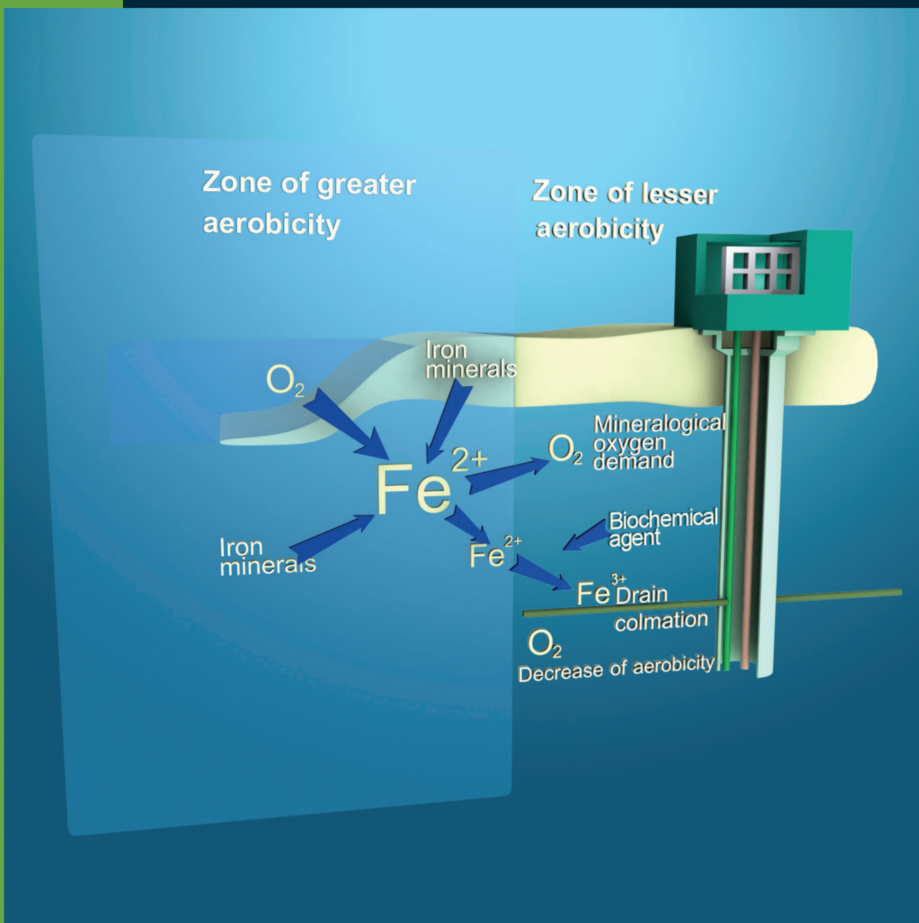
IWA SPECIALIST GROUND WATER CONFERENCE



International Water Association

Jaroslav Černi Institute for the Development of Water Resources

Belgrade Water Supply and Sewerage Company

PROCEEDINGS

08-10 September 2011, Belgrade, Serbia

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INTRODUCTORY ADDRESS

Groundwater is a precious resource for life on our planet. It represents the largest accumulation of water in the world, accounting for more than 97% of all fresh water on Earth (not counting glaciers and permafrost). Groundwater maintains river levels during periods of low flow, and supports a large number of ecosystems. Most oases and springs in arid zones rely on groundwater.

The hydrosphere is only about 10 kilometers thick (Figure 1). However, it is a prerequisite for life on planet Earth. Groundwater is an integral part of the water cycle. However, because of its specific features, in addition to consideration within the framework of overall water management, it must also be specifically addressed.

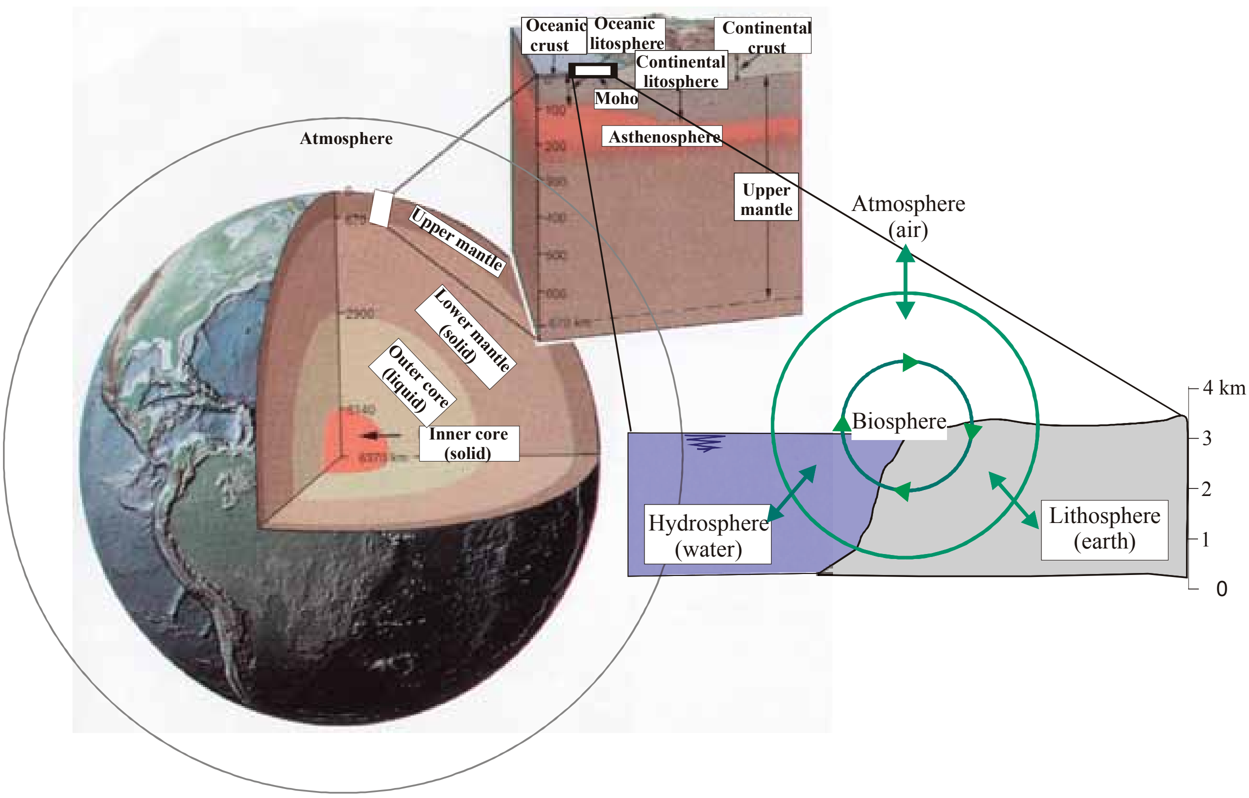


Figure 1: The Earth's spheres (Milovanović D. and Boev, 2001, modified, supplemented)

Groundwater is a source of drinking water supply for more than half of humanity. It is very popular because of the wide-spread confidence in its natural quality and because it is readily accessible. Groundwater flow is slower than river or stream flow by several orders of magnitude. As a result, a substance dissolved in groundwater interacts with rocks and is exposed to other highly-complex processes which lead to transformation, generally improvement, of water quality and to mineralization of organic matter. The aquifer medium can be viewed as a complex physical and biochemical reactor, which we must take into consideration when we assess approaches to groundwater use and protection.

Following a period of abundance, when water demand was easily met, we entered a period of depletion of water resources. This depletion resulted from population growth, industrial development, and increasing use of water for irrigation and other human needs. The main signs of depletion are water quality pressures and degradation, and excessive use of water from certain resources.

The need for sustainable and adaptive water management has been identified in order to ensure ongoing protection and conservation of water resources, and adaptation to global constraints and changes. These primarily include climate change, natural and social constraints, and potential socio-economic changes in the future.

Although efforts are being made to mitigate man's role in climate change, such as by the 2005 Kyoto Protocol[1], it is evident that there is still a difference of opinion with regard to the approach to be followed, as the 2009 Copenhagen Summit[2] has shown. At the same time, there are demands for adaptive water management, such as those voiced at the 5th World Water Forum[3] in Turkey in 2009, aimed at developing our ability to adapt to the challenges, constraints and changes.

The achievement of the necessary sustainability and adaptivity of water management requires the efforts of and cooperation between global institutions such as the IWA[4], UNESCO[5], FAO[6] and the World Bank. Also needed is a concerted effort of regional organizations and managers of large river basins and groundwater basins, for example the ICPDR[7], IAWD[8], ORASECOM[9], and the Joint Commission for the Study and Development of the Nubian Sandstone Aquifer. There is increasing insistence on joint, both bilateral and multilateral, management of transboundary water bodies.

The conference ahead of us is the first IWA Specialist Groundwater Conference. We expect this Conference to recognize the specificities of groundwater and the need for effective conservation of groundwater through sustainable and adaptive management.

The Conference also purports to use and develop the outcomes of the IWA Regional Groundwater Conference held in June 2007 in Belgrade, including the book Groundwater Management in Large River Basins[10] published by IWA Publishing.

1 *The Kyoto Protocol is a protocol to the United Nations Framework Convention on Climate Change, signed in Kyoto, Japan in 2005*

2 *The 2009 United Nations Climate Change Conference, commonly known as the Copenhagen Summit, was held in Copenhagen, Denmark*

3 *World Water Council's 5th World Water Forum was held in Istanbul, Turkey in 2009*

4 *The International Water Association*

5 *United Nations Educational, Scientific and Cultural Organization*

6 *Food and Agriculture Organization of the United Nations*

7 *The International Commission for the Protection of the Danube River*

8 *The International Association of Waterworks in the Danube Catchment Area*

9 *The Orange-Senqu River Commission*

10 *Groundwater Management in Large River Basins; Eds: Milan Dimkic, Heinz-Jurgen Brauch and Michael Kavanaugh, 2008*

This IWA-backed specialist conference is held under the auspices of the Serbian Government and the Serbian Academy of Sciences and Arts.

The IWA, IAWD, ICPDR and IAH[11] have all made major contributions during the preparatory stage of the Conference.

The main organizers of the Conference are Jaroslav Černi Institute for the Development of Water Resources and Belgrade Water Supply and Sewerage Company, aided by the Serbian Water Protection Society and the Serbian Association of Water Technology and Sanitary Engineering.

The objectives of the Conference are grouped under four themes:

Theme 1: Preparation and implementation of the groundwater component of water management plans for large basins

This theme is consistent with the current momentum seen in Europe and throughout the world, to develop and implement surface water and groundwater management plans within the framework of sustainable and adaptive water management. The aim is to bring face-to-face and compare the positions and agendas of different global and regional organizations, as well as of different countries. The focus is on challenges brought about by global changes, especially climate change and socio-economic changes.

Theme 2: The importance of the aerobic state of groundwater, and the processes which are driven by the level of aerobicity

This theme is increasingly at the forefront of groundwater research. The various processes associated with groundwater quality transformation and the rate of water well ageing largely depend on the aerobic state of the aquifer. This aerobic state is especially significant in bank filtration and artificial recharge, as well as for the mineralization of the organic component, particularly micropollutants in groundwater. Additionally, the correlation between well ageing expressed via hydraulic losses at well screens and aerobic indicators of groundwater is of major scientific and economic importance.

Theme 3: Climate change and its impact on groundwater

This theme is highly stimulating. Climate change is becoming an increasing challenge, but its framework has not been sufficiently defined to steer water management. The issue which arises is the definition of global climate change, including the relationship between global, regional and local changes. Also challenging is the correlation between regional climatic parameters and the condition of watercourses and aquifers. This condition affects the underlying assumptions of surface water and groundwater management.

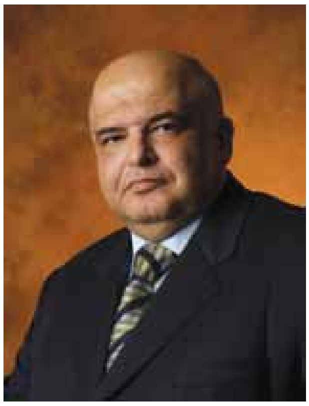
Theme 4: Management of urban groundwater basins: mitigation of water quality impacts from anthropogenic threats

This theme befits the transition from a period of depletion to a period of sustainable and adapted responses to the threat to water. It is a customary topic of the IWA Groundwater Group and the Conference purports to build on its efforts.

11 The International Association of Hydrogeologists

As you know, this is a two-day Conference. On the first day, invited papers will be presented in a plenary session. These papers will address groundwater management plans and their implementation. Various global organizations (the IWA, IAH and UNESCO), then regional organizations (the ICPDR and IAWD), and finally two countries (Austria and Serbia) will present their agendas in this area. One invited paper each has been prepared under Themes 2 and 3, which will also be presented at the plenary session.

On the second day, papers addressing the four themes will be presented at breakout sessions. More than 50 papers, featuring contributions by scientists and engineers from more than 20 countries, attest to the importance and appeal of this Conference.



Chairman of the Programme
and Scientific Committee

KEYNOTE PRESENTATIONS

IMPLICATIONS OF OXIC CONDITIONS IN ALLUVIAL GROUNDWATER

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Abstract: Alluvial groundwater is a very important resource for drinking water supply and is a source of water for baseline flow in rivers and wetlands. Groundwater self-purification processes are of extreme importance for the protection of this vital resource, as well as from the standpoint of groundwater resource utilization. The existence of self-purification processes de facto makes groundwater aquifers equivalent to physico-chemical reactors. Of major importance with regard to the quality of baseline flow in rivers, and to the transformation of water quality within an aquifer and along the groundwater flow path to the production well, are the redox conditions in the field and the degree of oxicity of the water within the aquifer. This paper provides an overview of the processes which define the baseline quality and the transformation of groundwater quality: oxic conditions, biochemical processes of nitrification and denitrification, reduction and oxidation of iron and manganese, and reduction and oxidation of sulphur. Questions pertaining to the transformation of groundwater quality are extremely important in groundwater use and protection and in the application of bank filtration and artificial recharge methods. Oxic conditions also determine the character and rate of well ageing in alluvial aquifers. Testing of the wells of the Belgrade Groundwater Source (Belgrade, Serbia) indicates that the dominant clogging process is incrustation with iron deposits. Changes in local hydraulic resistance at well screens, which occur as a result of clogging, are linked to the following main indicators: the redox potential and the concentration of ferrous iron. The authors draw a conclusion that long-term operation and the design of wells to be placed in anoxic groundwater are highly dependent on biochemical processes. For wells under high oxic conditions, the seepage stability and maintenance of a laminar flow regime of the groundwater are important factors. The paper also attempts to explain the mechanisms that lead to a particular set of oxic conditions in groundwater and the impact of such conditions on the processes that take place in a typical alluvial aquifer. The section of the paper which deals with well clogging correlates the kinetics of the development of hydraulic losses at the well screen to dominant oxic conditions in groundwater and the predetermined indictors of the degree of oxicity. It is shown that biochemical well clogging calls for stricter well design criteria with respect to the entrance velocity at well screens than is the case with traditional design criteria when applied to conditions of highly-reduced oxygen concentrations (low degree of oxicity) and low to medium anoxia in alluvial groundwater.
Keywords: groundwater, alluvium, aquifer, oxicity, well clogging, baseline water quality, groundwater quality.

INTRODUCTION

Groundwater represents the largest accumulation of fresh water in the world and accounts for over 97% of all fresh water on the planet Earth (not including glaciers and permafrost). The remaining 3% is mainly comprised of surface waters (lakes, rivers, wetlands) and soil moisture. Groundwater maintains river levels in periods of low water as well as a large number of associated ecosystems.

It is estimated that more than 50% of the water supply in the world comes from groundwater; in Europe, this figure is over 60%. In Serbia, about 70% of the water supply comes from groundwater (Dimkić et. al., 2007a), of which more than 50% traces to alluvial aquifers.

According to Schmidt et al. (Schmidt et al., 2003), most of the potable water in Germany is supplied through bank filtration; more than 300 waterworks use bank filtration and roughly 50 plants are based on artificial groundwater recharge. Through the application of bank filtration and artificial recharge, water is additionally purified by filtration through the aquifer, which is a very important addition to the treatment of river water and decreases the risk of accidental pollution.

Alluvial groundwater owes its “popularity” to availability, i.e. its proximity to the place where groundwater is utilized. There are different types of alluvial water sources:

- Small sources located at some distance from the river, where the percentage of inflow from the river represents only a small fraction of the resource,
- Sources located adjacent to the riverbank where the inflow from the river is considerable, and
- Sources for which artificial infiltration is used, and the resource is river water.

The methods of bank filtration and artificial recharge are important for water supply. Undesirable substances and pollutants are removed from river water by filtration through alluvial sediments. With the application of these methods, the degree of oxicity in an alluvial aquifer depends on a number of parameters, and primarily on:

- the oxygen concentration in the river/artificially infiltrated water,
- the content of organic matter in the river/artificially infiltrated water, and that already present in the aquifer,
- the content of oxidizable mineral matter in the aquifer;
- diffuse intrusion of oxygen into the aquifer,
- the hydrodynamic character of the groundwater flow from the river to the well.

In other words, the level of oxicity in an alluvial aquifer depends on the oxygen saturation of the river water, the oxidation and reduction processes of organic and inorganic matter, and the degree of oxygen restoration in the waters of the alluvial aquifer.

Figure 1 shows a schematic longitudinal section of an alluvial aquifer. The aim of this figure is to show that the manner and the outcome of sedimentation and deposition processes are different for different river reaches, with different consequences on the oxicity of the aquifer and the associated processes of groundwater quality transformation.

The sections of the riverbed in higher parts of the river valley are formed from coarse materials and are mainly characterised by oxic groundwater conditions and good connectivity between the river and the underground water-bearing layer. Along the middle sections of the river, the flow spreads out and becomes calmer, and coarse sediments are replaced by fine-grain sediments containing a greater proportion of clay minerals. The alluvial deposits of the downstream sections of large rivers are characterised by an even greater prevalence of fine-grain alumosilicate sediments, often with elevated concentrations of iron and manganese. The groundwater, on its passage from the river to the well, loses a part of its dissolved oxygen due to oxidation of the dissolved organic matter present in the infiltrating water or due to oxidation of the organic matter present in the riverbed and in the aquifer substrate. Besides the consumption of oxygen due to the oxidation of organic

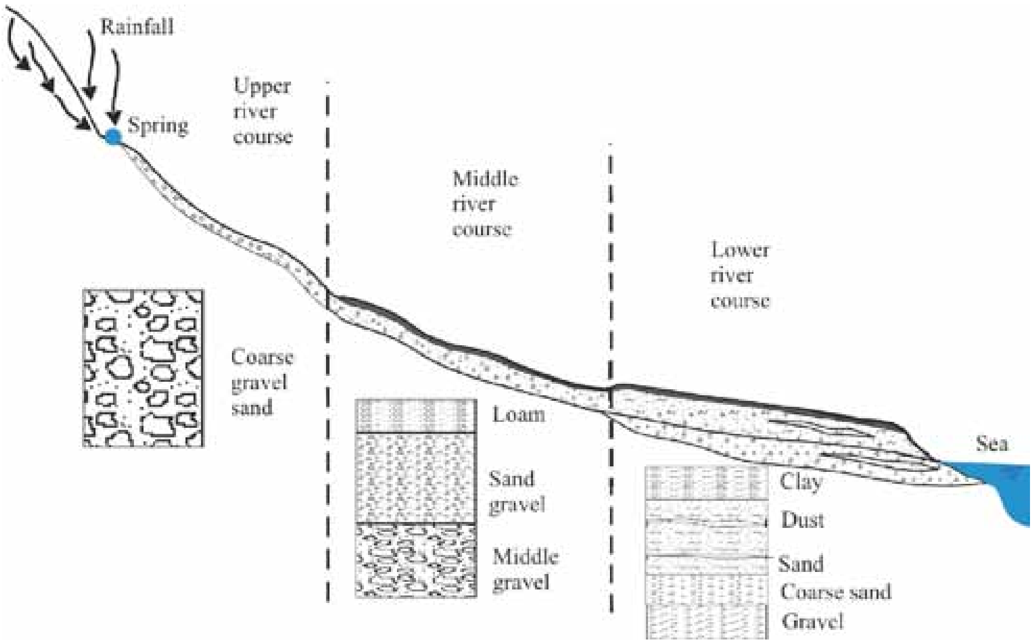


Figure 1: Change in grain size of an alluvial aquifer along the river course (Dimkić et al., 2011d)

matter, oxygen is also consumed for the oxidation of inorganic matter. The oxidation of minerals (inorganic), especially those containing iron and manganese in low-valence forms, often appears to be an especially important mechanism of oxygen consumption in groundwater. Therefore, the occurrence of highly aerobic conditions in groundwater is more frequent in the alluvion of the upstream river sections than in the alluvion of the downstream sections of large rivers.

The following all depend on the degree of oxicity of an aquifer (Dimkić et al., 2011d):

- the baseline water quality of groundwater,
- the self-purification processes of groundwater,
- the processes of well ageing,
- the way in which pollution spreads,
- the required degree of technological intervention in the aquifer required to maintain well performance (e.g. artificial underground removal of iron or arsenic), etc.

CHARACTERISTIC CONDITIONS AND PROCESSES OF GROUNDWATER TRANSFORMATION DEPENDING ON THE OXIC STATE OF THE AQUIFER

Phases of river water filtration

Along the course of groundwater flow, from an open water flow to water intake structures, there are four areas which may be considered to act as filter layers for the filtration of water from the river to the well, Figure 2.

Phase 1 – filtration through the riverbed. Phase 1 is characterised by fine-grain sediments, pronounced oxicity, high sorption potential for organic and other substances dissolved in water, and high biochemical activity;

Phase 2 – filtration under oxic conditions in the aquifer. The oxygen dissolved in the water is used for the oxidation of organic matter and other redox processes. Of special interest here is the consumption of dissolved oxygen for the oxidation of ferrous iron minerals present and their conversion into insoluble ferric forms.

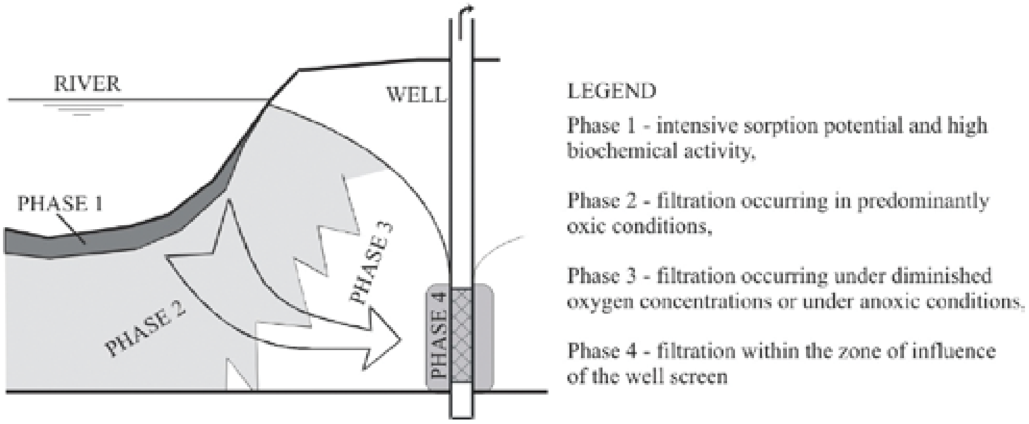


Figure 2: Phases of water filtration from the river to the well (Dimkić et al., 2011d)

Phase 3 – filtration at reduced oxygen concentrations or under fully anoxic conditions. Here water quality transformation processes have a different character than those occurring in Phase 2. Fe^{3+} is transformed into Fe^{2+} by redox reactions and ferrous iron, being soluble, increases the total concentration of iron in the groundwater.

Phase 4 – filtration in close proximity to the well. It takes place in an area where mechanical, chemical and biochemical changes occur in the aquifer and around the well screen zone, due to intensive processes at the aquifer/well screen interface. Under anoxic conditions in the aquifer and with more positive redox conditions in the well itself, at the aquifer/well screen interface there is an area where Fe^{2+} reverts to Fe^{3+}. This often causes rapid well ageing and is generally the reason for increased well maintenance costs.

It should be noted that Phase 3 may be absent if oxygen concentrations in the aquifer are high (at or near saturation). Furthermore, the presence of anoxic conditions in the well itself does not mean that the processes of water quality transformation from the river to the well are the same or of a similar character; the contrary is most often the case with both oxic and anoxic processes occurring at the same time, during water flow to the well.

Natural processes which lead to the baseline quality of groundwater

The baseline quality of groundwater implies a natural quality which develops without anthropogenic impact and is solely the result of the dissolving of minerals of the sediments through which the groundwater flows, the oxidation-reduction processes which take place, and the quality of the aquifer recharge. The baseline quality of groundwater is relatively stable at a given point under relatively stable conditions. The baseline quality of groundwater of different aquifers may be very different, and even vary within the same aquifer (albeit to a lesser extent).

Nelson (2002) identified three main factors which influence the solubility of minerals in groundwater: the types of minerals which constitute the water-bearing layer, the length of contact between water and the minerals, and the chemical condition of groundwater.

Precipitation tends to dissolve minerals in water-bearing layers being recharged. The longer the water is in contact with the minerals, the possibility of reaction with the minerals is greater.

The self-purification potential of an aquifer is the capability of improving the initial water quality through filtration in the aquifer. The self-purification potential depends on the time and length of the filtration media, the conditions in the aquifer, and the flow dynamics (Dimkić and Keckarević, 1990). In the event of a disturbance in the water quality, the self-purification processes tend to restore the quality to the baseline level (Dimkić et al., 2008a, 2008b).

Processes which are especially significant for the formation and achievement of a baseline level of groundwater quality are processes of selective transport and transformation of groundwater quality.

Processes of groundwater quality transformation

Groundwater quality changes in response to two basic mechanisms:

- In the first case, the quality of the inflowing water is stable and shows small to moderate variations over time. In this case the quality of groundwater in the aquifer basically stays unchanged;
- In the second case, there is a rapid and significant change in the quality of infiltrating water (e.g. accidental pollution, Dimkić et al., 2008b). In such a case the quality of groundwater can also change significantly.

In both cases there is a sequence of processes and associated parameters which lead to groundwater quality transformation (Table 1):

Table 1: Purification processes in an aquifer (Dimkić, 2007)

<table>
<tr><td rowspan="3">Transport via liquid phase</td><td>Convective transport of solute</td><td>1.1 Convection</td></tr>
<tr><td rowspan="2">Dispersion/diffusion of solute</td><td>1.2 Diffusion</td></tr>
<tr><td>1.3 Dispersion</td></tr>
<tr><td rowspan="6">Transfer from liquid to solid phase</td><td rowspan="3">Transfer of solute from solid phase into solution</td><td>2.1 Desorption</td></tr>
<tr><td>2.2 Rock dissolution</td></tr>
<tr><td>2.3 Transfer of solid into solution</td></tr>
<tr><td rowspan="3">Transfer of substance from solution to solid phase</td><td>2.4 Physical sorption</td></tr>
<tr><td>2.5 Chemical sorption</td></tr>
<tr><td>2.6 Precipitation</td></tr>
<tr><td rowspan="4">Loss of a particular substance from the aquifer</td><td rowspan="2">Degradation processes</td><td>3.1 Biodegradation</td></tr>
<tr><td>3.2 Chemical oxidation-reduction processes</td></tr>
<tr><td rowspan="2">Other processes</td><td>3.3 Radioactive decay</td></tr>
<tr><td>3.4 Evaporation</td></tr>
</table>

When the baseline quality of groundwater is altered by pollution, the processes shown in Table 1 lead, over time, to the restoration of baseline groundwater quality. In such cases, the aquifer medium acts like a physical and biochemical reactor with respect to the groundwater.

Notes on purification effects in the application of the bank filtration method

The bank filtration method is used in water supply systems to utilize the benefits from the efficiency of purification processes occurring in the aquifer. Self-purification processes during groundwater flow on its way to the well lead to the elimination or attenuation (to an acceptable level) of diverse undesirable substances found in river water.

The main advantage of using this method is the degradation of organic matter during filtration processes occurring within the aquifer. For example, at the Belgrade Groundwater Source (99 radial wells beside the River Sava), it was found that there is a decrease in the content of organic carbon from 2.5 mg/L in the river to about 1 mg/L in the groundwater. Similar results for the River Rhine and bank filtration were reported by Schmidt et al., 2003.

Transport through alluvial aquifers is associated with a number of water quality benefits, including the removal of microbes, pesticides, total and dissolved organic carbon (TOC and DOC), nitrate, and other contaminants (Schmidt et al., 2003, Dimkić 2007, Dimkić et al., 2008b, 2011c).

Organic substances generally do not dissolve well in water. Because of this and the chemical activity of microorganisms, relatively low concentrations of organic substances are found in groundwater. Aquifers in which oxic conditions prevail, and where oxygen concentrations are high, tend to support more intense biodegradation processes.

Sorption of an organic substance to aquifer material plays a dual role in relation to the overall biochemical oxidation of the substance in question. First, sorption can often significantly slow down the advance of an organic substance along the groundwater flow path (by a factor of ten, or hundred or even more). The sorbed organic substance is thus exposed to microbial activity for a much longer period of time. Second, a microbial agent “attacks” a sorbed substance differently than it does a substance dissolved in the water.

This is extremely important from the standpoint of substance transport through riverbed sediments, especially when one considers that these sediments are often made up of fine particles with a high sorption capacity. In general, when scientists and engineers assess the “purity” of sediments and the transformation of a substance infiltrated into the riverbed, they often do not attach sufficient significance to the role of sorption to riverbed sediment material.

Monitoring river water filtration in an alluvial aquifer over several years, Dimkić and Keckarević, 1990, JCI, 1983, JCI, 1983–1989a, JCI, 1983–1989b reported a decrease in the concentration of phenols, under oxic conditions in the aquifer, from 2–10 μg/L in the river to 0–2 μg/L in the wells. At the same time, the content of mineral oils decreased to approximately half of the amount present in the river water (Dimkić et al., 2008b).

Testing of phenol degradation in an oxic aquifer has shown very rapid degradation of phenols in groundwater (JCI, 1990, Dimkić et al., 2007b).

Even though degradation generally occurs more quickly under oxic conditions, some substances degrade only partially or not at all under such conditions, and degrade more rapidly in anoxic conditions.

In contrast to organic substances, one of the most important properties of inorganic substances with respect to groundwater is their solubility. A number of elements may be found in more than one valence, or oxidation state. Nine of the sixteen inorganic species for which EPA has specified maximum contaminant levels in drinking water, exhibit multiple oxidation states. These include antimony, arsenic, chromium, copper, lead, mercury, selenium and nitrogen. Consequently, reactivity, solubility and mobility in the environment of these and other redox-sensitive elements depends, in part, on redox conditions.

It is well documented that the solubility and transport, the kinetics of transformation and/or degradation, and much of other relevant chemistry of groundwater depends on the oxic conditions in the aquifer. Especially significant are the relations between the degree of oxicity and the concentrations and forms of nitrogen, iron and sulphur compounds present in groundwater.

Oxic/anoxic conditions in groundwater

Redox processes in groundwater generally depend on microorganisms which metabolise energy by enabling electron transfer from a donor (most often organic carbon) to an acceptor (in most cases an inorganic compound) (Jurgens et al., 2010). Certain electron acceptors release more energy than others and are the first to participate in redox reactions, while types that yield less energy enter into processes in a descending order of the energy they release. Redox processes last until all the available electron donors and acceptors are used. If the concentration of CO_2 is not a limiting factor, the processes will unfold according to the following sequence (Jurgens et al., 2010):

$$O_2 \rightarrow NO_3^- \rightarrow Mn^{4+} \rightarrow Fe^{3+} \rightarrow SO_4^{2-} \rightarrow CO_2 \quad (1)$$

with the greatest energy yield occurring from the reduction of oxygen, while nitrate reduction produces a somewhat smaller amount of energy. In order for bacteria to use the energy from the reduction of $Fe(OH)_3$ for biomass growth, it is necessary to reduce a large quantity of iron with large quantities of precipitates appearing as a by-product. Sulphate reduction produces the same results.

The identification of redox processes in groundwater and the associated redox categories to which they belong have been provided by USGS (Jurgens et al., 2010) and are shown in Table 2.

Table 2: Identification of predominant redox processes in groundwater and redox categories according to the methodology provided by USGS (Jurgens et al., 2010)

Redox category	Redox process	Half-reactions of electron acceptors
Oxic	O_2	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Suboxic	O_2 – Mn	
	O_2 – Fe(III)	
Anoxic	NO_3	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6\ H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$
	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$
	Fe(III)/SO_4	Fe(III) and (or) SO_4^{2-}
	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$
Mixed (anoxic)	Fe(III)-SO_4	Fe(III) and SO_4^{2-}
Anoxic	SO_4	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$
	CH_4gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$

Zobrist et al. (2000) provide a scheme of oxidation-reduction processes depending on the redox potential very similar to the classification in Jurgens et al. (2010), although this classification does not include processes in the suboxic zone.

The reactions of oxidation and reduction occur simultaneously, i.e. during reduction (accepting electrons), a simultaneous reverse process of oxidation must also take place (donating electrons). Also, not all molecules are oxidized or reduced at the same redox potential. With a decrease of the redox potential, the following reducing reactions will occur: transformation of nitrate into nitrogen gas, Fe^{3+} (insoluble) into Fe^{2+} (soluble), sulphate into hydrogen sulphide, and, at a very low redox potential, methanogenesis (Drever, 1982, Nelson, 2002).

CONDITIONS IN WHICH IMPORTANT PROCESSES OF GROUNDWATER QUALITY TRANSFORMATION ARE FOUND

Groundwater represents a complex heterogeneous electrolytic system within the environment in which it is located, which contains numerous inorganic and organic species in the liquid and solid phase.

Nitrogen - nitrification and denitrification

Nitrogen is present in the environment in a wide variety of chemical forms including organic nitrogen, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and nitrogen gas (N_2). Once nitrate reaches the groundwater, it tends to move with the groundwater without further reduction of concentration other than by dispersion.

Processes of the nitrogen cycle transform nitrogen from one chemical form to another. Many of the processes are carried out by microbes either to produce energy or to accumulate nitrogen in the form needed for growth.

The reduction of nitrate (denitrification) occurs at low oxygen concentrations (approximately 0.5 mg/L) and in the presence of organic substances (the source of carbon needed for cell synthesis), through the action of nitrate-reducing or denitrifying microorganisms. Nitrite is formed as the first product of reduction, and the denitrifying bacteria utilize NO3- as the electron acceptor and reduce it to NO_2^-, N_2O, or N_2. The elemental nitrogen escapes into the ground air. Since denitrifying bacteria require organic carbon as an energy source, denitrification occurs primarily in soils where organic matter is readily available. Under aerobic conditions, ammonia is oxidized to nitrite and nitrate by nitrogen bacteria (Matthess, 1982).

The biochemical processes of nitrification and denitrification have recently been described by Madigan et al. (2005).

Iron and manganese

The solubility of metals in natural waters depends on the oxidative condition of the mineral components (Table 3). Additionally, the dynamic interaction at the interfaces between liquid and solid phases is determined by the transfer dynamics of metals between the liquid and solid phases.

Table 3: Conditions in which certain significant substances are found in groundwater

Chemical formula	Oxidation state	Chemical formula	Oxidation state
MnO_2	4	Fe_2O_3	3
Mn^{2+}	2	NH_3	-3
FeOOH	3	NH_4^+	-3
$Fe(OH)_3$	3	N_2	0
$FePO_4$	3	NO_2^-	3
FeS_2	2	NO_3^-	5
$FeCO_3$	2	SO_4^{2-}	6

Concentrations of iron and manganese, as well as of most heavy metals, decrease during groundwater filtration as a result of sorption processes. In oxic environments, the decrease in concentration is caused by an ion exchange on the negatively charged surface of clay minerals, amorphous Fe_2O_3 and Al_2O_3 oxides and solid organic matter. In anoxic environments, the removal of a metal ion is predominantly followed by the formation of sulphides (Schmidt et al., 2003).

Iron is much more soluble in its reduced form (Fe^{2+}) than in its oxidized form (Fe^{3+}), where it usually appears as Fe_2O_3 or $Fe(OH)_3$). If the environment is such that a reduced iron form is produced, groundwater will contain higher concentrations of iron.

A variety of microorganisms can reduce ferric (Fe^{3+}) iron to the ferrous (Fe^{2+}) state. Fe^{3+} reduction can be coupled to the oxidation of a wide variety of both organic and inorganic electron donors because the reduction potential of the Fe^{3+}/Fe^{2+} pair is very electropositive.

The reduction potential of the Mn^{4+}/Mn^{2+} pair is very high and several compounds should be able to donate electrons to Mn^{4+} reduction.

Only a small amount of energy is available from the oxidation of iron from the ferrous (Fe^{2+}) to the ferric (Fe^{3+}) state, so iron bacteria must oxidize large amounts of iron in order to grow. The end product of this reaction is solid iron hydroxide.

The main bacterial strains participating in the oxidation of Fe^{2+} to Fe^{3+} are: Thiobacillus ferrooxidans, Gallionella feruginea, Sphaerotilus natans, and Leptothrix ochracea. Leptothrix and a few other bacteria can oxidize Mn^{2+}.

Sulphur

In groundwater, sulphur most often appears in the form of sulphate (SO_4^{2-}). If it occurs in the form of hydrogen sulphide (H_2S), an unpleasant smell of rotten eggs is present even at concentrations under 10 mg/L. Redox reactions cause sulphate reduction to hydrogen sulphide in anoxic conditions, in the presence of organic matter (dissolved organic carbon).

WELL AGEING CAUSED BY IRON

Well ageing is a term that entails processes on wells with multiple consequences. It takes place under certain conditions of combination and interaction of the aquifer skeleton, groundwater and the well. Ageing leads to deterioration of the abstraction features of a well – a reduction in yield and the deterioration of the well construction materials. Well ageing may even cause the cessation of well operation.

Well ageing due to well clogging with iron occurs when, under conditions of a relatively reduced redox potential, a sufficient quantity of dissolved iron reaches the well screen. More favourable redox conditions in the well should exist (more oxygen and/or a higher Eh value than in groundwater) to produce the following reaction:

$$Fe^{2+} - e^{-} => Fe^{3+} \tag{3}$$

These reactions occur with the catalytic effect of bacteria which use energy from the reaction and/or its products for their needs. Iron bacteria can be primarily anaerobic, optionally anaerobic or, rarely, slightly aerobic.

The transformation of Fe^{2+} into Fe^{3+} hardly ever occurs under extremely oxic conditions (Eh > 300 mV) and is of low intensity in low oxic environments (150 mV < Eh < 300 mV), but it occurs in anoxic environments. Besides oxicity, the grain-size distribution of the aquifer, screen quality and velocity of groundwater flow to the well are also important for the intensity and kinetics of the process. A well ageing study of the Belgrade Groundwater Source conducted in recent years (JCI, 2009), as well as a research project financed by the Ministry of Science of the Republic of Serbia (JCI, 2010), and a project of the Ministry of Agriculture, Forestry and Water Management of the Republic of Serbia (JCI, 2011) (both under way), all address the well aging problem at approximately 150 water supply and drainage wells, which operate under aerobic and anaerobic conditions.

Clogging of the well screen tends to occur through physical, chemical and biochemical processes. Based on extensive research conducted in Germany, Houben (2003a) reported that more than 80% of the studied wells were clogged with iron compounds. Detailed research on some 150 alluvial wells in Serbia has also shown that trivalent iron was the dominant cause of well clogging. Chemical corrosion is manifested by corrosion and destruction of the screen material and the well structure as a whole, while the consequence of chemical clogging is a deposit formed on the screen and around the well screen zone. Groundwater contact with air and the dissolution of gasses, especially oxygen, enhance the formation of deposits.

In alluvial aquifers, especially along the middle and lower reaches of big rivers, minerals containing Mn and Fe are usually deposited. Under such conditions, massive development of microorganisms occurs in the wells, especially of manganese and iron bacteria. The deposit formed is a product of their metabolism and of the bacteria themselves. Apart from clogging which is dominant in ecological micro-niches in contact with the well structure, bacteria appear to participate in the corrosion of the well screen material utilising it for their metabolic processes.

Above all, these causes of well ageing are responsible for a decrease in well yield and a shorter life-span. The ageing of the well screen is a significant question from practical and operational points of view. Both the total quantity of abstracted water and the cost of construction, operation and maintenance of the well depend on the stability of well yield and well longevity. In recent years, the introduction of new technologies (materials, design solutions and well construction) has contributed to the lowering of the risk of well ageing, although this problem is still present.

Well ageing has been the subject of research worldwide for quite some time. Initially, more attention was devoted to researching criteria important for well construction (well dimensions, characteristics of the screen, maximum permissible well yield, etc.), such that the focus was on hydraulic parameters, as a precondition for good quality and a long life cycle of the well (Sichardt (1928), Abramov (1952), Istomina (1957), Cistin (1965), Alekseev (1968), Gavrilko (1968), Pietraru (1982), Kovacs and Ujfaludi (1983), Gavrilko and Alekseev (1985), Vuković and Soro (1990), Vuković and Pušić (1992), etc.). Standard criteria for defining the permissible entrance velocity of groundwater into the well screen are most often related to grain-size distribution characteristics of the adjacent material and to the hydraulic flow regime (laminar or turbulent flow).

Experience has shown that, in a great number of cases, well ageing occurs due to chemical and biochemical processes occurring concurrently. Since the 1980s, many authors have studied these issues (Dubinina (1978), Howsam (1990), Leach et al. (1991), Borch, Smith, Noble (1993), Smith (1995), McLaughlan (1996), Cullimore (1993, 1999), Mansuy (1999), Houben (2003), Ellis (2006), Houben and Treskatis (2007), etc.). Chemical clogging with carbonate deposits has been studied to such an extent that LSI (Langelier Saturation Index, Langelier, 1936) and RSI (Ryznar Stability Index, Ryznar, 1944) were derived for quantifying the propensity of water for corrosion or encrustation. These indexes have a wider practical significance apart from wells.

CORRELATION BETWEEN THE KINETICS OF THE FORMATION OF LOCAL HYDRAULIC LOSSES (KLHR [1]) AT THE WELL SCREEN AND SOME INDICATORS OF OXIC CONDITIONS

Establishing a correlation between the kinetics of the formation of local hydraulic losses at the well screen and some indicators of oxic groundwater conditions is in fact a new engineering approach to the study of well clogging (ageing) under a given set of oxic conditions. This work is partly based on the results of many years of monitoring of the behaviour and processes in approximately 150 wells at several alluvial aquifers in Serbia. At locations with a high redox potential, no well clogging with iron deposits was observed. In relatively low oxic environments (150 mV < Eh < 300 mV, 0.2 mg/L < O_2 < 1 mg/L), iron clogging was found to be of low intensity. Under low or medium anaerobic conditions, iron clogging is frequently present. The most intensive and beneficial research of the clogging rate was possible at five radial wells of the Belgrade Groundwater Source with new (replaced) lateral screens. Changes in hydraulic resistance at the well screen were correlated with certain clogging indicators (Eh, Fe, bacterial count).

The clogging of a radial well lateral directly results in increased local hydraulic losses at the entrance to the lateral. The hydraulic parameter which can be used to quantify the extent of well clogging is Local Hydraulic Resistance (LHR), expressed as the quotient $\Delta S/v$, where ΔS is the local well drawdown (i.e., the difference in water levels between the well and a nearby piezometer), and v is the entrance velocity of groundwater into the well screen (discharge per surface unit) (Dimkić and Pušić, 2008c, Dimkić et al., 2011b).

1 KLHR – Kinetics of local hydraulic resistence variation

$$LHR = \frac{\Delta S}{v} \tag{4}$$

LHR variation over time may be expressed as

$$KLHR \approx \frac{\Delta(LHR)}{\Delta t} \tag{5}$$

where KLHR is the rate of change of local hydraulic resistance. The KLHR value is an indicator of the rate of LHR variation, i.e. the rate of well ageing.

Local hydraulic resistance at the wells of the Belgrade Groundwater Source was quantified based on the results of periodically performed pumping tests. This groundwater source is comprised of radial wells, located along the banks of the Sava River. The groundwater source has 99 radial wells and about 50 tube wells. The wells were built from 1953 to 1998 (Dimkić et al., 2007).

A constant decline in well yield has been noted at most of the wells since the beginning of their operation. Over time, this has become a serious problem for the entire groundwater source. The problem was addressed in three ways: construction of new wells (today there is virtually no suitable location for the construction of a new well within the present groundwater source), replacement of laterals, and repeated regeneration of laterals.

During the 2005-2008 period, old laterals were replaced at five wells (hereafter: new wells), through the application of a more modern technology and the installation of screen pipes made of superior material (Cr-Ni steel alloy), compared to the previous period. At the same time, comprehensive research was carried out at the groundwater source in order to establish a correlation between well yield and certain indicators of well ageing. The new wells were the focus of this research.

Plots of LHR variation over time are shown in Figure 3. Only the period of well operation with new laterals was analysed. The origin of the X-axis represents the time of installation of new laterals at each well.

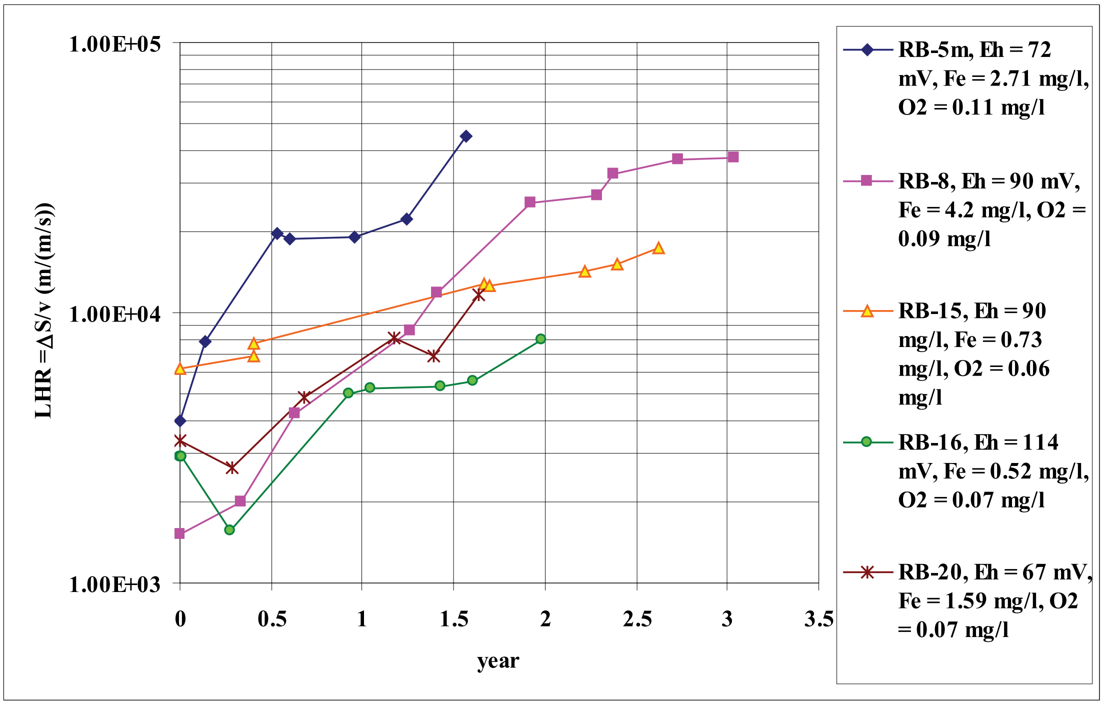
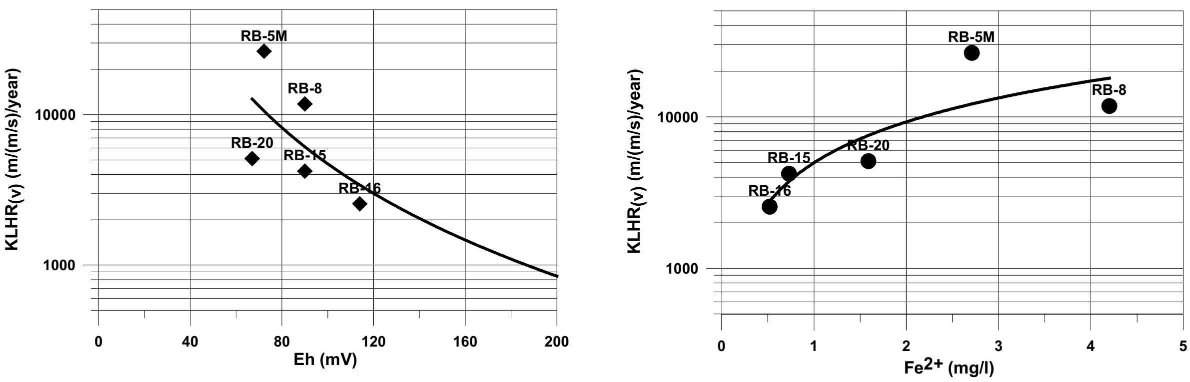


Figure 3: Change in LHR following installation of new laterals (Dimkić et al., 2011b).

The initial local hydraulic resistance, LHR, was of the same order of magnitude at all the wells (it was in fact hydraulic resistance without the influence of clogging). The resistance that developed due to clogging differed to a large extent at different wells. This difference corresponded to the difference between the Eh and Fe values of the individual wells. Based on the data shown in Figure 3, a simple calculation yielded the rate of LHR change (KLHR) in the studied time period.

Figure 4 shows the correlation between the iron concentration and the groundwater redox potential, and the intensity of KLHR. The plots should not be considered as universal. However, they certainly indicate the character of the relationship KLHR = KLHR (Fe, Eh, ...). It should be noted that all the discussed wells are actually in a slightly anoxic area. Taking into consideration the conditions found in the wells, the best fit line (KLHR = F_2(Eh)) is also shown for the wells which operate under more oxic conditions. It should be emphasized that no single parameter defines the KLHR value by itself, as this value is a result of the correlation of a set of interrelated parameters (Dimkić et al., 2011a).

$$KLHR = f_2\left(Eh, Fe, B\right) \tag{6}$$



$KLHR = F_1\,(Fe)$ $KLHR = F_2\,(Eh)$

Figure 4: KLHR as a function of iron concentration and redox potential of well water.

LIMITING ALLOWABLE WATER INFLOW VELOCITY AT THE WELL SCREEN IN RELATION TO GROUNDWATER OXICITY

Based on the results of research of these radial wells of the Belgrade Groundwater Source, a correlation was established between KLHR and the clogging indicators (q, Fe, Eh, B, Γ):

$$KLHR = KLHR(v, Fe, Eh, B, \Gamma) \tag{7}$$

where: v - well entrance velocity, Fe – iron concentration in the well water, Eh - measured redox potential, B – a quantity which describes the intensity of bacterial growth in the well, Γ – a quantity which depends on several parameters – well screen installation method, gravel pack and aquifer grain-size distribution.

In the above context, the clogging rate of a well also depended on the discharge during abstraction. There is the practical question of LHR estimation, which in a given time period should not exceed a (likewise) given value. For example, the annual increase in LHR should not exceed a certain value (allowed value - AV), in order to ensure well longevity. The following empirical expression is proposed:

$$\Delta S_{year} = v_{perm} \cdot KLHR_{year} \leq AV\ (m) \tag{8}$$

where ΔS_{year} is the proposed maximum permissible hydraulic resistance at the lateral as the annual average (m), and vperm is the permissible entrance velocity into the well (m/s).

Based on the above, the permissible entrance velocity of groundwater flow into the well (or lateral, in radial wells), taking the annual parameter change (i.e. the degree of oxicity) as a criterion, may be calculated as follows:

$$v_{perm} = \frac{\Delta S_{year}}{KLHR_{year}} \tag{9}$$

The concept of critical, maximum permissible entrance velocities into the well screen (vperm), has in practice until now been linked exclusively to the occurrence of seepage instability of the aquifer around the well screen zone (e.g., Sichardt, 1928, Abramov, 1952, Kovacs, 1983).

Here, however, an additional criterion is introduced, namely the concept of the permissible rate of well clogging, KLHR, i.e. the permissible drawdown, ΔS_{year}. It is assumed that both criteria should be fulfilled. Determining the vperm value and setting the dimensions of the well screen in order to meet the condition that the entrance velocity (v_{en}) should not exceed the permissible velocity ($v_{en} < v_{perm}$), does not ensure complete cessation of clogging of the laterals. It only reduces the process to a level which allows the annual increase in hydraulic losses between the outer environment and the inside of the lateral, to be smaller than the given value ΔS_{year}.

Furthermore, a correlation may be established between v_{perm} and the degree of oxicity of the groundwater, where the Eh level of groundwater is taken as an indicator. Figure 5 is a graphic representation of this approach in the form of plots of permissible velocities as a function of the increase in Eh, namely plots of permissible velocities based on the expressions proposed by different authors, where the occurrence of seepage instability (v) and vperm was taken into consideration as the sole criterion. It is assumed that the recommendation includes the laminar groundwater flow condition.

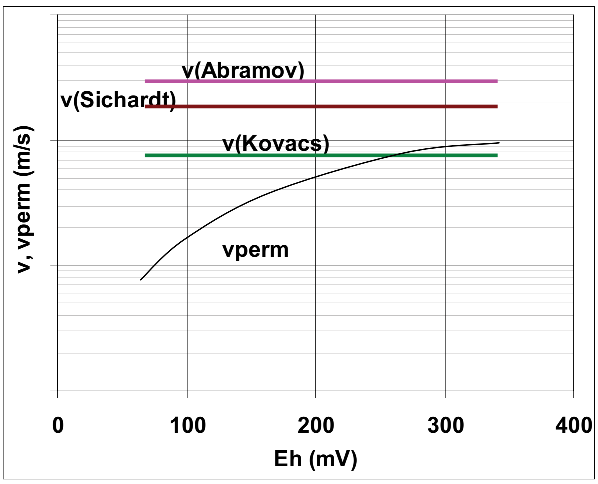


Figure 5: Graphic representation of the correlation between the entrance velocity at the well screen, v (standard criteria) and vperm depending on the degree of oxicity (expressed via the Eh of groundwater).

The example of the Belgrade Groundwater Source shows that vperm for nearly all the wells was much lower than that calculated using "standard" experimental formulas related to the seepage stability in the well screen zone. This is especially true of anoxic/suboxic water conditions, i.e. in this case for 70 mV ≤ Eh ≤ 150-200 mV.

For an analysis of higher oxic conditions (Eh > 200 mV), the results of the tests conducted at the wells of the Belgrade Groundwater Source, as well as at high oxicity wells of other groundwater sources („Ključ“ - Velika Morava, „Mediana“ - Nišava) were used (Dimkić et al., 2007c, 2011c).

These test results show that biochemical processes are relevant to the design of wells for slightly or moderately anoxic groundwater, 50 mV ≤ Eh ≤ 200 mV. None of the studied wells had Eh < 50 mV. For high oxicity wells, “standard” criteria of seepage stability and maintenance of a laminar flow regime apply.

CONCLUSIONS

Alluvial groundwater is extremely important for both human society and the natural environment. The oxicity in an alluvial aquifer is significant, for both the formation of the baseline groundwater quality and its transformation processes.

Bank filtration is a widely applied water supply method. The level of groundwater oxicity in the aquifer in the case of bank filtration depends on the oxygen saturation of the river water, the oxidation-reduction processes of organic and inorganic substances, and the level of oxygen renewal in the aquifer.

High oxic conditions occur more often in aquifers in the upper parts of a river basin than in central and especially lower parts of the basin. Besides the level of organic load, the mineralogical consumption of oxygen should also be taken into consideration. Minerals with ferrous iron content are particularly significant.

Under oxic conditions, oxidation takes place through the oxygen dissolved in water. Under anoxic conditions, biochemical oxidation is based mainly on nitrates, compounds of ferric iron and tetravalent manganese, as well as sulphates.

Oxic environments are generally more favourable for self-purification processes. However, some substances can also degrade in anoxic conditions. Knowledge of the effects that the degree of groundwater oxicity has on the baseline quality of groundwater and understanding of the process of purification of river water to the baseline quality level are fundamental for the design, use and protection of groundwater sources.

Well ageing due to screen clogging with iron deposits is a process of great economic significance. It predominantly occurs through the transformation of soluble Fe^{2+} into poorly soluble Fe^{3+}. In this paper, the correlation between the kinetics of local hydraulic resistance variation at the well and well clogging indicators is expressed as:

$$KLHR = KLHR(v, Fe, Eh, B, \Gamma) \tag{10}$$

With regard to groundwater source design, namely well discharge decline and well ageing, the oxic state in which biochemical processes become dominant is 50 mV ≤ Eh ≤ 200 mV. In this range of oxic conditions the critical well screen entrance velocity depends on biochemical parameters. In a highly oxic area, “standard” criteria - seepage stability and laminar flow of groundwater to the well - are the most significant criteria for well screen design and operation. It should be noted that wells where Eh < 50 mV were not studied.

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GROUNDWATER ISSUES IN LIGHT OF THE WATER FRAMEWORK DIRECTIVE IN THE DANUBE RIVER BASIN

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INTRODUCTION

The EU Water Framework Directive (WFD) aims to ensure that water is more effectively managed on a sustainable basis for the benefit of both society and the environment. It brings together management and protection aspects and covers both surface and groundwaters. For groundwater, the Member States must ensure that all groundwater bodies are of good status – in terms of water quality as well as quantity.

The Danube countries created a management arrangement to protect and restore the water resources of the Danube by signing of the Danube River Protection Convention (DRPC) in June 1994. DRPC entered into force on 22 October 1998 and it became an overall legal instrument for the cooperation and transboundary water management in the Danube River Basin. One of the major strategic goals of the Convention is to maintain and improve the status of surface and ground water resources, including both quality and quantity, and to prevent, reduce and control water pollution. To implement these goals the Danube countries have established the International Commission for the Protection of the Danube River (ICPDR). The Commission has created a set of Expert Groups to strengthen the proactive participation of all Contracting Parties.

The cooperation and management framework under the ICPDR was strengthened in 2000 when the DRPC signatories decided to make all possible efforts to implement the WFD throughout the entire basin. This included both EU member states and non EU countries. The Danube countries then agreed to produce a Danube River Basin Management Plan by the end of 2009, including national and basin-wide analysis of the status of Danube surface and groundwaters and agreed measures to address the existing problems. The Danube River Basin Management Plan and the Joint Programme of Measures – prepared as an integral part of it - aim for the achievement of environmental objectives of WFD to achieve good status of waters in the whole international basin.

In order to address the issues of groundwater management under WFD the ICPDR created a Groundwater Task Group. The activities of this expert body include identification of transboundary

GW-bodies of basin wide importance, development of guidelines for harmonised characterisation of groundwaters in the Danube River Basin, collection of information from groundwater chemical and quantity monitoring networks and preparation of reports to EC as required by the EU legislation including elaboration of Danube River Basin Management Plans.

WATER FRAMEWORK DIRECTIVE

WFD brought major changes into water management practices in the basin primarily by:
- setting uniform standards in water policy throughout the Danube River Basin and integrating different policy areas involving water issues,
- introducing the river basin approach for the development of integrated and coordinated river basin management plan,
- including public participation in the development of river basin management plans and encouraging active involvement of interested parties including stakeholders, non-governmental organizations and citizens,
- stipulating a defined time-frame for the achievement of the good status of surface water and groundwater.

The components of the Water Framework Directive dealing with groundwater cover a number of different steps for achieving good (quantitative and chemical) status by 2015. They require Member States to:
- Define groundwater bodies within River Basin Districts to be designated and reported to the European Commission by Member States. They must classify them by analysing the pressures and impacts of human activity on the quality of groundwater with a view to identifying groundwater bodies presenting a risk of not achieving WFD environmental objectives.
- Establish registers of protected areas within each river basin districts for those groundwater areas or habitats and species directly dependent on water. The registers must include all bodies of water used for the extraction of drinking water and all protected areas covered under the following directives: the Bathing Water Directive 76/160/EEC, the vulnerable zones under the Nitrates Directive 91/676/EEC, and the sensitive areas under the Urban Wastewater Directive 91/271/EEC, as well as areas designated for the protection of habitats and species including relevant Natura 2000 sites designated under Directives 92/43/EEC and 79/409/EEC. Registers shall be reviewed under the River Basin Management Plan updates.
- Establish groundwater monitoring networks based on the results of the classification analysis so as to provide a comprehensive overview of groundwater chemical and quantitative status.
- Set up a river basin management plan for each river basin district which must include a summary of pressures and impacts of human activity on groundwater status, a presentation in map form of monitoring results, a summary of the economic analysis of water use, a summary of protection programmes, control or remediation measures, etc. The first RBPM has been published in 2009, a review is planned every six years thereafter.
- Establish by the end of 2009 a programme of measures for achieving WFD environmental objectives (e.g. abstraction control, prevent or control pollution measures) that would be operational by the end of 2012. Basic measures include, in particular, controls of groundwater extraction, controls (with prior authorisation) of artificial recharge or augmentation of groundwater bodies (providing that it does not compromise the achievement of environmental objectives). Point source discharges and diffuse sources liable to cause pollution are also regulated under the basic measures. Direct discharges of pollutants into groundwater are prohibited subject to a range of provisions listed in the Article 11. The programme of measures has to be reviewed and if necessary updated by 2015 and every six years thereafter.

GROUNDWATER DIRECTIVE

The Groundwater Directive (2006/118/EC) establishes a regime which sets groundwater quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater. The directive establishes quality criteria and allows for further improvements to be made based on monitoring data and new scientific knowledge. This directive represents a response to the requirements of the Water Framework Directive (WFD) as it addresses the assessments on chemical status of groundwater and the identification and reversal of significant and sustained upward trends in pollutant concentrations.

Complementing the Water Framework Directive, the Groundwater Directive requires:

- groundwater quality standards to be established by the end of 2008;
- pollution trend studies to be carried out by using existing data and data which is mandatory by the Water Framework Directive;
- pollution trends to be reversed so that environmental objectives are achieved by 2015 by using the measures set out in the WFD;
- measures to prevent or limit inputs of pollutants into groundwater to be operational so that WFD environmental objectives can be achieved by 2015;
- reviews of technical provisions of the directive to be carried out in 2013 and every six years thereafter;
- compliance with good chemical status criteria (based on EU standards of nitrates and pesticides and on threshold values established by Member States).

Groundwater bodies of basin-wide importance in the Danube River Basin

The analysis and review of groundwater bodies (GWBs) in the Danube River Basin (DRB), as required under Article 5 and Annex II of the WFD, was performed in 2004 and identified 11 transboundary GWBs or groups of GWBs of basin-wide importance.

Transboundary GWBs of basin-wide importance were defined as follows:

1. Important due to the size of the groundwater body i.e. an area >4,000 km^2 or
2. Important due to various criteria e.g. socio-economic importance, uses, impacts, pressures interaction with aquatic eco-system. The criteria need to be agreed bilaterally.

Other GWBs, even those with an area larger than 4,000 km^2, that are fully situated within one country of the DRB are dealt with at the national level.

Transboundary GW-bodies of basin wide importance (ICPDR GW-bodies) are divided into national parts of ICPDR GW-bodies which can furthermore consist of a number of individual national GWBs. Only ICPDR GW-bodies and national parts of ICPDR GW-bodies are under the focus of the GW TG and TNMN Groundwater.

Analysis of pressures and impacts

The overall assessment of pressures on the quality of the 11 transboundary GWBs of basin-wide importance in the DRBM Plan showed that pollution by nitrates from diffuse sources is the key factor affecting the chemical status of these groundwaters. The major sources of this diffuse pollution are agricultural activities, non-sewered population and urban land use.

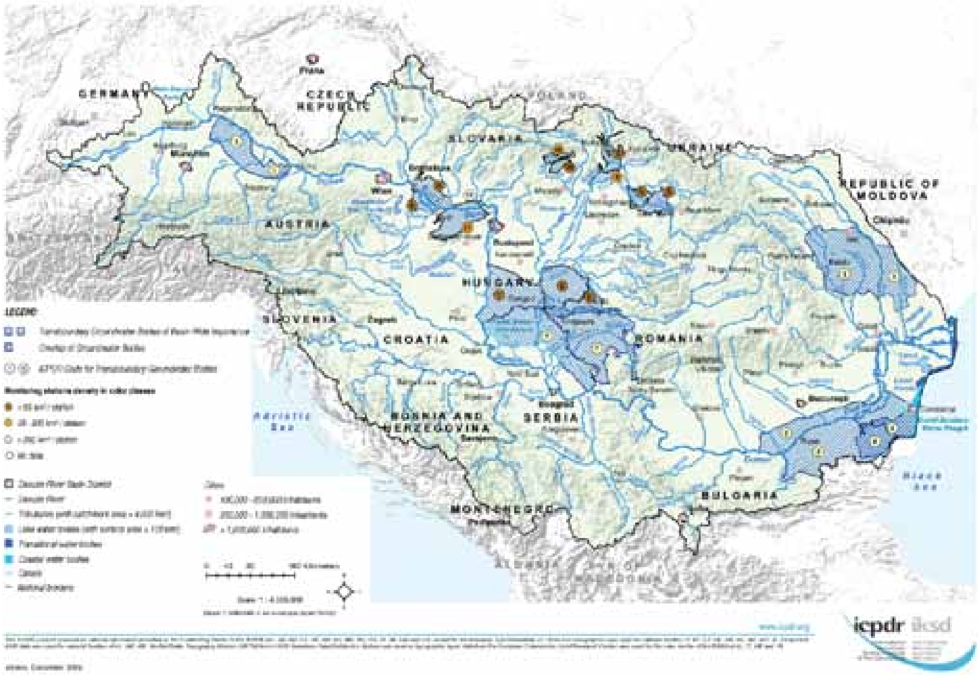

Figure 1: Danube River Basin District - Transboundary Groundwater Bodies of Basin-Wide Importance and their Transitional Monitoring Network

Furthermore, following types of point sources of pollution were found relevant:

- Leakages from contaminated sites;
- Leakages from waste disposal sites (landfill and agricultural waste disposal);
- Leakages associated with oil industry infrastructure;
- Leakages from septic tanks;
- Discharge of used thermal water.

Groundwater quantity in the DRB is affected by groundwater abstraction for drinking water supply or for industrial and agricultural purposes. The expected development of future water demand has to be taken into account when identifying water exploitation and protection strategies.

Groundwater status

According to the EU WFD, good chemical and quantitative status should be achieved for groundwater bodies. Groundwater status is determined by the poorer of its quantitative status and its chemical status. Good groundwater status means the status achieved by a groundwater body when both its quantitative and its chemical status are at least good.

A GW body has good quantitative status when the level of water in the groundwater body is such that the available groundwater resource is not exceeded by the long-term annual average rate of abstraction.

The groundwater body has a good chemical status when its chemical composition is such that the concentrations of pollutants do not exhibit the effects of saline or other intrusions, do not exceed the EU quality standards and do not pose any significant damage to terrestrial ecosystems which depend directly on the groundwater body.

Processing the data from the ICPDR groundwater monitoring programmes (Transnational Monitoring Network, TNMN), the results on status of the transboundary GWBs of basin-wide importance were presented in the Danube River Basin Management Plan.

Out of 11 transboundary GWBs of basin-wide importance (22 national parts evaluated), good chemical status was observed in all national parts of 8 transboundary GWBs (73%). In two additional transboundary GWBs, poor chemical status was observed in one national part. In only one GWB were all national parts found to be in poor status. Altogether, poor chemical status was identified in four out of 22 of the evaluated national parts of the 11 transboundary GWBs. Nitrates were the cause of the poor classification in each case.

Out of 11 transboundary GWBs (22 national parts evaluated), good quantitative status was observed in all national parts of 9 transboundary GWBs (82%). In two transboundary GWBs, good quantitative status was observed in only one national part. The poor quantitative status was caused in two cases by the exceeding of available groundwater resources; in one case by damage to terrestrial ecosystems and in one case by damage to surface waters (springs). In the case of the national part of one GWB, former mining activities still have an impact on the quantitative status. Herewith it has to be explained that poor status can be caused by more than one reason.

Gaps and uncertainties in the DRBMP

As the overall coordination of groundwater management in the DRBD started only during preparation of the Article 5 report in 2002, there were differences in the approaches taken in the WFD implementation throughout the Danube River Basin District. The Danube countries used a broad spectrum of different methodologies for:

- delineation and characterisation of GWBs;
- assessment of the risk of failure to reach good status;
- establishment of threshold values and status assessment.

Despite there was an overall coordination of the groundwater status assessment process, further harmonisation of the national methodologies is still needed. Data gaps and inconsistencies have become apparent in the underlying data, resulting in uncertainties in the interpretation of data. Furthermore, additional information may be needed for a proper assessment of the water balance. In addition, some countries have identified the need to expand the current monitoring networks to include monitoring stations along national borders, where transboundary GWBs are located. In some cases, countries have assessed the need to adapt their current monitoring programmes to collect more comprehensive information on groundwater quality and quantity.

To achieve a harmonisation of data sets for transboundary GWBs, there is a need for intensive bi- and multilateral cooperation. In addition, the interaction of groundwater with surface water or directly dependent ecosystems need further attention. At present, no harmonised system for coding the various layers of the GWBs is available. The issue of different groundwater horizons needs further discussion and clarification.

Joint Programme of Measures

The Joint Programme of Measures (JPM) builds upon the results of the pressure analysis, the water status assessment and includes, as a consequence, measures of basin-wide importance oriented towards the agreed visions and management objectives for 2015. It is firmly based on the national programmes of measures, which shall be made operational by December 2012, and describes the expected improvements in water status by 2015. Priorities for the effective implementation of national measures on the basin-wide scale are highlighted and are the basis of further international coordination.

The JPM represents more than a list of national measures as the effect of national measures on the Danube basin-wide scale is also estimated. The implementation of the measures of basin-wide importance is ensured through their respective integration into the national programme of measures of each Danube country. A continuous feedback mechanism from the international to the national level and vice versa will be crucial for the achievement of the basin-wide objectives, in order to improve the quantitative and chemical status of groundwater bodies.

In response to the pressures to groundwater quality and quantity the respective visions and management objectives have been adopted by the ICPDR.

The ICPDR's basin-wide vision for groundwater quality is that the emissions of polluting substances do not cause any deterioration of groundwater quality in the Danube River Basin District. Where groundwater is already polluted, restoration to good quality will be the ambition.

Taking into account that contamination by nitrates is a key factor against achieving good chemical status of a significant portion of the GWBs of basin-wide importance, and in line with the management objectives, it is essential to eliminate or reduce the amount of nitrates entering groundwater bodies in the DRBD. Prevention of deterioration of groundwater quality and any significant and sustained upward trend in concentrations of nitrates in groundwater has to be achieved primarily through the implementation of the EU Nitrates Directive and also the EU Urban Wastewater Treatment Directive.

To prevent pollution of GWBs by hazardous substances from point source discharges liable to cause pollution, the following measures are needed:

- an effective regulatory framework ensuring prohibition of direct discharge of pollutants into groundwater;
- setting of all necessary measures required to prevent significant losses of pollutants from technical installations;
- prevention and/or reduction of the impact of accidental pollution.

To avoid the presence of hazardous substances in groundwater aquifers, additional measures need to be taken as required under the following Directives:

- Drinking Water Directive (80/778/EEC) as amended by Directive (98/83/EC);
- Plant Protection Products Directive (91/414/EEC);
- Habitats Directive (92/43/EEC);
- Integrated Pollution Prevention Control Directive (96/61/EC).

It can be concluded that in agreement with the ICPDR's basin-wide vision, emissions of nitrates and relevant hazardous substances need to be sufficiently controlled so not to cause any deterioration of groundwater quality in the DRBD. Where groundwater is already polluted, restoration to good quality by a thorough implementation of the respective EU legislation is essential.

The ICPDR vision for groundwater quantity stipulates that the water use is appropriately balanced and does not exceed the available groundwater resource in the Danube River Basin District, considering future impacts of climate change. In line with this vision, the over-abstraction of GWBs within the DRBD should be avoided by effective groundwater and surface water management. Therefore, appropriate controls regarding abstraction of fresh surface water and groundwater and impoundment of fresh surface waters (including a register or registers of water abstractions) must be put in place as well as the requirements for prior authorisation of such abstraction and impoundment. In line with the WFD, it must be ensured that the available groundwater resource is not exceeded by the long-term annual average rate of abstraction.

The concept of registers of groundwater abstractions is well developed throughout the DRBD. The Ministry of Environment and Water in Bulgaria maintains a national register of abstraction permits. A central register of groundwater abstractions based on the National Water Law is updated annually in Slovakia. In Hungary, a Groundwater Abstractions register is published yearly and it contains data on the withdrawals of the operating, monitoring and reserve wells. In Bavaria, water suppliers are obliged to report annual data to local authorities on overall water abstraction and specific abstractions from spring sources. Bavaria and Austria cooperate on the annual preparation of a register of abstractions from the thermal water of the Lower Bavarian - Upper Austrian molasses basin (GWB1). In Romania, the national administration “Romanian Waters” maintains the national register of abstraction permits according to the National Water Law.

To prevent deterioration of groundwater quantity as well as the deterioration of dependent terrestrial ecosystems, solutions for the rehabilitation have to be explored. These should include restoration of wetland areas which are in direct contact with aquifers.

During completion of the River Basin Management Plan specific water-related problems for the significant water management issues were identified and the measures addressing those problems were proposed such as the need of continued reduction in organic and nutrient pollution loads throughout the basin principally through building of waste water treatment systems. The reduction of nutrients also needs to come about through improvement in agricultural practices and actions such as the reduction of phosphates in detergents. Even though these issues were addressed in connection with the surface waters a close link to groundwater bodies makes the proposed actions very relevant for groundwaters as well.

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ANCIENT AND PRESENT GROUNDWATER MANAGEMENT IN IRAN

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Abstract: Iran has an arid to semi-arid climate with an average precipitation of 250 mm. Water supply has been a continuous dilemma all throughout the country's documented history. The use of groundwater is unavoidable due to the lack of surface water in most parts of Iran and the seasonal nature of precipitation. Ancient Iranians managed these problems by extensive use of qanats, abanbars (small underground storages), and dams. A qanat is the most environmental method to withdraw groundwater by gravity without any energy costs, aquifer depletion, or evaporation. The overexploitation of most aquifers started in the 1960s. The main reasons were hydrological, economical, cultural, and social. The depletion of the aquifers, and consequently the water crisis, was not visible to the public for decades due to the high storage of the aquifers. The cultural and socio-economic reasons of groundwater overdrafts were population growth, economic development, urbanization, expansion of irrigated farm area, unauthorized construction of pumping wells, and use of modern technologies to easily construct more and more pumping wells. The impacts of groundwater overexploitation were the intensification of water scarcity, especially in draught years, the reduction or drying downstream qanats, wells and seepage to rivers, the degradation of groundwater quality and the increase of energy costs. Remediation methods include the reduction of overexploitation from aquifers by the use of intelligent meters, providing agricultural water from other sources, extending drip irrigation without using the water thus saved for cultivation of new farms, increasing water prices, increasing dry grain yield per unit volume of applied water, and conducting integration social researches for optimum farm management.

Keywords: Ancient water supply, water management, aquifer depletion, groundwater, qanat, overexploitation.

INTRODUCTION

Groundwater overdraft occurs when water abstraction exceeds water recharge in extensive areas and for long times, resulting in overexploitation or persistent groundwater depletion. Wade et al. (2010) provide a global overview of groundwater depletion (defined as abstraction in excess of recharge) by assessing groundwater recharge with a global hydrological model and subtracting estimates of groundwater abstraction. Their study was limited to sub-humid and arid areas. They reported that the total global groundwater depletion increased from 126 (±32) km^3 a^{-1} in 1960 to 283 (±40) km^3 a^{-1} in 2000. Groundwater overdrafts have taken place in numerous aquifers of the world. According to the United States Geological Survey, significant ground-water depletions have occurred in the High Plains' aquifers of the Midwest, many areas in the Southwest (AZ, CA, NM, NV, and TX), the Sparta aquifer in the Southeast (AR, LA, and MS), and in the Chicago-Milwaukee area (Covalla, et al., 2001). A global map of groundwater depletion for the year 2000 indicates that overdraft has occurred in central U.S.A., Spain, north-eastern China, India, Pakistan, Iran, Saudi Arabia, South Africa and Australia (Hanasaki, et al.; Wade et al. 2010).

The arid to semi-arid climate and limited surface water in most parts of Iran encouraged ancient Iranians to develop technologies such as qanats, abanbars, and water wheels to supply groundwater as efficiently as possible (FAO 2008). The qanat is the most environmental and sustainable method of groundwater withdrawal. The present system of water resource management in Iran has evolved, from its roots dating back half a century, under certain social and economic conditions such as population growth, urbanization, fundamental changes in the economic system, and modernization (Ardakanian, 2005). The economic development started by making the necessary water resources available by building dams, pumping up groundwater, and bringing in water from remote sources. Food security and sustainable agricultural productions were one of the main policies of the country. As a result of these policies and changes, the aquifers were partly depleted in order to provide enough food for 70 million people. The objective of this study was to determine the hydrogeological and socioeconomic reasons of aquifer depletion and to propose remediation methods.

POPULATION, CLIMATE, AGRICULTURE AND WATER RESOURCES

Iran covers a total area of about 1.65 million km^2, ranking 18th in the world. The total population was about 77.8 million in the year 2010, of which 30 percent are living in rural areas. About 52 percent of the country consists of mountains and deserts. Most parts of Iran are arid or semiarid. The main mountain range is the Zagros Mountains, stretching from the northwest to southeast, with numerous peaks exceeding 3,000 m amsl (above mean sea level), surrounded high interior basins. The High Alborz Mountains are located near the Caspian Sea, including the country's highest peak, namely Damavand, with an elevation of 5,610 m. amsl. The center of Iran consists of several closed basins and the eastern parts are covered by two uninhabited salt deserts.

Iran has a variable climate. In the northwest, winters are cold with heavy snowfall, springs and falls are relatively mild, while summers are dry and hot. In the south, winters are mild and summers are very hot. The center of Iran receives ten centimeters or less precipitation annually and it is very hot. The climate of Iran is generally arid to semi-arid and precipitation mainly occurs in late fall, winter and early spring., except for the Caspian Sea coasts in which precipitation occurs throughout the year. The annual precipitation ranges from 50 mm in the deserts to 2270 mm near the Caspian Sea, having an average of 250 mm. The temperature varies from -30°C in the northwest high mountains up to 55°C in the interior.

The average annual volume of rainfall is 412 billion cubic meters (BMC), of which, 92 BCM flows as surface run-off, 25 BCM directly recharges the aquifers and the rest is evaporated (Assadollahi, 2009). External water resources from neighboring countries account for 13 BCM/

year, therefore the total renewable water resources are estimated at 130 BCM/year. The total groundwater recharge is 56.5 BCM/year, by direct precipitation 25 MCM/year, surface run-off 13.2 MCM/year, and agricultural and municipal return flow 18.3 MCM/year. Part of the data presented for water resources is shared by surface and groundwater. The total water use is about 90 BCM, of which 93 % is used for agriculture and the rest for municipal uses and industries. Per capita, water usage was about 7000 and 2000 m^3/yr in 1956 and 1996, respectively, and it is predicted to reduce to less than 1300 m^3/yr in 2021. Groundwater is exploited by 37,000 qanats, 124,000 springs and 625,000 wells (Assadollahi, 2009).

Irrigated and dry farming cover 8 and 6.5 million ha (Foghi, 2003). Agriculture is mostly practiced on small farming units. From 1960 to 1993, the number of farming units increased from 1.8 to 2.8 million units, such that 72.5 percent of the landholders cultivated less than 5 ha, 22.5 percent between 5 and 20 ha, and only 5 percent more than 20 ha (FAO, 2008). Agricultural land is not a major constraint. The major constraint is the availability of water for the development of these lands. Most of the farming units are scattered within up to five different locations. The overexploitation of groundwater started about 50 years ago in some aquifers and gradually spread to most of the aquifers. However, it has recently decreased significantly by the enforcement of governmental laws. Groundwater overexploitation varies each year, resulting in an estimated average of about half a meter drop in the water table per year. Most of the overexploitation happens in the basins where less surface water is available.

The long-term objective of the Islamic Republic of Iran's Water Resources Development Plan is focused on the control and regulation of surface-water through storage dams. The numbers of dams under operation, construction and study are 588, 137 and 546, with regulated water capacities of 30.1, 12.1, and 14.8 BCM, respectively (IWPRDC, 2011). These dams also provide recreational facilities, flood control and often hydropower generation. In addition, extensive small artificial recharge basins were constructed to recharge the aquifer.

ANCIENT GROUNDWATER MANAGEMENT

Iran is among the countries with the earliest evidence of agriculture, with records going back to 4000 BC. Water supply has been a constant issue since the beginning of the country's recorded history. Most rivers in Iran are seasonal, therefore they are not capable to supply the needs of urban settlements and agricultural lands during the summer. Iranians learned to design and implement techniques for harvesting groundwater and surface water resources for irrigation including qanats, abanbars, water wheels, dams of various types, and water measurement instruments (FAO 2008).

The qanat (Kariz) was invented by Iranians in the Achamenid Era (550 to 330 BC), more than 2500 years ago (Lightfoot, 2000; Forbes, 1964; Salhi, 2008) and it spread to Egypt, Levant, and Arabia (English, 1968; Goldsmith and Hilyard, 1984). The qanat is a gently sloping conduit, draining large quantities of the groundwater of the surrounding aquifer to the surface by the use of gravity, without any pumping. The conduits are connected to the surface by a series of vertical shafts. The qanat starts at the foothills, mainly alluvium fan, where a conduit is constructed below the water table. The slope of the conduit floor is less than the slope of the corresponding ground surface, therefore the conduit eventually reaches the surface. Bybordi (1974) discussed the hydraulics of the qanat system. The conduits are usually 50 to 80 cm wide and 90 cm to 1.5 m high. The qanat length varies between 1 km and 70 km. One of the oldest and best known qanats is situated in Gonabad City, which is still providing drinking and agricultural water to nearly 40,000 people, after 2700 years. This qanat with a length of 33 km meters contains 427 vertical wells and has been constructed based on different scientific principles of physics, geology and hydraulics (UNESCO, 2007). While most archeological sites present themselves in their full splendor to every visitor, the qanat run invisibly underground, spreading over wide areas. Few people realize their value to a civilization, nor give the builders the credit and respect that they deserve (Richardson, 1983). The following are the outstanding characteristics of qanats:

1. Water is transported over long distances in hot dry climates without loss due to evaporation.
2. The essential quality of a qanat is that it taps the groundwater potential only up to, and never beyond, the limits of natural replenishment and, as a consequence, does not upset the balance of hydrological and ecological equilibrium of the region (Richardson, 1983).
3. A qanat is capable of draining the aquitard below the water table over a long distance, providing sufficient water, in contrast to the negligible discharge by pumping wells.
4. No electricity is needed to raise the water to the ground surface.
5. It is a remarkable social phenomenon. Qanats require collective and cooperative work, because individual farmers possessed neither the capital nor the manpower that was needed for construction and maintenance of the qanat system (Balali, 2009).

It is estimated that approximately 50,000 qanats were in use in Iran, with an average discharge and length of about 20 l/s and 5 km, respectively (Kuros and Labbaf-Khaneiki, 2007). These qanats once provided as much as 75 % of the water used in Iran, and irrigated about half of the land under cultivation (Wulff, 1968; Kheirabadi, 1991). Presently, there are more than 624,838 (Assadollahi, 2009) deep and semi-deep water wells throughout the country, many of which are being exploited without permit. The excessive exploitation of water through these wells has resulted in a negative water balance in most areas, such that out of 609 aquifers, 270 have a negative balance and further exploitation is prohibited. The excessive exploitation resulted in water table drop, aquifer depletion and abandoned qanats at an accelerating rate (Balai, 2009). The role of qanats in securing all of the functions of water in Iran has decreased from 75 per cent prior to 1950, to 50 per cent around 1950, and to 10 per cent in the year 2000 (Haeri, 2006; Yazdi and Khaneiki, 2007; Balali, 2009). The socio-economic reasons for qanat abandonment are as follows:

1. Farmers started to express their admiration for new pumping well technologies, because drilling a well took less than a month, while the construction of a qanat would sometimes take tens of years.
2. If the farmers wanted to increase the discharge of a qanat, they had to extend the tunnel, which would take two or three years, whereas it was easy to increase the discharge of a pumped well by deepening the well.
3. The costs of qanat maintenance are quite high, not comparable to pumped wells. In addition, budget collection from tens of qanat stockholders is no longer an easy task after social and economic changes.

An “abanbar” is a traditional water reservoir used to store drinking water in Iran. The water storage space is located below the ground surface. The reservoir is protected from wind, dust, bird droppings, evaporation, and pollution by a dome-shaped roof. Several wind towers around the dome let the dry desert air blow into and out of the dome, thus cooling the water. The reservoir is not accessible from the outside to maintain the quality of water. A tap is connected to the reservoir a few centimeters up to a meter above the reservoir bottom and this tap is accessible by a few, or at most, tens of steps. Abanbars were a routine part of life in desert regions, and were to be found in cities, villages, caravanserais, mosques, main roads, and farms.

Dam construction in Iran dates back to the Achamenid Era. The Shushtar Hydraulic System was built on the Karun River in the 5th century B.C. (Sanizadeh, 2008; UNESCO, 2009). It consists of a unique and exceptionally complete example of the hydraulic techniques designed globally and developed during ancient times to aid in the occupation of semi-desert lands (UNESCO, 2009). It is rich in its diversity of civil engineering structures, such as a regulating and diversion dam, a bridge, and two main canals. It made possible multiple uses of water across a vast territory, including the urban water supply, agricultural irrigation (4000 ha), fish farming, mills, transport, defense system, etc. (UNESCO, 2009). Various types of dams were constructed in ancient times such as the 700 and 900 year-old Saveh and Sheshtaraz gravity dams, respectively, the 700 year-old Kebar arc dam with an arc radius of 38 m, and the 400 year-old Akhlamad buttress dam (Sanizadeh, 2008).

The advanced knowledge of the Persians concerning groundwater is demonstrated by a recently discovered book by Mohammed Karaji, an Iranian scholar of the eleventh century A.D. entitled: “The Extraction of Hidden Waters”. Biswas, 1970 and Pazwash et al., 1980 presented a summary of Karaji’s book as follows: “Karaji was familiar with the general concepts of the hydrological cycle, but he never featured the whole cycle as we know it. Karaji and other Persian scholars were familiar with the basic hydrologic, geologic, and engineering principles associated with groundwater. Karaji himself exhibited skills and expertise regarding the classification of soils, the search for fresh water and the different types and hydraulic characteristics of aquifers, and invented ingenious devices employed in surveying and tunneling. Much of Karaji’s book deals with the techniques of exploring for groundwater, mainly how to dig wells and qanats. The methods he describes are still used in many parts of the Middle East and Asia.”

PRESENT GROUNDWATER MANAGEMENT

Most of the karstic and alluvium aquifers of Iran have been overdrafted since about 50 years ago through the construction of numerous illegal wells and the exploitation of more water than the permissible discharge rate. The main reasons of groundwater overdraft are hydrological, economical, cultural, and social. A significant volume of water in excess of the average recharge water is stored in all the aquifers to provide enough pressure-head to push the water toward the discharging zones such as springs, rivers and adjacent aquifers. In this study, this volume is called the “minimum hydraulic storage” (MHS). The MHS may be dynamic or static, fossil or renewal water. It is not a part of the conventional water balance equation and can be withdrawn only once and cannot be replaced under over-pumping. The volume of MHS was so significant in most aquifers that it took several decades for it to be depleted as a result of overdrafting. Therefore, the water crisis was not observed until tens of years after the beginning of overdrafting in spite of the water table drop. The wells were further deepened to withdraw the MHS below the dropped water table. This period of overexploitation with no obvious signs is named “hidden water crisis period” in this study. The water crisis was only observed when a significant part of the MHS was withdrawn from the aquifer. It can be concluded that this hidden hydrogeological characteristic of an aquifer is one of the main reasons for the water crisis in Iran. During the hidden water crisis period, hydrogeologist predicted the upcoming water crisis in several plains of Iran, such as Jahrum, Darab, Estahban, Fasa, Arsenjan, Niriz, Kazeroun, and Sarvestan, etc., but in practice the overdrafting was not halted.

The impacts of groundwater overexploitation are (a) significant reduction of the discharge of downstream springs, qanats, exploiting wells and seepage to adjacent rivers; (b) irreversible land settling and loss of aquifer storage capacity; (c) water quality degradation; (d) intensification of water scarcity in draught years, and (e) increase of energy costs resulting in higher prices of agricultural products. The social, economic and cultural reasons of overexploitation are as follows:

1. The population of the country has increased about six times since 1900. The major part of the population change occurred in the 1960s and afterward due to the reduction of mortality and the increase of birth rate. Part of the population growth in the last decade has also been due to the immigration of Afghani refugees. The direct impact of population growth on water resources was the increase of potable and irrigation water demand (Ardakanian, 2005).

2. Industrialization and urbanization, as well as better education raised farmers' expectations for a higher standard of life. Since the farms were generally small, they could provide the economic expectations of only one of the farmers' offspring. The remaining offspring were forced to look for jobs elsewhere. Since the development plans were mainly focused on agriculture, there were no big industrial plants to employ the numerous farmers' offspring. Therefore the farmers constructed illegal wells or overexploited the existing wells, cultivated pastures or planted high-priced crops having high water consumption.
3. The unauthorized wells should have been plugged-off by law, but the society had sympathy for the low-income farmers, thus preventing law enforcement.
4. The all-inclusive water resource programs of the basins were not implemented due to the pressures of the locals, resulting in water crises in the other parts of the basins.
5. The hidden water crisis was not publicized by the mass media, village councils, and scientific conferences.
6. Groundwater was free and no flow-measurement devices were installed at the well discharge points to control the farmers' uptake.
7. The government heavily subsidized delivered water, modern pressurized irrigation systems, agricultural equipment, land leveling, fertilizers, pesticides, small rate loans, etc. In spite of all the government aids, the average irrigation efficiency is still less than 33 % and the average dry grain yield is about 750 gram per 1 cubic meter of applied water at the national level, significantly less than the world average values. The majority of farmers do not follow optimized irrigation schedules or scientific methods of cultivation, maintenance and harvesting.
8. The traditional flood irrigation method had a low efficiency due to high return flow. This return flow was withdrawn by downstream wells. Drip irrigation replaced traditional irrigation methods to solve the water crisis in some of the aquifers with a negative water-balance. The return flow saved by drip irrigation was used to cultivate new lands, therefore, intensifying the water crisis.
9. The local leaders controlled the water resources in most villages, but they lost their authority due to socioeconomic changes. These changes brought about, as a result of the adoption of development models imported from the West (Foltz, 2002), the demolishing of the traditional organized system, without creating new social orders.

The only way to overcome the water crisis is to raise the water table to the level it had before withdrawing the minimum hydraulic storage. This may take several decades. The remediation methods are classified into the following: (a) reduction of exploitation from the aquifer, (b) providing agricultural water from other sources, (c) improving irrigation efficiency, and (d) increasing the dry grain yield per unit volume of applied water. These methods are explained in more detail below.

The most effective method to reduce overexploitation is to install intelligent meters which deliver no more than a specific volume of water within a growing season. Such a meter can be very effective during drought years by fairly distributing the limited water among all the exploitation wells. Increasing water prices can also contribute to less consumption. Substitution water resources include: (a) the desalinization of seawater or saline aquifers, (b) the prevention of deterioration of water resources of evaporate formations and salt diapers, (c) the treatment of municipal and industrial wastewater, (d) the use of fossil water, and (e) the use of virtual water. There are a total of 120 salt diapers in Iran which deteriorate the quality of adjacent karstic aquifers. Even a few liters per second of brine having a total dissolved solid content of 330,000 g/l is enough to increase the salinity of karstic aquifers to levels unsuitable for agricultural purposes (Zarei and Raeisi, 2010). The desalinization of saline water aquifers is a promising option, especially by use of solar energy technology. A qanat at the contact of a salt diaper and a karstic aquifer can drain the salt diaper brine. Another option is to transfer excess water from basins with high surface water to areas having water shortage problems. This option is unlikely because there is no excess water in most of the basins. Cloud seeding is not a recommended method since most of the precipitation fronts terminate in Iran, and seeding them can create severe problems in deserts and nearby aquifers. Water inefficient crops which have large requirements of water per kilogram of product, like rice, may be imported as “virtual water”, to reduce the water demand.

Improving irrigation efficiency has been recommended in literature to reduce water withdrawal. However, the term “higher irrigation efficiency” can potentially be misleading in negative water balance aquifers. Reduction of return flow improves the irrigation efficiency, but it reduces the available water downstream. Therefore the term “evaporation loss prevention” is recommended instead of “improving irrigation efficiency”. This can be explained by considering that drip irrigation can significantly reduce the evaporation, thus enabling farmers to expand their original cultivation surface area, causing a shortage of water downstream. Therefore, drip irrigation is only recommended when the cultivation area is not expanded and the scientific criteria, especially crop-water requirements, are implemented. Land leveling reduces surface run-off and inundation in furrows and border irrigations, preventing evaporation from conveyance canals. Greenhouse cultivations are other ways to reduce water withdrawal from aquifers. All of the mentioned methods are capable to reduce the over-pumping if farm management is significantly improved. The essential requirements for proper farm management is the farmers’ cooperation, which itself requires the improvement of education and the alleviation of social and cultural constraints. For example, the integration of small farm units is rejected by the farmers. The solution of social and cultural problems requires extensive multi-disciplinary researches by a team of hydrogeologist, sociologist, psychologist, extension and education specialists, local religious leaders and local leading characters.

CONCLUSIONS

Most of the agricultural lands in Iran are located in arid and semi-arid climates with no precipitation during the summers. The use of the groundwater is unavoidable due to the lack of permanent rivers and the seasonality of precipitation. Iranians invented qanats to transfer groundwater by gravity to the surface without energy costs and evaporation. In addition, qanats do not cause overexploitation problem. They are also capable of draining considerable amount of aquitard water, compared to the negligible discharge of pumping wells. Population growth, urbanization, modernization of agricultural technologies, economic development, social and cultural changes, and the absence of big industries in rural areas to employ the number of farmers’ offspring in excess of the farms’ labor demands, have all lead farmers to extend their cultivated lands by constructing unauthorized pumping wells or withdrawing water over the permissible levels. The overexploitation resulted in the depletion of the minimum hydraulic storage. The volume of minimum hydraulic storage was so significant in most aquifers that the water crisis was not noticed until tens of years after the beginning of overdrafting. This period of overexploitation with no obvious signs is named the “hidden water crisis period” in this study. The impacts of overdrafting include water table drop, desolation of numerous qanats, reduction of discharge of downstream springs and wells, increased energy costs, increased groundwater contamination, and the intensification of water scarcity in draught years.

Remediation methods include reduction of exploitation from aquifers by use of intelligent meters, providing agricultural water from other sources, increasing water prices, using drip irrigation without extending farm areas, increasing dry grain yield per unit volume of applied water, and integrating research to encourage farmers to further cooperation for optimum groundwater management. New water supplies include desalinization of seawater or saline aquifers, prevention of intrusion of evaporate formations and salt diaper brines into karstic and fresh water aquifers, treatment of municipal and industrial wastewater, and the use of fossil and virtual water. Drip and sprinkler irrigations are recommended only if the farm area is not extended as a result of the saved water from return flow, as return flow is being used by downstream wells for irrigation. Using the saved water of return flow for cultivating new land only intensifies the water crisis in the basins. The transfer of water from other basins is no longer an option, because there is simply no excess water left. Cloud seeding is also not recommended, because it has severe impacts on the other parts of Iran with very low precipitation.

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Notes:

Extended Abstract
Invited Paper

GROUNDWATER IN THE DEVELOPING WORLD: AN ASSESSMENT OF SUSTAINABILITY IN A CLIMATE CHANGING WORLD

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INTRODUCTION

Globally, ground water use has undergone dramatic expansion over the past 50 years, with global abstraction rates increasing from an estimated 100-150 cubic kilometers in 1950 to 950-1000 cubic kilometers in the year 2000. Much of this growth is the result of agriculture where, for example, in Bangladesh, the area irrigated by groundwater (as a fraction of total irrigated area) grew from 4% to 70% between 1972 and 1999 (Mainuddin 2002). Additional concerns are that increasing water demands are also in response to urban growth and the population explosion. The result is that the growth in demands for water has been so large in the developing world in particular, that serious questions exist in terms of sustainability. In light of the combined effects of climate change and population growth, will larger groundwater withdrawals to meet the water supply needs be sustainable?

Currently it is estimated that 8.2% of annually renewable groundwater on a global scale is being extracted for human use but the regionality of the withdrawals are such that some regions are experiencing declining groundwater levels. While there are many advantages to use of groundwater as a water supply source, when available, globally only about 2% of all worldwide precipitation goes to groundwater. The bulk of global groundwater use is concentrated in a relatively few nations, namely Bangladesh, China, India, Iran, Pakistan, and the U.S.A., where approximately 80% of global groundwater use is presently concentrated.

Estimates of the extent and magnitude of global groundwater use are listed in Table 1 (after Shah et al., 2007). Globally, groundwater is estimated to provide about 50% of current potable water supplies, 40% of the demand of self-supplied industry, and 20% of water use in irrigation (after UNESCO, 2003). Using current trends and extrapolative models, Rosegrant & Cai (2002) predict global groundwater withdrawals to increase from 817 km^3/year in 1995 to 922 km^3/year by 2025.

In India and China (two of the world's largest users), use is predicted to increase by 27 km^3 by 2025 despite predicted reductions in the most severely mined areas.

Table 1: Extent and magnitude of the global groundwater revolution

Country/region	Annual groundwater use (km^3)	Number of groundwater structures (million)	Extraction/ structure (m^3/year)	Percentage of population dependent on groundwater
India	150	19	7900	55-60
Pakistan-Punjab	45	0.5	90000	60-65
China	75	3.5	21500	22-25
Iran	45	0.5	58000	12-18
Mexico	29	0.1	300000	5-6
USA	100	0.2	500000	<1-2

The nexus of increased groundwater use and the energy needs to pump the groundwater, demonstrates the important relationship between energy pricing and the influence on groundwater withdrawals. The pricing structure used in a number of countries is exacerbating the groundwater withdrawal issue where, in southern India for example, energy used in agriculture is free, and consequently, is bankrupting many electrical utilities.

The extrapolation to the future is foreboding as climate change will increase evapotranspiration rates and hence irrigation needs. It is noted that although rainfall rates are expected to increase in many countries, the increased intensity of the precipitation will not necessarily increase infiltration rates. The bases for these general characterizations are demonstrated in a case study application in Bangladesh.

CASE STUDY ASSESSMENT IN BANGLADESH

Figure 1 depicts the historical temperature trends in Bangladesh for annual/August and January conditions, all of which demonstrate statistically significant increasing trends. Climate change projections using four of the Global Circulation Models (GCMs) indicate the projected trends for Bangladesh represent continuation of increased temperatures, but with an increased rate of change with time. Some amelioration of the rate of these increased temperatures occur if the various countries attain their committed levels of emission reduction, but even under these assumptions, the expectation is there will be some increases in annual average temperatures, as depicted in Figure 2.

In parallel, there have also been some increases in precipitation, and the GCMs predict modest (e.g. approximately 15 percent) increases in precipitation rates into the future, as illustrated in Figure 3. However, it is important to note that the increases in precipitation rates are expected in one month, namely July, which is already a very wet month, as indicated in Table 2; for the considerable majority of the months, the precipitation levels are projected to decrease, such that in October, for example, the precipitation rates will decrease to 72% of current precipitation levels. Hence, when monthly conditions are currently 'wet', they will get wetter, and when monthly conditions are currently dry, they will get drier.

The projected increased temperatures translate to higher potential evapotranspiration rates, as indicated in Figure 4. These projections indicate that irrigation water demands will increase; with the lesser rates of precipitation, the result is that Bangladesh will look to greater withdrawals from groundwater to meet the water demands.

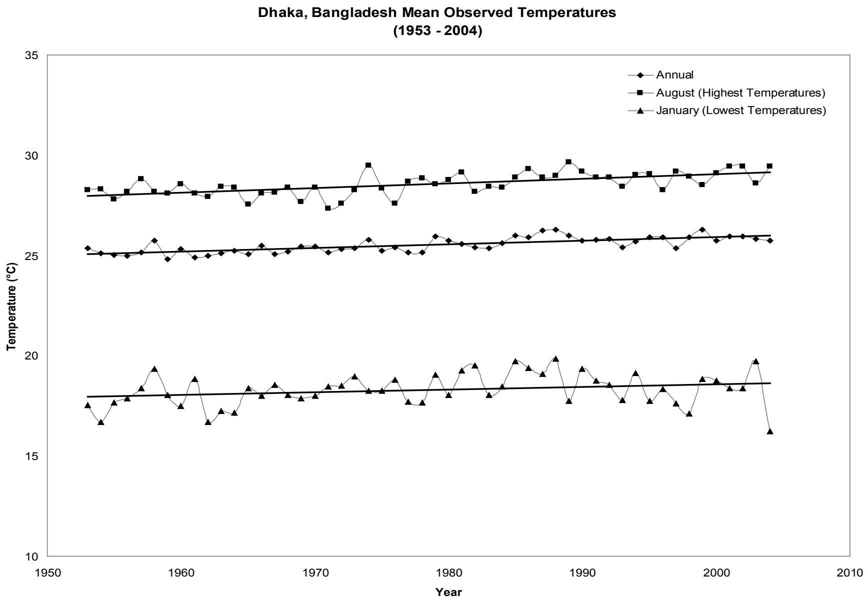

Figure 1: Historical Trends in Temperature in Dhaka, Bangladesh

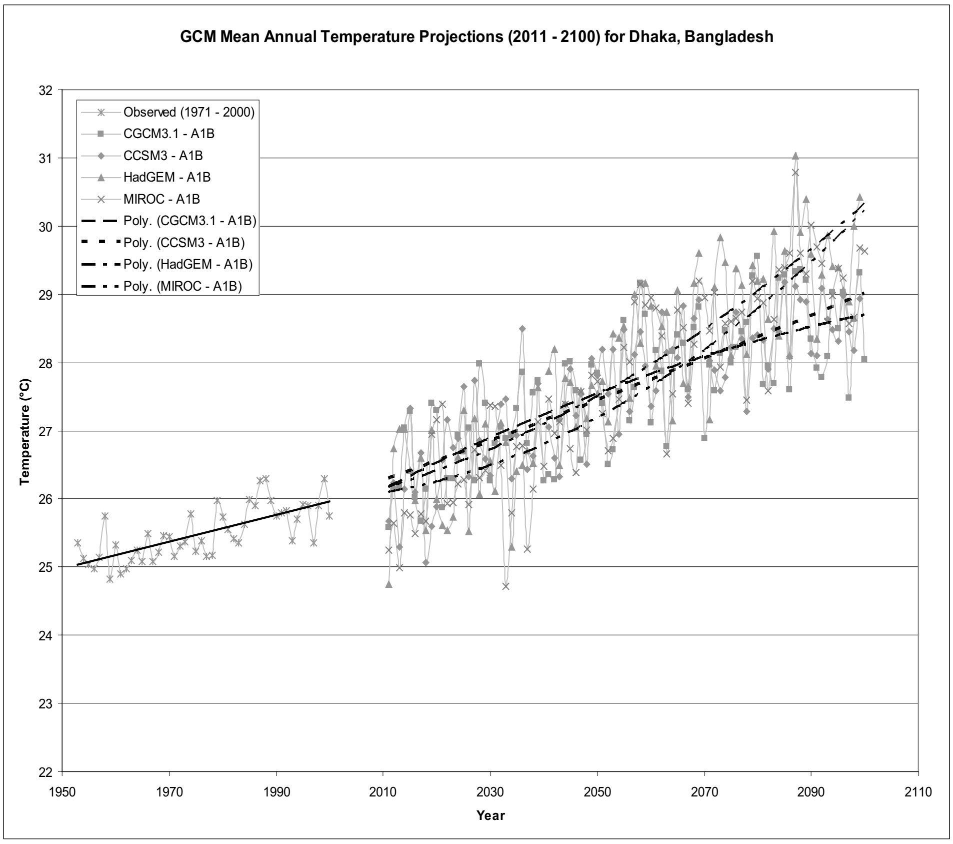

Figure 2: Projections of Annual Temperatures (2011-2100) for Different GCMs

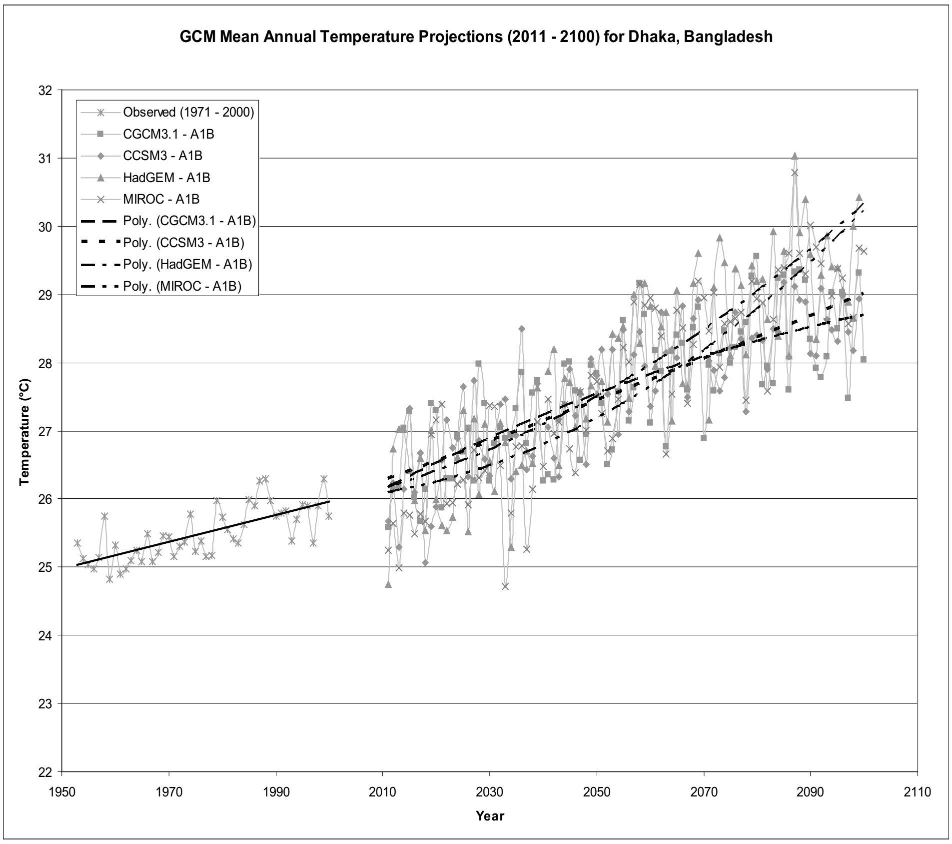

Figure 3: Annual Precipitation Quantities (Historical and Projected) for Dhaka, Bangladesh

Table 2: Ratios (Projected/Historical) for Precipitation in Dhaka, Bangladesh

Month	Projected Temp Change for Individual Months (ºC)	Precipitation in 2000 (mm/in month)	Projected Ppn in 2100 (mm/in month)	Ratio Ppn (2100)/ Ppn (2000)
January	2.0	118	98	0.83
February	2.5	93	89	0.96
March	2.2	106	95	0.89
April	1.5	102	73	0.71
May	2.0	108	78	0.72
June	1.4	104	75	0.72
July	1.6	431	542	1.26
August	2.2	431	432	1.00
September	2.4	283	262	0.92
October	2.2	159	115	0.72
November	1.7	100	75	0.75
December	1.8	104	81	0.78

While irrigation in Bangladesh is conducted primarily from its mega deltas, India's diversion from the Ganges using the Farruka Barrage may significantly decrease the flows in the Ganges which will exacerbate demands on groundwater. In this context, the current situation of declining groundwater levels must be considered. As Shamsudduha et al. (2009) indicate, although seasonality dominates the variance in groundwater levels in the shallow aquifers in Bangladesh, declining water levels indicate that the shallow aquifers are not being fully recharged each year under current conditions, where they are demonstrating a decline at the rate of 0.1 to 0.5 m/yr.

These results clearly demonstrate that there are areas of unsustainable groundwater withdrawal already being demonstrated. For the reasons indicated in the preceding sections of this paper in relation to climate change, widespread conditions of unsustainable appear to be poised to become much more challenging in the future.

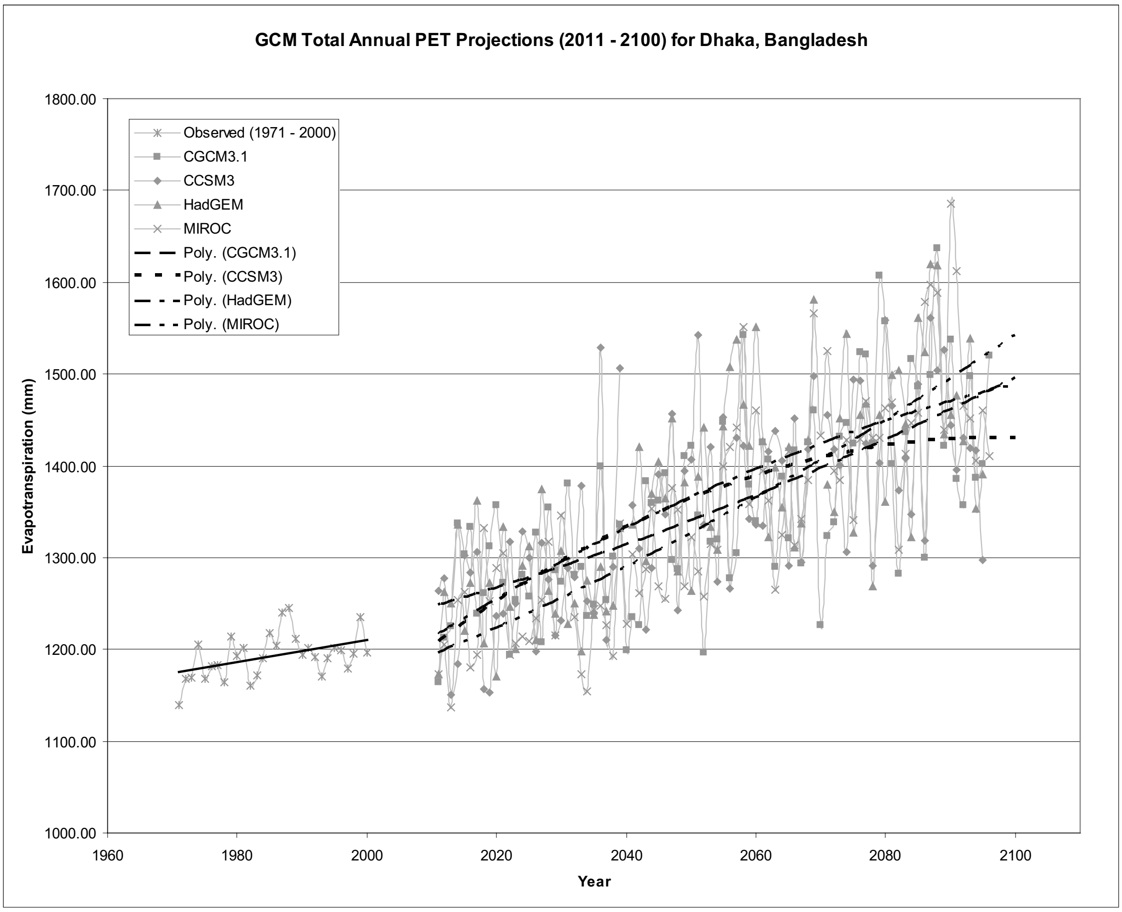

Figure 4: Historical and Projected Evapotranspiration Rates for Dhaka, Bangladesh

CONCLUSIONS

Groundwater withdrawals over the last four decades have been substantial and important, in meeting the burgeoning needs of the agricultural sector and increasingly so, the needs of the urban sectors. However, the ability to respond to the existing and projected increased needs, including the increasing populations, has limits. The situation, in light of climate change, however, is even more foreboding as the ability to rely on groundwater resources is going to be severely limiting. While issues of the challenges to sustainability were only demonstrated using one country (Bangladesh), the message is consistent across many parts of the world. The potential to use increased groundwater withdrawals as the response to climate change, is very limited in most countries.

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THEME 1:

PREPARATION AND IMPLEMENTATION OF THE GROUNDWATER COMPONENT OF WATER MANAGEMENT PLANS FOR LARGE BASINS

Invited Paper

MANAGEMENT OF TRANSBOUNDARY GROUNDWATER BODIES UNDER THE ICPDR

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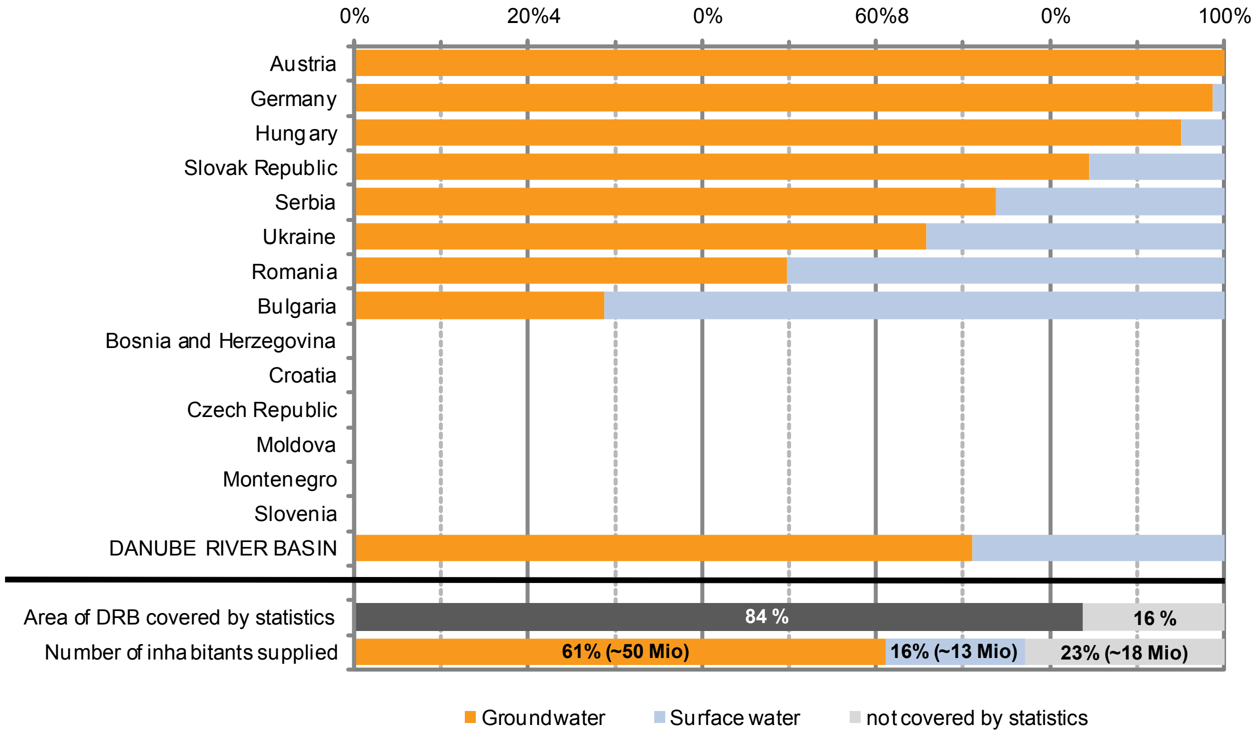
Abstract: Groundwater is of major importance in the Danube River Basin. At least 50 Mio of 81 Mio inhabitants in the Danube River Basin are served by drinking water from groundwater. To acknowledge this importance and to address the challenges of the implementation of the Water Framework Directive, the Groundwater Task Group was established within the ICPDR framework in 2004 to tackle all relevant groundwater issues of basin-wide concern. The Groundwater Task Group contributes to the transboundary harmonization of the implementation of the Water Framework Directive and the Groundwater Directive of Danube River Basin concern; it provides the ICPDR with information on the status of groundwater and coordinates the monitoring programmes necessary to ensure that the appropriate information is available. As ICPDRs focus is on issues of basin-wide importance, the groundwater domain of the ICPDR is focused on eleven bi-/multilaterally nominated important transboundary groundwater bodies of basin-wide importance.
Keywords: Groundwater management, Danube River Basin, Transboundary

INTRODUCTION

The importance of groundwater in the Danube River Basin (DRB) can be best pointed out by the fact that groundwater is the major source of drinking water. Best available data and estimates from eight Danube countries representing 81% of the population (~63 Mio) and 84% of the area of the Danube River Basin impressively demonstrate that about 70% of the drinking water is produced from groundwater, serving nearly 50 Mio (61%) of the 81 Mio inhabitants living in the Danube River Basin. In addition to the overall statistics for the whole Danube River Basin, Figure 1 illustrates the shares of groundwater and surface water as sources of drinking water production for the area of the DRB in the eight countries where data and estimates were available (ICPDR, 2010a).



Note: The statistics given for the countries do not refer to the countries as a whole but only to the areas of the Danube River Basin within these countries.

Note: Contrary to the definition in the OECD questionnaire, bank filtered water was agreed by the Groundwater Task Group to be considered as groundwater.

Reference year of the data: 2006 (Serbia), 2007 (Bulgaria, Germany, Romania and Ukraine), 2008 (Hungary, Slovak Republic), 2009 (Austria)

Number of inhabitants supplied: For 3.4 Mio inhabitants in Bulgaria, no information about the source of drinking water was available.

Austria:	Less than 1 % of drinking water is abstracted from surface water (negligible).
Bulgaria:	The share of population supplied by the different sources was not available.
Germany:	Number of inhabitants supplied is roughly estimated, based on the abstraction ratio and the total number of inhabitants.
Romania:	The figures of water abstraction for private households are only rough estimates based on a water consumption rate per capita of 112 l/day.
Serbia:	Presented data do not include water abstraction of the population of Kosovo. Data for public water supply were estimated based on the percentage of population living in the DRB part of Serbia. Data for the abstraction of private households were estimated, based on the percentage of population not connected to public water supply systems (approx. 20 % or 1.4 Mio. inhabitants).
Slovak Republic:	With respect to the SHMI categorization of the use of GW, data on private households were not available.
Ukraine:	The statistical data refer to water usage and not to water abstraction. Data refer to public water supply; the abstraction for private households is unknown.

Figure 1: Drinking water abstraction by source in the Danube River Basin (ICPDR, 2010a)

Due to the heterogenic situation in the Danube River Basin (e.g. different hydrogeological, topographic, climatic, pressure and pollution conditions), the share of groundwater used for drinking water purposes in the DRB part of the single Danube countries varies and ranges from 30% (DRB part of Bulgaria) to 100% (DRB part of Austria).

Apart from the drinking water aspect, groundwater is an important resource for industry (cooling purposes, food etc.), agriculture (e.g. irrigation) and thermal water supply (balneology, heating purposes). Furthermore, it plays an essential role in the hydrological cycle, being critical for the maintenance of wetlands and feeding river flows. It acts as an important buffer during dry periods and it provides base flow to many surface water systems.

GROUNDWATER TASK GROUP WITHIN THE ICPDR

During the process of implementing the EU Water Framework Directive (WFD, 2000/60/EC) throughout the entire basin of the Danube River and the preparation of the Danube River Basin Management Plan (DRBM Plan) many technical questions arose especially concerning the identification of transboundary groundwater bodies (GWBs) of basin-wide importance, bilateral agreements and harmonisation of the management activities. To address those challenges, the ICPDR Contracted Parties established the Groundwater Task Group (GW TG) in 2004 to deal with groundwater related issues of basin-wide concern.

Beside the key objective of the GW TG to support the implementation of the WFD and the EU Groundwater Directive (GWD, 2006/118/EC) in the Danube River Basin District, it also provides the ICPDR with information on the state of the ICPDR GW-bodies and, in line with the Danube River Protection Convention (DRPC) and the relevant EU legislation, coordinates the monitoring programmes necessary to ensure that the appropriate information is available.

The work programme of the GW TG is laid down in Terms of Reference and a mandate which specify responsibilities and main tasks and deliverables in the sector of groundwater management.

All the principles and decisions within the Groundwater Task Group are summarised in a guidance document (ICPDR Groundwater Guidance, ICPDR, 2010b) which is regularly reviewed and updated. It comprises the particular groundwater related procedures according to the needs within the ICPDR framework, provides brief technical information on the nomination, characterisation and grouping of GW bodies and necessary explanation on monitoring parameters, on aggregation procedures, on data reporting including reporting frequencies and templates, on the presentation of status and reporting on the programme of measures in order to contribute to a harmonisation and coordination of approaches within the Danube River Basin.

CONTRIBUTION TO THE IMPLEMENTATION OF EU LEGISLATION

The GW TG fosters and supports international coordination as required by the WFD and GWD and acts as a platform for facilitation and promotion of transnational coordination and harmonisation of their implementation by the ICPDR Contracting Parties.

It is not the aim of the GW TG to duplicate any assessments carried out by the Danube countries at the national level but to compile the available results as far as they are relevant on a Danube basin-wide scale. Following the subsidiarity principle of the implementation of EU legislation, Member States apply their own, national criteria and approaches (e.g. for the risk assessment, status assessment, establishment of groundwater threshold values, etc), which may lead to different results available for the national parts of the important transboundary groundwater bodies of basin-wide concern in the Danube River Basin (ICPDR GW-bodies).

Beside the identification of relevant GWBs, which is described in the following chapter, the GW TG dealt with groundwater related aspects of the analysis of pressures and impacts (Article 5 WFD), the identification of significant water management issues (Article 14 WFD), the report on establishing monitoring networks (Article 8 WFD) and of the Danube River Basin Management Plan 2009 including the Joint Programme of Measures (Article 13 WFD). Details can be found in the paper: Groundwater issues in light of the Water Framework Directive in the Danube River Basin.

TRANSBOUNDARY GROUNDWATER BODIES OF DANUBE BASIN-WIDE IMPORTANCE

In order to allow the ICPDR to focus on the issues of basin-wide concern, criteria were developed for identifying those transboundary GWBs which are of basin-wide importance. The selection criteria of "importance" do not only consider size (> 4,000 km²) but also importance due to various other criteria like pressures or utilization, which must be bilaterally agreed upon. Nevertheless, all nominated GWBs must be transboundary and bi-/multilaterally agreed.

Bilateral/multilateral discussions and agreements concerning the identification of such GWBs of basin-wide importance lead to the nomination of 11 important transboundary GWBs or groups of GWBs (ICPDR GW-bodies). ICPDR GW-bodies are divided into national parts of ICPDR GW-bodies which can furthermore consist of a number of individual national GWBs. Only ICPDR GW-bodies and national parts of ICPDR GW-bodies are under the focus of the GW TG and TNMN Groundwater.

Table 1 lists the 11 nominated ICPDR GW-bodies together with the Danube countries sharing the GWBs, the size of the GWBs, the thickness of the overlying strata, the bi-/multilaterally agreed criteria of importance as basis for nominating the GWBs and the groundwater chemical and quantitative status as reported within the DRBM Plan 2009 under the WFD.

Table 1: Nominated transboundary groundwater bodies of Danube River Basin wide importance

GWB Code	Countries	Size [km²]	Overlying strata [m]	Criteria for importance	Status	
					Quality	Quantity
GWB-1	DE-AT	5,900	100–1,000	Intensive use	Good	Good
GWB-2	BG-RO	30,147	0–600	> 4,000 km²	Good	Good
GWB-3	RO-MD	21,626	0–150	> 4,000 km²	Good	Good
GWB-4	RO-BG	7,027	0–10	> 4,000 km²	Good	Good
GWB-5	RO-HU	7,699	2–30	GW resource, DRW protection	Poor	Good
GWB-6	RO-HU	2,475	5–30	GW resource, DRW protection	Good	Good
GWB-7	RO-RS-HU	29,012	0-125	> 4,000 km², GW use, GW resource, DRW protection	G/G**/P	G/P**/P
GWB-8	SK-HU	3,363	2–5	GW resource, DRW protection	G/P	Good
GWB-9	SK-HU	2,216	2–10	GW resource	Good	Good
GWB-10	SK-HU	1,090	0–500	DRW protection, dependent ecosystem	Good	Good
GWB-11	SK-HU	3,811	0–2,500	Thermal water resource	Good	G/P

** based on risk assessment data G…Good, P…Poor

GROUNDWATER STATUS

As ICPDR's focus is on basin-wide concern and as decided by the GW TG, the result of the status assessment is illustrated for the whole national part of an ICPDR GW-body.

Criteria have been developed for the uniform presentation of status results at the basin-wide level, taking into account the status assessment at the level of national GWBs. These criteria included a commonly agreed concept of confidence of status presentation, which took into account the specific cases of aggregation of national-level GWBs to national parts of ICPDR GW-bodies.

If a national part of an ICPDR GW-body consists of several individual national-level GWBs then the poor status of only one national-level GWB is decisive for characterizing the whole national part of an ICPDR GW-body in poor status.

High confidence expresses that all national-level GWBs forming a national part of an ICPDR GW-body show the same status (either all good or all poor). Medium confidence is assigned when national-level GWBs show different status results within one national part of an ICPDR GW-body. Low confidence indicates that the status assessment is based on risk assessment data (see Figure 2). The level of confidence is color coded together with the groundwater status and illustrated in the maps on groundwater chemical and quantitative status.

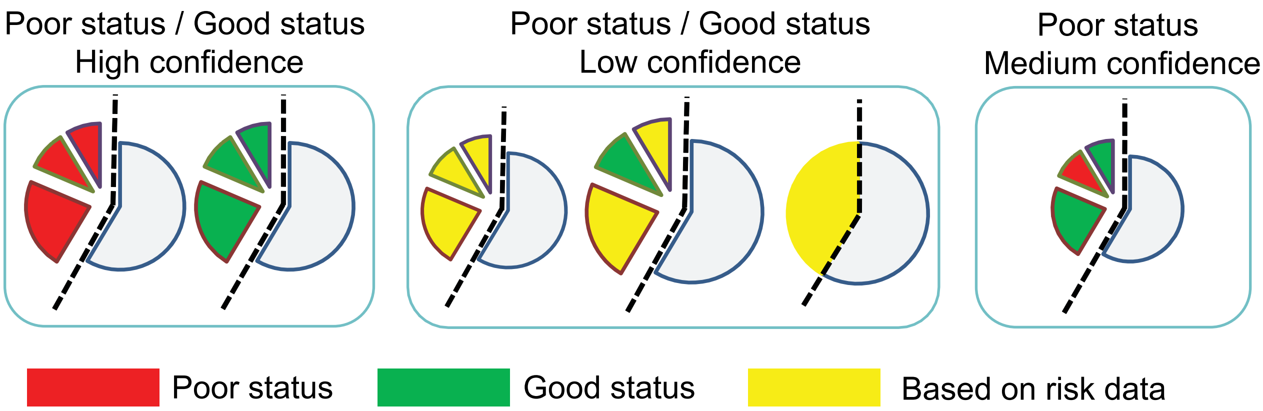


Figure 2: Concept of confidence in the groundwater status assessment (ICPDR, 2010b)

As reported in the DRBM Plan 2009 and listed in Table 1, in 8 out of 11 ICPDR GW-bodies all national parts are of good chemical status. In two ICPDR GW-bodies, poor chemical status was observed in one national part, in one GWB both national parts were identified to be in poor chemical status. The poor chemical status, which was identified for four out of 22 evaluated national parts of ICPDR GW-bodies, was caused by nitrates in each case and additionally by ammonium in one case.

Poor status can be caused by more than one reason. In addition to the failed general status assessment of the GWBs as a whole for nitrates in all national parts, in one case the WFD Article 4 objectives for associated surface waters could not be achieved for nitrates and increasing trends for nitrates and ammonium already exceeded the starting points of trend reversal. In one case the objectives of WFD Article 7 regarding the drinking water protected areas (avoid deterioration of water quality to reduce the level of purification treatment) could not be met for nitrates as well.

The results of the chemical status assessment (considering the confidence in the assessment) are illustrated in the following map (Figure 3).

Good quantitative status was observed in all national parts of 9 out of 11 ICPDR GW-bodies (Table 1), in two ICPDR GW-bodies, good quantitative status was observed in only one national part.

In two cases poor quantitative status was caused by groundwater abstractions exceeding the available groundwater resources; in one case by significant damage to groundwater dependent terrestrial ecosystems and in one case by damage to associated surface waters (springs). In the case of the national part of one GWB, former mining activities still have an impact on the quantitative status and for one national part over-abstraction lowers the groundwater tables, increases pumping costs for users and poses threats to an intrusion of deep mineralized waters. The results of the quantitative status assessment (considering the confidence in the assessment) are illustrated in the following map (Figure 4).

Based on the risk assessment and the status assessment programmes of measures have to be implemented and made operational by 2012 in order to enable the achievement of the environmental objectives laid down in Article 4 of the WFD by 2015 at the latest. At the basin-wide level ICPDR's Joint Programme of Measures builds upon the national programmes of measures but represents more than a list of national measures as the effect of national measures on the Danube basin-wide scale is also estimated.

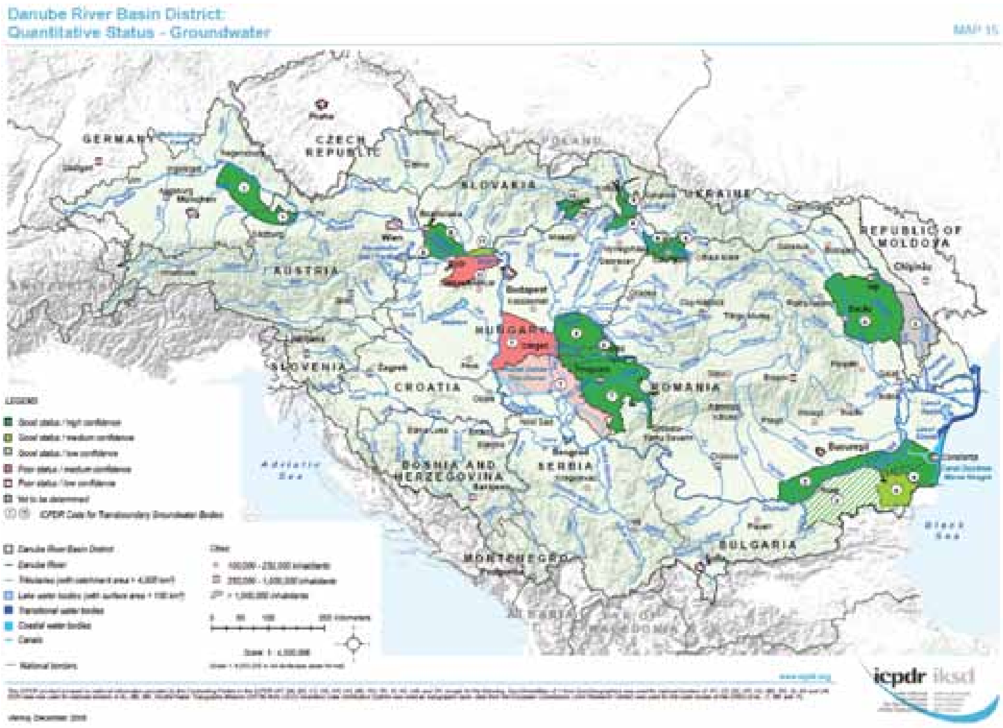


Figure 3: ICPDR GW-bodies – Chemical status of groundwater (ICPDR 2009)

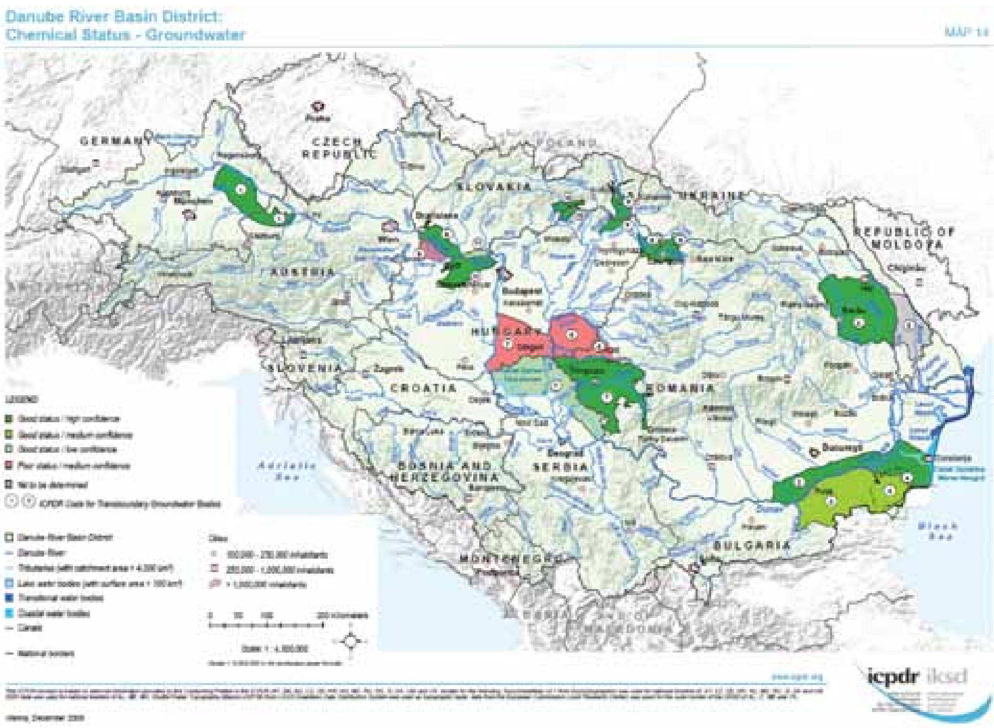


Figure 4: ICPDR GW-bodies – Quantitative status of groundwater (ICPDR 2009)

OUTLOOK

The implementation of the WFD and the GWD follows a cyclic procedure and future important steps in the implementation of EU legislation in the Danube River Basin District focus on:

- contribution to the progress report on the implementation of the Joint Programme of Measures which is due in 2012,
- further promotion and development of common conceptual models for the ICPDR GW-bodies,
- revision of the nominated ICPDR GW-bodies, and
- review and update of the Danube Basin Analysis (WFD Article 5) in the light of the second River Basin management Plan.

According to the ICPDR Transnational Monitoring Network for Groundwater (GW TNMN) it is foreseen to collect and present every 6 years monitoring data for a set of parameters for each GWB of basin-wide importance. The collection started in 2010 for the first time in order to provide an overview of the groundwater quality.

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Notes:

INVITED PAPER

INNOVATION AND EFFICIENCY FOR GROUNDWATER MANAGEMENT CHALLENGES FOR EUROPEAN POLICY

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Abstract: The new approach for water efficiency should bring down barriers to innovation in the field of urban and rural hydrology as well as of industrial water use. The main challenges for groundwater management are located in trans-boundary water management, in artificial groundwater recharge to meet water scarcity especially for drinking water supply and in the risk assessment for groundwater protection.
Keywords: European Commission, groundwater recharge, climate change, water treatment, networks

INSTRUMENTS OF THE EUROPEAN COMMISSION

The new position of European water policy is based on a sustainable and efficient water use and at the same time on an innovative development of water technology.

The "Water Supply and Sanitation Technology Platform WssTP" was promoted by EC to improve the efficiency of water research driven by industries enabling proper drinking water and sanitation services. This public-private co-operation should bring the research to the market. New initiatives represent a shift towards a stronger interest regarding water challenges that calls for stronger coordination, integration and innovation in Europe. The Pilot Program of WssTP is an organizational structure covering research and technology development. On the other hand a Task Force is a working group handling cross-cutting issues of several Pilot Programs. Most effective is the "Member States Mirror Group MSMG", an associated body of the WssTP consisting of official delegates from Member States and Candidate Member States. These official representatives transmit the interests of their states at the European level thus contributing to an European R&D strategy with the aim of more sustainable protection and utilization of water resources and provision of water services in Europe (WssTP 2010).

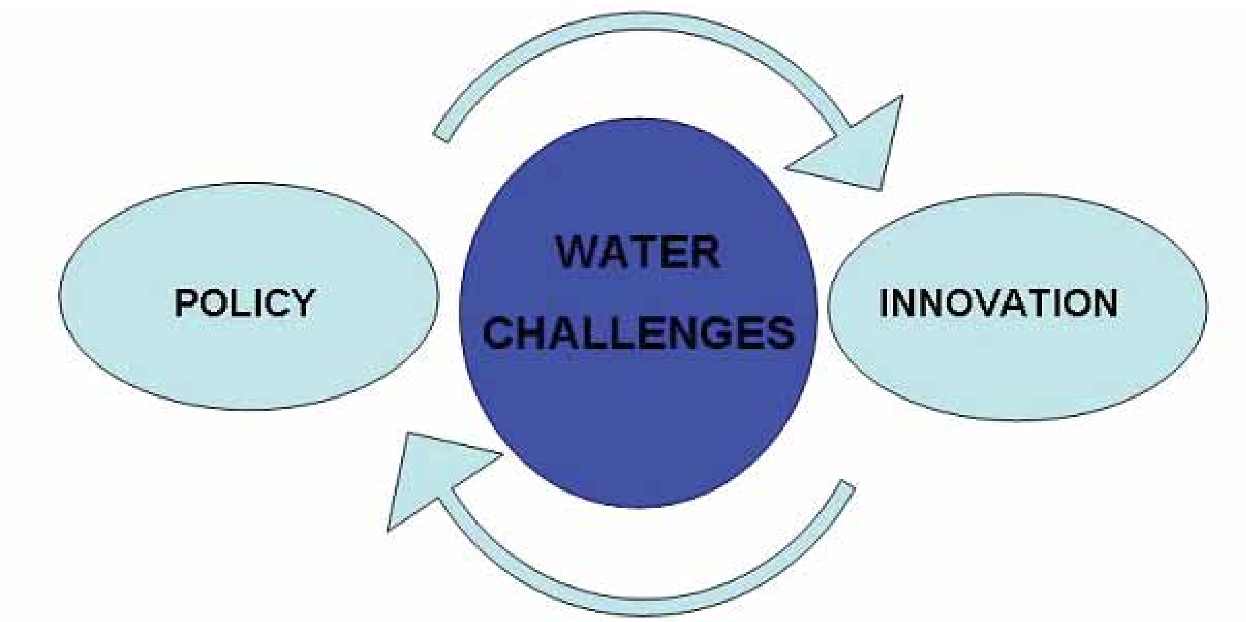

Figure 1: DG Environment (2011)

The Joint Program Initiative JPI on “Water Challenges in a Changing World” has the goal to harmonize national research programmes and to initiate public-public co-operation (JPI 2010). It is based on:

- the prevention of negative effects of bio-based economy on the water system,
- searching for a sustainable balance in the ecosystem,
- achieving healthier water systems for a healthier society and
- closing the water cycle gap by reconciling water supply and demand.

The research driven European Innovation Partnership EIP on “Water Efficient Europe” is considered as a synoptic “Europe 2020 Flagship Initiative” to ensure the availability of water for households, agriculture, industry and the environment. The key components are summarized in 3 work packages:

- water for urban areas
- water for rural areas
- water for industry

The programme should be executed by both, the DG for Environment and the DG for Research and Innovation, and it will also be operated by the DG Regio (DG Environment 2011).

Challenges for water management with special regard to groundwater

- The world population will increase between 2000 and 2050 by 47% from 6.1 billion in the year 2000. This will result in a need for more water for drinking and food production. Furthermore an impact on water infrastructure will reach remarkable dimensions.
- Climate change will increase disequilibria of ecosystems, floods and droughts will occur with higher frequency.
- The change to a bio-based economy will affect on groundwater storage because of altered infiltration conditions.
- Land use changes are usually associated with a higher need for water for agriculture and in many cases with a decrease of natural groundwater recharge.

HOW WE CAN MEET THESE CHALLENGES

Quality demands

A clear labelling of water withdrawal regarding the quality demands of end users is essential. One has to distinguish between water for drinking and for different uses in industry, agriculture and energy generation. The latter includes water power and geothermal use. With regard to drinking water globally it makes less than 10% of the whole water-use. Consequently we should follow the philosophy to provide the consumers, wherever possible, with natural untreated groundwater, based on a proper quantitative and qualitative protection. However, strategically quantity and quality requirements of the different user' branches have to be taken into account. The chemical composition of water for industrial use must fulfil special requirements. For tourism the sustainability of water supply is of major economic importance. Very essential aspects for agriculture are availability of water (surface water, groundwater) and optimised irrigation practices.

Groundwater utilization

Groundwater will be utilized preferentially for drinking purposes as a consequence of the risk of airborne pollution to water systems open to the atmosphere. This approach is backed once more by the accident in Fukushima 2011. There, long-lived radioactive isotopes were released to the atmosphere and the fallout reached the open reservoirs for drinking water storage. This induced a significant and dangerous radioactive pollution. When using groundwater, radioactive isotopes of Strontium-90 and Caesium-137 are retarded in the soil zone.

Climatic change

There are two possible approaches to meet climatic change: While mitigation aims at reducing the causes and negative impacts, adaption aims at learning to cope with the changes. For the water sector a combination of both strategies appears most promising. Water scarcity and droughts are expected to increase due to climate change, especially the increased frequency and severity of these extreme hydrological events are impacting civil society and ecosystems.

Regarding water supply, resources management with its quantity and quality issues should be kept for the future within public responsibility. On the other hand the provision of services and the maintenance of supply systems is becoming an important national and international free market and might be privatized.

Artificial groundwater recharge

Managed groundwater recharge comprises a wide variety of systems in which water is intentionally introduced into an aquifer (Grützmacher et al. 2010). The objective is to store excess water for times of low water availability and to reduce the risk of groundwater contamination by setting underground barriers. In the context of alternative water resources this technique could enable the efficient use of resources as raw water like storm water, high flows from springs, not contaminated surface water or collected precipitation water. In coastal aquifers saltwater intrusion and mixing processes decrease the reserve of fresh water resources. According to the seasonal changes of salinity, coastal aquifers can only be utilized in time periods, when the static pressure of the fresh water component is high and the fresh/sea water interface in the aquifer is forced very much towards the sea. Recharge of fresh water from this period through well galleries and infiltration ponds will create a hydraulic barrier protecting wells further inland from saline intrusion. Alternatively, the coastal fresh water can be infiltrated into aquifers not connected to the sea and exploited in times of water scarcity.

Trans-boundary water management

In total there are 261 trans-boundary river or lake basins worldwide; 23 of them are located in regions with four or more adjacent states. Trans-national water use has become a factor for regional conflicts, because allocation of groundwater resources is associated with a disadvantage of down-river parts of a basin. The situation is further aggravated by technical constructions like dams or by water pollution. All these technical configurations should be regulated considering:

- the sources of transnational water use,
- why transnational water use became an international problem and
- water as a conflict factor.

Therefore, the establishment of an international convention on water allocation is essential. Eventually water should be considered as a catalyst for regional cross-border co-operation and not as a source of conflicts.

Disaster management

The effects of climatic change on the water cycle lead to disaster management recognizing extreme hydrological events and, therefore, require effective disaster management. Uplands and lowlands within river basins are linked through the hydrologic cycle. Thus, floods in the lowlands can be caused by storm events in higher located regions; droughts in mountainous areas, connected with a drastic decrease of runoff, can result in a lower groundwater recharge in the valley fields. To overcome the consequences of inundations and droughts, the development of emergency plans is essential. Closely linked to institutional arrangements are the necessary implementation tools, which can be grouped into legal arrangements, monetary incentives, technical assistance, education and specific research.

To overcome inundations and droughts the elaboration of emergency plans is essential including forecasting, planning and management of water utilisation. With regard to cross border water resources management the delimitation of catchment areas and the calculation of the water balance are necessary. For the case of floods caused by rain and snow melt events strengthened research efforts are required, how and in which magnitude water can be retained subsurface in mountainous regions in order to avoid large inundations in the lowlands. It is therefore essential to develop proper tools for the upscaling of data concerning underground storage capacities and water quality resulting prognosis models of groundwater recharge and quality, depending on a different density of input data and scale. From these basic ideas sustainable management strategies can be derived:

- detection of storage capacities in different geological units
- assessment of technical availabilities of artificial recharge in selected aquifers
- calculation of recession coefficients

Risk assessment for groundwater protection

There is a need for research regarding the mechanisms of recharge and the infiltration processes in hard rocks (carbonate and fissured rocks). This specially applies to areas where only scanty information about soil and vegetation is available. Unlike in the mostly plain areas in the Quaternary river valleys and basins, the infiltration process in mountainous regions is controlled by geological and pedological conditions. Apparently, besides the areal diffuse type, there is a considerable point and linear type of infiltration. Up to now the recharge to karst systems was understood to occur explicitly in preferred infiltration zones, particularly in dolines, sinkholes and other solution-created depressions. However, the contribution of the diffuse type of infiltration appears to be substantial. Therefore, risk assessment in such systems requires areal evaluation of the condition of the overburden of the mother rocks (soil, moraines, talus, weathering zone). Based on this, groundwater recharge in fissured hard rocks and karstified carbonate rocks can be reliably quantified. This information enables to perform detailed vulnerability analysis. This synoptic approach also requires the application of methods that complement each other. This involves methods for the exact determination of the areal precipitation, calculation of potential and actual evaporation by performing land-use mapping supported by satellite imagery. It can also be about the input concentrations of selected environmental isotopes or dynamics of geomorphologic developments.

The next step is the determination of potential hazards, estimation of the dangerousness of individual contaminants, their weighting and probability of occurrence of emissions. Finally, based on the vulnerability of hydrogeological systems and the potential hazards, risk evaluation is performed, which is of major importance for planning and decision for economic activities at catchment level. The application strategies are focussed on water economy and tourisms in high mountainous regions (especially winter tourism).

Hydrological data show different temporal and spatial scales. Therefore, different scaling algorithms are needed to transform the data into the so-called model scale, in which the required model is valid. In this case, it is, depending on the questions to be solved, necessary to upscale or downscale to closely approximate the model scale.

Specific water treatment

This is one of the main emphases in the water sector in order to develop affordable, effective and environmentally friendly treatment technologies in order to meet existing and future effluent quality requirements (3). The most promising advances have been made in membrane and nano technologies, applying, for example, reverse osmosis, low pressure reverse osmosis membranes or nanofiltration for the removal of trace components and microorganisms. Full scale installations of membrane plants in public water supply systems are continuously growing. Especially nanotechnology has a huge potential for improvements in the field of water treatment leading to the development of new organic and inorganic materials.

Quality assurance models

The development of appropriate quality assurance models is complementary and dynamic supplementary to the legal instruments (e.g. water law, drinking water decree, water quantity permitted to be utilised etc.). This, therefore, should be taken as an innovative step towards achieving optimized water resource utilization.

In this connection, the following questions should be clarified:

- Structural analysis and optimisation of water resources utilization in technical, organisational, legal and cost respects. The basis of any optimisation is the determination of the current water resource use. As the basis for rehabilitation and optimization strategies to be established, ascertaining the current situation and evaluating the water intake structures, water transportation and water distribution systems form the central issues of the technical aspects. In organizational and legal respects, matured organizational structures need to be evaluated with regard to their legal and structural advantages and disadvantages.
- Development of variables, of scaling and of multi criteria methods for evaluating the quality or quality changes of water taking the different quality requirements of end-users (drinking water

versus industrial water); comparison and further development of quality parameters of given benchmarking and yardstick competition systems.

- Development of methods for determining and evaluating resource conflicts and environmental impacts resulting from the use of water reserves and transportation within the catchment area and to other catchment areas. The influence of the biosphere in the channels, the impact on groundwater flow and the micro climate should be examined. Special consideration should be given to the impacts on emission condition in the waters. Competition situations in water utilization should be assessed. According to existing guidelines, especially the monetary value of ecology and resources should be worked out and taken into account in the water charges.
- Groundwater quality should be safeguarded using a monitoring system, comprising three components: data acquisition (methods, instrumentation and representative measuring points), data evaluation (analysis, statistics) and catalogue with intervention possibility. The evaluation should consider the influence of spatial and temporal interactions between geogenic, hydrologic and hydrogeological factors and anthropogenic impacts on water quality.
- Moreover, for the consideration of the scenarios, competitiveness in the market, the possibility of common use of network and the question of mixing different waters should be answered. In this connection, the technical problems should be taken into account, especially the hygienic and corrosive effect of the mixing of water with variable quality in a network. These aspects are of importance for the laying and running of major water lines needed to increase the safety of water supply of large regions.

DEVELOPMENT OF CLUSTERS AND NETWORKS TO INTEGRATE RESEARCH AND BUSINESS

The management of water resources represents an important future market and is, thus, of major relevance. Its full potential can be realized, if future developments are based on (I) an increased added value due to a bundling of resources, (II) an acquiring added value through sound political advice and directives, and (III) an added value by concentrated competence building.

For ensuring the successful accomplishment of an innovative collaboration the network-company's ownership is open for strategic business and scientific partners. This should provide a well balanced structure of the company taking into consideration the fair interests of both research and business. From these basic conditions the tasks and objectives can be deduced. The structural tasks include the utilization of the natural resource "water" for end users, the direct generation of scientific results with business enterprises, the orientation of R&D co-operation to perspective subjects and the development of an international and interdisciplinary platform. As regards the contents the focus is on groundwater pollution, new irrigation systems, the minimization of water utilization for industrial purposes through tailor-made managing concepts, the relation of the human-social environment to water borne problems, the use of water power and geothermal resources for energy generation, and the development of efficient and environmentally friendly technologies for cleaning waste water.

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Invited Paper

THE CURRENT STATUS OF GROUNDWATER MANAGEMENT IN AUSTRIA

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Abstract: Water is an indispensable resource for people and the environment. Therefore, it needs to be preserved in its original quality and quantity, for the widest possible types of uses. The EU Water Framework Directive (WFD) embodies this objective and thus requires all waters to achieve good status as a minimum until 2015 and principally prohibits any further deterioration. Austria is a country with an abundant availability of water, only a small proportion of which is used. The country's fundamental objective of water management is its protection and sustainable use. Thus, full-scale groundwater protection has a long-term tradition in Austria. Accordingly, this great experiences exist in managing groundwater. EU water legislation, in particular the Water Framework Directive (WFD) and the Austrian Water Act with its linked ordinances, create the legal framework for this. The following paper provides an overview of the main geographical conditions, the public administration structure and the water management in Austria. The emphasis is laid on the existing groundwater resources and groundwater monitoring as well as on the level of groundwater protection. Furthermore, a summary is given of the actual WFD implementation activities with respect to the results of the quantitative and qualitative groundwater status assessment, to the national water management plan and to the degree of the current programmes of measures.
Keywords: groundwater, groundwater protection, groundwater monitoring, national water management plan, programmes of measures

GENERAL CONDITIONS

For the implementation of river basin management plans it is necessary to take into consideration the geographical conditions as well as the existing administrative structure and the current situation of water management. These elements represent an essential framework for the development of the required plans and measures.

Geographical Fundamentals

Austria is a small, predominantly mountainous country geographically located in Central Europe. It has a total area of 83.859 km^2. Currently Austria has nearly 8.3 million inhabitants.

The territory can be divided into three distinct geographical areas. The largest part of Austria (62%) is occupied by the mountains of the Alps in the western part. The eastern part of Austria shares the Pannonian Plain. The granite massif of the Bohemian Forest, a low mountain range, is located north of the Danube Valley and covers the remaining 10% of Austria's area.

Land-use patterns in Austria change from Alpine to non-Alpine regions. Approximately one-tenth of Austria is barren or unproductive land, that is, extremely Alpine or above the tree line. Just about 47% of Austria is covered by forests, the majority of which lie in the Alpine region. Less than one-fifth of Austria is arable land and suitable for conventional agriculture. The percentage of arable land in Austria increases in the East as the country becomes less Alpine. More than one-fifth of Austria is covered by pastures and meadows located at varying altitudes. Almost half of this grassland consists of high Alpine pastures.

Due to the topographical conditions, the populated areas are concentrated in the river valleys and on the hilly landscapes and plains in the north and south/east of the country. It is also these areas which, because of the favourable climate and the soils, are mainly used for agriculture.

The territory of Austria features a diverse lithologic composition and structure. Several hydrogeological provinces can be distinguished within the territory, characterized by both specific geological compositions and specific hydrogeologic properties. The groundwater stored in porous media in valleys and basins with mainly Quaternary sediment, and the karstic groundwater in the northern and southern Limestone Alps, represent Austria's most important groundwater resources. Local thermal springs and mineral water sources are also of particular importance.

Austria is part of three international River Basin Districts. The main part of the Austrian territory (~80,700 km^2 or 96%) is located in the Danube River Basin. The Rhine River Basin covers approximately 2,400 km^2 (3%) and the remaining part of around 900 km^2 (1%) is situated in the Elbe River Basin. So, water from the Austrian territory is drained to two seas – the North Sea and the Black Sea.

Public Administration

As a federal republic, Austria is divided into nine provinces ("Länder"). These nine states are further divided into 84 regional districts. Districts are subdivided into about 2400 municipalities. Local competencies are granted to both districts and municipalities, and some major cities. The provinces are not mere administrative divisions but also have certain legislative power independent of the federal government. The provinces are also responsible for the implementation of most parts of the federal water legislation.

The main instrument for water management is the Austrian Water Act, which regulates the use and protection of water resources. The Water Act generally requires that water uses must be permitted. Within the frame of the Austrian Water Act, a number of ordinances concerned with groundwater management have been enacted. These regulations establish, in particular, requirements of monitoring and protection of groundwater as well as the stipulation of quality threshold values.

For the implementation of the WFD it was necessary to divide Austrian territory into eight planning units, which are assigned to the three international River Basin Districts. For the delineation of these planning units only hydrological criteria were taken into account, irrespective of national borders. Water management in these planning units must be carried out in a coordinated manner by the public administrations in the concerned federal states.

Water Management

Water balance

In general, Austria enjoys a mostly favourable hydrological situation. Characteristic for the Austrian water management situation is the comparatively large abundance of water.

For the time period from 1961 to 2000, the annual mean values are 1,100 mm for precipitation and 600 mm for run-off, leaving 500 mm for evaporation. The annual precipitation varies from more than 2,500 mm in the west to around 500 mm in the east. This run-off combined with the 320 mm of water that flows in from surrounding countries, add up to a total annual run-off of approximately 920 mm per year.

Precipitation and the inflow from bordering countries result in a fresh-water volume of 120 billion m^3/year, of which 84 billion m^3 are available for use. Approximately one third of this is groundwater.

Water utilization

The average total annual consumption of freshwater is about 2.6 billion m^3/year (only 3% of the available amount). Water utilization in Austria is divided into three sectors: municipal, industry and agriculture. More than two-thirds are used by industry and agriculture.

The main consumer of Austrian freshwater resources is the industry. More than 50% is used in this sector. The requirement of freshwater for municipal use (household and trade) is about 1.0 billion m^3/year. In comparison to other countries and the worldwide average, the use of water for irrigation and livestock farming is low. Only 5% of the freshwater is used by this sector. This can be attributed to the high precipitation on the one hand, and the small area of arable land on the other hand.

Water supply

In contrast to many other countries where drinking water is produced by multi-stage chemical treatment of surface water, Austria uses mainly groundwater resources (wells and springs) which are available in a largely natural quality. This is first and foremost the result of the high standard of groundwater protection in Austria.

From 8.3 million Austrian inhabitants, about 7.2 million, i.e. 87% of the population, live in areas provided by a central water supply plant. Roughly 1 million people get their water from private wells and springs.

Public water supply is mainly provided for by local authorities and local authority associations. More than 1900 water utilities and more than 4000 water associations provide Austrians with high quality drinking water in accordance with the drinking water ordinance. In the last years an increasing number of private companies have been founded to supply villages and cities with drinking water. These private companies are owned predominantly by the authorities (municipalities).

The current sources of Austria's drinking water are spring water (50%) and groundwater (50%). Treated surface water is used for drinking water only in exceptional cases and on a very small scale.

In Austria currently the average daily consumption of drinking water is about 135 l/inhabitant and day. This value has not changed or even slightly decreased over the last decades. Taking into account the water use of industry and businesses, the average daily water consumption is about 230 l/inhabitant.

GROUNDWATER IN AUSTRIA

In Austria groundwater is very important for water supply as well as economic development. The basic elements for sustainable managing of this resource are the delineation of management areas (groundwater bodies), a comprehensive quantitative and qualitative groundwater monitoring just as strategies for groundwater protection. These elements also represent an essential framework for the development and implementation of river basin management plans.

Location and Boundaries of Groundwater Bodies

Based on the Austrian geological structure, a distinction can be made between groundwater in porous media like porous bedrock and areas of gravel and crushed stones, groundwater in fractured media like in fractured layered non-karstic bedrocks, groundwater in karstic bedrocks and deep groundwater bodies.

For the identification of groundwater bodies, delimitation criteria such as size, homogeneity (geological and hydro-geological), utilisation, economic importance, risk potential, as well as the existing national monitoring network and the importance of groundwater for water supply, have to be taken in to account.

In accordance with the horizontal guidance document “Identification of Water Bodies” (2003), groundwater bodies should be delimitated in a horizontal and a vertical manner. According to the criteria given in the guidance paper, a distinction between single porous groundwater bodies, and groups of ground water bodies, as well as surface near groundwater bodies (shallow aquifers), and deep groundwater bodies (approx. below more than 200m) has been made.

In particular with respect to the different geological strata a further distinction was made between porous, fractured and karstic types of aquifers.

The analysis of groundwater bodies was based on 64 identified individual shallow groundwater bodies covering a total area of 9,669 km^2, 62 groups of groundwater bodies, with a total area of 74,039 km^2 and on one individual deep groundwater body (thermal groundwater body), as well as 8 groups of deep groundwater bodies. All single groundwater bodies are located in porous media and the groups of groundwater bodies assigned to the predominant part of the aquifer type (porous, fractured or karstic).

Groundwater Protection

In Austria, full-scale groundwater protection has a long tradition. Enormous investments were made to secure the high quality of the majority of domestic groundwater resources.

As already pointed out, the main groundwater resources in Austria are to be found in the karstic regions and in the valleys and basins with mainly quaternary sediments. The different pressures (agricultural land use, settlements, traffic …) create possible impacts on these high quality groundwater resources. In order to avoid pollution and ensure the future use for drinking water purposes, groundwater resources have to be protected as strictly as possible. Hence the Austrian Water Act entails the principle of an overall protection of groundwater. Drinking water standards represent the basis for quality targets in groundwater.

With the aim of protecting water supply plants, the Austrian Water Act also requires the establishment of protection areas. Such areas can be established to protect both water supply plants in operation as well as groundwater resources reserved for future supply. In such areas the use of land or water and the operation of existing or future plants or installations may be prohibited or limited by an official regulation issued by the Water Act Authority.

The basis for the delimitation and prescription of measures for groundwater protection zones and groundwater prevention areas in Austria is the technical directive W 72 “Schutz-, und Schongebiete” (ÖVGW, 1995). This directive defines 3 different types of protection zones, which are the basis for groundwater protection zones (prescribed as decree) or groundwater prevention areas (issued as ordinance). Groundwater prevention areas are issued when it is necessary to prevent large areas. It is also possible to issue prevention areas for future groundwater use.

At present, about 200 large protected areas, with an average surface area of about 38 km², and a large number of smaller ones (1900), have been installed in Austria. This area comprises a total of about 10 % of Austrian territory.

Groundwater Monitoring

The protection and management of groundwater would not be possible without the knowledge of the quantitative and qualitative condition of our groundwater. Therefore, a systematic and comprehensive water monitoring system was established in Austria quite some time before the WFD introduced such requirements.

According to the “Wasserkreislauferhebungsverordnung 2006” (ordinance on the monitoring of the water cycle) and the former “Hydrographiegesetz” (Act on hydrographical data), the survey of the water cycle operated by the Hydrological Service in Austria involved the observation of precipitation, evapotranspiration, air and water temperatures, water level, discharge, sediment and suspended load, subsurface water, groundwater and springs.

Presently the monitoring network for groundwater quantity comprises about 3450 groundwater level gauges, 200 groundwater temperature gauges, 87 spring gauges and 14 stations for the unsaturated zone. The systematic quantitative groundwater monitoring started in early 1940.

The Austrian programme for monitoring groundwater quality covers the entire national territory with a dense network of sampling sites. A uniform measurement methodology ensures the production of high quality data. The development of a network of sampling sites for groundwater and monitoring according to uniform criteria for parameter selection, frequency and methodology, started in 1992.

The water quality in Austria has been consistently monitored by private and public contractors commissioned by the Federal Ministry of Agriculture and Forestry, Environment and Water Management (BMLFUW). The sampling site network for groundwater currently comprises about 2000 groundwater sampling sites and 230 springs.

Physical-chemical parameters are monitored 4 times a year at groundwater and spring sampling sites. As for physical properties and chemical parameters, the monitoring programme aims at the comparison of the monitoring results collected throughout the country, allowing at the same time for an adjustment of selected parameters. Certain basic parameters are monitored at all sampling sites continuously. Other parameters, for which an overview of the entire country is required, are monitored at all sampling sites for a limited period (usually one year), at the beginning of a monitoring cycle, and measured a second time after 6 years (“initial monitoring”). In case of non-significant concentrations, these parameters are no longer taken into consideration during operational monitoring (“repeated monitoring”). Special parameters are specifically analysed in groundwater areas either according to local utilisation and impacts or in case of explicit requirements of certain EU directives.

Consequently, for a large number of identified groundwater bodies or groups of groundwater bodies, sufficient data are available to describe their quantitative and qualitative status.

The data collected during the quantitative and qualitative monitoring programmes are published by the BMLFUW in reports like the “Hydrological Yearbook” and the “Water Quality Report”. These data provide the basis for implementing the risk and status assessments required by the WFD.

RESULTS OF GROUNDWATER STATUS ASSESSMENT

The results of the status quo analysis have been laid down in the Austrian "Summary Report" (2005). This report was prepared in compliance with the requirements of the WFD. It comprises a description and classification of water bodies, and a review of the impacts of human activities on waters, including a first assessment of the compliance with the quantity and quality objectives.

The qualitative and quantitative monitoring sites within the different groundwater bodies were reviewed in accordance with the requirements of the WFD. In some cases the investigations showed that it was possible to reduce the monitoring sites without changing the representativeness. In other cases the monitoring network had to be supplemented to reach the required degree of representativeness. The density and distribution of the monitoring stations has been set up according to the pressures and hydrogeological and natural conditions. All in all, the monitoring network had been optimised. The results are contained in the summary report of the monitoring programmes pursuant to Article 8 of the WFD.

Based on the results of monitoring for the years 2003 – 2008, the qualitative and quantitative status assessment was accomplished with the developed methodologies.

Chemical Status

For the chemical status assessment, two criteria have to be taken into account. A groundwater body will in a good chemical status, if in a considered time period

- less than 50 % of the monitored sites are endangered (a monitoring site is considered as endangered if the arithmetic mean of a measured parameter in a time period of six years is higher than the respective national threshold value);
- no sustainable upward trend (a sustainable upward trend is detected if in a time period of six years the arithmetic mean of a measured parameter has a significant upward trend and the trend line exceeds 83% of the respective national threshold value).

The quality of groundwater in Austria is more or less satisfactory, particularly in the western provinces of Austria. In the south-eastern and eastern regions of Austria which are subject to intensive agricultural use, the concentrations of nitrate, atrazine and desethyl-atrazine are significantly higher.

The results of the chemical status assessment reveal that most groundwater is of good chemical status. Three bodies of groundwater that are used intensively for agricultural purposes in the east of Austria are exceptions on account of nitrate. They fail to meet good chemical status and have been classified as areas in which measures are to be taken. In accordance with the precautionary principle and to guarantee groundwater as drinking water in the long-term, a threshold value for nitrates of 45 mg/l has been established.

For other pollutants such as, for example, pesticides, orthophosphate, ammonium and nitrite, threshold values are exceeded although this does not lead to failing good chemical status.

At present, 14 observation areas (body of groundwater in which at least 30% of the monitoring stations exceed the national threshold values for a pollutant) have been identified. This means that while the good status will be reached, first steps for identifying the causes of pollution have to be taken. Such observation areas are to be seen as pre-stage, before groundwater bodies are classified as areas of poor status.

With respect to the agricultural land use, the deadline for achieving a good status may still need to be extended to 2027 for the three groundwater bodies without good chemical status due to nitrate. The extension is necessary on account of the long residence time of groundwater, often more than 30 years. For this reason a reduced input of nitrate leads to a reduction in groundwater very slowly. The heterogeneous conditions of soil and ground, as well as the change of climate, have a great influence on the processes of degradation and elution. As regards the concentrations in groundwater, the precipitation situation and the resulting renewal rate of groundwater (distribution over time and its extent) do, of course, play a very important role. Therefore, forecasts about the development over time of the effects of measures are very difficult. Due to the natural conditions in Austria, the concentrations of nitrate in groundwater cannot be reduced to the threshold value of 45 mg/l by 2015 in the three groundwater bodies without good chemical status.

Nevertheless, the national water management plan requires that local and/or regional pollution sources, especially in the proximity of drinking water abstraction points, should be reduced or eliminated by 2015.

Quantitative Status

The following criteria for the quantitative status assessment for single groundwater bodies and groups of groundwater bodies have been identified:

- Single groundwater bodies with a sufficient data base are considered as being in a good quantitative status if for at least 60 % of the monitored sites the average groundwater level exceeds the characteristic low groundwater level.
- Single groundwater bodies with an insufficient data base or groups of groundwater bodies are considered as being in a good quantitative status if the abstraction does not exceed 90% of the estimated available groundwater resource.

The Austrian ordinance for monitoring the quality and quantity status of the water bodies ("Gewässerzustansüberwachungsverordnung" GZÜV) stipulates for each groundwater body or groups of groundwater bodies the method (groundwater level or groundwater resource) to monitor the status.

The actual results of the investigations following the risk assessment indicate that there is no need to change the evaluation of the quantitative status of the groundwater bodies and groups of groundwater bodies. All groundwater bodies in Austria can be reported as in a good quantitative status. Long-term abstraction does not exceed the available groundwater resource.

NATIONAL WATER RESOURCE MANAGEMENT PLAN

The first National Water Resource Management Plan was elaborated in a long term process over many years, appropriate to the specifications of the Water Framework Directive. In the year 2009, the draft of the plan was subject to a public consultation. Altogether approximately 400 comments were received. They were all accounted for in the further steps of the elaboration. The final version of the plan was published at the end of May 2011. The legal implementation was done with the ordinance to the National Water Resource Management Plan. This ordinance was also enacted at the end of May 2011.

In this ordinance, the environmental objectives as well as the public policy in water management laid down in the national water resource management plan were declared mandatory. Henceforth the legal requirements are also available to implement the programme of measures.

The national water resource management plan was arranged in the following main chapters:

- Analysis of the characteristics of the groundwater bodies
- Review of the impact of human activities on groundwater
- Economic analysis of water use
- Monitoring
- Environmental objectives for groundwater
- Programme of measures

Programme of measures

Appropriate to the possible impacts on groundwater, there are different types of impacts specified. These types are the basis for the generation of the programme of measures. The following types of impacts are definite:

- pollutants from point sources
- pollutants from diffuse sources
- abstraction of groundwater
- artificial recharge of groundwater

Special measures for all these types of impacts were elaborated. With these measures the targets of the National Water Resource Management Plan shall be reached. Therefore the following general instruments were identified:

- prevent and limit the output of nitrate
- legislative policy
- control and supervision
- research and development projects
- educational projects
- financial development scheme

According to the results of the status quo analysis and the status assessment, the focus of the first programme of measures is on the type of impact “pollutants from diffuse sources”.

In Austria, special instruments and measures are implemented on the basis of the Water Act with the corresponding regulations since a long time. Subsequently, the essential measures which are laid down in the National Water Resource Management Plan are taken up.

An additional important legal regulation is the nitrates action programme. With it the EU nitrate directive was implemented in Austria. This programme makes a contribution to the reduction of the impact on groundwater due to nitrate. Through the forceful implementation of the nitrates action programme, the diffuse emissions into groundwater will be further reduced.

Further, an important instrument for the qualitative management and protection of groundwater is the Austrian programme for sustainable agriculture (“ÖPUL”). This programme contains financial incentives for voluntary measures in agricultural land use. Also, special regional groundwater projects can develop on this programme. On the basis of these programmes, further improvement of groundwater quality in the problematic areas is expected in the next years.

With regard to placing of plant production products on the market and the control of pesticides, several legal regulations exist in Austria. These should account for the prevention of potential groundwater pollution by pesticides and their metabolites. In addition to the programmes of enhanced advice agriculturists about the use of fertilizer and pesticides, systematic control of the abidance by the legislation and obligations represents an important instrument of the programme of measures.

These activities should be continued during the next years. In particular the mentioned control should be done on a larger scale.

So far performed measures should be supported in the next years by target-oriented investigations, research and development projects as well as by surveys and special monitoring programmes concerning the application of fertilizer and the risk potential of pesticides. An evaluation of the reached awareness shall be conducted. For the next planning period, the results of the evaluation and the results of the implemented monitoring programme will be taken into consideration for the revised version of the programme of measures.

CONCLUSIONS

Austria started at an early stage with the systematic investigation of the quantitative and qualitative groundwater situation. The generated data provide a valuable basis for the delineation and characterisation of the groundwater bodies and for the quantitative and qualitative risk and status assessments, as well as for the development of the national water management plan and for the implementation of the programme of measures.

The first National Water Resource Management Plan was elaborated in a long-term process over many years, appropriate to the specifications of the Water Framework Directive. This plan is a comprehensive planning instrument for the regime of water management in Austria. In the year 2009, the plan was subject to a public consultation and the final version was enacted at the end of May 2011.

The programme of measures is based on already existing instruments and measures. Therefore, the programme is a target-oriented extension of so far strategies for qualitative and quantitative groundwater protection in Austria. This concerns especially the sustainable reduction of the impact on groundwater due to nitrate. The experiences with the implementation of the programme of measures and the achieved successes will show if it is necessary to adapt the measures for the next planning circle.

The first National Water Resource Management Plan is a further important step toward a comprehensive and sustainable groundwater protection policy in Austria. But this step does not guarantee protection and there will always be new challenges to confront for the management of groundwater resources.

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Notes:

Invited Paper

PROGRESS AND IMPROVEMENT OF THE STATUS OF GROUNDWATER IN SERBIA

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Abstract: The paper presents some recent data on hydrogeology and an overview of current groundwater utilisation and protection in Serbia. Over the past several years, national legislation in the water sector has been upgraded and adapted to the EU WFD, including several large projects for groundwater assessment and protection initiated or conducted in order to improve the status and standards of the national water sector. These activities included the establishment of a new national groundwater monitoring network, the study of aerobic-anaerobic conditions in the major alluvial aquifer systems, surveys for the opening of several new groundwater sources, the optimisation of artificial recharge for its wider application in practice, the management of major transboundary aquifers, and assessment of the possible impact of climate change. The approach is aimed to improving the status of groundwater and further contributing to its more sustainable use in the future.
Keywords: groundwater, water supply, protection, WFD, Serbia

INTRODUCTION

Serbia is relatively rich in groundwater reserves, deposited in different aquifer systems and unevenly distributed across the territory. The major groundwater reserves are accumulated in thick Quaternary and Neogene intergranular aquifers. Alluvial aquifers of large rivers (the Danube, Sava, Velika Morava and Drina) are particularly important and widely used for drinking water supply. Karstic aquifers dominate the southwestern and eastern regions of Serbia. These regions abound in springs which are generally vulnerable to considerable discharge fluctuations. Precipitation, watercourses, and groundwater provide Serbia with quite a favourable water regime: although Serbia is one of the largest food producers in the Balkans, only some 1-2% of its arable land is irrigated. Water deficiencies are found in the south of Serbia, as well as in a central region of Serbia (Šumadija).

Most resources deliver a good natural groundwater quality. The main exception is the northern province of Vojvodina. This province is part of a large flat depression of the Pannonian Basin, with very thick Quaternary and Neogene sediments and sub-artesian aquifers. Organic material has been deposited in the natural sediments, and groundwater is frequently loaded with organic substances, ammonia, and occasionally also arsenic or boron.

Roughly 90% of the population has access to the public water supply [2]. Furthermore, some 75% of water for public water supply is abstracted from groundwater resources. In some areas, currently tapped resources are unable to quantitatively meet the population's water demand. However, there are other considerable groundwater resources especially in the alluvia of large rivers or in karstic aquifers which are still under-exploited. Artificial recharge is also not used to a large extent: only about 1 m^3/s of water is delivered by such sources, which is less than 5% of the estimated potential [2]. There is the need to upgrade protection of groundwater resources. Additionally, large undertakings are required to improve river water quality, since rivers are a precious natural resource and a source of alluvial aquifer recharge. Maintenance of water sources and water supply systems will also have to be improved.

BRIEF GEOLOGY AND HYDROGEOLOGY OF SERBIA

The complex geology of Serbia and adjacent areas has produced hydrogeological heterogeneity and considerable variety in aquifer systems and groundwater distribution. Several hydrogeological provinces can be distinguished within the territory, characterised by both specific geological compositions and specific hydrogeological properties (Fig.1) [3]. Therefore, the region is characterised by the presence of formations with small groundwater reserves (Palaeozoic formations, magmatic and metamorphic rocks, Jurassic and Cretaceous flysch or deeper, thick sedimentary complexes), as well as Mesozoic carbonate rocks, and Tertiary or Quaternary alluvial and terrace deposits which can be very rich in groundwater. Recent alluvial deposits and fans of major rivers such as the Danube, the Sava, the Drina, and the Velika Morava, constitute by far the richest aquifers which supply major towns. Neogene and Pleistocene sediments tapped by many boreholes are the main sources of water supply for numerous cities and villages in the northern province of Vojvodina (the Pannonian Basin), as well as settlements in inter-mountainous basins in the central and southern parts of Serbia [4].

In accordance with the Water Master Plan [2], the hydrogeological units in Serbia have been classified as follows: the Bačka and Banat Region (comprising N and E parts of the Pannonian Basin); the Srem, Mačva and Sava/Tamnava Region (SW Pannonian Basin and NW Dinarides); Southwest Serbia (SW Dinarides), West Serbia (W Dinarides), Central Serbia (Serbo-Macedonian Massif and the Šumadija-Kopaonik-Kosovo Zone), and East Serbia (Dachian Basin and Carpathian-Balkan Arch) (Fig. 2).

In the Bačka and Banat Region, Neogene and Quaternary sediments are up to 4500 m thick, but major subartesian and artesian aquifers are of Quaternary age, tapped up to a depth of 230m (Kikinda). Groundwater abstraction from the "Basic Water-Bearing Complex" (BWC) accounts for more than 60% of overall abstraction in this province [5]. The previously registered significant drawdown in some areas (i.e. Kikinda up to 0.5m/a) has relatively stabilised due to lesser consumption as a result of economic stagnation during the 1990s. However, hydrodynamic analyses of the impact of abstraction in this region indicate that under current conditions the rate of abstraction is more than 1 m3/s higher than the rate of recharge [5]. Water quality is generally protected from human activity by thick, overlying impervious sediments but, as previously stated, groundwater is highly loaded with organic matter and ammonia (and often arsenic). The alluvial aquifer of the Danube provides water supply for the cities of Novi Sad, Pančevo and Apatin near the Danube. The rate of water abstraction from alluvial aquifers is roughly 2 m^3/s.

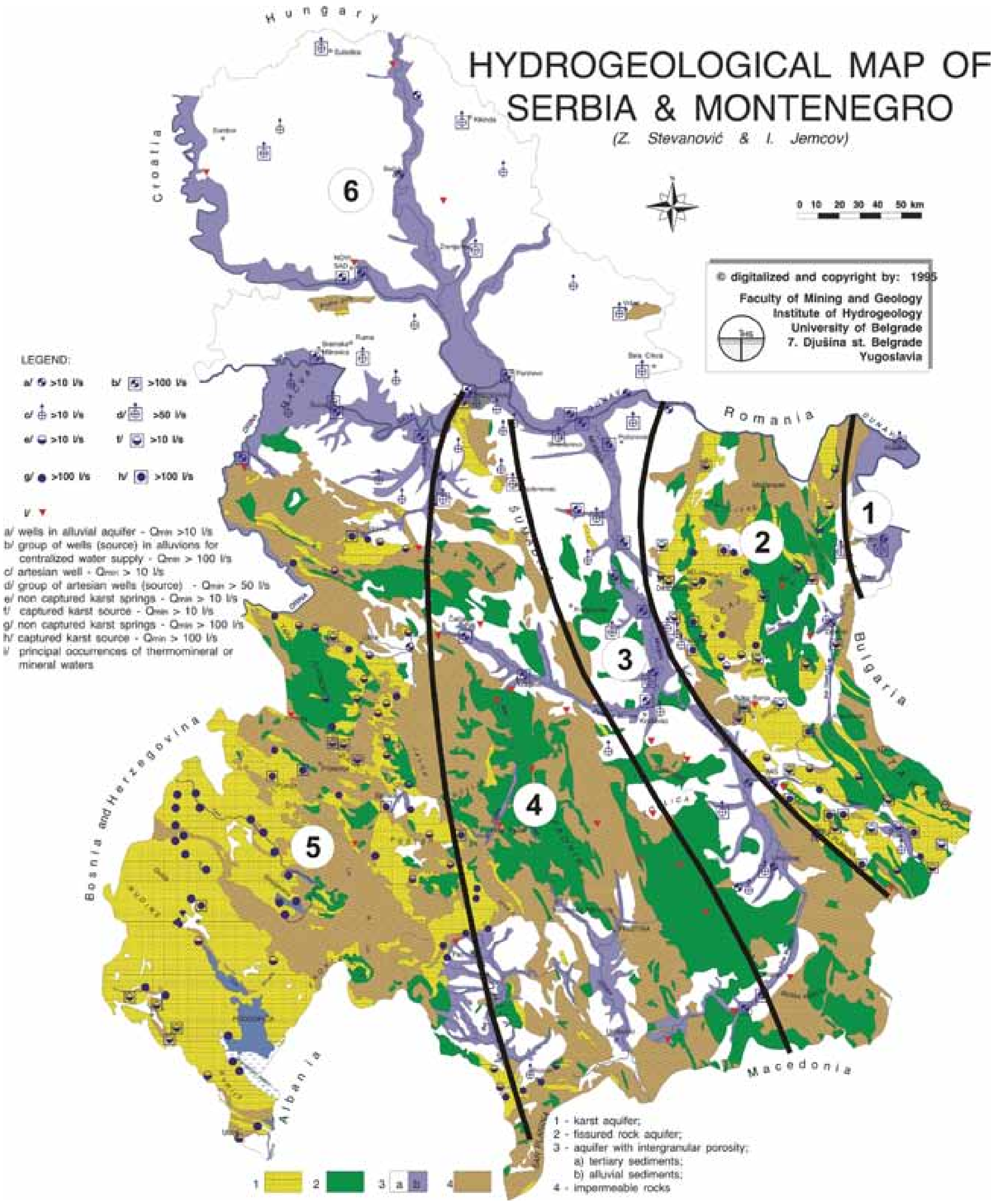

Figure 1: Hydrogeological Map of Serbia and Montenegro with hydrogeological provinces in Serbia – Dachian Basin (1) Carpathian-Balkan Arch of East Serbia (2), Serbian Crystalline Core (Serbo-Macedonian Massif, 3), Šumadija-Kopaonik-Kosovo Zone (4), Dinarides of West Serbia (5), Pannonian Basin (6).

The Srem, Mačva and Sava/Tamnava Region is characterised by thick water-bearing alluvial and terrace sediments (up to 30m), which can be found in the Mačva area (sediments of the Drina River). Closer to Belgrade, the Sava alluvium is also 20-30 m thick and holds a major water source for the City of Belgrade, including radial wells located along the banks of the Sava River. The current rate of water abstraction from this source is 4-5 m^3/s [6], although the potential is considerably higher.

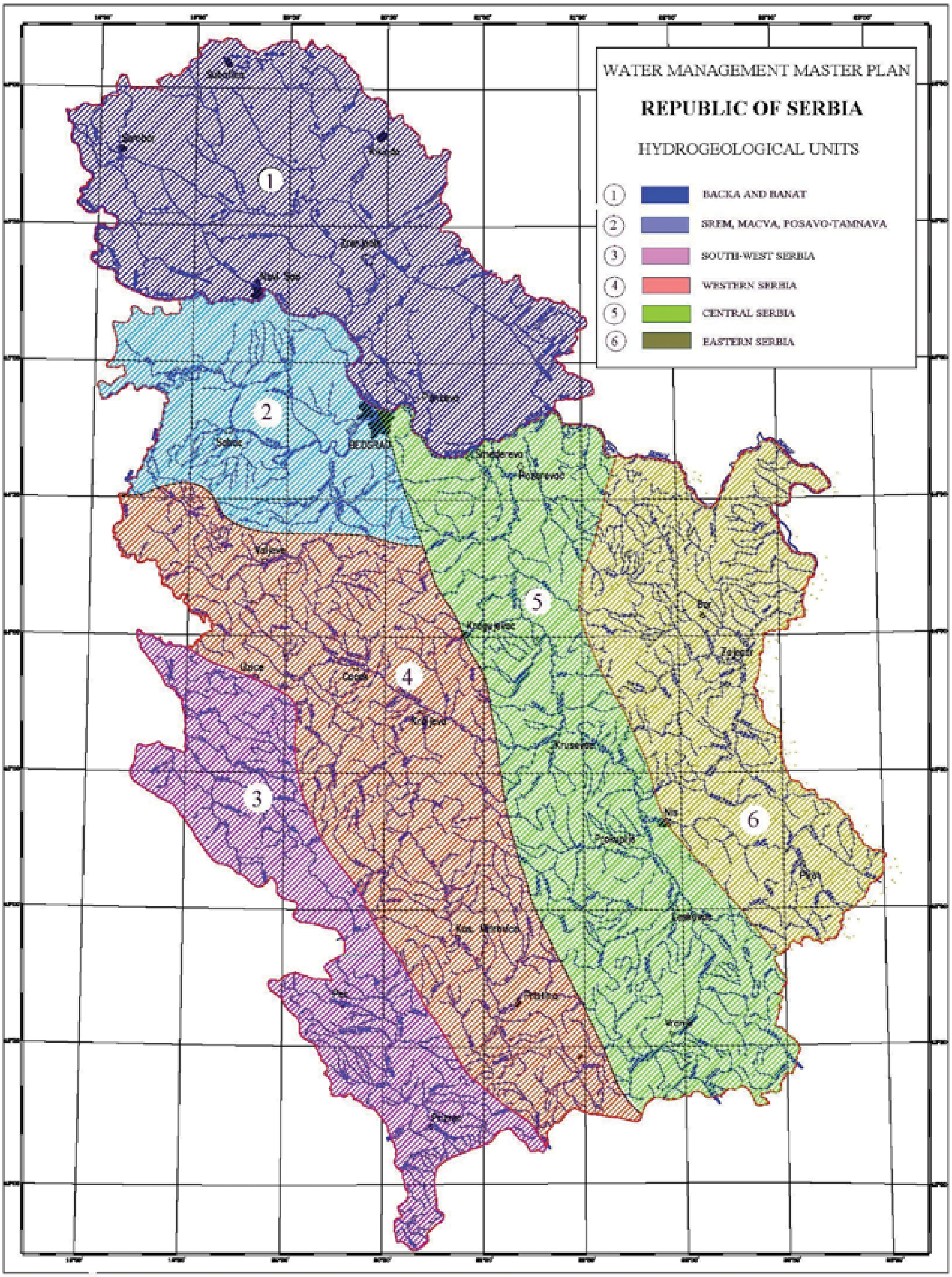

Figure 2: Hydrogeological units of Serbia (according to [2]).

The most important hydrogeological formation in South-Western Serbia is comprised of extensively karstified Middle and Upper Triassic limestones. They are extremely thick in the southern part of the region, where they constitute a single limestone unit between the Pešter Plateau and the northern edge of the Metohija Valley. This part of the country's territory infiltrates large amounts of precipitation and is abundant in karstic groundwater. Among numerous karstic springs, eleven have a minimum discharge of more than 1000 l/s of water [7, 8]. Here intergranular aquifers in alluvial and lacustrine sediments are less significant and their abstraction potential is rather limited.

The most important hydrogeological formation in the Dinaric Mountains of the Region of Western Serbia is comprised of extensively karstified Middle and Upper Triassic limestones. They are extremely thick in the southern part of the region, where they constitute a single limestone unit between the Pešter Plateau and the northern edge of the Metohija Valley. Among numerous karstic springs, eleven have a minimum discharge of more than 1000 l/s of water [7]. Here intergranular aquifers in alluvial and lacustrine sediments are less significant and their abstraction potential is rather limited.

In the Region of Central Serbia, the most important aquifer is the alluvial aquifer of the Velika Morava River (6-60 m thick). Another important water-bearing medium is the Danube alluvium along the stretch from Kostolac to Golubac, which is 15-30 m thick [1]. Groundwater in these alluvial aquifers is exposed to strong anthropogenic impacts and this is why protection of river water quality is extremely important (although the minimum flow of the main national watercourse, the Velika Morava River, can be as low as 40 m^3/s or less during autumn months). Main Neogene aquifers are found in the Leskovac and Jagodina-Paraćin basins. Groundwater resources within intergranular aquifers in the central and southern parts of this region range from low to considerable.

The East Serbia Region is characterised by highly karstified Upper Jurassic and Lower Cretaceous limestones of the Carpathian-Balkan Arch and a portion of the Dachian Basin. This region features a large number of karstic springs, 16 of which have a minimum yield of more than 100 l/s [8]. Large alluvial aquifers are rare (the Nišava and Beli Timok basins). The artificially-recharged Mediana water source in the City of Niš is the focal point of this city's water supply, especially during lean water periods [9].

CURRENT GROUNDWATER UTILISATION

Groundwater is a traditional water supply resource: The proportion of groundwater use in Serbia relative to the overall water supply is similar to that which exists in most European countries. Although groundwater abstraction within the territory of Serbia dates back to Roman times, the beginning of organised public use of groundwater (excluding tapping of minor springs) is associated with the year 1850 when an "artesian well" was bored in Banatski Karlovci (Vojvodina) [5]. By the end of the 19th century artesian wells were drilled in all major urban areas of Vojvodina (Subotica, Sombor, etc.) and in Central Serbia (e.g. Paracin, Smederevo, Mladenovac, Negotin). Abstraction and use of groundwater for modern water supply systems began in 1892, when the Makiš water source was developed for Belgrade's water supply [6]. Public (municipal and industrial) water supply in Serbia became fully developed during the second half of the 20 century (since the 1960's), when most of the current water supply systems were built. Since that time, groundwater abstraction has been extensive, as a result of expanding economic activity, primarily industrial and agricultural. Based on available data, more than 1000 water sources have been developed in Serbia, including tapped springs.

Surface water is used to a significant extent mostly in the southern part of Serbia, from river reservoirs which equalize discharge fluctuations in this region relatively poor in water. Also, almost 3 m^3/s of total water consumption of the City of Belgrade is from the surface water resource of the Sava River, planned to be expanded up to 5 m^3/s in the near future.

Based on the Water Master Plan of Serbia [2], the total yield of active groundwater sources is roughly estimated at 23 m^3/s (Table 1). The total currently abstracted volume is slightly lower and amounts to roughly 600x106 m^3/year, equivalent to an average abstraction rate of some 19 m^3/s. More than half of the abstracted water is groundwater from alluvial aquifers.

Table 1: Groundwater source yield in Serbia by type of water-bearing medium (l/s) [2],

Region	Alluvial aquifers	Quaternary subartesian aquifers	Neogene aquifers	Karstic aquifers	Fissured aquifers	Total
Bačka and Banat	1454	3570	431	0	—	5455
Srem, Mačva, Sava/Tamnava	6974	340	506	30	—	7850
Central Serbia	2585	—	845	430	—	3860
East Serbia	620	—	60	1711	—	2391
SW Serbia	242	—	140	1614	—	1996
West Serbia	1051	—	60	397	17	1525
Total	12926	3910	2042	4182	17	23077

Karstic aquifers in East and Southwest Serbia are outcropped in areas with relatively high precipitation levels. Tapped springs are generally characterised by high discharge fluctuations. Water quality is good to excellent, and the catchment areas are usually sparsely populated. However, low spring yield during dry periods is a problem for most waterworks. Hydrogeological surveys and feasibility studies undertaken during the last two decades made it possible to identify favourable conditions for artificial control of karst aquifers in several locations. Based on these results, several successful systems were constructed mostly in East Serbia (Bor, Niš, Ćuprija, Knjazevac) [10, 11].

With regard to major cities, groundwater sources are used to supply Niš, Novi Sad (and all major towns in Vojvodina), Jagodina, Paraćin (and most of the cities in East Serbia), Novi Pazar, etc. The rate of groundwater abstraction for large municipal centres varies over a wide range, from 10-20 l/s to more than 4 m^3/s. The towns that use surface water exclusively are Užice and Priština, whereas Belgrade, Zaječar, Valjevo and some other cities combine surface and groundwater. Belgrade residents consume water which originates from thick alluvial deposits of the Sava River (near its confluence with the Danube), or treated river water. The groundwater is tapped by numerous conventional drilled wells and about 100 radial (Ranney) wells (av. 4.7 m^3/s). The second largest source of alluvial groundwater is supplying Novi Sad from the Danube alluvium (1.5 m^3/s). The City of Niš combines groundwater supply from the artificially-recharged Mediana source in the alluvium of the Nišava River (Q=0.6 m^3/s) with karstic waters tapped at several springs (Krupac, Ljuberadja, Mokra, Divljana).

GROUNDWATER POTENTIAL AND ARTIFICIAL RECHARGE PROSPECT

Based on research conducted to date, the current yield of groundwater sources (Table 1) is roughly 30% of the groundwater potential which could be used in the future (approx. 67 m^3/s) [1]. This estimate is based on the volume of groundwater, excluding the application of artificial recharge methods or regulation of karstic springs (Table 2).

Table 2: Estimated groundwater potential in Serbia (excluding artificial recharge) (m^3/s) [1]

Alluvial	BWC	Neogene	Karst	Fissured	Total
43.80	5.46	3.95	13.70	0.20	67.11

In addition to natural groundwater potential, extra amounts of groundwater can be obtained through artificial recharge methods, from water sources developed in alluvial plains and by controlling karstic springs. According to the Water Master Plan of Serbia and based on current information, artificial recharge (AR) can provide an additional 40 m^3/s of water; added to amounts extractable without the use of AR, the total is approximately 107 m^3/s [1, 2]. If we compare the contributions by potential future groundwater resources, AR can essentially double the yield of alluvial aquifers and ensure sustainable and environmentally safe water use.

Such an optimistic view is based on several currently functional AR sources in Serbia. The largest AR source is the above-mentioned “Mediana” source of water supply for the city of Niš where AR not only resolves water supply reliability, but contributes to groundwater quality improvement and protection [9]. In order to protect this groundwater source from contamination from an electronic industry, remediation of the contaminated part of the groundwater source and construction of safety structures (such as an impervious concrete-bentonite barrier and a system of 6 drainage wells) were undertaken. Following extensive investigations, planning, and design, complete remediation and protection were achieved. The rate of water abstraction was increased to about 500-600 1/s by the AR system consisting of an intake from the Nišava River, a pretreatment station, 9 recharge ponds, 80 shallow drilled wells and a water distribution system.

Similarly, AR has recently been introduced to the “Ključ” source of the City of Požarevac in order to increase its capacity, but also to dilute groundwater and reduce the negative impact of the nitrates present in this zone. During the 2004-2006 period, a hydraulic barrier and 6 infiltration ponds were built to direct groundwater flow and prevent water from flowing towards pumping wells. The water for the ponds is delivered from the Velika Morava alluvium, from a distance of about 1.5km (Fig 3a,b).

Figure 3a,b: Recharge pond at the Ključ source, during construction (a) and during operation (b).

The other main aquifer system successfully regulated at several locations is karstic. Widespread karstic areas, abundant reserves, and excellent quality of karst groundwater have been the reasons for its extensive use in water supply systems throughout the country. In total, 70 karstic sources have been tapped for public water supply, with the estimated minimal capacity exceeding 4.5 m^3/s. Most of the large cities in East and West Serbia currently use karst groundwater for their water supply; however, due to an unstable flow regime when only natural springflow is tapped, numerous problems arise during the recession period (summer-autumn). To overcome this problem, several systems for artificial control of the karst aquifer (mostly in East Serbia), have recently been constructed and they significantly improved the water supply situation. The applied measures are not typical AR, but regulation structures enable faster aquifer recharge and recovery [10].

The largest regulation system was constructed for a mining and industrial complex in the City of Bor. Following extensive and complex hydrogeological research in the 1990s, four production wells (Fig. 4) were drilled in the vicinity of the natural Mrljiš spring [10]. Several pumping tests confirmed their composite capacity in the range from 240 to 320 l/s, creating a depression in the Mrljiš spring zone of less than 2 m (low flow period). The optimal extraction rate of the source, compared to the minimal springflow, increased almost four-fold. The system has been operational since 2002, including a monitoring system on the nearby Crni Timok River to ensure ecological flow for dependent ecosystems downstream.

Figure 4: Over-pumping well IEBOG-4 near the Mrljiš karstic spring (Source: Bor Waterworks).

"Modro Oko" (Blue Eye) in the Village of Krupac is one of the five karstic springs tapped for the water supply of Niš. It drains the southern part of the Svrljig Mountains (>100 km^2), and is characterised by high discharge variation (~ 40-11.000 l/s). Aqua-speleological exploration of deep siphonal channels enabled the installation of high-capacity pumps. Based on pumping test results (250 l/s), it was assumed that continual extraction during periods of low flow will be possible so that two new wells were drilled. The tapped amount of water is six times greater than the extreme minimal natural springflow and can be replenished by new recharge during the winter season [11].

GROUNDWATER QUALITY AND PROTECTION

Sanitary control of drinking water quality is under the jurisdiction of the Ministry of Health and the National Institute for Public Health, including its regional offices. All waterworks also test the basic chemical and bacteriological quality of raw-water and treated-water samples.

Groundwater quality is being systematically monitored through an alluvial aquifer monitoring network. This activity falls within the scope of the Hydrometeorological Service of Serbia, which also monitors the quality of watercourses at designated stations. Furthermore, water quality is monitored at abstraction points and groundwater is occasionally tested under various projects. Systematic monitoring of Neogene and karstic aquifers has not yet been established. Generally speaking, there is a considerable diversity in natural groundwater quality and human impact on this quality in Serbia. It depends on the type and properties of the resource itself, as well as its vulnerability and the pressures to which it is exposed.

As previously discussed, groundwater from the BWC in Vojvodina has high baseline concentrations of organic matter ($KMnO_4$ demand can exceeds 20 mg/l, e.g. at Odžaci), arsenic, iron and manganese. The iron content was found to be as high as 3 mg/l in some samples. The BWC groundwater has low concentrations of manganese, nitrites, and nitrates. Generally, the water is of the sulphate-hydrocarbonate type, with a mineralisation level of around 450-750 mg/l [5].

Inadequate protection of alluvial aquifers has, in some places, resulted in water quality changes caused by anthropogenic impacts. A typical example is the alluvium of the lower course of the Velika Morava River which is threatened by high nitrate concentrations due to uncontrolled wastewater discharges and agricultural pressures [12]. Groundwater from the aquifer formed in Neogene sediments is characterised by slower water recharge and exchange, mineralisation can be as high as 1400 mg/l, while iron and manganese content is lower than in the alluvial aquifer. Exceptions can be found only in areas where there is a hydraulic connection between Neogene aquifers and overlying Quaternary aquifers.

With regard to water quality, karstic water resources have a special place in water supply systems. The properties of this water are very favourable, mineralisation is low, and they, as a rule, meet chemical standards. Occasional bacterial contamination is eliminated through chlorination and a large number of water supply systems do not use any additional treatment methods prior to delivery. Another problem related to water quality is an occasional increase in turbidity during flood periods. Most of the karstic areas in Serbia are not populated, which is favourable from the perspective of pollution prevention and protection. On the other hand, discharge characteristics of karstic aquifers are not conducive to protection, in view of the size of karstic channels, caverns and fissures which constitute privileged pathways of circulation. High groundwater flow velocities have been confirmed by a relatively large number of tracer tests. They allow for pollutant transport to a distance of up to 10 km during a single day [7, 8].

The largest Serbian cities, Belgrade and Novi Sad, have batteries of radial wells located along the banks of the Sava and the Danube, respectively. Unfortunately, there is a conflict between the need of the cities to occupy riverbanks and the imperative to protect water sources from pollution. Sanitary protection zones have been identified only for large sources of water supply but, even where they have been identified, examples of active and systematic protection are rare.

IMPACT OF GROUNDWATER QUALITY ON SOURCE PRODUCTIVITY AND AGEING OF WELLS

Groundwater is generally preferred because of its quality, pleasant taste, agreeable temperature, and proximity to the point of water consumption.

Throughout the world, there is increasing reliance on subsurface filtration of groundwater as part of the drinking water preparation process. The ultimate goal of filtration through an alluvial aquifer, or bank filtration, is to attain the baseline quality of groundwater; in most cases, long-term water quality impacts tracing to human activity are largely eliminated and the consequences of accidental pollution of groundwater, or of the river that recharges the aquifer, mitigated. When the size of safeguard zones of sources of drinking water supply and the constraints that apply to them are defined, it is necessary to properly consider the baseline quality of the groundwater, the quality of the surface water that recharges the aquifer, the potential and actual human pressures on surface water and groundwater quality, the purification potential, and the aerobic state of the groundwater. This is also true of problems related to the design of a groundwater source and its water regime. The rate of abstraction and the operating mode of the source determine the groundwater flow velocities, which in turn govern water quality transformations and the purification potential of groundwater, but also affect the performance and ageing of groundwater abstraction facilities.

Apart from purification effectiveness, current groundwater quality, oxic state and regime have a major effect on both the rate of well ageing and the well maintenance approach, whose economic significance is considerable.

A series of capital research projects addressing alluvial groundwater have been undertaken during the past five years [25, 26, 27]. Their main goal was to assess the purification effectiveness of the bank filtration method at a number of large existing or potential sources of drinking water supply located in the alluviums of Serbia’s largest rivers. Special attention was devoted to the removal of hazardous substances [27], and to substances which have not yet been regulated (emerging pharmaceuticals) [28].

Bank filtration was found to be highly effective in the degradation of organic substances and in the removal of organic micropollutants. For example, it is interesting to note that at the Belgrade Groundwater Source (Sava River alluvium, 99 radial wells), transformation of the Sava River bank filtrate leads to a DOC reduction from an average of 2.5 mg/l in the river water to slightly more than 1 mg/l in the raw well water. Additionally, the raw water abstracted at this site complies with all drinking water standards, except for slightly elevated iron and manganese concentrations.

A considerable degree of removal or reduction in concentrations of significant emerging pharmaceuticals was noted on the way from the large rivers to the wells of alluvial drinking water sources [29].

Well ageing due to biochemical clogging was monitored at a large number of important sites relying on bank filtration or AR. The indicators which were monitored included the Redox potential, O_2 content, iron concentration in water, entrance velocities at well screens, grain-size distributions in the vicinity of well screens, and the like. The results highlight the effect which the occurrence of iron minerals in water has on the achievement of a certain oxic state of the groundwater, and on the rate of clogging of well screens [30, 31, 32]. Biochemical clogging is now recognised as a major challenge for alluvial sources with a low oxic state of groundwater, and it should certainly be an important criterion in the selection and design of groundwater abstraction sites and facilities.

Alluvial sources are likely the most important drinking water supply resources in a large number of countries, including Serbia. Figure 5 shows the trend of $KMnO_4$ demand of the Sava River and of the raw water abstracted at the Belgrade Groundwater Source.

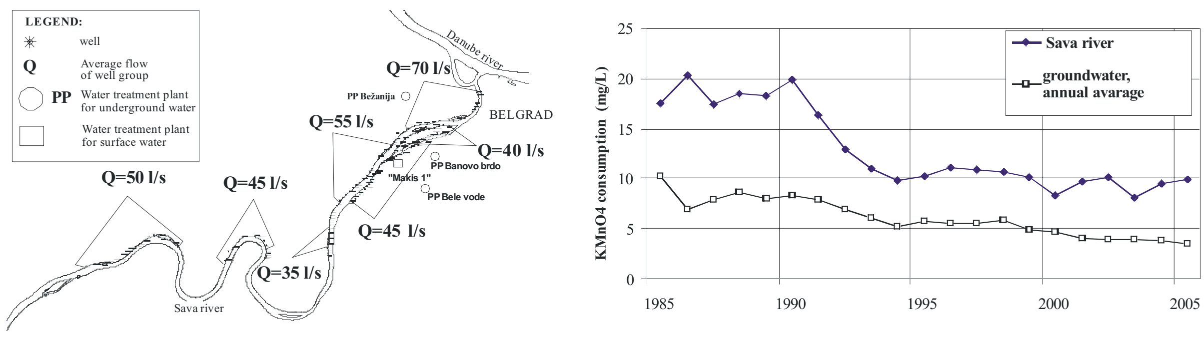

Figure 5: Belgrade Groundwater Source – radial (Ranney) wells along the Sava River banks and representation of estimated average monthly $KMNO_4$ demand of the Sava River water and blended groundwater at the source (Source: [29]).

Of course, river water quality is extremely important, as a starting point for achieving good water quality after bank filtration. This requires relatively positive trends of the three largest rivers (the Danube River, the Sava River and the Tisza River). The quality trends of the fourth largest river, the Velika Morava, are generally stagnant. Figure 6 shows water quality variation of the Danube River over the past 15 years, via the BOD parameter.

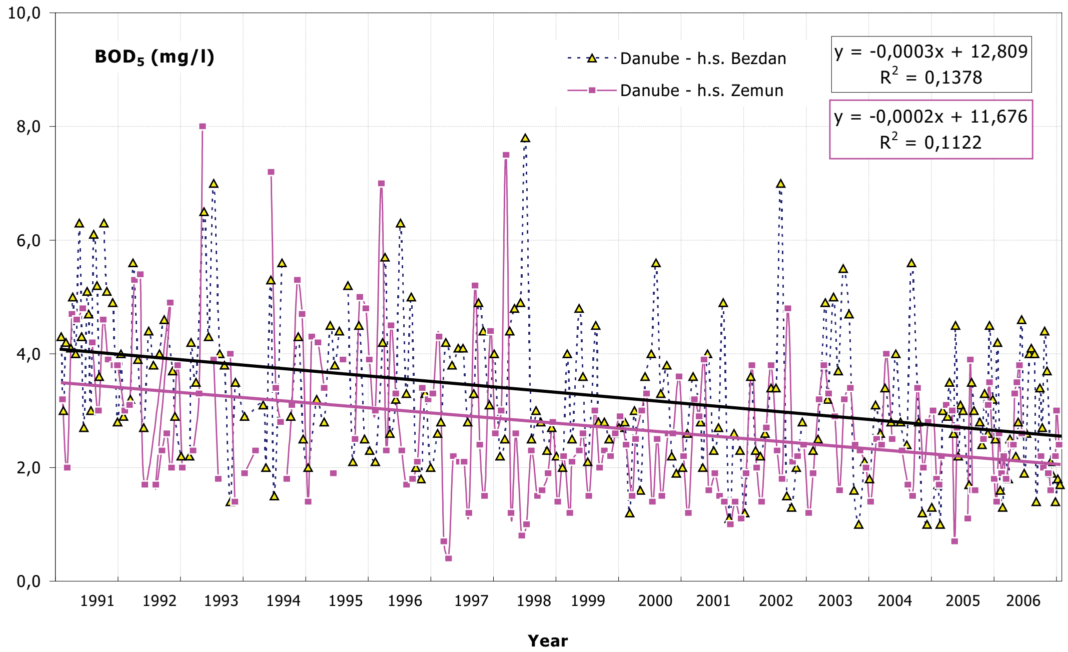

Figure 6: BOD_5 of the Danube River at the border between Serbia and Hungary, and immediately upstream from Belgrade, 1991-2008 (Source: [29])

GROUNDWATER-RELATED LEGISLATION IN SERBIA

Serbian groundwater legislation is comprised of several acts, which mainly address the issues of the quality and protection of groundwater as a part of the environment and the water cycle. These documents include: the Water Law (Official Gazette of the RS 30/10), the Code of Practice for the Classification and Categorization of Groundwater Reserves (Official Gazette of the SFRY, 1978), the Geological Exploration Law (Official Gazette of the SRY, 1995), the Law on the Determination and Classification of Natural Mineral Resources and Data Presentation (Official Gazette of the SRY, 32/98), the Code of Hygienic Practice for Drinking Water (Official Gazette of the SRY 42/98), the Environmental Protection Law (Official Gazette of the RoS 135/04), the Strategic Environmental Impact Assessment Law (Official Gazette of the RoS 135/04), the Law on Integrated Prevention and Control of Environmental Pollution (Official Gazette of the RoS 135/04), and the Code of Practice for Safeguard Zones of Water Sources and their Preservation (Official Gazette of the RoS 92/08).

The most important act dealing with groundwater is the Water Law. Upon its entry into force in 2010, governmental policy recognised groundwater issues and their specifics in a proper way. Major tasks on the implementation of the Water Law are related to the protection of groundwater sources, the maintenance and upgrading of existing sources, and the development of new sources. The Water Law introduces water management planning, through preparation of documents, including:

- The Water Management Strategy for the territory of the Republic of Serbia;
- The Water Management Plan;
- The annual Water Management Programme;
- Plans which address protection against the adverse effects of water (flood risk management plan, the general flood defence plan, etc.)

Another legal act which has a major influence on the protection of groundwater for drinking water purposes is the Code of Practice for Safeguard Zones of Water Sources and their Preservation (Official Gazette of the RoS 92/08). This Code requires the establishment of three safeguard zones for groundwater sources, whose perimeter is defined using a criterion based on the time of water travel through the saturated zone (the maximum time it takes for a contaminant to reach the abstraction point). This is a widely used criterion that should provide confidence that the concentration of contaminants will be reduced to an acceptable level.

Based on this Code, physical protection of groundwater abstraction facilities must be provided in the 1st protection zone, in order to prevent rapid ingress of contaminants or damage to the wellhead. The 2nd protection zone is based on a minimum 50-day travel time, sufficient to reduce pathogens to an acceptable level that can be removed in the treatment process. The 3rd zone is based on a minimum 200-day travel time, estimated to be needed for natural purification processes (dilution and effective attenuation of slowly degrading substances).

Problems in the implementation of the protection concept based on travel time arise when it is applied to existing groundwater sources, in areas where there is already a developed land-use pattern, such as agricultural production, industry, municipal infrastructure, and the like. In such cases, certain restrictions must be imposed on the activities of other land users, especially in the 2nd and 3rd protection zones. In the case of large groundwater sources near urban areas and a specific land use environment, certain restrictions could severely limit land development. In such cases, besides the travel time approach, more sophisticated methods for the definition of sanitary protection zones are used.

Although specific approaches to the definition of sanitary protection zones generally require a much greater knowledge of local conditions, the benefits can be mutual, for water supply operators (waterworks) as well as other land users. In view of the importance of drinking water sources, the design of groundwater source protection zones must also address the principle of characteristic parameters. In effect, this is a "...set of substances present in the water, whose characteristics can be used to define the water production line with an adequate degree of reliability". These substances may have such characteristics because of their: mobility in groundwater, harmful effects, (non-)sorbability, (non-)degradability and potentially-high concentrations.

Most important activities in the legislation area which lie ahead are those concerning the development of by-laws, addressing the establishment of GW quality threshold values, status assessment methodologies and groundwater monitoring.

IMPLEMENTATION OF THE EU WFD IN THE FIELD OF GROUNDWATER IN SERBIA

Although not obliged by national laws, by ratifying the Danube River Protection Convention (DRPC) in 2003, Serbia became actively engaged in the implementation of the WFD as a full member of the International Commission for the Protection of the Danube River (ICPDR). Serbia took part in the preparation of the 2004 Roof Report for the Danube River Basin District and in the development of the Danube River Basin District Management Plan (DRBMP, 2009), as well in the preparation of RBMPs for sub-basins of the Tisza River (completed in 2010) and the Sava River (in progress).

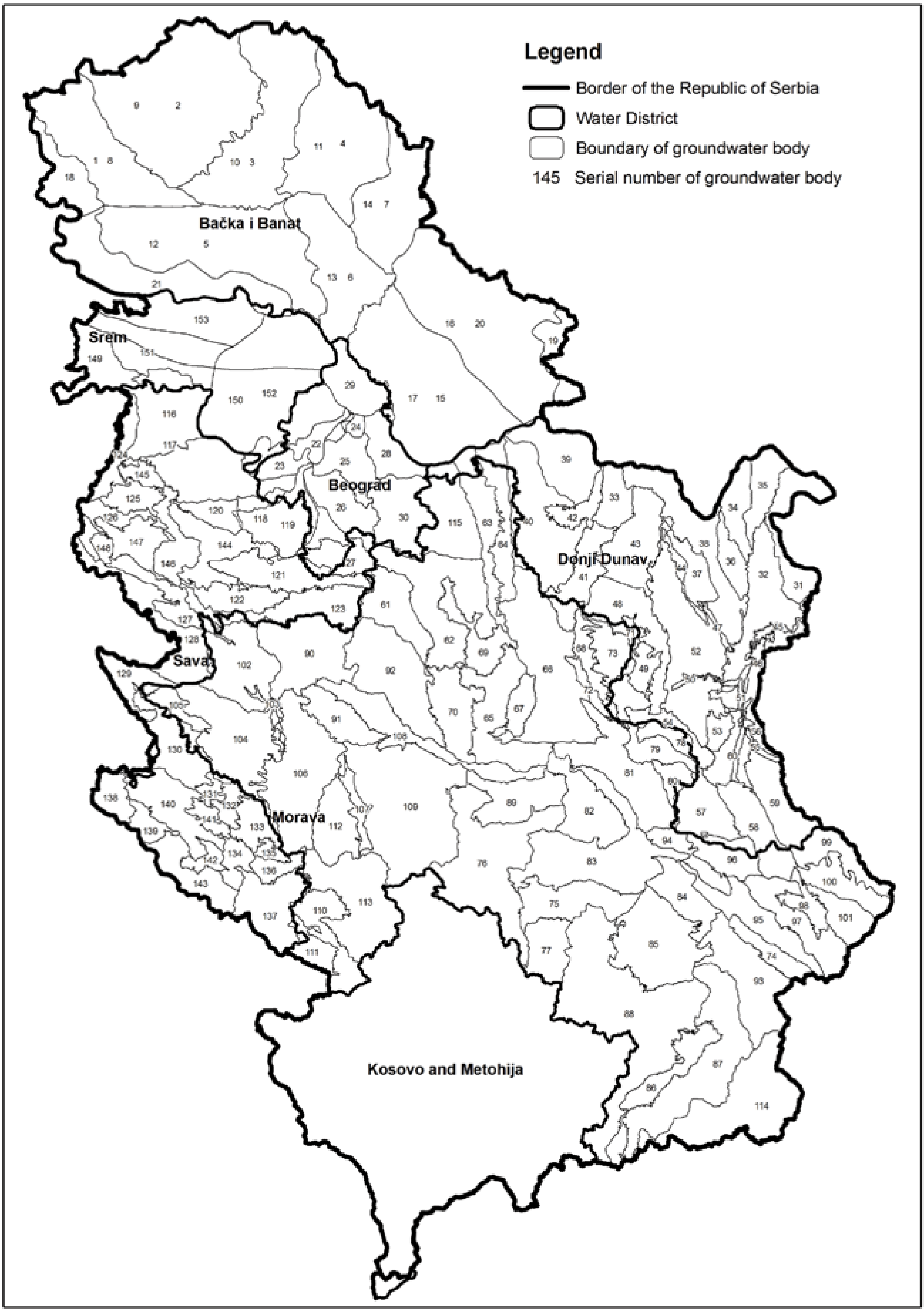

Figure 7: Map showing designated groundwater bodies in Serbia
(Source: Code on the Designation of Surface Water and Groundwater Bodies, Official Gazette of the RoS 96/10).

By adopting the Water Law in 2010, Serbia fully accepted the standards, terminology and goals declared in the WFD. A set of bylaws have been drafted, among them the Code on the Designation of Surface Water and Groundwater Bodies (Official Gazette of the RoS 96/10). 153 groundwater bodies (GWBs) have been identified in Serbia, as shown on the map in Fig. 7. Based on aquifer types, all GWBs were divided into: porous (Quaternary and Neogene), karstic and fissured.

In order to enable accurate assessment of the status of groundwater, GWBs have been identified as coherent units in the river basin to which environmental objectives must apply. Criteria for the delineation of the GWBs were based on local geological and hydrogeological conditions and data availability on natural conditions and pressures. In general, the hierarchical approach (groundwater → aquifer → groundwater body), recommended by CIS Guidance Document no. 2, was followed. During the process of delineation of groundwater bodies in Serbia, the principle criteria were the geological characterisation of the rock mass, hydrogeological boundaries and present quantitative pressures (groundwater use). The GWBs were designated according to a combination of criteria including the geological type, borders of the surface catchment areas and present anthropogenic pressures.

At present, groundwater resources are monitored at several levels: national level, municipal (town) level, and water supply source level, as well as in a portion of the riparian lands of the Danube, Sava, and Tisa rivers which are within the reservoir zone of the Iron Gate Dam. A state network of monitoring stations under the responsibility of the Hydrometeorological Service of Serbia-HMS (total number approx. 500) has been established for continuous monitoring of quantity and quality characteristics of surface water and groundwater regimes; the network is divided into monitoring areas corresponding to the basins of major rivers or large water-bearing strata within Quaternary sediments. Systematic monitoring of Neogene and karstic aquifers has yet to be established.

As for nearly all chemical monitoring points in Serbia (approx. number 70, Fig. 8) the monitoring frequency is once per year. About 50 different parameters are analyzed on a regular basis. These parameters include the main cations (i.e., Na^+, K^+, Ca^{2+} and Mg^{2+}), the main anions (Cl^-, SO_4^{2-} and HCO^{3-}), and the three nitrogen components (NH_4-N, NO_2-N and NO_3-N), which are major indicators of agricultural impact on shallow aquifers. The redox-sensitive parameters, iron and manganese, are part of the monitoring programme, as are the heavy metals Zn, Cu, Cr, Pb, Cd, Hg, Ni and As. Furthermore, measurements for groundwater contamination originating with certainty from non-geogenic sources are also included. Some prominent pesticides, like Lindane, Atrazine, Simazine, Propazine, Aldrin, Endrin, and Methoxychlor, and other organic chemical substances like PCB's (potential anthropogenic contaminants), are also covered by this programme. As far as chemical analysis is concerned, all major components - other than lightly volatile halogenated hydrocarbons (typical point-source related substances - defining the groundwater quality according to the EU WFD or the EU GWD), are covered by the regular groundwater quality monitoring programme. Additionally, water quality is monitored at abstraction points and groundwater is occasionally tested under various projects.

Due to uneven coverage of the groundwater monitoring network and programmes, information on chemical and quantitative status of GWBs in large parts of Serbia is very limited or missing. This presents a major obstacle for reliable groundwater status assessment of a large number of GWBs, so only an assessment of the risk of failing to achieve WFD Art. 4 objectives is available in some cases.

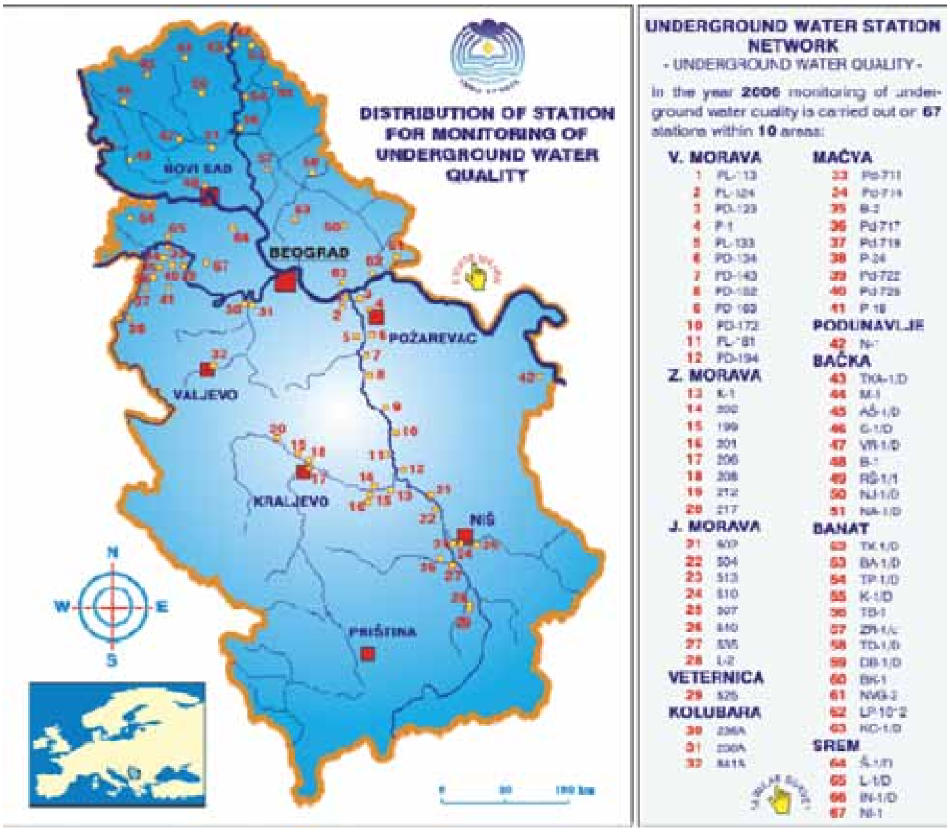

Figure 8: Groundwater quality monitoring stations in Serbia (Source: HMS).

Chemical risk assessments were made on the basis of the type of land use and the substances present, as indicators of potential diffuse sources of pollution (use of CORINE Landcover 2000), the location and potential impact of point sources of pollution, and natural protection of groundwater bodies from possible pollution from the ground surface. To assess the risk of failure to achieve good chemical status due to diffuse sources of pollution, a risk map was compiled based on natural characteristics and pollution susceptibility (vulnerability map), and on local facilities and activities which might contribute to pollution (land use map). Like quantitative risk assessments, they were based on available results of national monitoring programmes, as well as on the results of monitoring programmes conducted for other purposes (i.e. calculation of groundwater reserves). For groundwater bodies where no quantitative monitoring exists, the groundwater balance is estimated using available data on precipitation, abstraction, etc. The risk of failing to achieve good quantitative status was assessed based on the criteria that average GW abstraction over several years is less than 50% of the groundwater recharge, that there is no substance intrusion into the body caused by a change in the GW streaming direction, and that associated surface ecosystems are not endangered by GW abstraction. In case one or more of these criteria are not fulfilled, the GW body is "at risk".

It is, therefore, necessary to expand the existing groundwater monitoring network to encompass all aquifers, through the inclusion of groundwater user facilities (water supply systems, industry, agriculture) and the establishment of new monitoring sites. Monitoring data are to be used to verify risk assessments and complement human impact assessments. Groundwater monitoring delivers information required for the assessment of long-term trends resulting from the alteration of natural conditions and human activity, as well as data needed to evaluate the effectiveness of programmes of measures undertaken to improve groundwater status.

Since groundwater is an integral part of the water cycle, a groundwater balance assessment is required for the development of sustainable planning. In line with these planning and management needs, several projects, such as “Groundwater Balance in Serbia” and “Monitoring of GW Resources in Serbia” are in progress. Their main goals are to provide a groundwater balance assessment, upgrade groundwater monitoring and set up a groundwater information system as a part of the integrated water information system. One of the outcomes of the project Monitoring of Groundwater in Serbia will be a Groundwater Vulnerability Map for the country as a whole, in the scale 1: 500,000. Although the methodology for this kind of mapping was developed during the past two decades and is well known, this was one of the first attempts to generate such a map on a regional (national) scale. The problem of hydrogeological complexity of the territory was overcome by selecting special criteria and approaches. This map is supposed to provide a basis for planning on a regional scale and contribute to the preparation of national and regional master plans, water master plans, RBMPs, as well as various studies of the protection of nature and geodiversity sites [15].

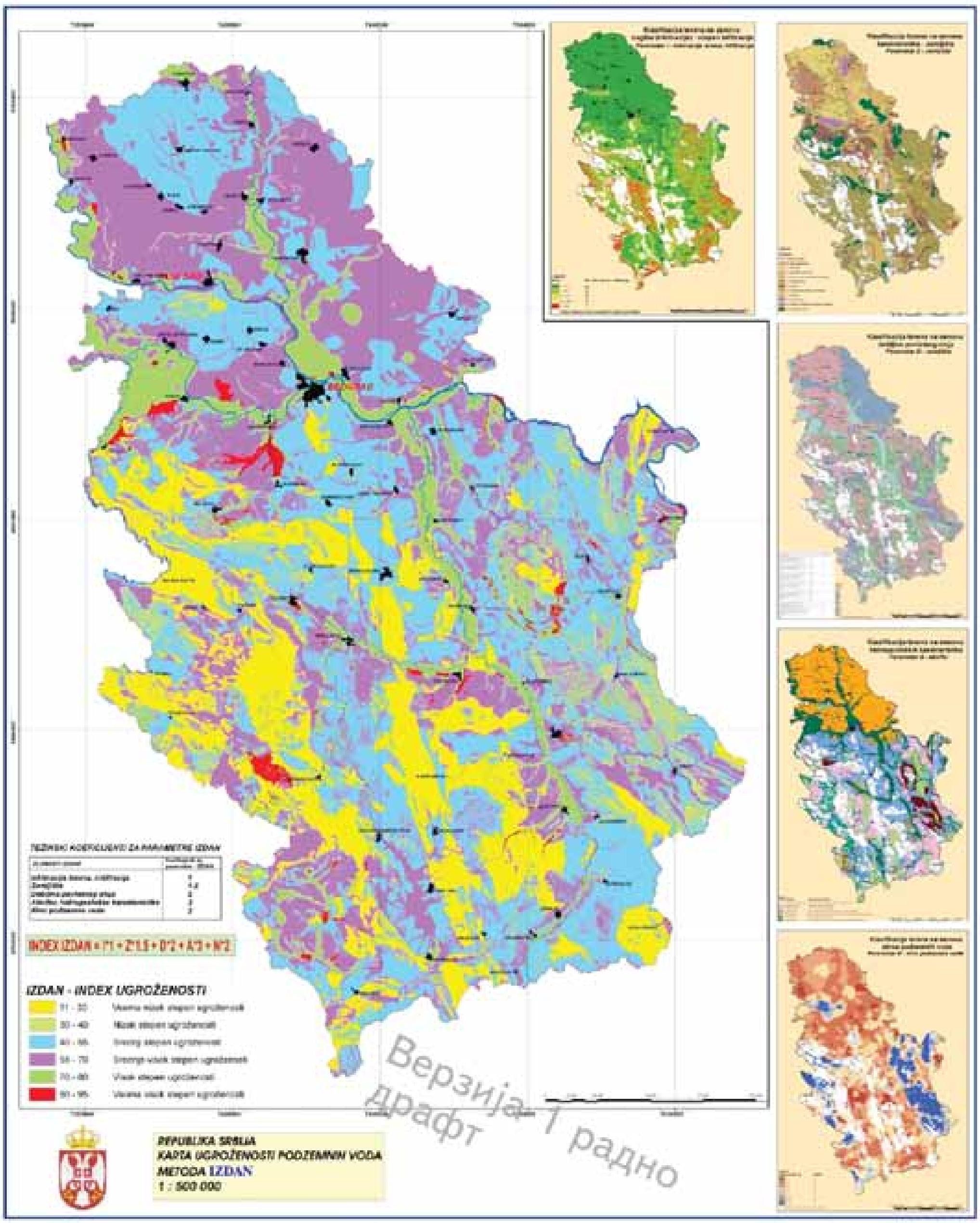

Figure 9: Groundwater Vulnerability Map of Serbia - draft [15]

TRANSBOUNDARY AQUIFER ASSESSMENT AND MANAGEMENT

During the past several years, increasing attention has been paid to the identification, assessment and management of transboundary aquifers. Some of these activities were synchronised through direct bilateral communication of national institutions (ministries and their bodies) [16], others were undertaken by UN-coordinated action (UN/ECE) [24], while some resulted from EU funded projects [18].

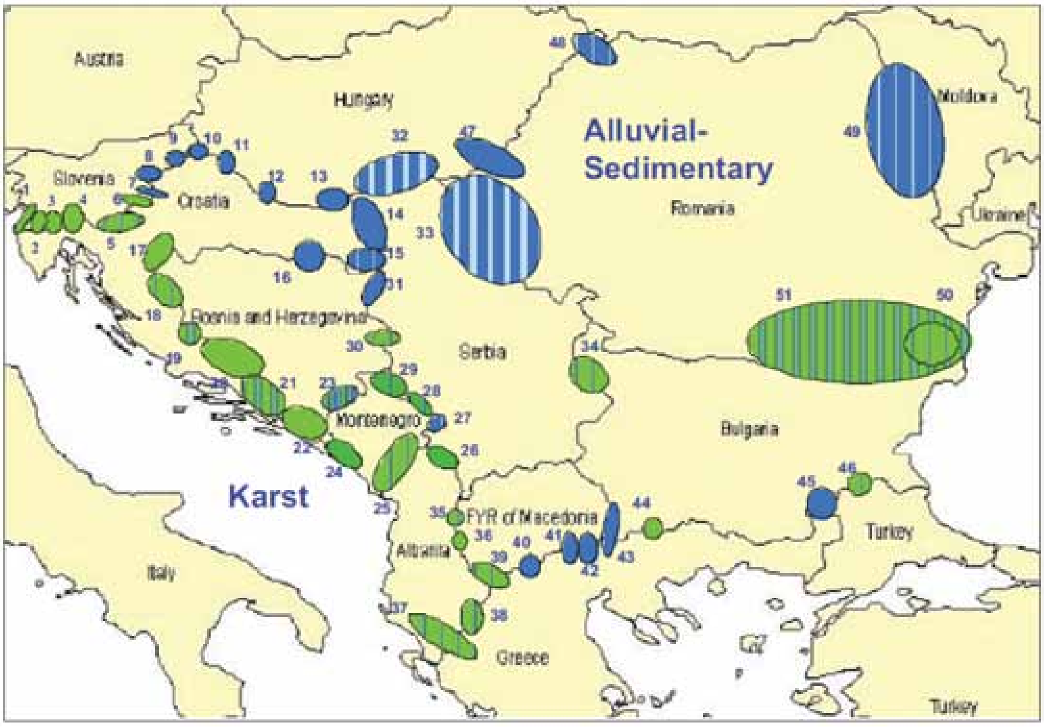

Figure 10: Distribution of transboundary groundwaters in the SEE region (Source: [24])

“Sustainable Development of Hungarian-Serbian Transboundary Aquifer (SUDEHSTRA)” is a good example of recently successfully implemented transboundary water projects. The project was focussed on groundwater resources of the thick Tertiary aquifer layers deposited in the Pannonian Basin between the Danube and Tisa rivers and shared by the two countries. This groundwater is vital for the economy and society in this part of SE Europe, where nearly one million inhabitants along the border use the groundwater for drinking and other purposes. Experts of the two countries worked jointly on this “mirror” project, aimed at improving the knowledge of the common groundwater resource and establishing a basis for its sustainable utilisation and protection [18].

GROUNDWATER USE AND PROTECTION PROSPECTS IN SERBIA

Groundwater is a very important component of the organically integrated water system. Resolution of numerous, extensive and not particularly easy problems will require an appropriate institutional set-up, legislation, and an adequate funding system. Major tasks are related to the development of new sources, wider application of artificially controlled aquifers, the maintenance and upgrading of existing sources, and the protection of groundwater sources.

General activities in the area of groundwater in Serbia which lie ahead could be summarised as:

1. Enforcement of GW legislation (implementation of the Water Law and related bylaws, establishment of safeguard zones…);
2. Preparation of studies and planning documents (development of River Basin Management Plans, Groundwater Balance, Groundwater Monitoring System Design);
3. Development of groundwater monitoring and information system as a part of the Water Management Information System;
4. Achievement of systemic and financial prerequisites for adequate use and protection of groundwater resources;
5. Development of regional groundwater sources (regional water supply systems for Vojvodina, review and upgrading of sources for Belgrade's water supply, improvement of water supply in the Lower Morava Basin);
6. Protection of groundwater bodies and protection of groundwater sources of water supply.

National groundwater reserves are being assessed through one of the strategic projects (Groundwater Resources Assessment of Serbia – Control and Development of Aquifers), by leading national institutions in the groundwater sector (along with Monitoring of Groundwater of Serbia). At this stage, preliminary analyses revealed that new groundwater sources could be developed in intergranular and karstic aquifers, with abstraction rates of 5m^3/s and 2m^3/s, respectively.

In certain parts of the country the development of regional water supply systems appears to be a prudent solution. In Vojvodina, regional systems should deliver water from alluvial aquifers of the Danube (Apatin-Sombor and Kovin-Dubovac areas) to Northern Bačka and Northern Banat [20, 21].

Consideration has to be given in the future to the largest national system - Belgrade's water source and the problems facing its 99 radial wells (declining yield, conflict with the expanding city, too-wide or too-narrow sanitary protection zones, and the like). Solutions are being sought through revision of this source's configuration and its protection zones. It is also necessary to re-define maintenance procedures for water abstraction wells and the water source as a whole. Judging by all indicators, it will be necessary to develop two new AR sources of water supply [22, 23].

Problems associated with protection of groundwater against nitrate pollution in the alluvium of the Velika Morava must be addressed more actively in the future. Solutions are being sought in regulation of wastewater disposal and agricultural production. Furthermore, new water sources should be developed or the existing ones protected, often by means of AR.

The creation of systemic and financial prerequisites for proper use and protection of resources is a precondition for a fully-functional water sector. Water tariffs in Serbia vary by consumer category and average approximately 0.35 €/m^3. A charge of 0.35-0.5 €/m^3 is currently collected for the production of 1 m^3 of clean water and the disposal of 1 m3 of wastewater. This is, of course, inadequate, and the situation has not changed during the past five years [1]. It is estimated that the total charge for 1 m^3 of drinking water and 1 m^3 of collected and adequately treated wastewater should amount to 1.2-1.4 € [19]. Such tariffs would cover operating costs, capital-intensive maintenance, and new capital projects. These tariffs should be reached gradually (over several years), in order to adapt the entire system to a higher revenue stream and not to unduly burden family budgets. Consideration should also be given to the fact that water management is an integrated process, and that activities aimed at improvements in water abstraction, water protection, and protection against the adverse effects of water should be undertaken in parallel. It is estimated that investments in the water sector at a level of 6 ·109 € [19] will be required to meet municipal water demand, regulate the water sector, and fully meet requirements arising from the WFD. Primary capital-project investors must include the government (wide-ranging projects, which require funding incentives), municipalities, and the private sector. This will require legal, financial and institutional improvements in the water sector. These prerequisites are related to the establishment of an appropriate social system which includes [19]:

- adequate capacities and set up of the government apparatus,
- appropriate scientific, professional and economic capacities,
- appropriate legislation, and
- financial instruments (water tariffs and appropriate financial institutions).

Investment preparation in this area must be provided on a timely basis, through adequate research, investigation, planning, design, engineering, and administrative processes.

The water tariff increase must reflect economic principles and requirements relating to planning, operation, maintenance, depreciation, and new investments in the area of groundwater utilisation and protection of specific groundwater resources used for water supply.

In order to ensure sustainable water supply in the future and expand existing groundwater systems, it will be necessary to plan and implement adequate research and technical measures. In view of the fact that two main groundwater categories are used, one related to karstic and the other to intergranular aquifers, the methods for any interventions relating to their control are quite different and should be adapted to local circumstances accordingly.

In terms of groundwater protection, the following aspects remain prioritised:

- Protection of surface water which recharges groundwater,
- Regulated wastewater treatment and disposal,
- Agricultural production harmonised with groundwater protection requirements, and
- Regulation of water source protection zones.

Proposed protection must be practicable and effective, in order to avoid major conflicts with other users of respective areas and to efficiently protect the water resources. In addition to the above, adequate knowledge and utilisation of the aquifers' self-purifying potential are needed to successfully address and complete these tasks.

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Notes:

Full Paper

GROUNDWATER IN THE TISZA RIVER BASIN MANAGEMENT PLAN

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Abstract: Aiming at the objectives set by the EU Water Framework Directive (2000/60/EC), Tisza countries (Ukraine, Slovakia, Hungary, Romania and Serbia) agreed to prepare the International Tisza River Basin Management Plan (ITRBMP), integrating the issues on water quality and water quantity, land and water management, floods and drought. Groundwater bodies (GWBs) are important sources for public water supply, industry and agriculture in the Tisza River Basin. The countries in the region, with the exception of Romania, depend mainly on groundwater sources to meet their drinking water needs (ICPDR, 2008). Based on common agreed criteria, 85 GWBs were identified as of basin-wide importance, putting them in focus concerning pressure analysis, status assessment and implementation of measures in order to achieve good quantitative and chemical status. Main reasons causing poor chemical status of some GWB's in the Tisza River Basin (TRB) are the pressures on the quality by nitrates from diffuse sources, which are the agricultural activities, non-sewered population and the urban land use. The assessment of pressures on the quantity status shows that the over-abstraction prevents achieving of a good quantitative status for 19 GWBs. Basic measures, listed in Annex VI, Part A of WFD, are foreseen as key instruments in achieving good chemical status and reversal of any significant and sustained upward trends in the concentrations of nitrates in groundwater in the Tisza River Basin. To address the quantity issues, controls of the abstraction of fresh surface water and groundwater and impoundment of fresh surface waters including a register or registers of water abstractions are foreseen as key measures.
Keywords: groundwater, management plan, measures, status, Tisza River Basin

INTRODUCTION

In 2004 Tisza countries (Ukraine, Slovakia, Hungary, Romania and Serbia) signed the Memorandum of Understanding - Towards a River Basin Management Plan for the Tisza River, aiming at the objectives set by the EU Water Framework Directive (2000/60/EC). Countries agreed to prepare the International Tisza River Basin Management Plan (ITRBMP), the document which should integrate the issues on water quality and water quantity, land and water management, floods and drought. In order to harmonize the approach for the Tisza sub-basin level with the approach already implemented on the Danube Basin level, same Significant Water Management Issues (SWMIs) are adapted for the Tisza River Basin that impact the water quality of surface and groundwater-organic pollution, nutrient pollution, hazardous substances pollution and hydromorphological alterations. Additionally, water quantity has been identified as a relevant water management issue in the Tisza River Basin, and three issues of concern for the integration of water quality and water quantity are floods and excess water, droughts and water scarcity and climate change. Main management objectives for the Tisza River Sub-basin are to describe the measures that need to be taken to reduce/eliminate existing significant pressures and to improve the linkage between measures on the national level and on the basin and sub-basin level for surface water and groundwater.

DELINEATION OF GROUNDWATER BODIES

According to Annex II of the WFD: “Member States shall carry out an initial characterisation of all groundwater bodies to assess their uses and the degree to which they are at risk of failing to meet the objectives for each groundwater body under Article 4. Member States may group groundwater bodies together for the purposes of this initial characterisation.” In order to focus their activities on issues of basin-wide importance, Tisza countries have agreed to select only important GWBs to be included in the Integrated Tisza River Basin Management Plan (ITRBM Plan) and JPM. For that purpose a size threshold of more than 1,000 km^2 was defined for both transboundary and national for GWBs. Additional criteria for selection of transboundary GWBs (if the size was less than 1,000 km^2) were: socio-economic importance, uses, impacts, pressures, interaction with aquatic ecosystems, etc. Based on the data collected by GW characterization templates from all five Tisza countries 85 GWBs of basin-wide importance were identified (51 transboundary and 34 national) (Table 1, Fig.1).

Table 1: Overview of number and size of important GWBs in the Tisza River Basin (ICPDR, 2010).

	Number of GWBs			**Size of GWBs**	
Country	**National**	**Transboundary**	**Total**	**Area Range (km^2)**	**Total Area (km^2)**
UA	3	6	9	290-4.769	24.569,27
SK	5	2	7	598-4.107	12.283,00
HU	19	25	44	491-5.037	80.924,77*
RO	3	8	11	1.358-15.995	42.049,00
RS	4	10	14	1.013-2.643	22.750,68*

** In HU and RS there is overlapping of shallow and deep GWBs*

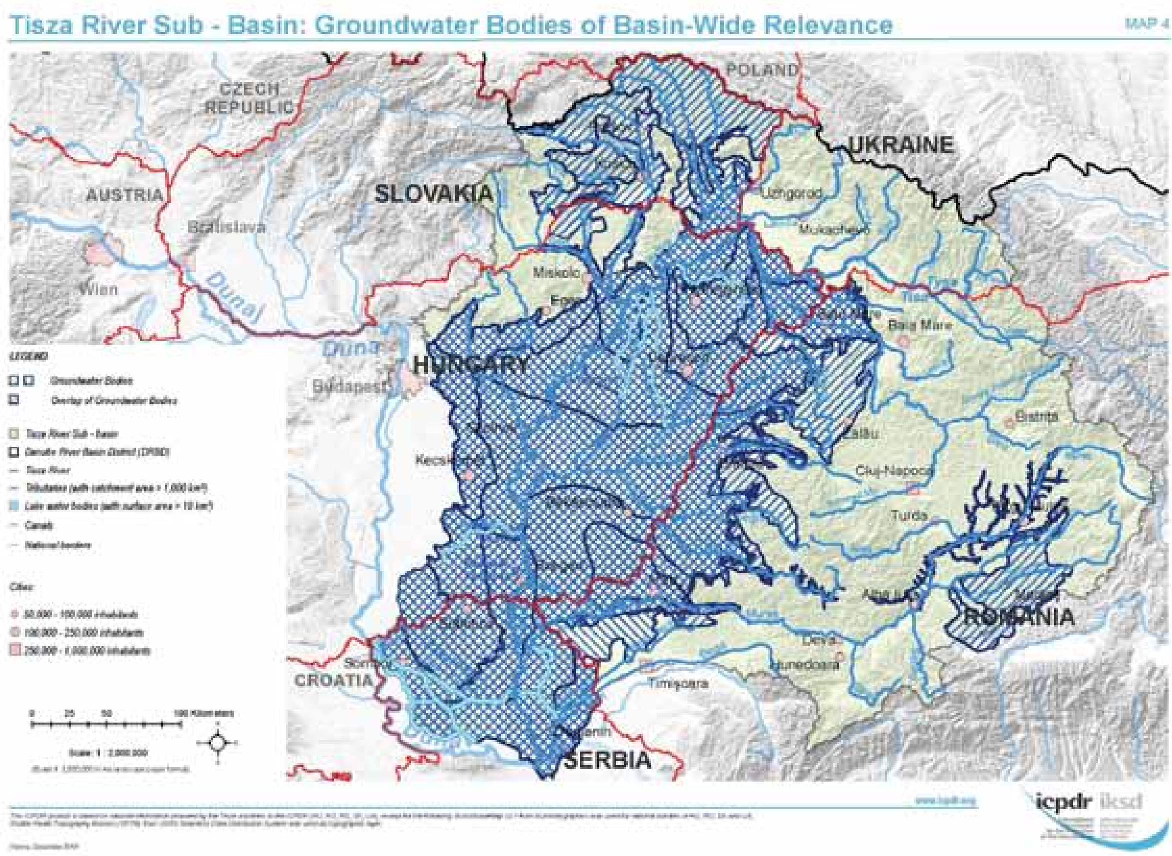

Figure 1: Groundwater bodies of basin-wide importance in the Tisza River Basin (ICPDR, 2010).

The GWBs were generally delineated according to a combination of criteria including the geological type and the borders of the surface catchment areas. Thermal water bodies were sometimes additionally separated on the basis of their temperature. Sand, gravel, silt, clay and boulder are the main components of the aquifers of the important GWBs.

SIGNIFICANT PRESSURES ON GROUNDWATER QUALITY AND QUANTITY

The main reasons for the pollution of the groundwater in the Tisza River Basin are:

- water pollution caused by intensive agriculture and livestock breeding,
- insufficient wastewater collection and treatment on municipal level,
- inappropriate waste disposal sites,
- urban land use,
- insufficient wastewater treatment at industrial enterprises.

Main reason causing poor chemical status of some GWB's are the pressures on the quality by NO_3^- and NH_4^+ from diffuse sources, which are the agricultural activities, non-sewered population and the urban land use (run-off from urban, paved areas). Problems with diffuse pollution in some cases are coupled with quantity issues, like over-abstraction. Main identified point sources of pollution of groundwater are:

- Leakages from waste disposal sites (landfill and agricultural waste disposal);
- Leakages from contaminated sites;
- Mine water discharges;

Those leakages lead to occurrence of other substances in GW bodies such as TCE (one GW body) at concentration levels over the threshold values.

Groundwater quantity is affected by groundwater abstraction for drinking water supply, industrial, cooling plants and agricultural purposes (Fig.2).

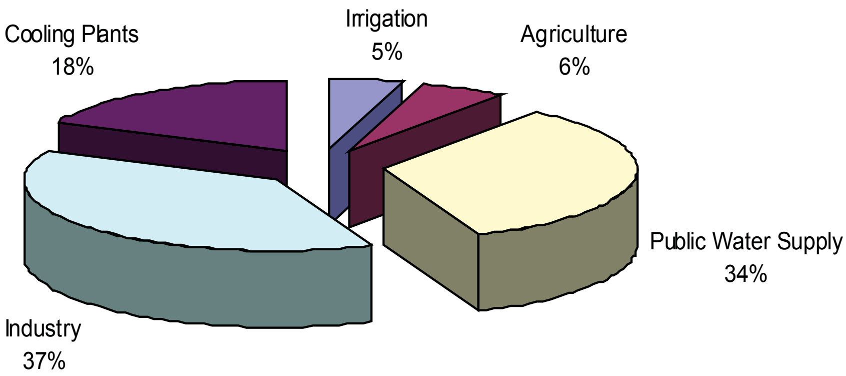

Figure 2: Estimation of the % of different groundwater use in the Tisza River Basin (ICPDR, 2008)

Among different types of groundwater utilisation, abstractions for agriculture and irrigation have comparable significance to that of drinking water. It can be deduced that impacts on quantity status of groundwater in some countries (Hungary, Serbia) are widespread (reduction of borehole yields, significant water level decline and water shortage for depending ecosystems).

GROUNDWATER STATUS ASSESSMENT-METHODOLOGY AND RESULTS

Tisza countries have established different status assessment methodologies, generally following the principles set up in the CIS Guidance Document No. 18 “Guidance on groundwater status and trend assessment” and/or based on results of other projects on national level.

In Hungary, methodology for status determination comprises a series of classification tests (for both quantitative and chemical status). For chemical status assessment, these tests cover drinking water source protection areas (for present drinking water sources and those designated for future drinking water abstraction), surface water bodies, groundwater dependent wetland and terrestrial ecosystems potential. For shallow and karstic GWBs in particular, tests are performed regarding pollution by nitrate and ammonium. Quantitative status is determined by performing three kinds of tests: water balance tests, surface water tests and tests of groundwater dependent wetlands and terrestrial ecosystems. GWB is considered to be in poor status if 20% of its area has continuous decreasing of water level or the groundwater abstraction exceeds the available groundwater resource. As regard to groundwater dependent water bodies, the GWB is classified as in poor status if the remaining spring rate or base flow in the river is smaller than the ecologically required flow, due to reasons of groundwater abstraction.

In Romania, the methodology for the chemical status assessment followed the recommendations of EU Working Group C. The first step was to check for any exceedance of threshold values (TVs). If there is exceedance of some chemical parameters than the tests are carried to assess if the total area of exceedance is greater than 20% of the total area of the GWB (limit for poor status assessment) or there is significant diminution of associated surface water chemistry and ecology due to transfer of pollutants from the GWB. The load of the pollutant transferred from the GWB to the surface water body is compared to the total load in the surface water body (not to exceed 50%). Also, tests are performed for analysis of transfer of pollutants from the GWB to groundwater dependent terrestrial ecosystems (GWDTEs), and drinking water protected areas (DWPAs), to check if there is evidence of increased treatment due to changes in water quality.

To assess chemical status in Slovakia, the proposed methodology stems from the feasibility of the input information, conceptual model and the hydrogeochemical and hydrogeological interpretation of conditions in the Slovak Republic. The TV was determined as a half the interval between the determined NBL and the reference (national drinking water standard). Criteria for assessing the groundwater chemical status for this test were drinking water standards and TVs. In the case of non exceedance, the GWB is recommended to be of good chemical status for the relevant parameters. An acceptable extent would not exceed 20% of the total GWB. To determine the overall quantitative status for GWBs, four tests were applied: water balance test, groundwater level and discharge test, surface water flow test and GWDTEs test.

Serbia has not yet established a groundwater monitoring programme according to the requirements of the WFD so only the risk assessment was done. Chemical risk assessment was analyzed on the basis of combining the type of land use and natural protection of the groundwater bodies.

Ukraine has not yet established a status assessment methodology.

A summary overview of the chemical and quantitative status for the important transboundary and national GWBs is presented in Table 2.

Table 2: Overview of chemical and quantitative status of important GWBs in Tisza Basin (ICPDR, 2010)

Status of GW bodies		UA		RO		SK		HU		RS		Total TRB	Total
		Nat.	Tran.	Nat.	Tran.	Nat.	Tran.	Nat.	Tran.	Nat.	Tran.		
Chemical Status	Good	no data	6	2	7	5	2	17	21	4	10	74	85
	Poor		0	1	1	0	0	2	4	0	0	8	
Quantitative Status	Good	no data	6	3	8	5	2	14	18	2	5	63	85
	Poor		0	0	0	0	0	5	7	2	5	19	

The results of chemical status assessment show that out of 85 groundwater bodies of basin-wide importance 74 water bodies (87%) have good chemical status. Out of this number, there are 49 transboundary and 25 national GWBs. Eight GWBs have poor chemical status and for three GWBs there are no data about chemical status (Fig.3).

The poor chemical status is either caused by values higher than the groundwater quality standard for nitrates, or by values higher than the TVs for other substances individually established by the Member States. It has to be stated that poor status in some cases is caused by more than one pollutant. Table 3 gives an overview of GWBs in poor chemical status by countries, caused by different pressures.

It can be noticed that poor chemical status of groundwater in most cases is caused by extensive agricultural activities and non-sewered settlements, by rule for shallow GWBs with overlying strata less than 5 meters. In such cases, the characteristics of the strata separating an aquifer from the land surface, in terms of how easily pollutants can reach the aquifer from the ground surface, show low capacity to attenuate the pollutants. Evidently, high vulnerability of some GWBs, combined with absence of wastewater collection & treatment systems and/or use of fertilizers requires application of systematic measures for improving the quality of shallow groundwater.

It is important to mention that in several cases the poor groundwater quality is naturally derived, as a result of geochemical characteristics of sediments. Chemical components such as iron, manganese, ammonia, NOM, methane, arsenic can be dissolved from rock by subsurface flow, which according to environmental isotope studies (Deâk, 1995) has been taking place for more than 10.000 years. The concentration of these components in groundwater often exceeds the drinking water quality standards, as it is the case of arsenic in parts of Slovakia, Hungary, Romania and Serbia (Csalagovits, 1999)(Gurzau, 2001) (Dimkic et al., 2010).

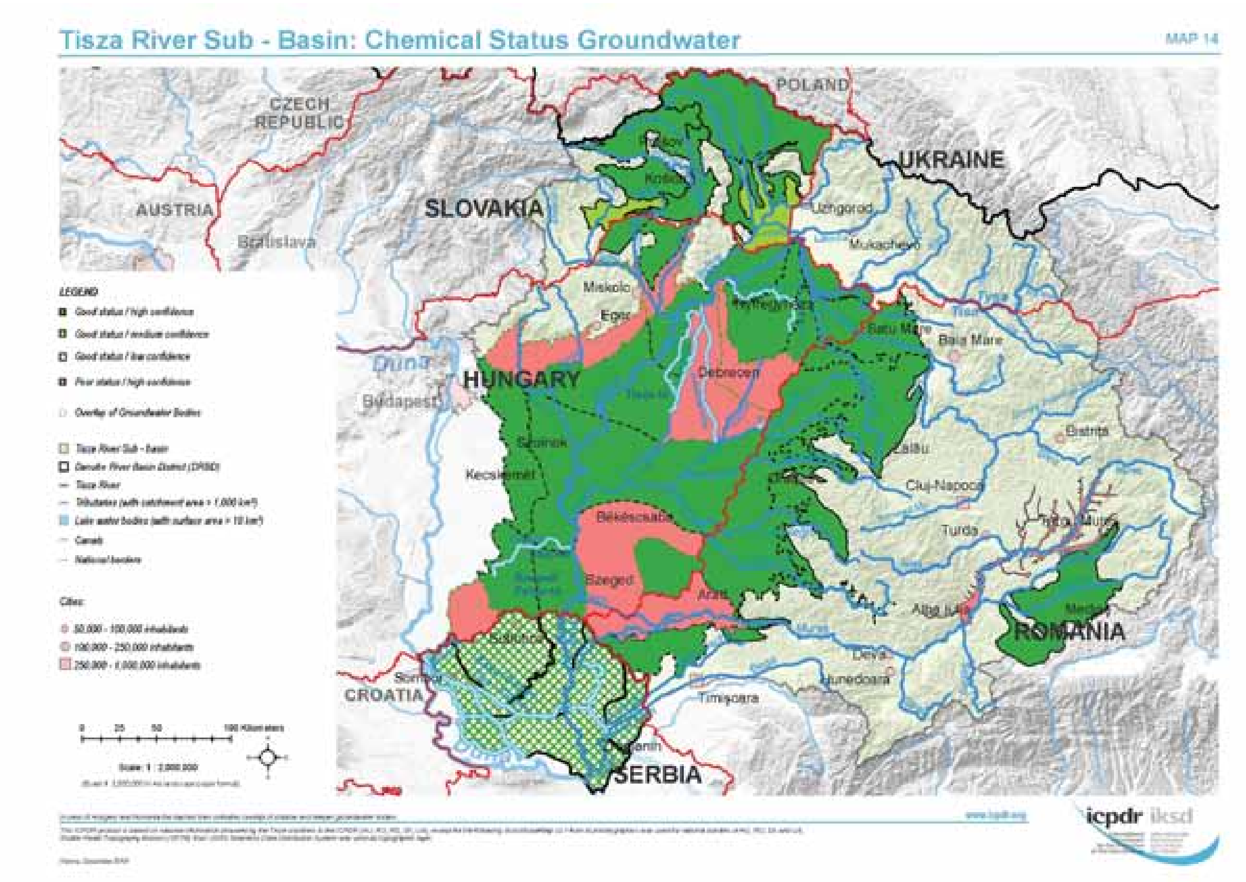

Figure 3: Chemical status of important GWBs in the Tisza River Basin (ICPDR, 2010)

Table 3: Pressures causing poor chemical status of important GWBs in the Tisza River Basin (ICPDR, 2010)

Sources	Number of GWBs with poor chem..status /Pressures posing poor chem..status	UA	RO	SK	HU	RS	Total TRB*
Point sources	Leakages from contaminated sites	-	-	-	2	-	2
	Leakages from waste disposal sites (landfill and agricultural waste disposal)	1	-	-	-	-	1
	Leakages associated with oil industry infrastructure	-	-	-	-	-	0
	Mine water discharges	1	-	-	-	-	1
	Discharges to ground such as disposal of contaminated water to soakways	-	-	-	-	-	0
	Other relevant point sources	-	-	-	-	-	0
Diffuse sources	Due to agricultural activities	4	2	-	6	-	12
	Due to non-sewered population	4	2	-	2	-	8
	Urban land use	-	-	-	5	-	5
	Other significant pressures	-	-	-	-	-	0

The results of quantitative status assessment show that out of 85 groundwater bodies of basin-wide importance good quantitative status was maintained in (case of) 63 water bodies (74%), out of which 39 are transboundary and 24 national GW bodies (Fig.4). 19 groundwater bodies have poor quantitative status (7 national and 12 transboundary) and for 3 GWBs data on quantitative status were not available.

In most cases poor quantitative status is caused by exceeding available groundwater resource due to abstractions for different purposes (agriculture, public water supply and industry), (Table 4).

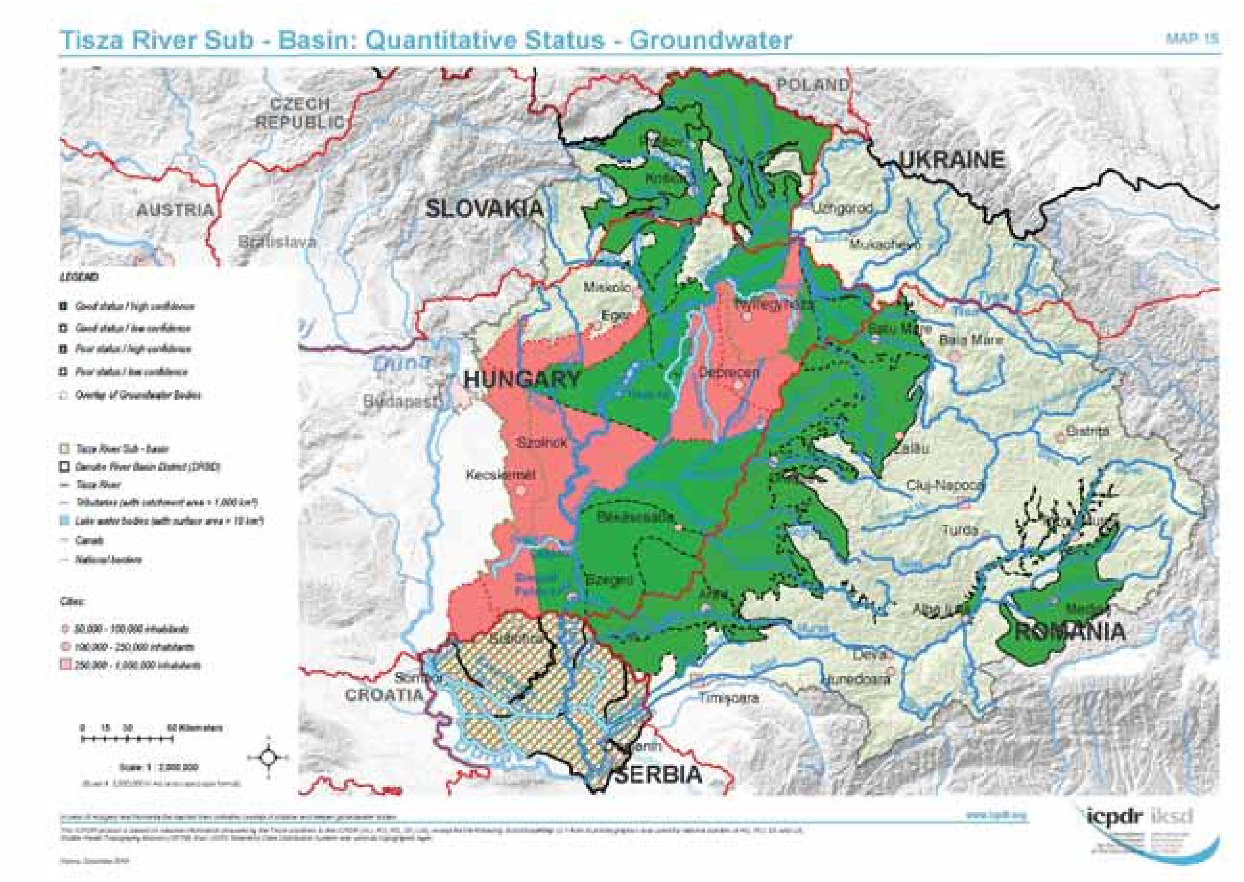

Figure 4: Quantitative Status of important GWBs in the Tisza River Basin (ICPDR, 2010)

Table 4: Different pressures causing poor quantitative status of important GWBs in Tisza Basin (ICPDR, 2010)

Press.	Number of GWBs with poor quant.status / Pressures posing poor quant.status	UA	RO	SK	HU	RS	Total**
Water abstractions	Abstractions for agriculture	-	-	-	-	7	7
	Abstractions for public water supply	2	-	-	-	7	9
	Abstractions by industry	-	-	-	-	7	7
	IPPC activities	-	-	-	-	-	0
	Non-IPPC activities	-	-	-	-	-	0
	Abstractions by quarries/open cast coal sites	-	-	-	2	-	2
	Other major abstractions*	-	-	-	10	-	10

**Other major abstractions include: illegal water abstraction and indirect abstraction by drainage and gravel pits;*
***Poor status can be caused by more than one type of pressure*

PROGRAMME OF MEASURES FOR GW QUALITY AND GW QUANTITY

According to the WFD, river basin management plans and programmes of measures are developed on three levels in the Danube RBD:

1. The international level (Part A);
2. The national level (Part B) and/or the internationally coordinated sub-basin level (Part B) for selected sub-basins (such as the Tisza River Basin) and
3. The sub-unit level (Part C).

ITRBMP is internationally coordinated at level B and is based on findings and actions on the national (or sub-unit) level. The interrelation between the different levels should provide the achievement of the objectives on all levels in the most efficient way.

The ICPDR's Tisza basin-wide vision for GW quality is that the emissions of polluting substances do not cause any deterioration of groundwater quality in the Tisza River Basin. Where groundwater is already polluted, restoration to good quality will be the ambition. For groundwater quantity, the Tisza basin-wide vision is that water use is appropriately balanced and does not exceed the available groundwater resources in the Tisza River Basin, considering future impacts of climate change.

The adopted programme of measures for groundwater responds to all identified significant pressures in order to achieve the agreed management objectives and visions on the basin-wide scale. It builds upon the results of the pressure analysis, the water status assessment and includes the measures of basin-wide importance oriented on the agreed visions and management objectives. It is based on the national programmes of measures (for EU member states these shall be made operational until December 2012), however the specific situation in the non-EU countries has been taken into account.

Results of the chemical status assessment clearly show that contamination by NO3 and NH4+ from diffuse sources is the main reason for putting GWBs in poor status in the Tisza RB. Hence, these substances have been identified as target substances to improve groundwater quality, through the reduction of the load to underground. Basic measures, listed in Annex VI Part A of WFD, are foreseen as key instruments in achieving good chemical status and reversal of any significant and sustained upward trends in the concentrations of nitrates in groundwater in the Tisza River Basin. Depending on the origin of the pollution load, this should primarily be done through the implementation of the Directive 98/83/EC (Nitrates Directive) and also the Directive 91/271/EEC (Urban Waste Water Treatment Directive). Where drinking water source are endangered, basic measures through the implementation of Drinking Water Directive (80/778/EEC) as amended by Directive (98/83/EC), should provide improvement of quality of groundwater. As regard to the presence of hazardous substances in the groundwater aquifers, additional measures have to be taken as required under the Drinking Water Directive (80/778/EEC), Plant Protection Products Directive (91/414/EEC), Habitats Directive (92/43/EEC) and Integrated Pollution Prevention Control Directive (96/61/EC). In specific cases (for example in urban areas), supplementary measures such as management of urban run-off and control of diffuse pollution in urban areas must be implemented, in addition to basic measures.

According to WFD (Annex V), in order to maintain good quantitative status it must be ensured that the available groundwater resource is not exceeded by the long-term annual average rate of abstraction. Furthermore, any damage to groundwater dependent terrestrial ecosystems must be prevented for the same cause. Most measures addressing poor quantitative status of groundwater bodies in the Tisza River Basin are based on implementation of appropriate controls of the abstraction of fresh surface water and groundwater and impoundment of fresh surface waters including a register or registers of water abstractions. Additionally, other measures such as change in drainage system, cessation of illegal abstractions, use of crops with low water demand and as well as application of water-saving irrigation technology should also be applied in order to improve the water de-balance. Slow and insufficient recharge of deep aquifers in some parts of the Tisza River Basin, followed by several decades of intensive public water supply, resulted in over-abstraction. Sustainable solutions for future water supply in such cases include measures on investigations for alternative water sources.

CONCLUSIONS

Results of the status assessment clearly show that contamination by nitrate and ammonium from diffuse sources is the main reason for the poor status of groundwater bodies in the Tisza River Basin. The main reasons for pollution in the Tisza River Basin are similar to the Danube River Basin, though with the addition of mine water discharges as well as with quantity issues such as over-abstraction. Therefore, the basic measures listed in WFD Annex VI Part A, are foreseen as key instruments in achieving good chemical status and reversing any significant and sustained upward trends in the concentrations of nitrates in groundwater in the Tisza River Basin.

To prevent pollution of groundwater bodies by hazardous substances from point source discharges liable to cause pollution, an effective regulatory framework has to be put in place prohibiting direct discharge of pollutants into groundwater and setting all necessary measures required to prevent significant losses of pollutants from technical installations. It is also necessary to prevent and/or reduce the impact of accidental pollution incidents.

Illegal water abstraction and indirect abstraction by drainage may be a significant and specific problem in the Tisza River Basin concerning quantitative status. Implementation of appropriate controls of the abstraction of fresh surface water and groundwater and impoundment of fresh surface waters including a register or registers of water abstractions are foreseen as key measures for addressing poor quantitative status of groundwater bodies in the Tisza River Basin. Since the agriculture is one of the key activities causing significant alterations mainly through water abstractions, other measures (change in drainage system, cessation of illegal abstractions, the use of crops with low water demand, as well as the application of water-saving irrigation technology), should also be applied in order to avoid groundwater depletion.

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Notes:

Full Paper

CHARACTERIZATION OF THE VENETO HIGH PLAIN'S UNSATURED AQUIFER FOR THE WATER BALANCE TOOL OF THE LIFE + PROJECT TRUST (NORTH EAST ITALY)

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Abstract: In the last decades the water table of the High Veneto Plain - HVP (North East Italy) has decreased also because of over-exploitation; considering the negative impacts of expected intensification of water scarcity due to climatic changes on the groundwater, the conservation of the north phreatic aquifer is become a crucial problem, especially in relation to the south artesian ones, which guarantee water supply for human activities and are directly recharged from it. Inside the Life + Project TRUST, first, the aquifer has been precisely studied in order to reconstruct by the means of geostatistical methods its geometries and minimum, medium and maximum volumes (water-holding capacity related to water banking) and monitor its time-space evolution and, then, a specific Water Balance Tool has been implemented. It allows to estimate the climate change impacts on the hydro-geological balance (from mountain basins to crops and irrigation networks) and water reserves; it permits also to evaluate the effectiveness of adaption measures (as Managed Aquifer Recharge - MAR), assuming different management scenarios, other than to support institutions in sustainable River Basin Management (RBM) in the light of WFD 2000/60/CE.

Keywords: Life+ Project TRUST, phreatic aquifer, High Veneto Plain, geostatistical interpolation, Water Balance Tool, WFD 2000/60/CE

INTRODUCTION

This study has been conducted by the Alto Adriatico River Basin Authority (responsible for the implementation of the RBM Plan of the Eastern Alps District for WFD 2000/60/CE) and the SGI-Studio Galli Engineering, within the Project TRUST (Tool for Regional scale assessment of groUndwater STorage improvement in adaptation to climate change), of which this work constitutes a fundamental part. TRUST is funded by the 2007 LIFE+ Environment Policy and Governance Program of the European Commission and by the Italian Ministry of Environment and falls under the "Climate Change" area focusing at the impact on EU natural resources of temperature potential increase due to greenhouse gas emissions. TRUST aims specifically to study the impacts on water resource status and its availability in the North East Italy.

This area is characterized by a wide hydro-geologic reservoir having a social, economic and environmental value because it allows, starting from meteorological processes (mainly rain and snow precipitations), the storage and the release of waters in the environment, guarantying the water supply for human activities. The NE Italy system is yet turns out to be extremely vulnerable in relation to the climate changes and the management and the use of its waters: in the last 30-40 years the water table has slowly but progressively decreased (Figure 2), numerous wetlands have been desiccated and the aquifers have been depressurized, mainly in relation with, largely past, over-exploitation. These effects could worsen as droughts and water scarcity are expected to intensify in the next decades in relation to the predicted climate changes (Dazzi et al., 2000). Still, groundwater can remain the primary water source if managed in a sustainable manner, starting from its physical characterization, and - even better - if recharge is established.

The current work wanted right to update the quantitative status of the groundwater present in the HVP (Cisotto et al., 2007), implementing the characterization of the phreatic aquifer's geometries and water levels, the reconstruction of maps and models and the monitoring of its time-space evolution; in particular, it was expected to compare different interpolation and geostatistical methods during numerical map elaboration. Then, the groundwater quantitative status had to be combined and analyzed as a whole with the climate general circulation models and TRUST catchment scale hydrological surface model and crop's water deficit estimations by a specifically implemented Tool For Modeling Water Balance. This tool had to identify adaptation measures based on artificial aquifer recharge (as MAR) to mitigate and/or reverse the water levels decline and to restore groundwater status, other than to provide innovative and specific decision tools useful for the entities involved in river basin and water resource management in the project area.

GENERAL SETTING AND DATA

The HVP is bounded on the West by Lessini and Berici hills and to the East by the Livenza river (Figure 1) it is part of the NE Italy alluvial plain (Dal Prà & Antonelli, 1980), which extends southwards of the pre-alpine system in the Veneto and Friuli regions and lays on a structured basement of various age rocky formations; this large plain is characterized by a flat topography and it is crossed by numerous rivers flowing into the Adriatic Sea. From North towards South, the Veneto Plain can be subdivided into distinct hydro-geological areas: the Higher Plain (the studied one), characterized by homogeneous coarse grained sediments, prevalently gravel, of alluvial fans, hosting a wide-spread unconfined aquifer; the transitional resurgence belt naturally originated by outcrop of the phreatic water table due to shallow impermeable materials; the Lower Plain, made of finer and alternated materials, mostly sandy and silty layers, originating a complex system of superimposed artesian aquifers and aquicludes down to over 500 m b.s.l., other than a shallow unconfined aquifer.

Figure 1: General setting showing the modeled area hydro-geological sectors: 1-Alta Pianura (AP) Vicentina Ovest; 2-AP Vicentina Est; 3-AP Brenta; 4-AP Trevigiana; 5-Piave Sud Montello; 6-Piave Orientale; 7-Monticano.

These ones, which guarantee a considerable water supply for human activities (domestic, drinking, agricultural, industrial uses, etc.), are directly recharged from the northern one which is a reservoir absorbing and storing the water contributions mainly from river dispersion.

In order to dispose of needed data for the Balance Tool and the reconstruction of the HVP aquifer, a geodatabase has been set up: it includes hydrological data (rainfall, snow, temperature, humidity, wind, flows and hydrometric levels, etc), land use, agronomic and hydro-geological data (water levels, pumping rates, total depths, permeability, etc.), mainly related to the TRUST period 01/01/2000-31/12/2008 (Figure 7). In particular, groundwater raw data acquired since the 70s and coming from 300 boreholes of the regional network of ARPA (Regional Agency for Environmental Protection), provinces and other institutions (i.e. Centro idrico Novoledo) have been analyzed.

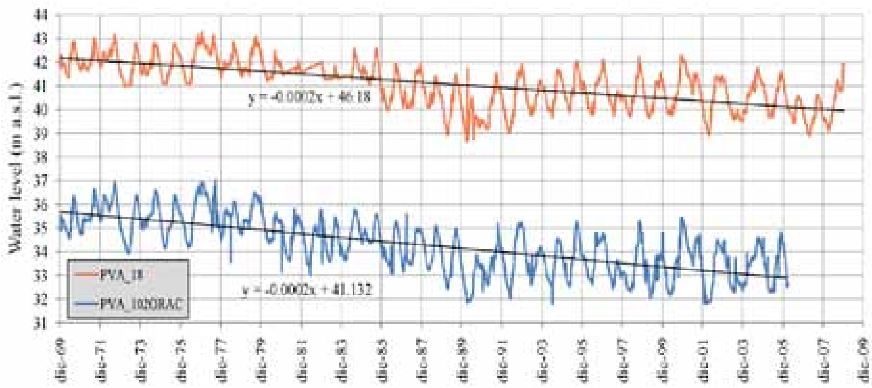

Figure 2: Example of long series (1969-2009) for HVP wells: regression lines show clearly the decrease trend of last decades.

These data have been acquired, with both traditional (manual) than automatic (datalogger) methods, during measure campaigns completed by several subjects and with various frequency.

INTERPOLATION METHODS

In order to reconstruct representative water table surfaces for extreme hydro-geologic conditions, it was necessary to identify brief periods having an evident prevalent regime, a significant observations number and a sufficient spatial wells distribution on the modeled area.

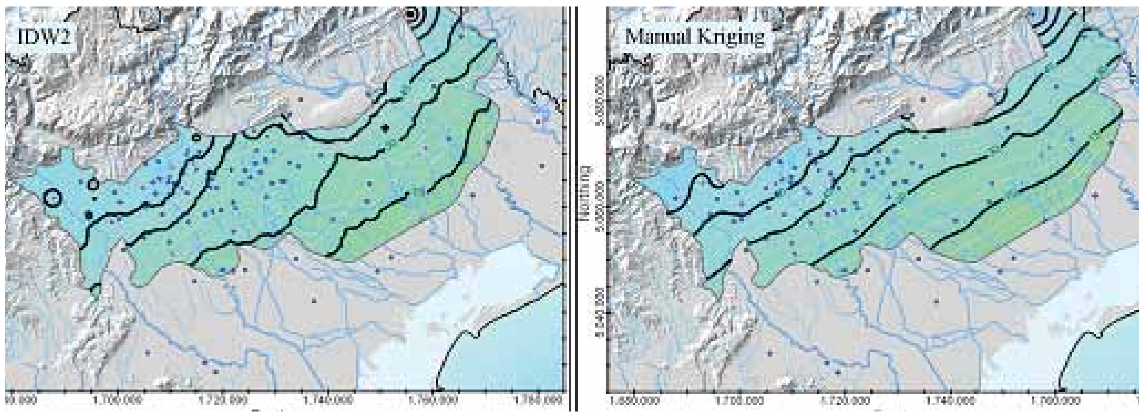

Figure 3: Comparison of IDW2 (bull's eyes effect visible) and Kriging (based on manual variogram analyzis and linear detrending) gridding methods for dataset A (100 points irregularly spaced.

These data have been statistically analyzed on frequency histograms (mean, median, skewness, kurtosis, standard deviation, etc), spatially filtered and selected (relating to clusters presence, outliers and reliability) and subdivided in a training and validation dataset, for maps elaboration and final predictability evaluations. In order to verify the estimated values reliability and to establish the most appropriate operating practice in treatment conspicuous amount of data, a particular attention has been given to the application of various gridding methods, mostly used in hydrogeology. Several grids have been computed adopting different spatial computational steps and applying simple and deterministic algorithms (as triangulation, natural and nearest neighbor, or IDW - Inverse Distance Weighted, with various exponents and samples search parameters) up to stochastic evolved methods, as universal kriging (Figure 3).

The latter included a iterative definition of variogram grid parameters and number of neighborhoods, analysis of experimental variogram for the individuation of derive anisotropies and theoretical best fitting variograms, both for the original than for the residuals data (computed in relation to different order polynomial trend surfaces), also considering nugget effects errors. The studied data turned out to be strongly influenced by an evident regional ENE trend which is logically related to the groundwater flow direction; then, a 1st order regression linear detrending has been applied.

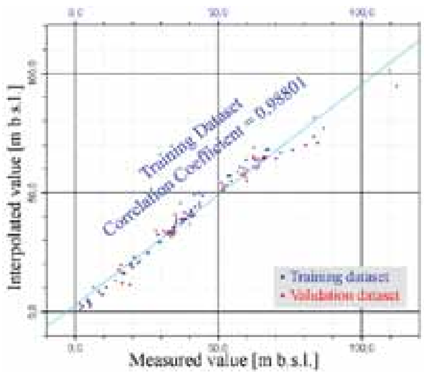

Figure 4: Accuracy diagram and correlation coefficient between measured and interpolated measures.

For every grid, the measured vs interpolated data differences have been represented in Krajewski diagrams (Figure 4) and the statistical (mean, standard deviation, root mean squared) errors have been computed.

Before compare the resulting groundwater volumes, the grids, polygonally filtered on the HVP domain used in the balance model, have been low- and high- filtered with the topography ground surface (from the regional 20*20m DEM) and with the Quaternary bottom (Dazzi et al., 2000) ones; where necessary, the elaborated grids have been smoothed in order to highlight low rather than high spatial frequency local anomalies. The maps were then compared to each other in order to highlight strengths and limitations of applied interpolation techniques, also mapping the reciprocal residuals and showing the most critical areas.

THE WATER BALANCE TOOL

The statistical elaboration of the groundwater levels has been also implemented in the large scale groundwater balance model developed. This predictive tool is based upon the hydrodynamics schematization of the HVP system, subdivided into distinct hydro-geological sectors; it has been built using Mike SHE software as a finite element model combining numerical algorithms with the implemented GIS database. The model analyzes as a whole the variation of the factors affecting the hydro-geological balance taking into account the interrelations among the hydro-geological sectors, the surface hydrological network and watersheds in order to simulate groundwater flow: the model structure includes some modules calculating infiltration processes, interactions between river network and groundwater, exchanges with adjacent aquifers and anthropic impacts.

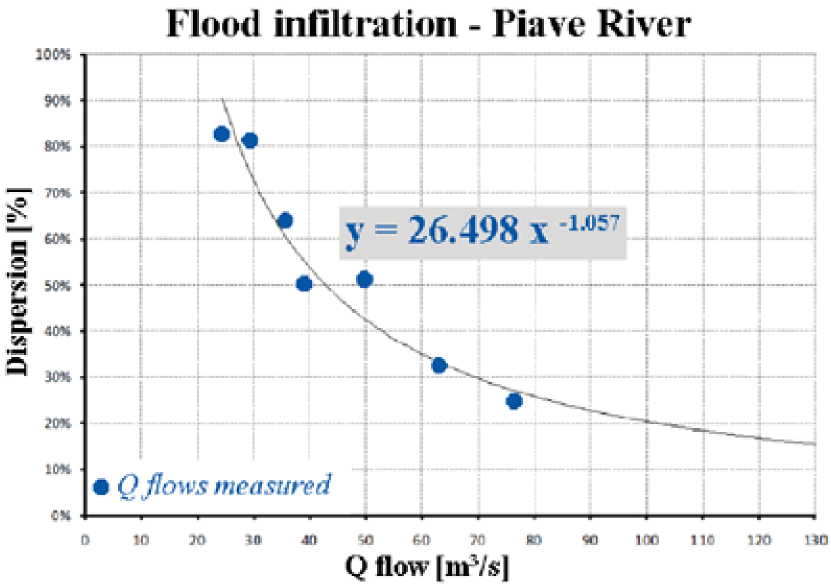

Figure 5: Percentage of dispersion versus discharge along Piave River.

The fraction of effective precipitation has been estimated starting from geodatabase data, time and spatial well distributed, that allowed the identification of precipitations and evaporation phenomena.

The water deficit affecting summer crops in the HVP has been simulated developing a specific application (Baruffi et al., 2010) that analyzes agronomic and land-use data with GIS Model Builder tools and by the means of innovative remote sensing identification methods: this work has allowed to solve out hydraulic balance for surface soils and terrains in order to delimitate potential water deficit (or surplus) areas.

A catchment scale hydrological surface model (Ferri et al., 2010) has been developed to simulate the hydrological response of the mountain basins, drained by the HVP flowing rivers; the discharge hydrographs at the alluvial plain tops have been assessed by a distributed model and a geomorphoclimatic approach. The river network has been simulated with Mike 11, a software based on the finite difference method to perform water surface profile calculations for steady gradually varied flow. This fluvial model has been coupled with Mike SHE to simulate the interaction between river flow and groundwater.

Experimental acquisitions of river-bed infiltration have been executed in order to reconstruct the discharge flow (in river) vs the losing flow (in aquifer) chart (Figure 5), in different hydro-geological conditions and with different river flows: a series of surveys has been conducted with traditional and modern (Acoustic Doppler Current Profilers) methods. The aquifer water withdrawals have been evaluated adopting different methodologies depending on type, quality and quantity of available data. In particular, with the collaboration of irrigation consortia, all data regarding the irrigation network, extension and typology of irrigation have been collected. Their positioning and seasonal variability have been implemented in the groundwater model by a specific module simulating all these withdrawals.

After the required model implementation with all the potential inflows and outflows, the groundwater -flow simulations for the TRUST period have been completed. The model set up has been validated with particular reference to water table statistic elaborations and average water balance information from previous studies, in order to assess the hydro-geological sector conditions.

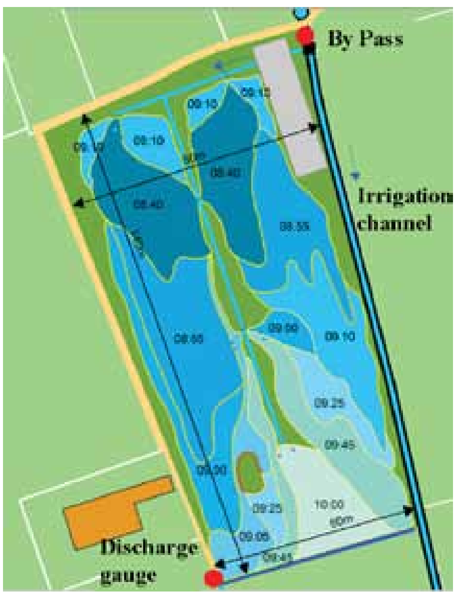

Figure 6: Testing of recharge using irrigation network: experimental area and map of infiltration timing.

The climate change scenarios have been obtained from the CMCC-MED global circulation climate model providing plausible scenarios SRES-IPCC of greenhouse gas emissions (A1B and A2) in the Mediterranean region for the 20th and 21st centuries defining the future water availability in the studied area and predicting future precipitation and evapotranspiration patterns.

The results of this climate model have been implemented in the groundwater system in order to evaluate the impacts on future demand and aquifer recharge considering all the factors affecting the hydro-geological balance through all the described tools. The land use evolution leads to an increased future water demand, while the precipitation decrease-trend reduces surface infiltration; both of them have been calculated with the application for water deficit affecting summer crops. Besides, climate changes cause minor flows in river network originating then lower fluvial dispersion (evaluated by river model).

Soil infiltration flow rates campaigns have been organized nearby the reclamation irrigation network, in specific areas equipped for surface irrigation practices. Operative conditions and results have been compared in relations with different crop terrains or natural vegetation, irrigation schemes and duration, i.e.: forest areas of infiltration with canals and dispersing grounds with fast-growing trees; grass stable fields (Figure 6) with surface irrigations up to 12 consecutive hours; plowed field, after a recent removal of poplar wood, with surface irrigations of several days.

These campaigns furnished crucial data for both the implementations and the validation of water balance tool: infiltration discharge turned out to vary from 15 up to 150 l/s for hectare; in particular, for the typical HVP coarse terrains, the specific infiltration value of about 50 l/s/ha has been measured.

RESULTS AND CONCLUSION

The water level grids for the extreme hydro-geological conditions have been computed in the TRUST period, both considering the min and the max absolute values for all the geodatabase boreholes, than in occasion of representative events of groundwater regime. They allows to define the 3D geometries of the underground volume interested by the water excursions, to characterize its evolution in the last years and to quantify the effective amount of water reserves, once evaluated the aquifer efficient porosity. The total aquifer has been supposed, even if in a elementary way, as a homogeneous volume superimposed on the bedrock surface; Table 1 shows the total volumes computed by “manual” kriging (that included a directionated variogram analysis and a detrend regression) as accepted for Mike She model, for medium (A), maximum (B) and minimum (C) events; the maximum difference of estimated aquifer volumes obtained comparing the used interpolation methods is also indicated. Their related water volumes have been calculated supposing an effective porosity between 15% and 25%.

Table 1: Volumes of total aquifer and groundwaters for Water Balance Tool compared with the maximum difference of estimated volumes obtained with different algoritm.

Dataset	Reference Period	Assumed Volume AQUIFER [$10^9 m^3$]	Assumed Volume WATER [$10^9 m^3$]	Max ΔVolume AQUIFER [$10^9 m^3$]	Max ΔVolume WATER [$10^9 m^3$]
A - med	02/08/04-30/08/04	**847,49**	127,12 - 211,87	**45,78**	6,87 - 11,45
B - max	02/11/05-23/02/05	**848,13**	127,22 - 212,03	**32,06**	4,81 - 8,02
C - min	01/02/05-23/02/05	**845,66**	126,85 - 211,42	**45,56**	6,83 - 11,39

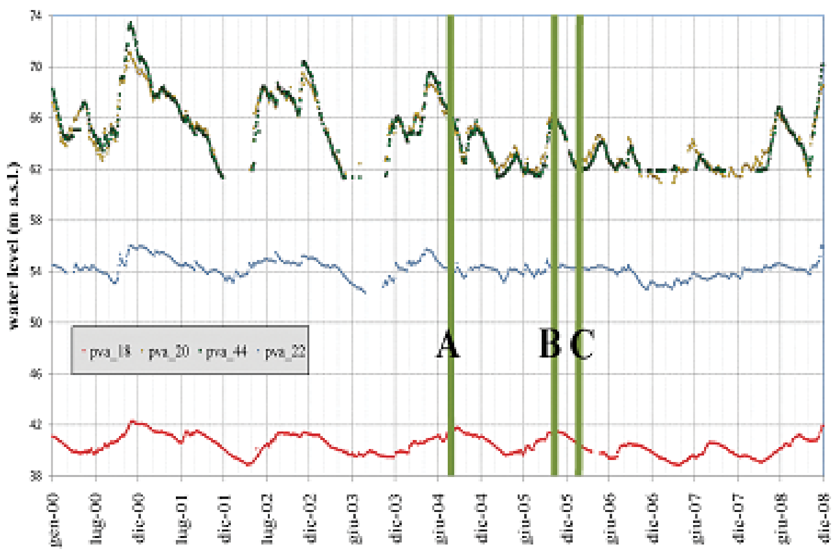

Figure 7. The graph zooms in the TRUST period and shows the dataset of max-med-min regimes.

The schema evidences how the evaluation error can be remarkable in term of aquifer and water absolute volumes and highlights the importance (and the need) of validate the used interpolating method before using the elaborated grids and maps in hydro-geologic applications. Analogous quantifications have been completed considering the volumes differences in relation to a constant grid representing the regional regression polynomial trend for the extreme value of minimums in TRUST period and considered as minimum water reserve.

On a long period, time-series show evidently the progressive lowering (locally up to 10 cm/year) of the water table in the upper plain since the 70's; the maximum absolute values reach 8-10 meters and without measure actions, this trend will progressively continue.

The historical series, on a short period (Figure 7), have allowed to detect seasonal fluctuations and their time-relation with rain and river inputs, other than to identify the presence of underground circulating recharged and drainages.

This modeling tool allows to evaluate, for homogeneous hydro-geological areas, the effectiveness of practices to protect and restore the quantitative groundwater resource, such as artificial Managed Aquifer Recharge – MAR; this objective is established both in quantity (volumes) than in temporal (at least on a seasonal scale) terms, in order to foster the water-holding capacity (water banking) of the aquifers. The potential water banking assumes different management scenarios, incorporating climate change issues and defines adaptation measures to mitigate the impacts of drought and water scarcity on the aquifer, allowing the water table to be preserved and the groundwater exploited in a sustainable way according to the WFD 2000/60/CE guidelines.

On a large scale the total potential groundwater storage is consequently estimated, the actual uses sustainability is verified and a cost-benefit analysis of aquifer protection best practices is allowed, giving altogether complimentary guidelines to the WFD Common Implementation Strategy (CIS) ones and for the river basin management plans. The groundwater model has implemented direct recharge interventions in order to compensate future climate change for an annual amount ranging from 150 to 200 million of cubic meters.

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Full Paper

ASSESSMENT OF GROUNDWATER LEVEL DECLINE OF A STRESSED AQUIFER IN BANGLADESH USING HISTORICAL DATA

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Abstract: In this paper, the application of a geostatistical method using the Kriging interpolation technique was undertaken to produce a simulated groundwater surface of Dhaka City to visualize groundwater level mining with the implementation of historical data. To predict the spatial and temporal variability of groundwater level of Dhaka City, GIS was used for the application of ordinary Kriging method with cross-validation leading to the prediction of groundwater levels. The semi-variogram of groundwater levels was best-fitted by a spherical model and Cross-validation prediction errors are satisfactory. In general, the results indicate that the trend of GWL lowering during the last 30 years in the city is substantial and a clarification of the picture of the most GW critical zones within the upper Dupitila aquifer is obtained. Urban dynamics, such as lateral spread of the urban area, may directly correlate to the GWL level mining phenomena over the past three decades. The spatial GWL distribution indicates lateral flow of groundwater from the nearby zones to the central part of the city that may trigger transport of pollutants from surrounding rivers, which are connected directly with the upper Dupitila aquifer, to the center of the City. Also, this temporal variation and spatial variation will clearly facilitate the preparation of a groundwater model. Recommended is to expand the current monitoring network by installing new piezometers, starting form the critical zones of GWL mining such as Zone 04. The recommended monitoring network may be divided into two networks, such as major and minor networks. The spatial distribution of the GWL provided in this study only estimates the groundwater level condition of the upper Dupitila Aquifer. The spatial and temporal distribution GWL in the lower Dupitila Aquifer has not yet been well investigated. The next step for groundwater management in this region is possibly to continue with more focus on the study of the GWL dynamics of both aquifers, considering the recent focus of DWASA strategy.

Keywords: Groundwater level, geostatistical analysis, Kriging method, stressed aquifer, Dhaka city

INTRODUCTION

Dhaka City has had immense problems concerned with flooding and drainage congestion during Monsoon in the past. Dhaka City is now also facing problems of water supply shortage. At present, 75% of Dhaka City is supplied water by the Dhaka Water and Sanitation Authority (DWASA), 83% of which comes from groundwater sources via 518 deep tube-wells (DTW) and 17% of which is supplied by three major surface water treatment plants. The recent concern of Dhaka Municipality is the continuous lowering of the groundwater level. The population of greater Dhaka is presently about 13 million (DWASA supplies to 8.6 million people) and according to growth trends, the population may reach 22 million by the year 2025. A proper groundwater management plan is therefore quite necessary to handle this alarming situation concerning water supply. A spatial and temporal determination of the variability of the groundwater level (GWL) in the aquifer is the most basic information for groundwater management studies, including information on parameters such as water balance, natural recharge estimation, etc. (Kumar and Devi, 2006).

A number of studies have already been involved with the analysis of the groundwater level condition of Dhaka City (e.g. Hoque et al. 2007; Akhter et al. 2009), but a proper geostatistical analysis was never undertaken to produce a smooth and reliable contour map. Hoque et al. (2007) analysed the spatial and temporal variation of the GWL in the aquifer of Dhaka City using the Kriging interpolation method with a linear variogram (default option in ArcGIS) but the researchers did not check any other non-linear variogram. Akhter et al. (2009), and Ahmed et al. (1999) also produced their own spatial contour maps of the GWL in Dhaka City but did so without any geostatistical procedures.

In this paper, the application of a geostatistical method using the Kriging interpolation technique was undertaken to produce a simulated groundwater surface of Dhaka City to visualize groundwater level mining with the implementation of historical data.

STUDY AREA DESCRIPTION

The study is focused on Dhaka Metropolitan City, DND (Dhaka Narayanganj Dam) area, Narayanganj municipality. The area is located between 23035´ to 23054´ North latitude and 90020´ to 90033´ East longitude and has a dimension of 370 km2. This area is surrounded by the Tongi Canal to the north, the Turag-Buriganga River system to the west, the Balu River to the east, and the Sitalakya River to the south. The Dhaka City area experiences the Indian Ocean monsoon climate with four meteorological seasons: pre-monsoon (March to May), monsoon (June to September), post-monsoon (October to November) and dry (December to February). Long-term annual rainfall is in the range of 1700 to 2200 mm. About 80% of rainfall occurs from June to September (JICA, 1991). Monthly average temperatures range between 250C and 310C.

Since 1963, DWASA has been responsible for the supply of drinking water as well as the collection and disposal of domestic sewage and storm water from Dhaka City and Narayanganj (Haq, 2006). For operational purposes, the entire service area for DWASA has been divided into seven zones; six of them within the Dhaka Municipality and one zone representing Narayanganj. Recently, DWASA subdivided Zone 5 into three further zones, namely Zone 05, Zone 08, and Zone 09; also, Zone 04 has been subdivided into Zone 04 and Zone 10 for management purposes. In this study we maintained the old subdivision for the analysis purposes, because most of the information is based on the old management zones.

Overview of geology and hydrogeology of the study area:

The geology of the study area is characterized by Quaternary alluvial sequences, which commonly show good aquifer properties. The study area consists of the southern half of the Madhupur tract, which is surrounded by the flood plains of Jamuna, Ganges, and Meghna Rivers (DWASA, 2006). The study area is characterized by a 400-500 m thick unconsolidated sequence of fluvio-deltaic sediments, which is overlain by the Modhupur and/or flood plain clay materials (5 m to 25 m thick) (Hoque, 2004; Hoque et al., 2007). The subsurface lithologies reveal that the aquifer and aquitard layers don't have similar gradients as the surface topography, and the aquifers are separated by an aquitard/aquiclude. The subsurface geology (within 300 m of depth) of Dhaka city can be generally subdivided into seven layers (DWASA, 2006). The upper aquifer is directly connected to the surrounding rivers. The aquifers of Dhaka City generally possess large transmissivities and storage coefficients and the hydraulic conductivity values of the aquifers are moderate (DWASA, 2006).

GROUNDWATER EXPLOITATION HISTORY OF DHAKA CITY

The first groundwater (GW) development in Dhaka City was initiated by the Department of Public Health Engineering in 1949. In the 1960s, groundwater was the principal water supply source. By the year 1966, groundwater covered almost 75% of the total drinking water supply (Ahmed et al., 1999) and in 2010, groundwater abstraction increased ca. 70 times compared to the GW extraction in 1966. If the population growth maintains the current trend, then drinking water demand will increase by an additional 80% until 2025. According to the record of DWASA, in 1970 only 49 DTWs were functioning whereas the current number is 518. Besides these DTWs, a number of private production wells are operating to withdraw groundwater from the upper Dupitila aquifer.

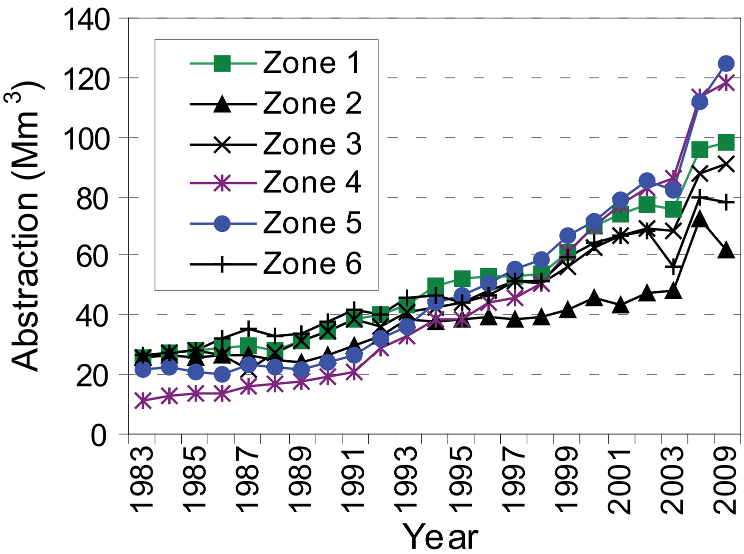

Figure 1: Historical development of groundwater abstraction in six zones of Dhaka. Abstraction data from year 2004 to year 2008 is missing (after Hoque et al. 2007).

MATERIAL AND METHODS

The data, used in this study, were provided by the Groundwater Circle II (GWC II), a branch of the Bangladesh Water Development Board (BWDB). GWL data of 14 observation wells from the year 1965 were collected but for spatial analysis purposes data from the years 1980 to 2005 were used in this study. Data for the last week of December of the respective years of all monitoring wells were used to construct GWL elevation-contour surfaces for the years 1980, 1990, 2000, and 2005. Missing data were filled by correlation analysis using SPSS (Statistical Package for the Social Science) software.

Exploratory spatial data analysis (ESDA) was undertaken using ArcGIS software for the water level to study data distribution and trend analysis. ESDA is an extension of EDA to detect spatial properties of data. ESDA is used to scrutinize the data in different ways, and to give an in-depth understanding of the investigated phenomena to make better judgment on the issues regarding the data (Haining and Wise, 1997; Hamad, 2009).

A normal score transformation of the data was performed using WinGslib software. Using ArcGIS software, semi-variogram, and covariance modelling, model validation using cross validation. GWL surfaces generation was undertaken by using Ordinary Kriging method.

GEOSTATISTICAL ANALYSIS

The GWL data of the study area are not normally distributed and therefore the data were transformed to find a normal distribution pattern. After checking several transformation procedures, the transformation was performed by the normal score (NS) transformation method. The transformed data were used for further geostatistical analysis in ArcGIS. The anisotropy of the groundwater level drop was checked and no significant differences were observed. Figure 3 (below left and right) shows the experimental semi-variogram model together with the covariance plot (Figure 3). Table 1 gives the overview of the fitted semi-variogram parameters. Low nugget to sill ration reflects the highly spatial structured GWL distribution. In order to verify the semi-variogram model and to evaluate the prediction values, cross validation was performed. Table 2 gives the overview of the statistical analysis for prediction analysis. As Root Mean Square Standardized (RMSS) prediction error of spherical semi variogram model is close to 1, better than others (e.g., circular, exponential etc.), this model was used for all prediction. The average standard error and the mean standardized prediction are very small, indicating good further accurate prediction analysis. After model validation, GWL surface was generated using an ordinary Kriging method. The interpolated data (100 m grid size) was back-transformed and analysed in ArcGIS.

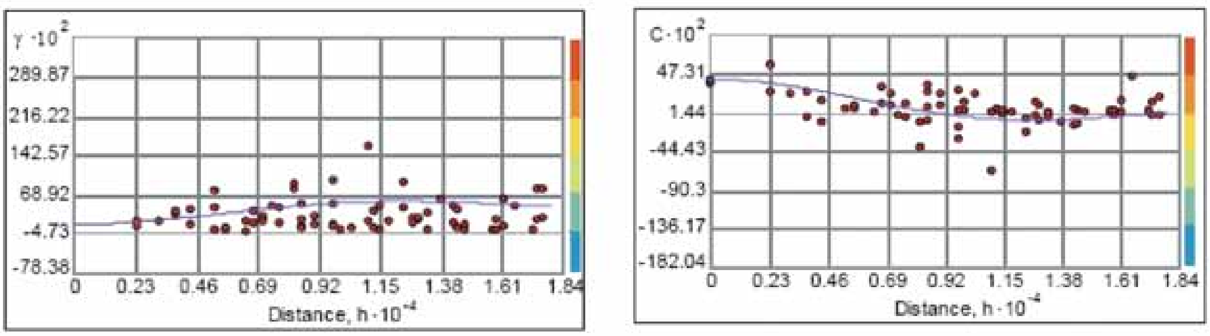

Figure 3: Modelled semi-variogram and covariance plot.

Table 1: Tables showing parameters for the best fitted semi-variogram.

Model	Spherical
Partial Sill	1
Nugget	0.18
Lag Size	7.184
Number of Lags	7
Angle Direction	58,7
Angle Tolerance	45

Table 2: Prediction errors for groundwater levels in Dhaka

Mean	0.077
Root Mean Square	0.5869
Average Standard Error	0.734
Mean Standardized	-0.068
Root Mean Square Standardized	0.841

RESULTS AND DISCUSSION

In order to understand the trend of GWL mining in Dhaka City, the spatial distribution of groundwater levels were generated for every 2 years between year 1980 and 2005. GWL surfaces of the years 1980, 1990, 2000, and 2005 are shown in Figure 4. The spatial distribution of groundwater level data shows that in the year 1980, the overall GWL of Dhaka City was relatively high. In about 90% of the places in Dhaka city, the GWL was in the range between -2 m and +7 m relative to the PWD (Public Works Datum). In almost the entire area of Zone 03 and some parts of Zone 04, 05 and 06, the GWL was comparatively lower, ranging between -9 m and -3 m below PWD (Figure 4a). In general, by December 1980, the GWL of the central and western part of the city is relatively lower compared to other parts of the city. At the end of 1990, the GWL depression spread widely, centering the central part of the city (ranges between -10 m to -15 m). The GWL status at the end of year 2000 (Figure 4c) shows that the trend of GWL lowering continued in Zone 05, 06 and some parts of Zone 03 and 04. The cone of depression is seen at the central part of the city, as of the year 1990. The 2005 GWL surface indicates a wider cone of depression especially in Zone 04 and the sharp GWL depression is moved to the southwestern part from the central part of the city. The spatial GWL distribution indicates lateral flow of groundwater from the nearby zones to the central part of the city, which is in agreement of the result showed by Hoque et al., 2007.

Figure 5 shows the GWL mining situation in Dhaka City during three time periods, such as between the years 1980 and 1990 (Figure 5a), between the years 1990 and 2000 (Figure 5a), and between the years 2000 and 2005 (Figure 5c). From Figure 5a, it is clear that during the years 1980 to 1990, the average GWL drop is 12 m. This is due to the construction of DWASA production wells. During the period of 1980 to1990, 34 production wells had been constructed in the city. About 85% of the wells were concentrated in the central part of the city and therefore the enormous abstraction caused GWL lowering below the central part of the city. During the years 1990 to 2000, another 193 production wells were constructed in the City. This amount is 6 times higher compared to the period between 1980 and 1990. The need of fresh water for a growing population had triggered in increase in new production wells in the city at that time. The effect of high abstraction during this time period is shown in Figure 5b. This figure shows that the GWL mining area, in other words, the 'critical area', was moved to Zone 05 and 06 during the years 1990 to 2000. The GWL decreasing part of the aquifer moved to the north part of the city. During these 10 years, average GWL level drop in Zone 06 and 05 was 31 m which is about 2.5 times greater than that of during the period of 1980-1990. Figure 5c shows that only by 5 years from 2000 to 2005, groundwater level had declined about 30 m below the PWD in zone 04. The rate of groundwater level decline is 5.0 m per year over this time span at this zone, which shows that the rate of GWL mining is increasing at an alarming rate. In general, the results indicate that the trend of GWL lowering during the last 30 years in the city is substantial and a clarification of the picture of the most GW critical zones within the upper Dupitila aquifer is obtained. The results clearly show the effect of pumping on the aquifer, which is GWL lowering. Urban dynamics, such as lateral spread of the urban area, may directly correlate to the GWL level mining phenomena over the past three decades.

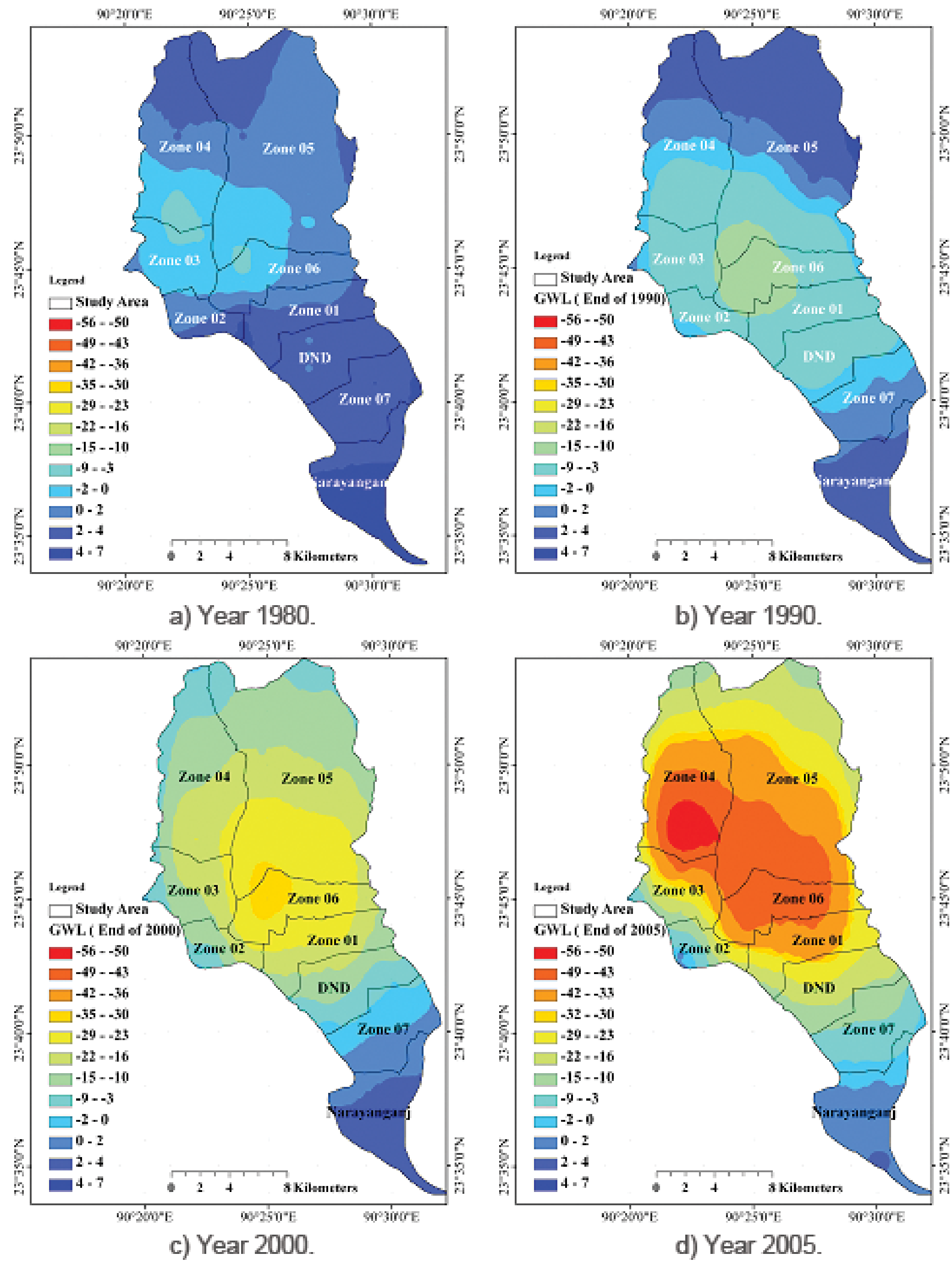

Figure 4: Spatial distribution of groundwater level at the end of year 1980, 1990, 2000, and 2005.

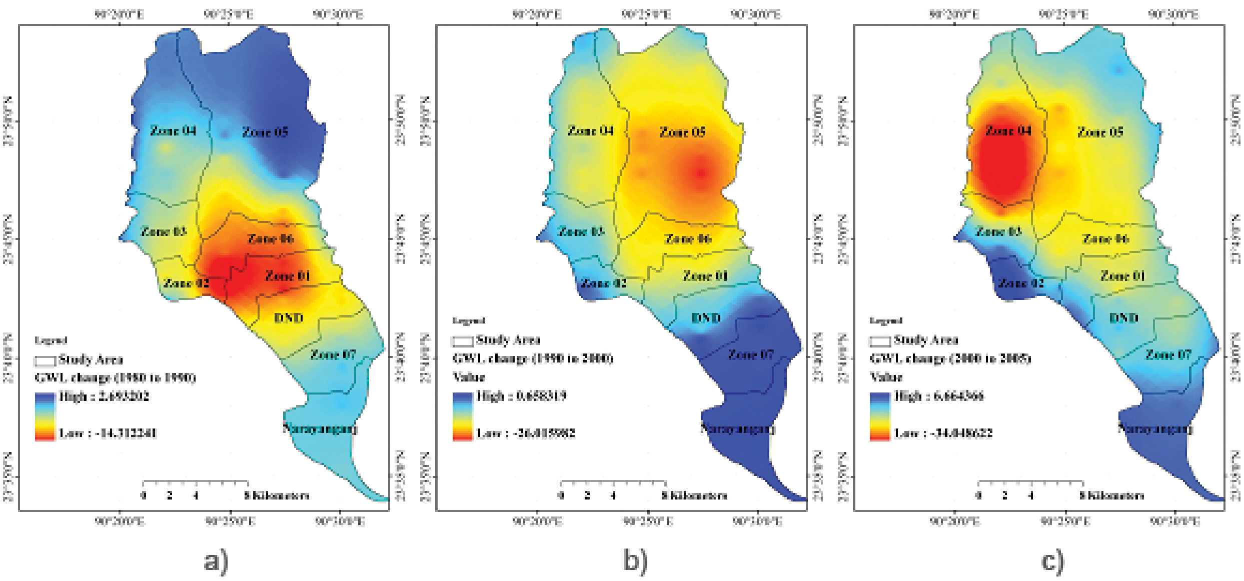

Figure 5: Groundwater level drop (a) from year 1980 to 1990 (b) year 1990 to 2000 and (c) year 2000 to 2005.

CONCLUSION AND RECOMMENDATIONS

Geostatistical methods have been already practiced as applicable and reliable tools for better management of water resources. It is without any doubt that currently groundwater management is of real need to strengthen water supply conditions in Dhaka City. This study clearly shows the ability of geostatistical analysis to predict groundwater levels where no observation data have been made available. With the understanding the spatial variation of the GWL, DWASA can further plan for future resource exploitation, such as installation of new pumping wells, demarcation of groundwater critical zones and the installation of new monitoring network. Also, this temporal and spatial variation will clearly facilitate the preparation of a groundwater model.

Recommended is to expand the current monitoring network by installing new piezometers, starting form the critical zones of GWL mining such as Zone 04. The recommended monitoring network may be divided into major and minor networks. The major network may consists of a denser network of monitoring wells and should be located in the most vulnerable GWL mining areas. The minor monitoring network may be relatively less dense and should occupy the rest of the city area.

The spatial distribution of the GWL provided in this study only estimates the groundwater level condition of the upper Dupitila Aquifer. The GWL distribution in the lower Dupitila Aquifer has not yet been well investigated. The next step for groundwater management in this region is possibly to continue with more focus on the study of the GWL dynamics of both aquifers.

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Extended Abstract

MODEL BASED QUALITY MANAGEMENT OF GROUNDWATER RESOURCES - CATCHMENT AREA LIEDERN, GERMANY

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INTRODUCTION

Freshwater abstracted from groundwater systems is one of the most important water resources used for alimentation, sanitation and industrial processes. A decline in groundwater availability due to climate change or overexploitation has direct implications on social and economic developments (Custodio 2002). However, a still underestimated problem in water management is the decreasing usability of resources caused by a progressing deterioration of groundwater quality. As a consequence, the maintenance of water supply relies more and more often on extensive and costly treatment steps. Furthermore, incrustations or the erosion of wells and ductworks often complicate the production of freshwater (Houben 2003). Still recent practices of economic resources control are based on water balance calculations but in most do not consider hydrogeochemical processes affecting water quality.

This study is focussed on the development of a model based instrument that supports a sustainable quality management of groundwater resources. Exemplified on the catchment area Liedern (BEW GmbH; Bocholt, Germany) site specific questions and economic needs of the water supplier are discussed and transferred into a management tool. The resulting tool serves as a communication platform between complex scientific expertises and economical implications. The tool enables to assess future trends in raw water quality, to test the efficiency of agricultural measures as an instrument of quality improvement and to control the quality of measures by establishing a model based monitoring system.

METHOD

The prognosis and planning instrument is based on a reactive transport model that couples hydrogeochemical and hydraulic processes using a hybrid approach (Kübeck et al. 2009). Groundwater flow and interacting surface water systems are simulated by means of the program SPRING® (König 2004). Model results of the geohydraulic simulation are transferred into a hydrogeochemical model using the conception of stream tubes. Thus, the temporal development of groundwater composition is calculated as a function of flow time and flow path through the three dimensional aquifer. Along the flow path physical, chemical and biological processes lead to an alteration of groundwater composition. For modelling hydrogeochemical processes between aqueous, solid and gaseous phases are calculated using the thermodynamic based program PhreeqC (Parkhurst & Appelo 1999) and the data base wateq4f (Ball & Nordstrom 1991). Kinetically controlled reactions like the microbial degradation of organic carbon are expressed by the multiplicative Michaelis-Menten equation:

$$\mu = \mu_{\max} \cdot \prod_i \left(\frac{c_i}{K_{S_i} + c_i} \right) \tag{1}$$

where the rate of chemical turnover (μ [mol/(l•s)]) is calculated as a product of the maximal reaction rate (μ_{max} [mol/(l•s)]) and a term that describes the influence of the concentration (c [mol/l]) of all reactants (i) and the affinity constant (KS).

Besides aquifer characteristics like transmissibility and geochemical-mineralogical composition, the occurrence of these processes is strongly affected by the influx of dissolved substances into the aquifer. Numerous studies indicate an exposure of groundwater resources not only by local contamination sources or infiltrating surface water but mainly due to regional long-term applications of agricultural additives (Strebel et al. 1989; Postma et al. 1991; McLay et al. 2001). In agriculturally dominated regions mass balance calculations provide information about the excess amount (surplus) potentially leached into the groundwater. Nitrate concentrations in shallow groundwater are, compared to the calculated N-surplus, most likely decreased due to denitrification and degassing of nitrogen within the unsaturated zone. However, the N-surplus reflects the temporal development of the nitrate concentration by trend (Hatch et al. 2002). As nitrate concentration and water constituents like chloride, sulphate, sodium and potassium in shallow groundwater correlate (Karr et al. 2001; Böhlke 2002) the input of solutes into the groundwater can be estimated as a function of the N-influx. Element specific transfer functions derived from data of the surface near groundwater are used for calculation.

$$c_i(t) = a \cdot c_N(t) + K \tag{2}$$

where the slope a determines the relation between element and nitrogen concentration (c_N) and the intercept K defines the solute concentration derived from elution processes and dry deposition. Electrical charges of aqueous N- and S-species are balanced by earth alkali elements (calcium and magnesium).

$$c_i(t) = \frac{c_N(t)}{2} + c_S(t) \tag{3}$$

Physicochemical parameters like pH, EH and the distribution of species between aqueous, solid and gaseous phases are calculated using an equilibrium approach.

CASE STUDY OF LIEDERN (BEW GMBH BOCHOLT, GERMANY)

Bocholt is located in the agriculturally dominated Lower Rhine region, close to the German/Dutch border. Water supply in Bocholt and the surrounding area relies on the extraction of freshwater from Quaternary sediments (sand and gravel). In the past water was primarily produced in Liedern and the pumping station Mussum nearby. In 1999 an additional facility was built in Schüttensteiner Wald. Although the application of fertilizers on agriculturally used land in the catchments has been very similar, high nitrate concentrations are only measured in raw water from Mussum. Whereas, the pumping station Liedern extracts a raw water with high iron and manganese concentrations of about 3.5 and 1 mg/l, respectively. Here, nitrate concentrations were low (7 to 10 mg/l) over the whole production period while hydrocarbonate concentrations increased from 110 to 260 mg/l. In Liedern sulphate concentrations increased until 1980’s from 60 to 140 mg/l and have been constant until now (see Fig. 2).

In this context, water suppliers are particularly concerned whether nitrate concentrations in raw water of other pumping stations will increase; and if so, how much time will be left until nitrate concentrations exceed the legal limitation of 50 mg/l (98/83/EC, WHO 2008)? Furthermore, what can be done to slow down this development? Another point that has been raised is the incrustation of wells and ductwork. In particular, the efficiency of freshwater production in the pumping station Liedern is influenced by a fast clogging of wells due to ironhydroxide precipitation. In this context, water suppliers ask whether groundwater quality may change in future causing an increasing precipitation rate of solids. Linked to this, water treatment may be also influenced in its performance.

Model conception

The pumping station Liedern consists of two well galleries each with 7 production wells and a total production rate of about 3.8 Mio m^3/a. Raw water from the northern and southern gallery is mixed (ratio 43.6 : 56.4) within a manifold. As shown in Fig. 1 groundwater flows in western direction towards the well galleries. The catchment area is about 20 km^2 and comprises mainly arable land and urban area (Bocholt). Within the catchment the total groundwater recharge is 4.2 Mio m^3/a. About 1.1 Mio m^3/a surface water from the nearby river Aa and 0.35 Mio m^3/a lake water infiltrate into the aquifer. Within a small section of the Aa groundwater exfiltrates into the river (0.96 Mio m^3/a). In agricultural areas a canal system drains about 0.9 Mio m^3/a groundwater.

Data of the N-influx between 1950 and 2005 are deduced from N-surplus calculations of North-Rhine-Westfalia (UBA 2007). In a first modelling approach surface water quality is assumed to be constant in time. The chemical composition of surface water is derived from measurements in 1996.

The catchment is subdivided into 11 zones (gallery north and south; see Fig. 1). Each zone is represented by a stream tube of a mean flow time and flow path through the three dimensional aquifer. Between 1976 and 2006 about 10 % of the grassland was ploughed up. In this process N-compounds mineralize and high nitrate concentrations (model assumption: 250 mg/l) are leached into the groundwater. Within the unsaturated zone the nitrate loaded seepage water reacts with mackinawite (FeS) and calcite. Along the flow path groundwater reacts with the solid phases of the sediment. In some parts of the catchment the groundwater percolates surface near peat lenses which causes high DOC concentrations in the shallow groundwater. Depending on the flow time and reactant concentration the DOC concentration decreases due to oxidation.

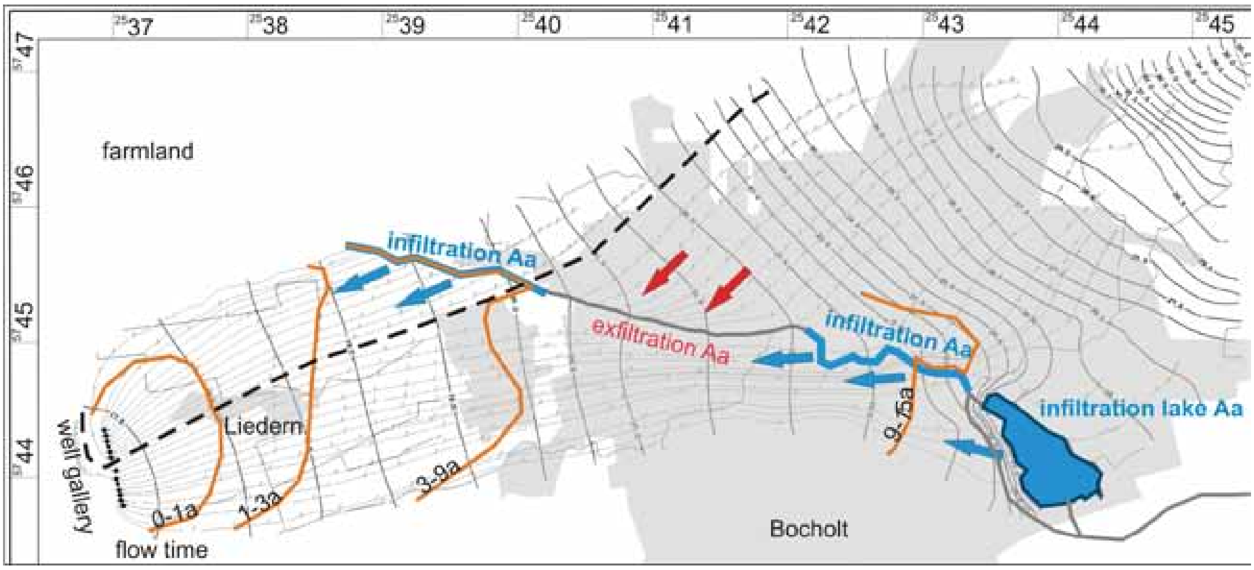

Fig. 1: 2D groundwater flow of the catchment area Liedern, Bocholt (BEW GmbH, Germany) (grey lines represent groundwater flow paths, orange lines indicate zones of different flow times).

Groundwater recharged in the west of Bocholt flows through oxidized sediments in the upper part of the aquifer. These sediments contain small amounts of calcite (< 0.03 wt %) and organic bound carbon (OC < 0.2 wt %). After percolating the upper aquifer part, groundwater recharged in the area of Bocholt and eastern parts of the catchment infiltrates into the deeper sediments. Here, the sediment contains pyrite (average 0.04 wt %) as well as small amounts of calcite and OC.

Within the aquifer organic bound carbon (dissolved and distributed in the sediment) reacts successively with dissolved oxygen and nitrate (Eq. 4, 5). After depletion of both reactants sulphate is used as electron acceptor (Eq. 6). Depending on the pH the produced $CO_{2(aq)}$ reacts with water to hydrocarbonate (Eq. 7).

$$CH_2O + O_2 \rightarrow CO_{2(aq)} + H_2O \tag{4}$$

$$CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow CO_{2(aq)} + 0.4N_2 + 1.4H_2O \tag{5}$$

$$CH_2O + 0.5NO_3^- + H^+ \rightarrow CO_{2(aq)} + 0.5NH_4^+ + 0.5H_2O \tag{6}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \tag{7}$$

Nitrate reduction in the deeper aquifer part is driven by oxidation of pyrite-S. In this process, ferrous iron and sulphate are released into the groundwater (Eq. 8). Under oxidizing conditions ferrous iron reacts with nitrate and precipitates as ironhydroxide (Eq. 9).

$$FeS_2 + 2.8NO_3^- + 0.8H^+ \leftrightarrow Fe^{2+} + 2SO_4^{2-} + 1.4N_2 + 0.4H_2O \tag{8}$$

$$Fe^{2+} + 0.2NO_3^- + 2.4H_2O \leftrightarrow Fe(OH)_{3(s)} + 0.1N_2 + 1.8H^+ \tag{9}$$

In the system calcite buffers the pH due to dissolution or precipitation.

Model results

Model results are divided into a retrospective and prospective part. The retrospective simulation period enables to test model plausibility by comparing model results with measured data. As shown in Fig. 2 modelled concentration of iron, sulphate, calcium and magnesium agree with measured raw water composition. Nitrate and hydrocarbonate concentrations reflect the temporal development of measured data.

In the prospective modelling period different N-influx scenarios are calculated (model input; see Fig. 2). For scenario 1 no changes in N-influx are assumed, no grassland is ploughed up and surface water quality remains unchanged. In scenario 2 and 3 agricultural measures are planned for 2012 reducing the absolute N-influx into the groundwater. In both scenarios N-influx is reduced by 50 % on an area of about 1 000 m^2. While scenario 2 calculates measures in the direct vicinity of the wells, in scenario 3 N-influx is reduced in the north of Bocholt. Results of both model scenarios are plotted in Fig. 2. In scenario 1 nitrate concentrations increase after 2008 at 10 mg/l and remain stable until 2050 while iron, sulphate and hydrocarbonate concentrations decrease slightly. The reduction of N-influx in scenario 2 leads to a decrease of nitrate concentration after 2016. Here, calcium and hydrocarbonate concentrations decrease slightly while iron and sulphate remain constant. In scenario 3 nitrate concentrations does not change, whereas iron concentrations decrease after 2028.

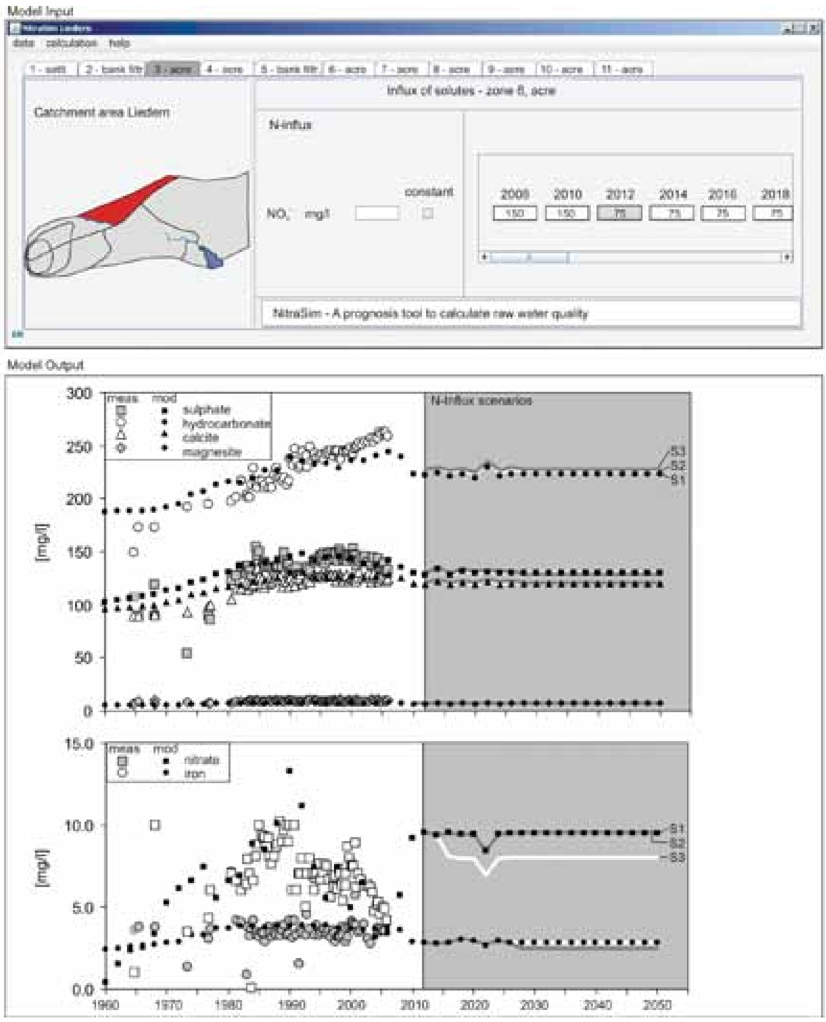

Fig. 2: Input structure of N-influx scenarios (scenario3) and model output of raw water composition. The retrospective model part compares model results and measured data. N-Influx scenarios (S1, S2, S3) are compared in the prospective part.

DISCUSSION AND CONCLUSIONS

In water management it is often assumed that a reduction of the solute influx into the groundwater in general improves raw water quality. However, preventive measures in different parts of the catchment area may provide contrary effects. Exemplified on the case study Liedern (BEW GmbH; Bocholt, Germany) it is shown that aquifer characteristics like flow pattern and geochemical-mineralogical composition of the aquifer strongly affect the results of agricultural measures in terms of efficiency and time.

Model results reveal a strong relation between N-influx and hydrocarbonate concentration. Nitrate concentration in the upper aquifer part is mainly influenced by oxidation of organic carbon. In this context, the spatial distribution of peat lenses, the intensity of DOC release and the reaction rate are important factors influencing groundwater quality. Within the deep aquifer part pyrite reacts with groundwater recharged in the eastern section of the catchment area. A reduction of the N-influx within this region does not affect nitrate concentration in raw water as long as a sufficient amount of pyrite is available within the sediment. However, nitrate concentration of the infiltrating groundwater determines the iron and sulphate amount released due to pyrite oxidation (scenario 3). In contrast, model results show a decrease in nitrate concentration in the raw water as a result of agricultural measures in the direct vicinity of the well gallery (scenario 2).

Within the production well iron loaded groundwater mixes up with oxidized groundwater of the upper sediment. The dissolved ferrous iron reacts with nitrate and precipitates as amorphous phase ($Fe(OH)_3$). The amount of solids precipitated may be affected by the amount of ferrous iron released due to ploughing up of grassland and oxidative dissolution of pyrite in the deeper sediment.

In summary, future raw water quality (in particular nitrate concentration) in Liedern depends on time and site specific N-influx rates, the amount of reductive capacity available (DOC, OC and pyrite) and the mixture of different groundwater within the well. The simulation of model scenarios enables to evaluate the impact of factors like a decreased N-influx, very small pyrite content in the deep sediment or a changing mixing ratio in the well on raw water quality. Based on this, effective strategies may be developed protecting groundwater resources.

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Notes:

Full Paper

FUZZY LOGIC AND SENSITIVITY ANALYSIS FOR THE CLASSIFICATION OF GROUNDWATER POLLUTION RISK

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Abstract: The work described in the present article aims at supplying an environmental planning tool able to define a groundwater risk hierarchy index in the function of some intrinsic characteristics of uncontrolled landfills and the territory where they are located. The risk assessment was carried out with a conceptual model, which includes groundwater vulnerability and the intrinsic hazard of landfills. In particular, in order to define the hazard of landfills, the fuzzy logic theory was applied. The fuzzy approach was then combined with the sensitivity analysis in order to overcome the problem of uncertainty associated with both the input data and the implemented fuzzy model, and at the same time to reduce the subjectivity. The assessment of groundwater vulnerability was carried out with the GNDCI-CNR method. This method, which does not need numerical input parameters, is particularly suitable for a large territory characterized by many geological, hydro-geological and morphological features, in which data and information are often unavailable, generic and territorially inhomogeneous.
Keywords: Fuzzy logic, Groundwater pollution risk, Sensitivity analysis, Uncontrolled landfills

INTRODUCTION

Pollution and management of the environment are serious problems which concern the entire planet; the main responsibility should be attributed to human activities that contribute significantly to damage the environment, leading to an imbalance of natural ecosystems. Contamination of groundwater from diffuse or point sources of pollution affects many industrialized countries. In particular, water pollution from nitrates or from landfills in different European countries tends to become a true environmental catastrophe. In order to evaluate in a timely manner and mitigate the risk of contamination of groundwater a model of hierarchical classification has been developed. This allows you to identify which sites require priority and should be reclaimed.

The developed conceptual model was applied to the Region of Basilicata for the assessment of the pollution risk of aquifers which underlie some uncontrolled landfills, identified in the surveys carried out in 2002 on the national territory by the "Corpo Forestale dello Stato" ("Italian Forest Rangers").

The conceptual model is based on fuzzy logic and provides groundwater vulnerability and intrinsic hazard of landfills.

The fuzzy logic theory, developed for the very first time by Zadeh in 1965, is used today in several fields; at the beginning it was adjusted to modify the concept of binary logic by approaching it to the human way of thinking and abandoning, in particular, the true/false bivalence, and eliminating well-known paradoxes.

The earliest practical fuzzy logic applications, however, only date back to the beginning of the nineties, mainly to control industrial processes and household electrical appliances, and means of transport. Later on, this approach was used in several fields, such as the environment, to identify the hazard connected to oil drilling waste (Rehan Sadiq et al., 2003), botany to identify an index of habitat suitability for Tugai forests (N. Rüger et al., 2004), in the hydraulics or water management to classify water quality and its subsequent treatment (Ni-Bin Chang et al., 2001) or to assess water quality as a function of algae growth (S. Marsili-Libelli, 2004), in the assessment of the transport of dangerous materials on roads and ducts (S. Bonvicini et al., 1998), in pedology to model and simulate soil processes (A. B. McBratney et al, 1997), and finally in hydro-geology for the identification of the vulnerability of aquifers (A. Gemitzi et al., 2006).

Given the wide use of this methodology in the environmental field, we decided to apply it to the problem of waste, which has been for years at the core of political and environmental discussions on an international and European scale. Intervening punctually and comprehensively on all the sites involved in illegal waste disposal is often impossible due to the lack of proper economic availability and human resources. It is thus necessary to identify a methodology which, cost-effectively, quickly and immediately identifies the most critical situations for the environment. This is a typical characteristic of the fuzzy logic which is used in this work as the basis in the data elaboration, thus being an extremely important decisional tool to optimise technical and economic resources.

Through this fuzzy approach we assessed the risk of pollution of some aquifers which are under 118 uncontrolled landfills present in Basilicata (Southern Italy). These are located between the districts of Potenza and Matera, each of which is characterised by morphological, hydro-geological and environmental parameters, such as: water table depth, leachate production, waste volume and type, soil coverage, landfill activity and proximity to superficial water. Some of them were obtained by means of GIS applications. In particular, in order to define the hazard of landfills the fuzzy logic theory was applied. The fuzzy approach was then combined with the sensitivity analysis in order to overcome the problem of uncertainty associated with both the input data and the implemented fuzzy model, and at the same time reduce subjectivity [1]. The assessment of groundwater intrinsic vulnerability was carried out with the GNDCI-CNR method. This method, which does not need numerical input parameters, is particularly suitable for a large territory characterized by many geological, hydro-geological and morphological features, in which data and information are often unavailable, generic and territorially inhomogeneous.

The sensitivity analysis allowed us to perform a series of simulations characterised by different input parameters to the model.

The results obtained from the simulations underwent several statistical analyses, in order to identify which fuzzy scheme could represent in the best possible way the distribution of input data. After determining the groundwater intrinsic vulnerability, the last phase was the creation of a final fuzzy inference characterized by the inherent vulnerability of the aquifers and the hazard of landfills. The output result of the inference was a fuzzy environmental risk index in the range 0-1, which was reclassified afterwards for the determination of 5 risk classes (Very low, Low, Medium, High, Very high). Through the proposed fuzzy model, together with the combined sensitivity analysis, it was therefore possible to classify each site within a risk scale enabling us to understand which one requires to be checked more urgently, to do instrumental surveys and, if needed, to do restoration and reclamation.

MATERIALS AND METHODS

The fuzzy model for groundwater pollution risk

The pollution of groundwater in nearly all cases is due to anthropic activities. The sources of groundwater pollution are in fact associated with a wide range of industrial, agricultural, commercial and domestic activities. Added to these are those activities or environmental transformations that, even if not directly pollutants, can contribute significantly to the transmission of the impact directly to groundwater.

In particular, the present study assessed the risk of pollution due to uncontrolled landfills.

The risk assessment was carried out through a conceptual model based on fuzzy logic which provides the inherent vulnerability of the aquifers and the hazard of landfills. The assessment of the aquifers vulnerability was carried out through a hydro-geological zoning method made for homogeneous areas: GNDCI-CNR method (Civita M., 1988). The hazard of landfills, however, was determined through the use of fuzzy logic (Caniani et al., 2010), by considering the various parameters of landfill descriptors.

The parameters considered were estimated or measured by the census of the State Forestry (“Italian Forest Rangers”), in fact the leachate production, volume, acclivity and proximity river index were calculated on the basis of other known information, using GIS tools and historical hydrological data. In order to reduce the number of rules and manage the algorithm easily, the parameters previously indicated were used to define three different fuzzy inferences, as shown in the conceptual diagram in Fig. 1. The results obtained through the first two fuzzy inferences, defined as site vulnerability and landfill potentiality, respectively, were then aggregated to the crisp parameter called landfill conditions, obtaining the hazard index of each landfill.

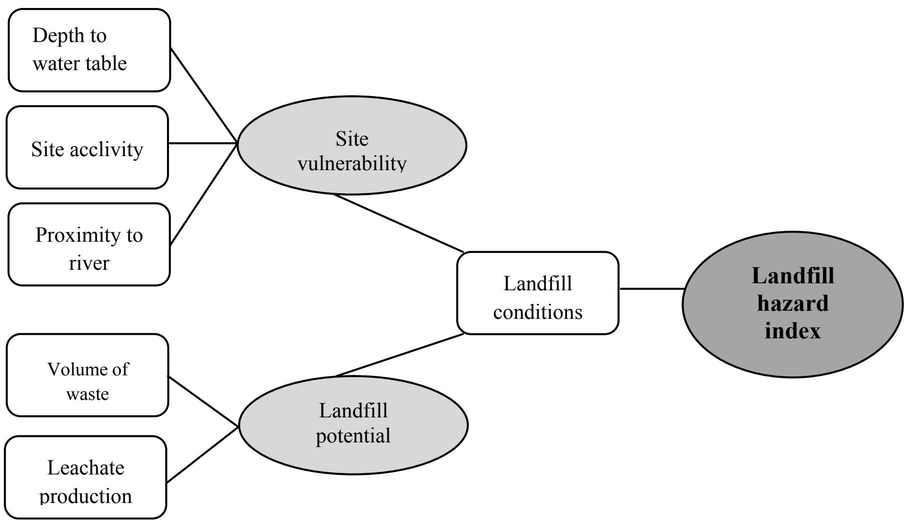

Figure 1: Conceptual diagram of the implemented fuzzy model.

Site vulnerability, defined through acclivity, water table depth and watercourse proximity, allowed us to obtain the site's propensity to be contaminated because of possible leachate infiltration. In fact, in the assignment of the rules, we defined that the increase in vulnerability is favoured by low slopes, proximity to surface watercourses (meant as index, so the higher the index the higher the proximity to rivers), and reduced depth of the water table. On the contrary, the landfill potentiality evaluates the probability of a landfill to release contaminants depending on the waste volume and leachate production. Therefore, with the increase of these two factors, such potentiality will increase as described by the fuzzy rules. The procedure to determine the landfill hazard index combines the results obtained by the two previous fuzzy diagrams with the addition of the landfill conditions. The basis of the fuzzy inference was drawn up keeping in mind that with the increase of values of the three parameters of the subset there is an increase of the hazard of landfills. Moreover, in order to determine the hazard of landfills and to face the risk of subjectivity, and to overcome the problem of uncertainty, linked both to the starting data and the developed model, we had to resort to a sensitivity analysis through which we analysed several fuzzy patterns. The different fuzzy patterns differ for membership functions and method of defuzzification. For each of the fuzzy inferences we defined: the type of membership function, membership classes (very high, high, medium, low, very low), fuzzy rules "if-then" and defuzzification method. The fuzzy rules were defined whereas the risk of pollution of the aquifers increases with the intrinsic vulnerability of aquifers and the hazard of landfills.

A membership function is a function which associates a value (usually numerical) with the level of membership to the set. By convention, the real number which represents the level of membership takes a 0 value when the element does not belong to the set, 1 when it belongs to it completely, and intermediate when a real number belongs to you in part. Membership functions can be of several types: the simplest are made up by straight lines, while the most used are the triangular and trapezoidal functions. There are other more complex functions, i.e. the Gauss function made up of a simple Gaussian curve and the Gauss2 function given by the fusion of two different Gaussian functions. Moreover, among this type of functions, there is the bell membership function (Gbell) which is a hybrid of the Gaussian function, it is mainly used to manage non-fuzzy sets. In order to face a possible asymmetry, in fact, we can use another type of function, such as the sigmoid function which may have both left and right asymmetry, and with a horizontal asymptote. In addition to this one, we have further asymmetric functions, the Dsigm and Psigm membership functions. Three more membership functions correlated with them are the functions Z, S and Pi; the first one is an asymmetric function open to the left, the second is open to the right, while the third one is asymmetric but closed to both its ends.

The rules are not represented by complex mathematical models, but from simple linguistic expressions, which are turned into mathematical formalism by the language "if-then" of the fuzzy logic. The rules are usually made up of an "if-then" structure, which in its turn is made up of an antecedent which defines the conditions, and a consequent which defines the action. The fuzzy output obtained by inference is often unusable, and therefore must be converted back to the deterministic value through an operation called defuzzification. To achieve these results, different methods of calculation have been proposed, the most widely used of which are the following: Centroid method: the chosen numerical value for the output is calculated as the centre of mass of the fuzzy set; Bisector method: the output is the abscissa of the bisector of the area subtended to the fuzzy data set; middle of maximum method: the output value is determined as the average of maximum values (Mom: middle of maximum); largest of maximum method: the output numerical value is calculated as the maximum of the maximum (Lom: largest of maximum); smallest of maximum method: the output value is represented by the output minimum value (Som: smallest of maximum).

The study described above was combined with the assessment of the intrinsic vulnerability of aquifers using the GNDCI-CNR method. This methodology allowed us to assess the groundwater vulnerability on the basis of a zonation of the territory in homogeneous areas from the hydrogeological point of view. The vulnerability is rated as qualitative and based on a comparison between the hydrogeological structure under study and the hydrogeological structures proposed by the method. These structures are attributed a variable degree of vulnerability. In particular, the vulnerability map (Figure 2) was obtained by taking into account different hydrogeological structures proposed by the method and by assigning degrees of intrinsic vulnerability provided by the method: extremely elevated, EE, elevated, E, high, H, medium, M, low, L, very low, VL (M. Civita, 1990).

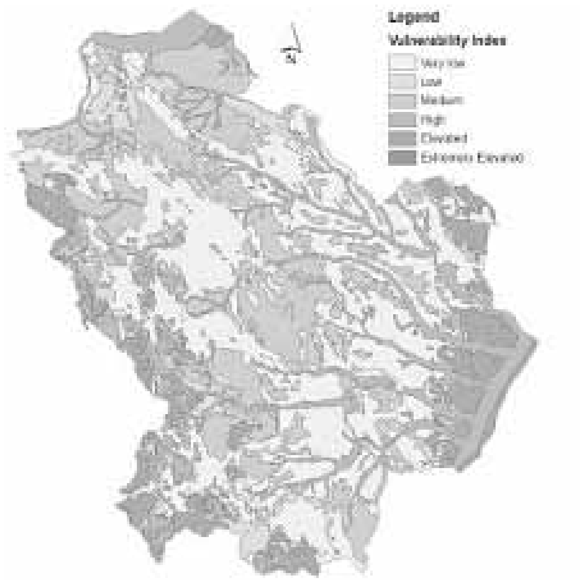

Figure 2: Map of the intrinsic groundwater vulnerability

The groundwater vulnerability was converted into a score and was integrated to the hazard of landfills in another fuzzy scheme to assess the risk of pollution of the aquifers. In the present case, with the conceptual model (Fig. 3) it was therefore possible to determine a ranking of sites at risk of pollution and then at the same time make a hierarchy of sites needing remediation and environmental restoration.

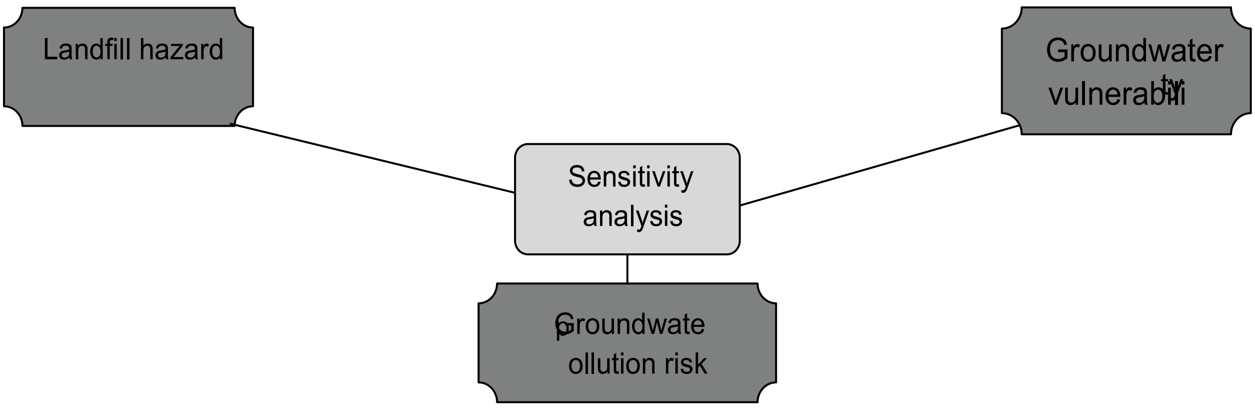

Figure 3: Fuzzy conceptual schema for pollution groundwater

RESULTS AND DISCUSSION

The work described dealt with the study of the risk of contamination of some aquifers in Basilicata (Southern Italy) the base to 118 uncontrolled landfills. In order to reduce further subjectivity and refining the model under examination, we used a sensitivity analysis which allowed us to perform a series of simulations characterised by different model input parameters. Through this analysis, which is complementary to fuzzy analysis, we wanted to identify the best result in terms of risk. Such a sensitivity analysis was performed by repeating the whole fuzzy inference procedure, modifying only one membership function or defuzzification method at a time, keeping constant all the other variables, thus performing 55 different simulations.

The results obtained from the simulations underwent several statistical analyses, in order to identify which fuzzy scheme could represent in the best possible way the distribution of input data (depth to water table, site acclivity, proximity to watercourses, waste volume, leachate production, and landfill conditions). For this purpose we carried out an earlier analysis related to the variability of the starting data sample, by adopting afterwards a criterion to make a comparison with the results obtained from fuzzy simulations. To this end, in order to make a comparison in terms of data dispersion, we deemed it necessary to identify, for each uncontrolled landfill, an average value obtained through the average of the parameters which characterise it, opportunely standardised, thus obtaining a data set characteristic of input data directly comparable with the results of simulations. A first simple and immediate approach to measure variability is the evaluation of the variation range, namely the difference between the maximum and minimum value, which gives indications on data dispersion; small values of this range show that data are similar to each other, while high range values prove a high dispersion. Such a criterion is not completely advantageous since the values of the minimum and maximum within each distribution could simply be outliers, so we used the standard deviation and variance calculations which gave information related to dispersion: null values show that the data are equal to each other (and thus equal to their average), while high values show the presence of a high dispersion. In order to choose the most appropriate fuzzy scheme to represent input data we compared the two dispersion indices (standard deviation and variance) of all the distributions with those of the input data, in order to identify the distributions whose values of deviation and variance can be compared with those related to input data.

In the case under analysis, the distributions which showed, in the several fuzzy schemes, a higher resemblance with respect to that of input data, are those obtained through implementing in the model either the membership functions Gauss2, Gbell, Trapezoidal and Triangular together with the Centroid defuzzification method, or the membership functions Gauss, Trapezoidal and Pi, together with the Bisector defuzzification method.

In order to overcome the difficulties met in the choice of the best fuzzy model, we carried out an F test to compare more precisely the variances related to the distributions corresponding to each fuzzy model and to the starting data. What we observed from the analysis of deviation was confirmed by the F test which highlighted, as the best model, the Centroid defuzzification method associated with the trapezoidal or GBell membership functions which give comparable results (Table 1).

Table 1: F test results

	Gauss2	Triangular	Trapezoidal	Gbell	Gauss	Disig	Psig	Pi
Centroid	0.692	0.594	0.969	0.966	0.280	0.001	0.001	0.479
Bisector	0.687	0.945	0.945	0.030	0.940	0.118	0.114	0.815
Mom	0.009	0.009	0.009	0.009	0.012	0.008	0.011	0.013
Lom	0.009	0.009	0.009	0.018	0.012	0.010	0.014	0.023
Som	0.026	0.025	0.025	0.012	0.021	0.087	0.094	0.093

After having determined the hazard of landfills, the intrinsic groundwater vulnerability was assessed by the GNDCI_CNR method described in paragraph 2.1. The intrinsic vulnerability and the hazard of landfills inserted in a fuzzy model provided the groundwater pollution risk. The fuzzy inference was formed using the hazard index of landfills as input data and the classes of vulnerability converted into numerical values. During fuzzification, the Centroid method of defuzzification and trapezoidal membership functions was chosen. The latter functions are subdivided into five separate sets: very low, low, medium, high, very high.

The environmental risk index, obtained through the chosen fuzzy scheme and characterised by the trapezoidal membership function and the Centroid defuzzification method, was successively revised for a classification of groundwater pollution risk in linguistic terms (Very low, Low, Medium, High, Elevated), using a cumulated frequency distribution curve (Figure 3), and dividing the classes at the points on the curve where a clear slope variation is observed.

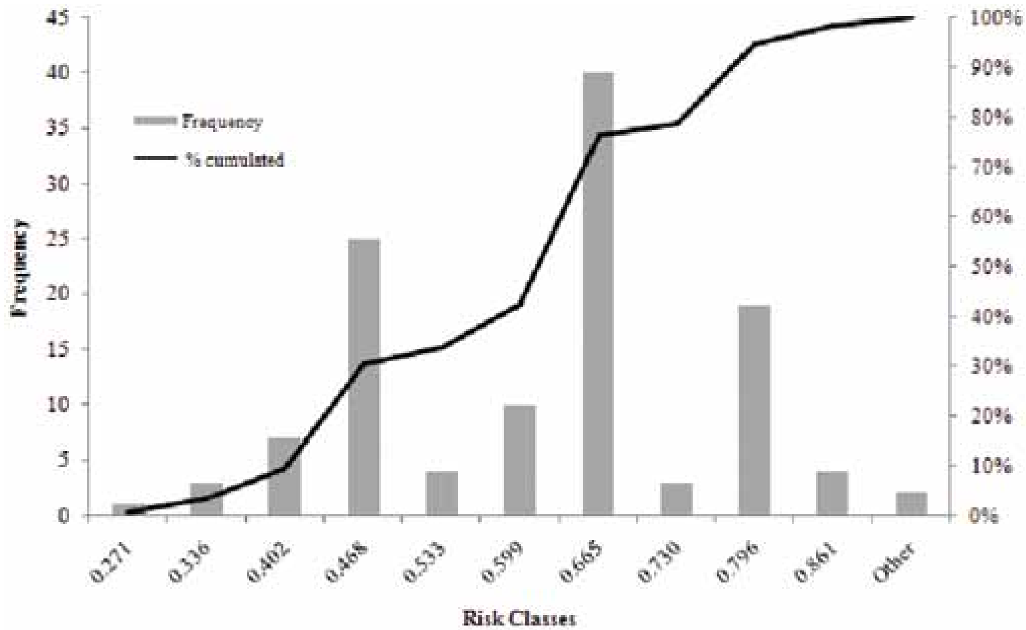

Figure 4: Cumulated frequency curve

The graphs in Figures 4 and 5 show, respectively, the percentage and spatial distribution of the groundwater pollution risk.

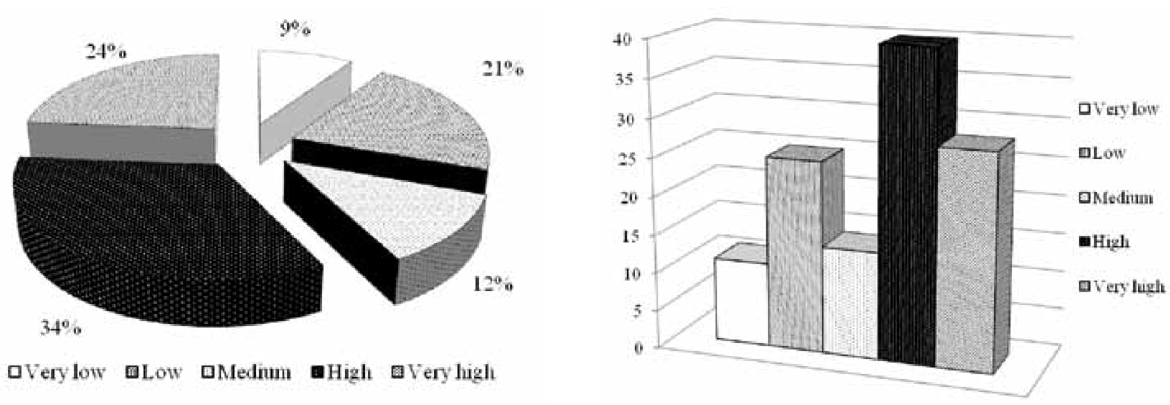

Figure 5: Percentage distribution of groundwater in pollution risk classes

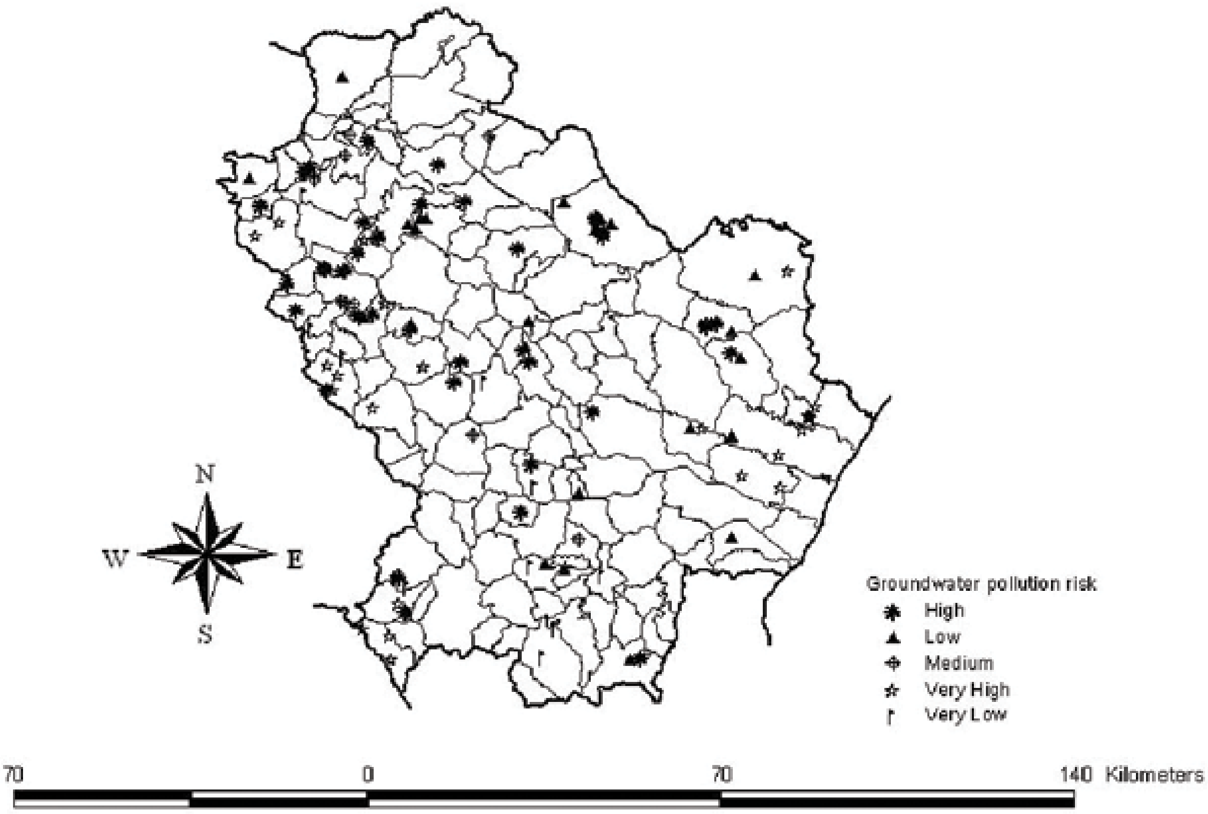

Figure 6: Groundwater pollution risk map of aquifers in Basilicata

The results of the fuzzy scheme previously described show that the methodology identifies a small percentage of very low (9%) and medium (12%) groundwater pollution risk. In fact, the cake diagram and the histogram show that the majority of groundwater has a low risk (21%), a high risk (34%) and a very high risk (24%) of pollution.

CONCLUSIONS

The fuzzy approach demonstrated to be a fast and effective method in the evaluation of groundwater pollution risk of some aquifers, and resulted in a quick and inexpensive method and a useful support to the decisions concerning the reclamation measures to adopt in the sites classified as hazardous.

Such a method allowed the identification of an environmental risk index for each site examined, then turned into nominal values, in order to perform a risk classification and, in turn, create a scale of priority measures. Such measures are addressed to a considerable percentage of sites; in fact, around 50% of them need urgent reclamation actions.

The present work suggests an innovative methodology characterised by the integration between the fuzzy approach and the sensitivity analysis, able to mitigate the problems connected to the subjectivity and arbitrariness of the evaluations based on the fuzzy approaches normally present in literature, especially as for the choice of the membership functions or the defuzzification methods. The proposed study, in fact, highlights how, by varying the choice of the membership functions or the defuzzification methods, it is possible to obtain extremely different, if not even contradictory results.

After these earlier results we aim at refining the model with its validation, or better, by carrying out detailed field analyses on the hazard of landfills (possible source of pollution for the aquifers), or by creating a neuro-fuzzy system where it is possible to let the system learn, through neural networks, the relationships existing between input and output.

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Notes:

Full Paper

THE EVOLUTION OF ROMANIAN GROUND WATER QUALITY LEGISLATION

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Abstract: The paper highlights all the changes in the field of ground water management in Romania, the possible effects these changes generate and the possible responses to the present requirements and exigencies or the legislation on quality protection of ground water. We present key subjects that will ensure sustainable management of this resource like: the main regulations developed and promoted in the 1990-2010 time period; sanitary protection areas; institutions with a role in the enforcement of the legislation.
Keywords: legislation, ground water, framework scheme.

INTRODUCTION

In Romania, in the past 20 years, an especially intense and complex activity took place to promote legislation in all political, economic and social fields. Special attention was devoted to the use of natural resources, including water resources.

In this context, an analysis of ground water legislation's evolution is a good opportunity to identify the main concepts and to highlight the importance of ensuring ground water quality. Ground water plays a strategic role in the drinking water services ensemble.

GROUND WATER – STRATEGIC RESOURCE

Ground water sources are a strategic source and have to be used sustainably and mainly as drinking water. This assertion is supported by many characteristics of groundwater, such as:

- The flow is relatively constant, both quantitatively and qualitatively;
- The natural conditions, especially for high depth sources, provide protection against pollution, in both the short and long term;
- Treating it to drinking water quality is, in the majority of cases, much simpler. Sometimes, no treatment is needed.

To meet sustainability requirements the use, conservation and protection of water sources imposes the development and the compliance of specific legislation.

GROUNDWATER MANAGEMENT ISSUE WITHIN THE LEGAL ENVIRONMENTAL REGULATIONS IN ROMANIA DURING 1990-2010

Respecting the requirements of sustainability, the development of the legislative package after 1990 was an intense activity that resulted in 236 regulations of which 162 were still valid in 2010 (Table 1). According to the Romanian legal practice, legal regulations include Laws, Governmental Emergency Ordinances, Governmental Ordinances, Governmental Decisions and Minister Orders. Activity specific standards were not included in this classification.

Table 1: Water related regulations adopted between 1990 and 2010

No.	Regulations	Still in force	Total annulled
1.	Laws	29	9
2.	Emergency Ordinances	11	2
3.	Ordinances	3	2
4.	Government Decisions	44	16
5.	Orders of the ministry	52	33
6.	Community legislation	23	12
Total		162	74

It is notable that the major regulatory acts of the Romanian legislation derive from two European Community Directives (Table 2):

- Directive 2000/60/EC on "Establishing a framework for Community water policy";
- Directive 2006/118/EC on "Protection of groundwater against pollution and deterioration".

Table 2: Matrix of regulations regarding the components of sustainable use of water sources

European legislation	Romanian legislation	Political strategies	Institutions	Management	Design/ construction	Use/ exploration	Quality	Financial
Directive 2000/60/ EC		X		X			X	
Directive 2006/118/ EC				X			X	
	1. Water Law no. 107/1996	X	X	X			X	X
	2. Minister Order no. 78/N /1998 for the approval of the design standard for building water catchments, Indicative NP 028-98				X	X	X	
	3. Governmental Ordinance no. 472/2000 regarding certain measures of water quality protection						X	

European legislation	Romanian legislation	Political strategies	Institutions	Management	Design/ construction	Use/ exploration	Quality	Financial
	4. Law no. 458/2002 regarding drinking water quality	X	X				X	
	5. Governmental Emergency Ordinances no. 107/2002 regarding the establishment of the “Romanian Waters” National Administration		X	X				X
	6. Mining Law no. 85/2003					X	X	
	7. Governmental Decision no. 898/2004 regarding the approval of exploitation instructions for ground water including fresh water/salt water transition areas				X	X	X	
	8. Governmental Decision no. 930/2005 for the approval of special norms regarding the characteristics of sanitary and hydrogeological protection areas.		X			X	X	
	9. Law no. 265/2006 for the approval of the Governmental Emergency Ordinances no. 195/2005 regarding environmental protection.	X					X	
	10. Law no. 51/2006 on community services and public utilities.		X		X			X
	11. Law no. 241/2006 on water supply and wastewater services.		X	X			X	X
	12. Governmental Decision no. 328 /2010 regarding the inflation index update of the contributions specific to water resources management, fees and fines			X				X

The presented legislation ensemble regulates various aspects of integrated water resources management, including ground water:

- The strategy and policy in this field in connection to E.U. legislation and to the entire Romanian economy;
- The institutions intended to apply and supervise the enforcement of legal provisions;
- Sustainable management of these vital resources;
- The design, construction, exploration and use of groundwater resources;
- The protection, preservation and quality assurance of these strategic resources;
- Economical issues that ensure population access to the water source, but also cover the costs imposed by the use of the resource.

The matrix in Table 2 identifies 12 main regulations and their objectives. The issues that determine sustainable management of groundwater bodies are spread evenly among the regulations.

INSTITUTIONAL ASPECTS

The analysis of the legislative developments includes the institutions that organize, assume, coordinate, apply and monitor the use of that legislation. Table 3 presents these institutions in relation to their tasks and responsibilities in sustainable use of water, including ground water. The matrix is organized according to the main phases of a centralized water/sewage system, namely:

- Intake;
- Use;
- Evacuation.

The involved institutions are listed according to the main components of national water sector operation. Among other components, we mention:

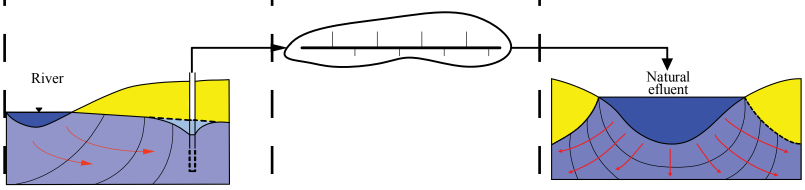
- The sector's strategy and policy;
- Consulting, design and implementation,
- Exploration and use;
- Education.

A great importance is given to water quality, including ground water quality. Table 3 lists the institutions involved in the conservation, assurance and monitoring of ground water quality either at the intake, distribution/use or disposal.

- Water companies have a prominent role providing water/sewage services. Public Health Departments control the respect of drinking water indicators. Basic tools in their activity are:
- Implementing sanitary protection areas as established in the cooperation between the "Romanian Waters" National Administration, local administration and water companies;
- Making regular analysis reports involving specialized laboratories at the Public Health Departments and the water companies;
- Preparing and implementing a water source and major sections of the centralized system of water/sewage monitoring plan.

The Monitoring system will result in a local and national network of licensed laboratories, a quality assurance system and a quality control system in each laboratory.

Table 3: Sustainable water use responsibilities and task matrix

Activities / Components	Intake	Use	Evacuation	Comments
				
A. Political Strategy	Ministry of Environment and Forests	Local Public Administration	Ministry of Environment and Forests	National strategy in environment protection Watershed management plan River basin development plan
B. Institution	„Romanian Water” National Administration	Public Health Department Environmental Protection Agency Water Supply Companies Consumer Protection	„Romanian Waters” National Administration Environmental Police	Monitoring Verification Inspection
C. Management	National Administration „Romanian Waters”	Water Supply Companies Private companies	„Romanian Waters” National Administration Water Supply Companies	Water management permit Water management license Contract
D. Designing/ construction/ consulting	Universities Design companies/ consulting Drilling companies	Universities Design companies/ consulting Drilling companies	Universities Design companies/ consulting Drilling companies	Prefeasibility studies (PS) Feasibility studies (FS) Technical design and manufacture Investment
E. Exploration/ usage	Water Supply Companies	Water Supply Companies Consulting companies Drilling companies	Water Supply and Sewerage Companies Consulting companies Drilling companies	Observation drillings Monitoring
F. Quality	Water Supply Companies „Romanian Waters” National Administration Public Health Department Environmental Protection Agency	Water Supply Companies „Romanian Waters” National Administration Public Health Department	Water Supply/sewerage companies „Romanian Waters” National Administration Environmental Protection Agency	Sanitary protection zones Analysis results Monitoring
G. Economic	„Romanian Waters” National Administration Water Supply Companies	Local Public Administration Water Supply Companies	„Romanian Waters” National Administration Water Supply/sewerage companies	Tariff Bills Penalties Contracts
H. Education/ specialized professional training	Universities Professional associations Training centers	Universities Professional associations Training centers	Universities Professional associations Training centers	Operating staff Management

MAIN LEGISLATION FRAMEWORK ON GROUNDWATER QUALITY PROTECTION

The most important law regulating sustainable water management is Law no. 107/1996, amended and supplemented, read in conjunction with the Government Emergency Ordinance no. 195/2005 on environmental protection, approved by Law no. 265/2006, amended and supplemented. The following paragraphs present important points of these regulations:

- Appropriate-quality ground water is intended primarily for public and animal farms water supply, and to ensure public health and hygiene. Other users require a water management authorization;
- The regulations aim at pollution prevention and elimination of pollutants from ground water to achieve a satisfactory quality for all ground water bodies by the end of 2015;
- The regulations aim at protection, improvement and restoration of all ground water bodies and the assurance of a balance between intake flow and ground water recharge in order to achieve good ground water status by the end of 2015;
- The action schedules and timetables are endorsed by river basin committees at the proposal of the national water authority and approved by governmental decisions. The schedules and timetables need to be developed and updated according to the Methodology and Technical Instructions for the development of guiding schemes approved by Order no.1258/2006, the “Romanian Waters” National Administration.

ADDITIONAL LEGISLATION ON GROUNDWATER QUALITY PROTECTION

The guideline scheme for planning and river basin management consists of two parts: the River Basin Development Plan (PABH) and the River Basin Management Plan (PMBH) (Figure 1).

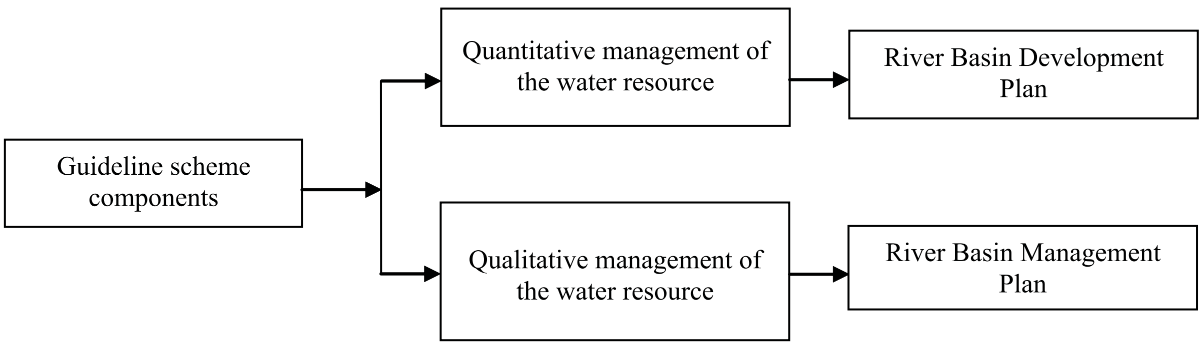


Figure 1: Components of the guideline scheme

Based on these documents, the identification and delimitation of groundwater bodies was performed using the following criteria: geological, hydrodynamic, qualitative and quantitative status of the water body. The delimitation of groundwater bodies was made only for areas where there are water supply significant aquifers with usable yields greater than 10 m^3/day. 129 ground water bodies have been designated in Romania, 19 of which are cross-border. 20 ground water bodies have been identified as being at risk for quantity and/or quality changes. The risk is due to historical sources of pollution, represented by large animal farms and/or agricultural infrastructure which have ceased or reduced operations, but also to current sources of pollution.

Groundwater resources are characterized by:

- The theoretical resource of 9.6 billion m^3 (representing 7.13% of total water resources) from which 4.7 billion m^3 low-depth water and 4.9 billion m^3 high-depth water;
- The usable resource of 5.4 billion m^3.

ESTABLISHMENT OF GROUND WATER SANITARY PROTECTION AREAS

This section presents the main points of the Government Decision no. 930/2005 for the approval of "Special Regulations on the nature and size of sanitary and hydro-geological protection areas". Compliance with this regulation plays a decisive role in groundwater quality protection. The regulation defines several ground water sanitary protection areas:

- Sanitary protection areas with a strict regime;
- Sanitary protection zones with a restriction regime;
- Hydrogeological protection perimeters.

In the sanitary and hydrogeological protection areas specific measures are required in order to avoid contamination of the water, lakes and medicinal sludge. Sanitary protection areas with a strict regime include the land around all the sources. Any activity or land use with a water contamination potential is forbidden.

Sanitary protection areas with a restriction regime cover the territory around the area with a strict protection regime, limited so that, by applying protective measures and depending on local conditions, the danger of deterioration in water quality is eliminated.

The hydrogeological protection perimeters include areas between the water intake and the water discharge at the surface of the ground water with natural occurring extraction (springs), drains and wells. When referring to pollution of groundwater bodies, reference is made to the following risks:

- Pathogen pollution: bacteria, viruses or other living organisms;
- Chemical pollution:
  - pest control substances in agriculture and forestry as well as compounds of nitrogen, phosphorus and potassium fertilizers;
  - industrial chemicals: phenols, tar, detergents, oil and oil residues, oil, liquid fuels, dyes, cyanides, heavy metals, etc.;
  - radioactive substances;
- Thermal pollution with high temperature waters discharged from industrial cooling units. In order to avoid any possibility of water contamination, sizing the buffer zones will take into account all local factors, natural and anthropogenic, including:
  - Geomorphological, geotechnical and geotectonic characteristics of the area;
  - The structure and hydrogeological parameters of the layers above the captured aquifer;
  - Hydrogeological parameters and structure of the captured aquifer;
  - Surface water quality if hydraulically connected to the captured aquifer;
  - Intake operating regimes;
  - Point and diffuse sources of existing pollution;
  - Other site-specific issues.

The principles of sizing the protection areas are specific to the local conditions of each intake:

- The underground travel time criteria of an active hydrodynamic water particle is usually used for the sizing of sanitary protection zones with a strict regime and restricted regime;
- The size of the protection area with a strict regime is determined based on a minimum 20-day pollutant travel time to the water intake through the underground. In the absence of detailed data for travel time calculations, the protection area stretches at least 50 m upstream, 20 m downstream and 20 m to the sides of the intake. The groundwater flow direction determines the upstream and downstream direction;
- The size of the protection areas with a restriction regime is determined taking into account an underground pollutant travel time of at least 50 days to the water intake;

- The sizing of the hydro-geological protected perimeter is needed for springs, drains and wells and for low-depth groundwater intakes. The sizing requires a detailed hydrogeological analysis, including considerations on the recharge area of the used water resources.

To respect the defined criteria, certain land-uses and activities are restricted or limited inside the sanitary protection areas. The land inside a strict regime sanitary area can only be used for the construction and installation of water supply equipment, for its operation and maintenance.

Both in groundwater abstraction areas with a strict protection regime and the shore areas with a strict protection regime for surface water sources are prohibited all activities planned for sanitary protection zone regime restriction, as well as:

- Constructions that are not directly related to the water supply;
- Blasting, digging and excavation of any kind;
- Storage of materials, except those strictly necessary for the operation of the water supply installations. Measures will be taken to prevent entry of any polluting substances into the soil;
- Installation of wastewater sewer systems with the exception of the sanitation system of the protected area. Measures will be taken to ensure the tightness of the sewer systems.

On agricultural land area with a strict regime of sanitary protection the following activities are prohibited:

- Use of chemical or animal fertilizers and plant protection chemicals;
- Irrigation with non-potable water;
- Planting of crops that require frequent care works or using animal traction;
- Grazing.

Farmland in sanitary protection areas covered by a strict regime will be operated only for perennial crops, straw and fruit trees, under conditions that do not cause degradation of the water works.

Land included in the sanitary protection zone under a restriction regime can be used for agriculture, but the following activities are prohibited:

- Use of natural and chemical fertilizer;
- Use of plant protection chemicals;
- Irrigation with sewage, even when treated;
- Installation of stables, cages of animals and animal waste storage;
- Grazing and silage fodder;
- Building greenhouses and fish ponds.

The norm approved by GD. 930/2005 provides for the organizing and conducting of a monitoring program. A monitoring program is required for drinking water intakes of over 100 m^3/day, to ensure sustainable use and to protect the ground water resources from overexploitation and pollution. Water intake owners are required to make observations and measurements regarding the evolution and development of ground water levels and quality, as measured in the exploitation wells. The records must be kept up to date and must be transmitted to the Water Basin Management Unit. The monitoring program is established by water management authorization.

For drinking water intakes of over 5,000 m^3/day, owners are required to install and operate several monitoring wells inside the protection areas. Well's location and technical features will be approved by the water permit. The observations and measurements will be performed both in the exploitation wells and in monitoring wells.

"Romanian Waters" National Administration establishes and maintains computerized records of sanitary protection zones and hydrogeological protection perimeters of each river basin and forwards them at the end of each calendar year to the specialized direction of the central public authority in the water sector – Environment and Forestry Ministry, for their inclusion in the register of protected areas.

CONCLUSIONS

This material discussed the current Romanian legislation and institutions regarding ground water protection. The development for the next 20-25 years should aim to achieve the sustainable use of groundwater resources. The main objectives will be:

- The prevention or elimination of pollutant infiltration into groundwater;
- The protection, improvement and restoration of all bodies of ground water.

The long-term objective of the strategy is to restrict ground water use to drinking water.

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LITHOLOGICAL AND HYDROGEOLOGICAL CONSIDERATIONS ON THE PHREATIC AQUIFER FROM BEGA – TIMIS INTERFLUVE , BANAT PLAIN, ROMANIA, WITH SPECIAL REGARD TO THE UNSATURATED ZONE (PROJECT CC WATERS)

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Abstract: CC WATERS Project - Climate Change and Impacts on Water Supply has as objective the optimization of water supply system management for the next decades under climate change in different areas of Europe (to find new solutions, sources, proposals for legislation amending). This paper presents a part of the project work, respectively lithological and hydrogeological characterization of phreatic aquifer in the pilot area of Banat Plain, with special regard to the unsaturated zone. Aquifer is developed in the floodplain and terrace alluvial deposits as well as interfluve areas in Upper Pleistocene-Holocene age. These deposits are characterized by lateral facies changes. Development in the unsaturated zone of clayey deposits with lenticular aspect determines in some areas that hydrostatic level to be ascensional, which is a peculiarity of the study area. Lithological and hydrogeological characteristics knowledge is very important to the elaboration of a correctly conceptual model. Consequently, a mathematical model of phreatic aquifer flow was made (will be the topic of another paper). This model was subsequently used to run some scenarios regarding the impact of climate changes on groundwater resources.
Keywords: lithologic facies, unsaturated zone, groundwater level

INTRODUCTION

In order to achieve the project CC WATERS Project - Climate Change and Impacts on Water Supply,and also the improvement of the water supply management system in what concerns the climatic changes, there have been chosen two pilot areas, Oltenia Plain and Banat Plain, the last area being the objective of this paper.

For each area there have been elaborated mathematical models of the groundwater flow (these will make the object of another paper), at which achievement, the knowledge of the lithological and hydrogeological characteristics of the phreatic aquifer had an important role.

General characteristics of the study area

From geomorphological point of view, the study area belongs to the Banat Plain situated in SW part of the country (Fig. 1). This is a recent subsidence alluvial plain with shallow valleys (2-4 m), strong meanders, deserted floodplains and buried terraces. It is partially covered with proluvial-deluvial deposits. Main rivers in the region are the Timis River, Bega Veche River and Bega Channel (Ardelean, Zăvoianu, 1979).

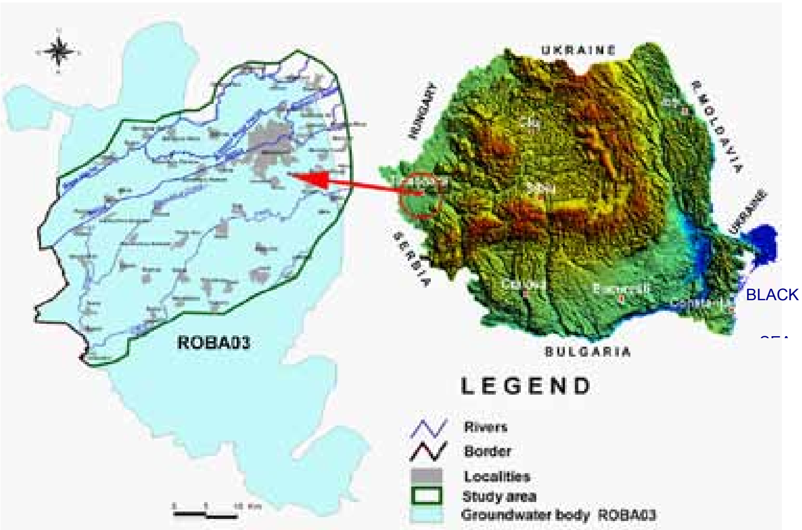

Figure 1 – The location of the study area

From geological point of view, the studied area belongs to the South East part of the Pannonian Basin. Its foundation is composed of Higher Precambrian crystalline. These are covered by discordant sediment deposits belonging to Cretaceous (Senonian), Cenozoic and Quaternary ages (Mutihac, 1990).

From a lithological point of view, the Pannonian Basin is composed of an alternation of sands, argillaceous sands, marls and clays, and subsidiary sand with gravels and sandstones. Quaternary deposits consist of sands and gravels, clays, and sandy clays with intercalations of silts. In addition to these, there are "red clays" from the Upper Pleistocene and loess deposits from the Upper Pleistocene-Lower Holocene (Ghenea, Ghenea, 1967, Drăgulescu et al., 1968).

From a hydrogeological point of view, the phreatic aquifer, which is the subject of this paper, is developed in the alluvial deposits of the floodplain as well as in the terraces and in interfluve areas. These deposits belong to the Upper Pleistocene-Holocene age.

Lithological and hydrogeological considerations on the phreatic aquifer from Bega – Timis interfluve

The study area is a part of the phreatic groundwater body ROBA03 (Bretotean et al., 2006) (Fig.1).

In order to characterize the phreatic aquifer, there have been elaborated, on the basis of the hydrological data of Hydrogeological Stations of I Order wells (usually setted on the water courses cross-section), belonging to the National Hydrogeological Network for phreatic aquifers, on several hydrogeological sections (Fig. 2).

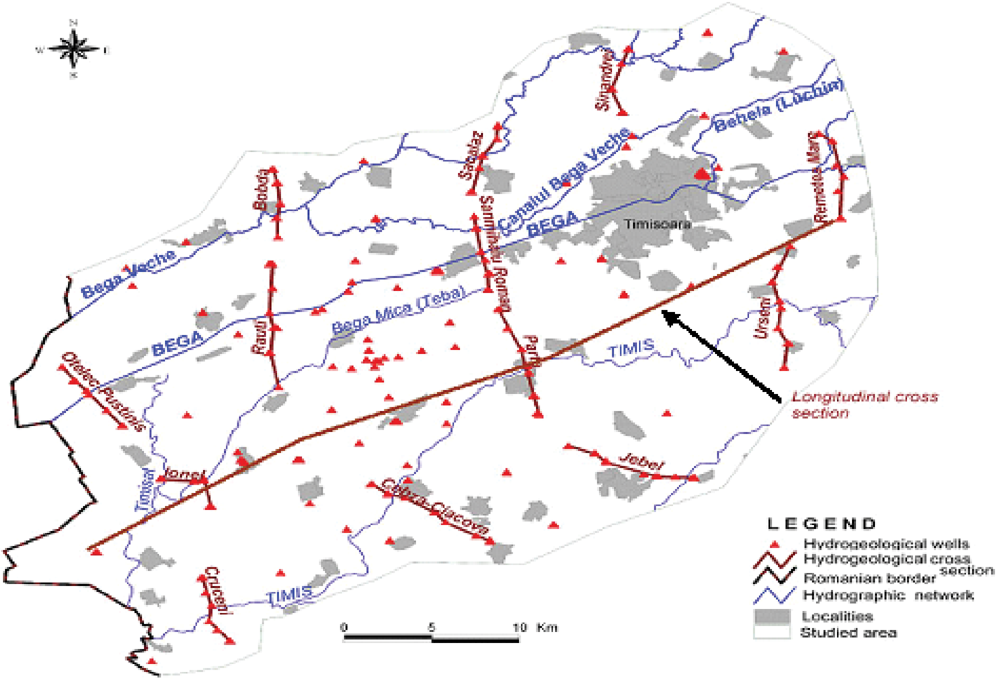

Figure 2 – The map with the location of the hydrogeological cross- section in the study area

From the analysis of these sections and the lithological data of the II order observation hydrological wells (situated on interfluve) results that the porous permeable deposits that quarter the phreatic groundwater body, are mainly made of fine sands – medium, subordinated medium coarse, frequently argillceus, at which there is added sands with small gravels (Fig. 3). These alternate with clays, sandy clays and/or silty and/or silty clays, and/or with clays, with calcalerous concretions. The presence of a relatively high proportion of the silt fraction is observed and the absence of coarse fractions, particularly boulders, can be noted.

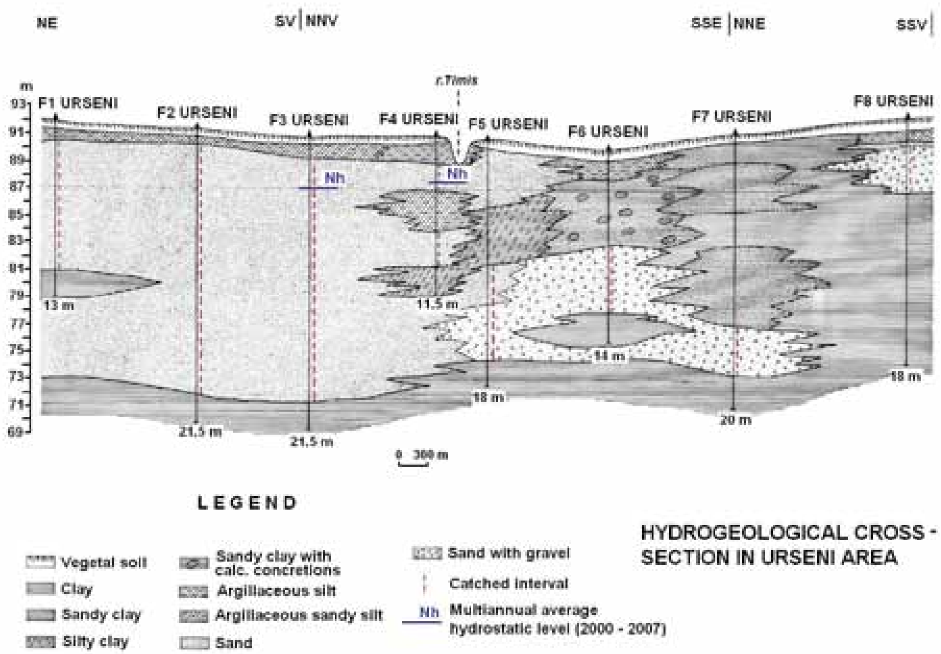

Figure 3 – Hydrogeological cross - section in the eastern part of study area (Urseni area)

The granulometry of the deposits decreases in the study area from north-east towards south-west, due to the decrease of the water courses transport power (Fig. 4).

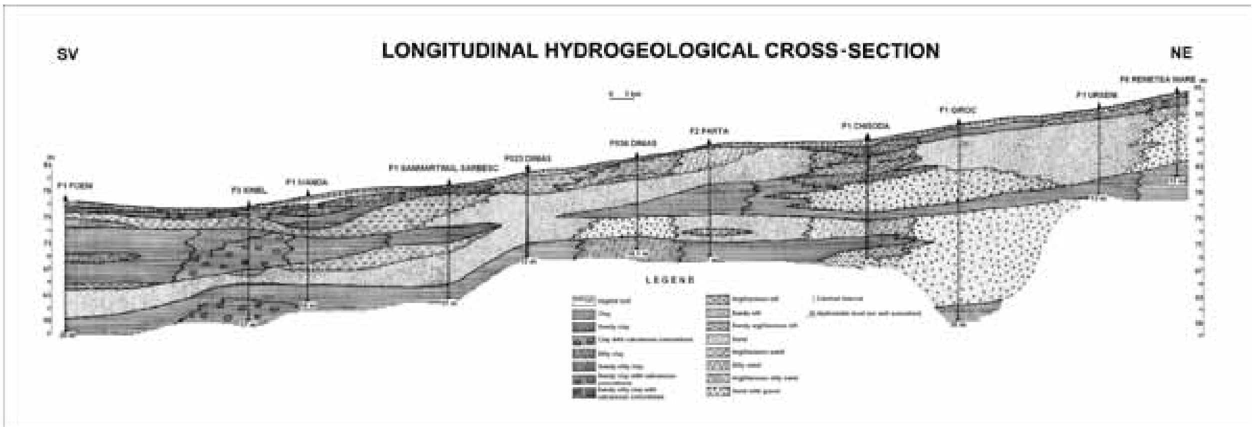

Figure 4 – Longitudinal hydrogeological cross - section in the Bega – Timiş interfluve

A characteristic of these deposits is the lateral facies variation, reflected by the horizontal and the vertical transition to deposits with different thickness and granulometry (Fig. 5).

The facies variation is gradual (from fine sand - to medium or coarse sand, with rare elements of small gravel at the beginning) or abrupt (the occurrence of loamy sand levels and silt and sandy clay and silt). Locally, sandy level lenses can occur showing a low development, isolated in clay and silt deposits (Figure 3). The facies variations are due to the deposit river-lake environment. This formed these deposits of alluvial or proluvial type. Processes that have characterized recently the subsidence of the area can be observed.

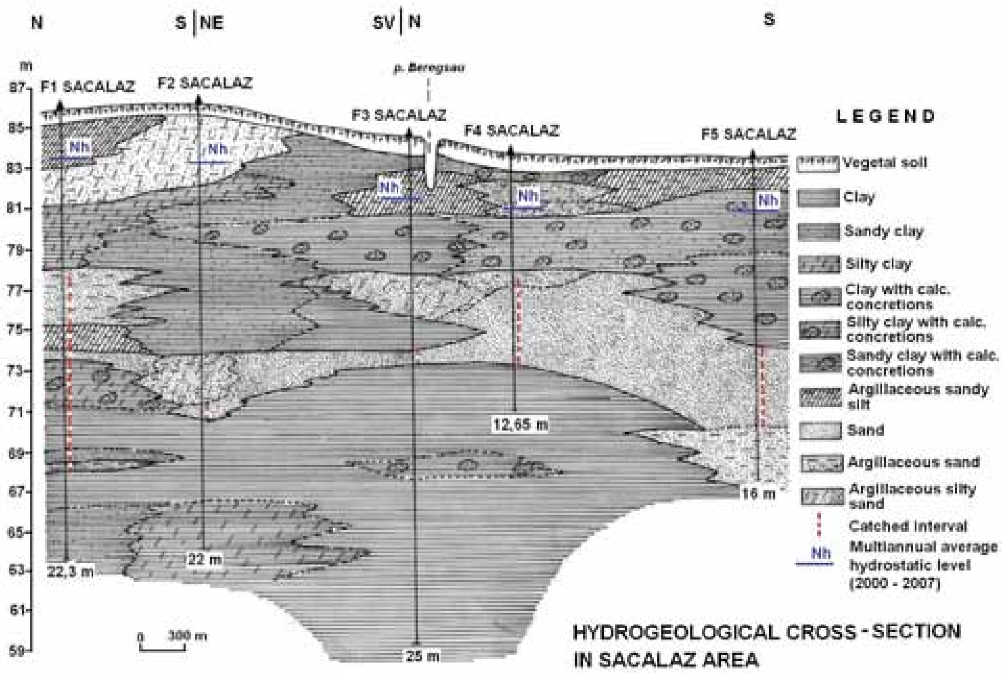

Figure 5 – Lithofacial variation of the alluvial-prolluvial deposits from study area (eg: Săcălaz area)

Some considerations regarding the unsaturated zone

From the hydrogeological cross-section analysis, of the lithological data of the hydrogeological observation wells of II order (situated on the interfluves) and of the medium multiannual depth of the piezometric level, there can be observed that the phreatic groundwater body from the study area is in complex hydrogeological conditions. This aspect is due to the intense facies variation (as mentioned before), as a direct effect of the characteristics and time and space evolution and of the depositional environment.

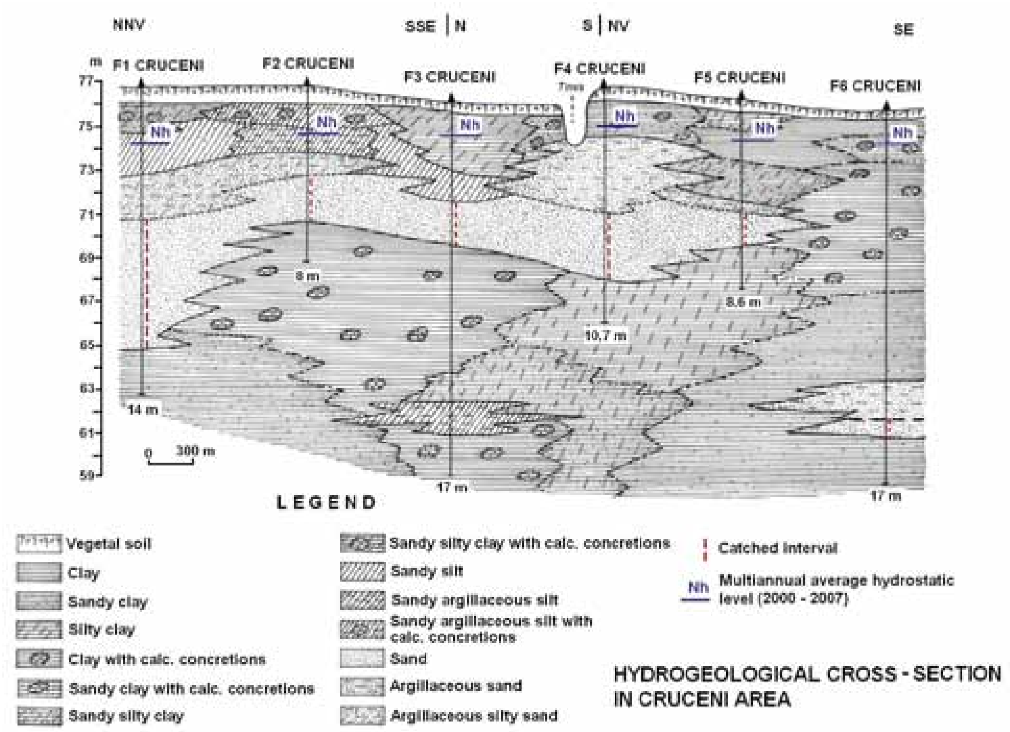

Figure 6 – Hydrogeological cross - section in the south western part of the study area (Cruceni area)

Due to this cause, in the upper part of the first porous permeable level, there are on relatively extended areas, but discontinuous, sandy and/or silty clays, and/or with calcareous concretion deposits, rarely compact clays, silts, sandy and/or argillaceous silts and/or calcareous concretions, having variable thicknesses.

These low permeable or semi-permeable deposits are laterally transiting to fine or medium, argillaceous and/or silty sands, which determine that in some areas the hydrostatic level to be free and in other areas the hydrostatic level to be ascensional.

CONCLUSIONS

From a lithological point of view, the alluvial-proluvial deposits which quarter the phreatic aquifer from the study area are mainly made from sands with different granulometries, subordinated sands with gravels, at which there are added intercalations of clays and silts. Characteristic of these deposits is the facies variation, on vertical and also horizontal.

The unsaturated zone is characterized through the presence of some argillaceous, silty levels, with a relatively extense area, but discontinuous, which makes that locally the hydrostatic level of the phreatic aquifer to be ascensional.

The thorough knowledge of the lithology of the deposits from the saturated zone and from the unsaturated zone lies at the basis of the elaboration of a correct conceptual model.

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INFLUENCE OF AQUITARD PARAMETERS UNCERTAINTY ON AQUIFER RECHARGE

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Abstract: Present evidence indicates that global warming of the atmosphere is taking place, and is influencing the water cycle. A major concern is the influence on the amount of fresh water. Having in mind that most of the fresh water is accumulated underground, special attention is devoted to infiltration and recharge of aquifers. To estimate aquifer recharge, one must have hydrological data such as rainfall, surface runoff and evapotranspiration. However, infiltration is affected by aquitard/soil characteristics as well. Field observations have shown that conductivity even in saturated soils is not uniform, and that it follows a log-normal distribution. When one deals with unsaturated soils, conductivity is usually estimated from the saturated soil characteristics, moisture potential and water content, so the uncertainty is even higher than in the case of saturated soils. This article will present a series of numerical experiments, which will model the conversion of rainfall into aquifer recharge during a period of one year. The process of infiltration is governed by the Richard's equation, using a stochastic set of soil parameter data, where the evapotranspiration is modeled by the Penman-Monteith equation (daily mean temperature, wind speed, relative humidity, and solar radiation are used to predict the net evapotranspiration). In addition, model inputs are daily average rainfall data. The results show severe effects of the soil parameters uncertainty on aquifer recharge, which should be considered in analyses of groundwater regimes.
Keywords: aquifer recharge, parameter uncertainty, geostatistical methods

INTRODUCTION

The process of infiltration plays an important role in a wide range of engineering practice. Infiltration from the surface is often the major recharge source for aquifers and therefore requires special attention in the process of groundwater modeling. Nevertheless, it is common practice in large scale groundwater modeling to consider infiltration as a calibration parameter with no significant insight into the processes in the vadose zone. Similarly, in applications of physically based distributed hydrological models, the infiltration estimate is of crucial importance, since the runoff is directly related. Moreover, the design and application of infiltration systems (e.g. infiltration trenches, soakways, etc.) as urban stormwater control systems, requires a detailed insight into saturated/unsaturated vertical flow (e.g. Fujita, 1984; Browne et al., 2008).

There are many field observations showing a highly heterogeneous nature of the soil material. This circumstance motivated researches in the last several decades to develop theories of groundwater flow in the probabilistic framework (e.g. Gelhar, 1986). However, these theories and investigations were mainly directed towards saturated, horizontal flow.

In this study, a vertical 1D numerical model is utilized to analyze the long term infiltration process and to evaluate the effects of aquitard heterogeneity on the annual recharge intensity of the aquifer. A numerical example consists of a 2m aquitard layer which drains under unit gradient at the bottom boundary (free drainage to phreatic aquifer is assumed). At the surface boundary, the observed daily precipitation is imposed, as well as the flux representing the evapotranspiration, estimated by the Penman-Monteith equation and observed meteorological data. A stochastic analysis is conducted by means of Monte Carlo simulations where material heterogeneity is generated in each realization based on assumed statistical parameters.

MODEL DESCRIPTION

The flow in the unsaturated zone is typically described by the Richards equation as:

$$\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial z}\left(K(h)\frac{\partial h}{\partial z}\right) + \frac{\partial K(h)}{\partial z} = 0 \qquad (1)$$

where t is the time, θ is the water content, z is the vertical coordinate (pointing downwards), K(h) is the unsaturated hydraulic conductivity and h is the pressure head. In order to solve the Richards equation, constitutive relations are required for the moisture characteristic curve and relationships between unsaturated hydraulic conductivity and either pressure head or water content. In this study, the Van Genuchten (1980) model is utilized:

$$\theta(h) = \frac{\theta_S - \theta_r}{\left[1 + (\alpha|h|)^n\right]^m} + \theta_r \qquad (2)$$

$$K(h) = K_S \frac{\left\{1 - (\alpha|h|)^{n-1}\left[1 + (\alpha|h|)^n\right]^{-m}\right\}^2}{\left[1 + (\alpha|h|)^n\right]^{\frac{m}{2}}} \qquad (3)$$

where θ_s is the saturated water content, θ_r is the residual water content, K_s is the saturated hydraulic permeability, m=1-1/n and α are the soil fitting parameters. Greater values of parameter α indicate a greater drainage potential as a consequence of a small capillary fringe zone. Parameter n is related to pore size and distribution in the soil – small values of n have the same effect as a higher frequency of smaller pores (Prasad et al., 2001).

The Richards equation has three distinct forms – pressure head (h) – based, moisture content (θ) – based, and the mixed form. Despite being mathematically equivalent, in this paper the mixed form is discretized, since it has been proven to have benefits in terms of mass balance preservation (Celia et al., 1990).

Two approaches are utilized for discretization of Equation (1) in this study, the finite element and finite difference methods, where both models showed similar results and efficiency. The applied discretization is implicit in time (Euler backward method), with a finite difference form as follows:

$$\left(-\frac{K_{i-1/2}^{n+1,m}}{(\Delta z)^2}\right)\cdot\delta_{i-1}^{m}+\left(\frac{C_i^{n+1,m}}{\Delta t}+\frac{K_{i-1/2}^{n+1,m}+K_{i+1/2}^{n+1,m}}{(\Delta z)^2}\right)\cdot\delta_i^{m}+\left(-\frac{K_{i+1/2}^{n+1,m}}{(\Delta z)^2}\right)\cdot\delta_{i+1}^{m}=$$
$$=\frac{1}{(\Delta z)^2}\left(K_{i+1/2}^{n+1,m}\left(h_{i+1}^{n+1,m}-h_i^{n+1,m}\right)-K_{i-1/2}^{n+1,m}\left(h_i^{n+1,m}-h_{i-1}^{n+1,m}\right)\right)-\frac{K_{i+1/2}^{n+1,m}-K_{i-1/2}^{n+1,m}}{\Delta z}-\frac{\theta_i^{n+1,m}-\theta_i^{n}}{\Delta t} \tag{4}$$

where $\delta_i^m = h_i^{n+1,m+1} - h_i^{n+1,m}$ is the iteration increment, m is the iteration index, n is the time step, and $i = 1, 2, \dots N$ is the node index.

The governing equation is inherently nonlinear and therefore requires iterative calculation in each time step. The Picard iterative procedure is applied with estimation of the unknown pressure height h^{n+1} using the latest estimates of C^{n+1} and K^{n+1} ($C \equiv d\theta / dh$ is the specific moisture capacity function).

Since modeling results are sensitive to hydraulic conductivity estimation between discretization nodes, the geometric average is utilized, based on the results of Haverkamp et al. (1979):

$$K_{i+1/2} = \sqrt{K_i \cdot K_{i+1}} \tag{5}$$

In order to improve model efficiency under highly dry conditions, the pressure head in previous equations is transformed by the following expression, as well as other dependent variables:

$$h' = \frac{h}{1-0.04h} \tag{6}$$

HETEROGENEITY REALIZATIONS

As emphasized above, evidence exist to confirm that soil characteristics vary greatly in space and a simple Van Genuchten model can hardly simulate the complexity of nature. Therefore, a decision was made to generate a random field of input parameters. The first parameter to be modeled is the saturated hydraulic conductivity. This physical quantity follows the log-normal distribution in space (e.g. Freeze, 1979). Generation based on this distribution cannot be done solely randomly; it has to include some degree of correlation between values.

Under the assumption that the hydraulic conductivity field is stationary, geostatistical methods can be used to generate new/extrapolate data from the measured data. First, the measured data have to be analyzed to find functions indicating spatial dependency between values based on their distance. The two common functions are the semivariogram $\gamma(z)$ – difference between variance and covariance, and the correlation coefficient $\rho(z)$ – ratio between covariance and variance, where z is the distance between two points. Hydrological models frequently use an exponential function to define the correlation coefficient:

$$\rho(h) = \exp\left(-\frac{h}{L}\right) \tag{7}$$

where L is the parameter–correlation scale. For example, at a distance equal to three correlation scales, the degree of correlation is negligible (<5%).

Uniform distribution is used to generate a set of random numbers on the domain (0, 1) which is a set of probabilities p(i). Using this probability set and the inverse log-normal distribution function, saturated hydraulic conductivity is calculated as:

$$K(i) = 10^{\text{norminv}\ (p(i), \mu_Y, \sigma_Y)} \tag{8}$$

where $i = 1, 2, \ldots M$ is the number of values generated in a node, μY is the mean value of Y = log(Ks), and σY is the standard deviation.

The Iman-Conover method (Iman&Conover, 1982) is used to induce rank-correlation to the randomly generated field. This method assumes that the correlation coefficient is a known value. A symmetric correlation matrix C is formed so that its elements ρ_{ij} represent the correlation coefficient between nodes i and j:

$$\mathbf{C} = \begin{bmatrix} 1 & \rho_{12} & \cdots & \rho_{1N} \\ \rho_{21} & 1 & \cdots & \rho_{2N} \\ \vdots & \vdots & \rho_{ij} & \vdots \\ \rho_{N1} & \rho_{N2} & \cdots & 1 \end{bmatrix} \qquad \mathbf{R} = \begin{bmatrix} Ks_{11} & Ks_{12} & \vdots & Ks_{1N} \\ Ks_{21} & Ks_{22} & \vdots & Ks_{2N} \\ \vdots & \vdots & Ks_{mn} & \vdots \\ Ks_{M1} & Ks_{M2} & \vdots & Ks_{MN} \end{bmatrix} \tag{9}$$

This matrix is of size NxN (where N is the number of nodes). The sample matrix R is formed of elements Ks_{mn} (m – sample index, n – node index), with each column representing sample set values in a particular node and rows representing a set of Ks values for all nodes per simulation. This matrix is of size MxN (where M is the number of simulations).

The Cholesky method is used to decompose matrix C to a lower and upper diagonal matrix. The upper diagonal matrix is used to transform sample matrix R to R*:

$$C = D \cdot U \qquad R^* = R \cdot U \tag{10}$$

Matrix R* has different values than R, but has nearly the same rank correlation as matrix C. The last step consists of a modification (perturbation of columns and rows) of matrix R in a way that value ranks in its columns correspond to value ranks in R*, without changing the actual values.

Numerical example

The matter of concern is aquifer recharge. The type of aquitard soil chosen for this experiment is sandy clay with typical values of soil parameters as shown in Table 1.

Table 1: Assumed soil parameters

Ks [m/day]	α [1/m]	θs [-]	θr [-]	n [-]
0.029	2.7	0.38	0.26	1.2

Ks value is the mean value used for log-normal distribution Y=log(Ks) and its standard deviation is μY = 1.0. For the correlation scale, a value of L = 1m was chosen, because correlation is negligible at a depth of 3m. These values have to be confirmed with a series of field investigations, involving taking samples at every 30 cm, estimating soil properties and finding the actual correlation scale.

Calculations are performed for a 2m deep zone, with equidistant numerical nodes at $\Delta z = 4$cm, which drains under unit gradient at the bottom boundary (phreatic aquifer is assumed). At the surface boundary, the observed annual precipitation is imposed, as well as the flux representing the evapotranspiration, estimated by the Penman-Monteith equation (Allen et al., 1998) and observed meteorological data. These data were taken from Hydrometeorological Service of Serbia's 2009 Yearbook for the station "Beograd" (Figure 1). The total rainfall in 2009 was 804.4 mm. The referent crop was 12cm tall grass. The initial condition in the soil was water content $\theta = 0.34$.

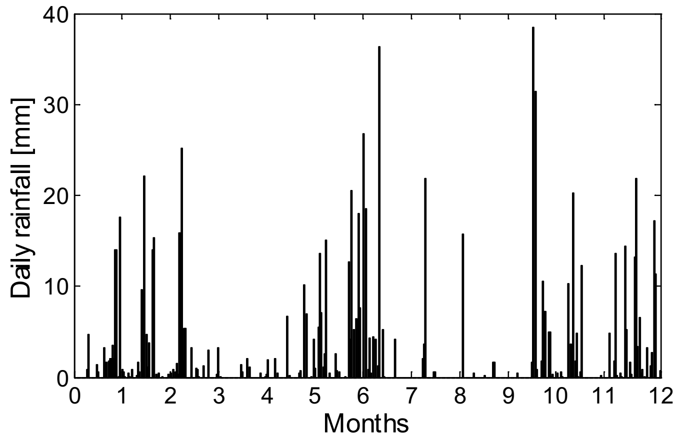

Figure 1: Input daily rainfall data, meteorological station "Beograd", 2009

RESULTS

A total of 200 simulations were performed, each lasting a whole year. Simulation results are volumes of water that infiltrate at a depth of 2 meters, i.e. the amount of water that recharges the aquifer. 200 data were processed and their statistics calculated. Figure 2 shows cumulative infiltration at 2 meters for 12 months. The range of yearly infiltrations is 0 – 323mm. The mean value shows that only 12% (99.5mm) of the total yearly rainfall recharges the aquifer. The maximum goes to 40% (more than the triple mean). Standard deviation is quite high and its value at the end of the year is 76.9mm (that is the order of magnitude of the mean value).

The next step is to compare the results of Monte Carlo simulations to the traditional model used for infiltration estimates. The standard model is a model of a homogeneous soil using the same parameters as shown in Table 1. As seen in Figure 3, a great difference exists in the two models' results. The homogeneous model (marked as standard model) simulation showed that 25% of rainfall infiltrates into the aquifer.

Monte Carlo simulations by the model described in this paper are tedious. However, the intention was to provide an appropriate estimate of equivalent hydraulic conductivity, knowing the statistics of the distribution it follows. In addition, the harmonic mean of Ks for each of the 200 samples is calculated (the equivalent Ks utilizing Darcy's law for steady flow) and the mean value of corresponding calculations is also shown in Figure 3. There seems to be a good match, however, models with equivalent saturated hydraulic conductivity have an even greater standard deviation (96.4mm).

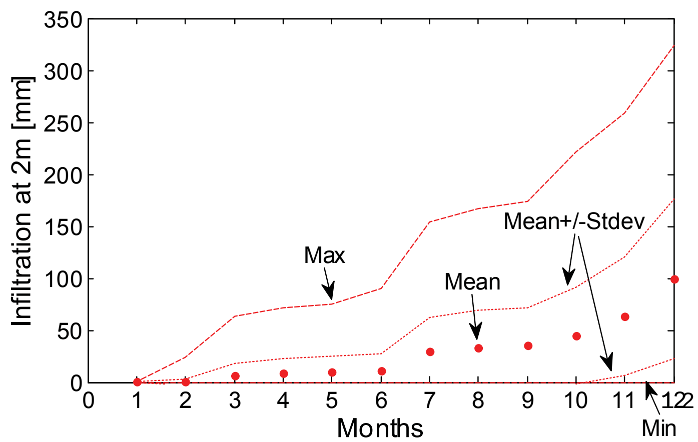

Figure 2: Simulation results and statistics – Infiltration at a depth of 2 meters

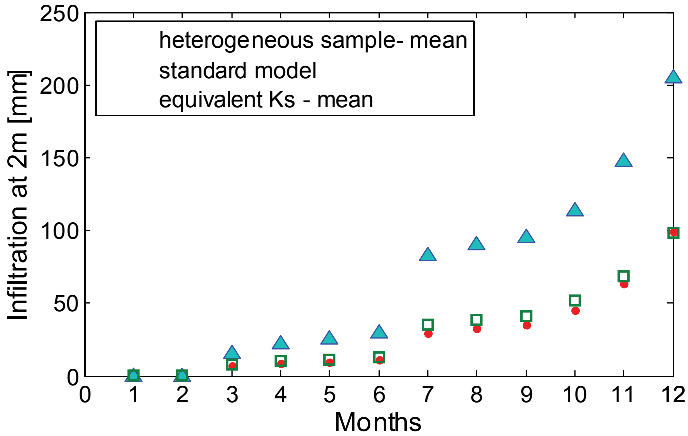

Figure 3. Infiltration at a depth of 2 meters – comparison of three models: heterogeneous sample, homogenous sample – standard model, and homogeneous sample – harmonic mean

CONCLUSIONS

An attempt was made to quantify soil heterogeneity influence on aquifer recharge. A probabilistic framework was used, this time for unsaturated vertical flow. The soil was described with widely used Van Genuchten relations. The saturated hydraulic conductivity was modeled with a log-normal distribution using an exponential model for the spatial correlation coefficient. Vertical filtration is modeled by the Richards equation, using both finite difference and finite element discretization methods, applied at a uniform numerical grid. Input data included rainfall daily and other meteorological data (in order to estimate evapotranspiration).

Results show great dissipation when the heterogeneity is taken into account, compared to the standard homogeneous model. The amount of rainfall that infiltrates when the heterogeneous model is used is 12%, compared to 25% of the homogeneous model. Actually, the results of the heterogeneous model show great variations: maximum infiltration is 40% of the rainfall, while standard deviation of results is 77% of the mean. The conclusion is that infiltration is highly sensitive to soil parameters and further numerical and field investigations are required to provide better quantification of the whole process, including stochastic characterization of the soil.

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Notes:

Extended Abstract

REMOTE SENSING AND GIS TECHNIQUES FOR ASSESSMENT OF SOIL WATER CONTENT IN ORDER TO IMPROVE AGRICULTURAL PRACTICE AND REDUCE THE IMPACT ON GROUNDWATER – CASE STUDY, AGRICULTURAL AREA ŞTEFAN CEL MARE, CĂLĂRAŞI COUNTY

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Keywords: classification, correlation, remote sensing, soil moisture content, spatial data

INTRODUCTION

The current agricultural practice in Romania consists of uniform irrigations, fertilizations and application of special treatments. This kind of procedure does not take into account the lithological, pedological and morphological features of the site. Therefore, there is a risk in some areas of irrigation and fertilization measures being over- or under-sized. Water excess causes an increase in nitro compound concentrations within the shallow aquifer.

The correlation of agricultural practice with land features brings a new series of direct benefits, such as:

- Improvement in fertilizer application, followed by a decrease of the negative impact on the environment, represented by soil and shallow aquifer pollution with nutrients;
- Major reducing of the amount of water used for the irrigations;
- Reduction of production costs caused by the decrease of consumption;
- A better correlation of cultivated species with the soil type.

At a local scale, terrain features can be assessed by classical methods, such as field analysis, measurements and mapping. For large cultivated areas, this methodology requires investigation and measuring points, followed by multiple analyses of soil and groundwater in order to determine the quality, leading to higher costs.

High-resolution Multispectral and Hyperspectral methods are used nowadays more and more for the improvement of agricultural measures and the diminution of the impact of agricultural activities on the environment (soil and shallow aquifer). Remote sensing emphasizes the spectral differences of the land surface. Depending on the wave length used and specific processing/interpretation, these could represent areas with different level of humidity, different textural character of the soil, and specific morphological aspects.

This study aims to correlate remote sensing data with field data in order to obtain a proper interpretation. All the information is the basis of the supervised classification, operated on the remote sensing images. The obtained classes from this process are associated with the features determined at the study stage.

The information resulting from specific processing of remote sensing data (obtained with the ENVI EX software) will represent the spatial database in order to develop a new GIS project (with ArcView10 software). Attribute associated data are the following:

- General data for the studied area – terrain morphology, climate, soil;
- Distinctive data related to agricultural exploitation – crop type, fertilization programme, irrigation, etc;
- Data obtained from sampling and field determination;
- Determination of the geographical coordinates in the field for all the used landmarks and for all the points, from which soil samples and groundwater samples were collected, was determined with the GARMIN GPSMAP 60CSx device.

Taking into consideration all the data, from the spatial analysis and by establishing different correlations, a new technology for the assessment of the agricultural practice in accordance with the land features was created.

The proposed technology was put in place within the agricultural area Ştefan cel Mare (44°25'36.59"N 27°38'27.21"E, elevation 70.5 m.), Călăraş County (Fig. 1), in both conventional and ecological crops.

The studied area is located within the "Romanian Plain", more exactly in the Hagieni Plain, from the Mărculeştiului Plain, between the Ialomiţa River and the Borcea Branch. The relief is specific, tabular plain covered by loess, fragmentary tabular plain covered by humus, piedmont–deltaic plain, also covered by loess, strong alluvial deposits - flood plain types, valley and also terrace. The hydrographical network is tributary to the Danube, which marks the county border in the south and southeast.

The soil structure is characterized by the following sequence: Chernozem, Cambic Chernozem, Alluvial Chernozem and brown and red soil (only in the western part of the county). The soil types were formed on the loess or loess deposits and the texture at their surface is medium. The moist phreatic soil appears only on limited surface.

Due to the high fertilization rate of the Chernozem and alluvial soils (which represent more than 97% of all soil), the entire area is used for intensive agriculture.

The temperate continental climate is characterized by hot summers and frosty winters, with the multiannual average temperatures between 10 and 11, with an average for January between 3 and - 4 degrees Celsius and for July between 22 and 23 degrees Celsius. The multiannual average for the precipitations is situated between 400 mm and 500 mm, with an average quantity between 30 and 40 mm in January, and between 40 and 60 mm in July.

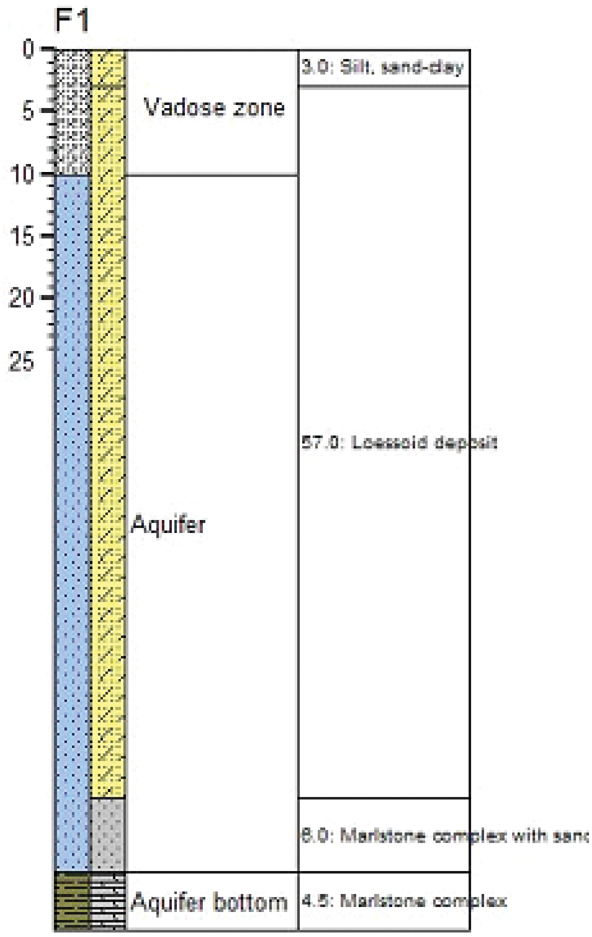

Fig. 1 Lithological column

Figure 1: Lithological column

Hydrogeological characterization

Analyzing the lithological data (Fig. 1) which describe the area, the following succession was determined (Bandrabur, Patrulius, 1974):

- 3 m deep from the land surface – silt and sand-clay from the Upper Holocene, interspersed in a loessoid sequence;
- between 3 and 60 metres deep – loessoid deposits from the Middle – Upper Pleistocene;
- between 60 and 66 metres - marlstone complex with 6-metre thick sandy seam on top (Middle Pleistocene).

METHODOLOGY

The working methodology is based on the correlation of remote sensing data with field observations. The aim is to identify key features and establish an interpretation pattern for the inhomogeneity elements highlighted by the remote sensing data.

Working field:
During the preliminary phase of data collection, five groundwater samples and nine soil samples were taken for laboratory analysis. For the shallow aquifer the determinations of pH and temperature were made in situ.

RESULTS

The results of the analytical stage are listed below:

GPS code	Sample ID	Terrain altitude (m)	Depth to groundwater level (m)	pH	Temperature °C
P004	P1	38	11	8.48	13.6
P005	P2	48	40	8.63	13.8
P006	P3	40	7	8.26	13.7
P011	P4	36	16-17	8.87	14.2
P012	P5	36	16-17	8.87	14.2

Laboratory determinations pointed out the following concentrations for nitrogen and phosphorus compounds within the water samples, compounds resulted from soil fertilization:

Sample ID	Nitrate mg NO_3/l	Nitrite mg NO_2/l	Ammonium mg NH_4/l	Total nitrogen mg N/l	Phosphate mg PO_4/l
P1	337,35	0,117	0,006	79,6	0,083
P2	80,51	0,040	0	19,7	0,033
P3	20,18	0,034	0	5,1	0,150
P4	51,187	0,036	0	12,8	0,271
P5	72,135	0,058	0,026	17,4	0,044

For the nitrate parameter, the maximum admissible concentration (MAC) for drinking water was exceeded for samples: P1, P2, P4 and P5. The significance of the overload is more important because of the relatively great depth of the groundwater level and the specific lithology (silty) of the vadose zone. These results show the scale of the pollution process, due to the high quantities of fertilizers used in agriculture.

The soil analysis results are listed below:

Sample ID	Total nitrogen %	Nitrate mg NO_3/kg [dry soil]	Nitrite mg NO_2/ kg [dry soil]	Ammonium mg NH_4/ kg [dry soil]	Phosphate mg PO_4/ kg [dry soil]
P1	0,267	7	0,925	10,9	0,21
P2	0,288	19	0,485	2,835	2,05
P3	0,279	19,2	1,4	4,445	0,575
P4	0,728	15,5	0,645	8,05	0,305
P5	0,303	22,5	0,72	5,3	0,355
P6	0,296	20,3	0,12	4,9	0,305
P7	0,125	21,75	0,19	7,2	0,35
P8	0,117	13,25	0,095	5,56	0,4
P9	0,178	21	0,11	6,85	0,42

The processing of the remote sensing data will be made taking into consideration the sample contents and the results of the field work.

The remote sensing images used were supplied by the FORMOSAT-2 satellite, created and operated by SPOT (Fig. 2). The criteria for this selection were determined by the low cost of acquisition, in comparison with other product, high resolution and favourable orbits (fourteen orbital revolution per day), with optimal coverage of the Romanian territory.

Figure 2: Demarcation of plots in the studied area (Formosat-2 multispectral image)

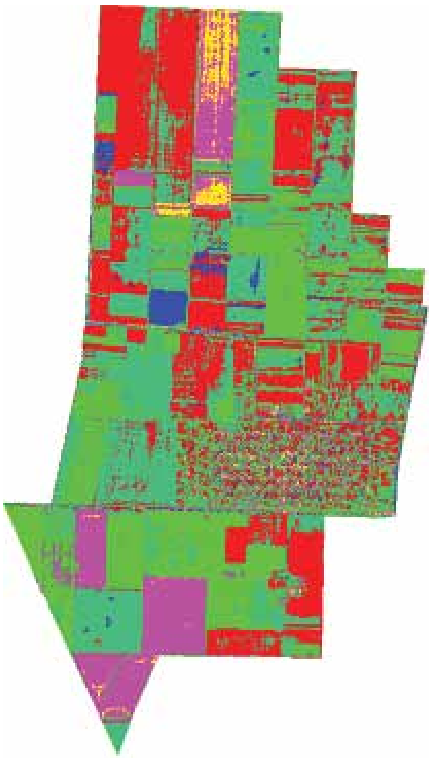

Figure 3: Result of unsupervised classification performed for study area

Such technology will be efficient for large cultivated areas and/or on land with a high diversity of crops or pedology. Using that technology, it will be possible to set up agricultural measures by interpretation of remote sensing data and also to reduce the impact of these activities on the shallow aquifer, an important drinking water source for rural communities.

The remote sensing images were rectified, and an unsupervised classification was performed (with the ENVI EX product), in order to correlate the spectral inhomogeneities within the field characteristics (Fig. 3).

The classes obtained from this stage represent the spatial database, which will be correlated with the observation and determinations from the field and laboratory.

CONCLUSIONS

Based on these correlations, the interpretation pattern for remote sensing data was established in order to become an important instrument for the evaluation and taking the right decisions for the improvement of the agricultural works and reduce the negative impact on the soil and groundwater.

As previously shown, the studied area is characterized by a moisture deficit (400 – 500 mm/an), which imposes the necessity of land irrigations.

Due to the specific and strong spectral response of the soil water content variation, the proposed methodology is very efficient for evaluation of soil water demand. The irrigation improvement will provide proper soil water content and therefore a reduction of water consumption and groundwater pollution.

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SOUTH DOBROGEA UNDERGROUND AQUIFERS AND THEIR EVOLUTION IN THE LAST 40-50 YEARS

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Abstract: The water company, RAJA SA Constanta, is a regional operator that ensures water supply to towns within Constanta County and 3 other surrounding counties. In Constanţa County, drinking water supply for over 700,000 inhabitants, is obtained in proportion of 95% from underground water. In recent years an increase in the nitrate content was found in the groundwater used for the water supply systems in rural areas and even larger town systems. Most were over the limit allowed by Law 458/2005 on drinking water quality. This led to the interruption of exploitation by underground water catchments by health authorities and their abandonment. This article presents data on the evolution of hydrogeological parameters and water chemistry of underground aquifers in southern Dobrogea exploited by water supply systems in the area. The causes of increases in nitrate content in groundwater, the time evolution of the content of nitrates and the measures to protect geological and groundwater abstractions exploited are analyzed. A case study will be presented for the Pecinega underground water source - located in the southern County of Constanta.
Keywords: water supply, nitrate, groundwater sources, aquifer, Sarmatian.

GENERAL DATA

The drinking water supply for Constanta County towns is almost exclusively from underground water sources. In the county there are about 100 captures of underground water with one or more drilled wells summing a total of 300 drilled wells with an installed capacity of about 8800 L/s.

Abstractions from the Barremian-Jurassic depth aquifer complex, have the largest share representing approx. 70% of installed capacity in the county. Abstractions of water from the medium depth Sarmatian aquifers are about 26% of installed capacity, and abstractions from shallow Quaternary groundwater aquifers are approx. 4% of installed capacity. In order to ensure sustainable exploitation of the two major aquifers the hydrogeological evolution of the main parameters - hydrodynamic flow and hydrostatic levels - and hydrochemical - groundwater chemistry was monitored.

Alarming increases in the concentrations of nitrates were recorded in over 30 cities in the county which are supplied with water mainly from medium-depth Sarmatian aquifers, a situation which was notified by the county's sanitary bodies. In some localities the use of underground water sources ceased and the search for water supply solutions for these villages of appropriate quality started. Thus 9 of the underground water Sarmatian aquifers were phased out.

GEOLOGICAL AND HYDROGEOLOGICAL CHARACTERIZATION OF THE STUDIED AREA

Southern Dobrogea represents a part of the Moesian Plateau, bound by the Capidava-Ovidiu fault to the north, the intra-Moesiana fault (Calarasi-Fierbinti-Shabla) to the south, the Danube to the west and the Black Sea to the east. This region covers an area of approximately 5000 km_2.

Formations of the Mesozoic and Neozoic are widespread in the area and include several sedimentary cycles separated by nearly horizontal discordants. Only a few of these formations are important in hydrogeological terms: carbonated sediments from the late Jurassic/early Cretaceous times with a thickness between 400-1200m in the entire area and which represents the main aquifer, the Eocene deposits and the Sarmatian limestone that make up the shallow aquifers.

Heterogeneous spatial distribution of Mesozoic formations, with wide variation in the profiles, suggests a process of sedimentation in a tectonically active area, which was divided into blocks with different positions (covered/uncovered) during the geological evolution. Boundaries of blocks, separated by almost vertical faults have evolved by successive movements that occurred in the Cretaceous and Paleocene tectonic phases.

The carbonated complex J3 - K1 develops at the whole Moesian plate, with a similar tectonic structure of southern Dobrogea. Stratigraphic thickness of this unit varies between 700 m and 1600m (in the Bucharest City zone and the north), but decreases to 100-300m in Giurgiu, near the Danube River (where the sequence is incomplete). Formations are inclined steeply to the north (through faults). The lower Cretaceous is found in several places: on the right bank of the Danube, upstream of the Ruse, between Ostrov and Cernavoda, along the valleys north of the Danube in Romania and Bulgaria (Fig. 1).

Lower aquifer (depth)

In the carbon complex of the late Jurassic/early Cretaceous there is a regional aquifer which covers the entire Moesian plate. In Romania, the main flow direction is W-E. The download to the Black Sea occurs mainly in the city of Constanta, through blocks bounded by the Capidava-Ovidiu and Cernavoda-Constanta faults (Mamaia Lake area).

The principal recharge area is located in the territory of Bulgaria. Between Cernavoda and Giurgiu, there is a complex hydraulic relationship between the aquifers and the Danube. In southern Dobrogea, the permeability of the tectonic blocks complex J_3 K_1 expresses the geological evolution of each block, which is less influenced by the actual dynamics of groundwater. Aquifer permeability values range from tens or hundreds to more than 150,000 m^2/day. The hydraulic slope is usually less than 0.05%. Hydraulic conductivity is usually more than 102 km/day and the storage coefficient varies between 10^{-3} and 10^{-4}. The aquifer is closed on 60% of southern Dobrudja. In the west and south of Cernavoda City, there is an area which presents conditions for openness. There the aquifer can be directly influenced by precipitations, seepage from irrigation systems and discharge from the upper aquifer.

Figure 1: Regional geological map aquifer J3-K1

Upper aquifer (shallow)

In the eastern half of the southern part of Dobrogea, the Sarmatian limestone layer forms a plate with a thickness of up to 150 m. The quartered aquifer in the Sarmatian limestone represents the main source of water supply for the southern coastal zone south of Eforie. The development of this aquifer is controlled by the existence of an impermeable layer of Senonian chalk. To the south and south east, Eocene and Sarmatiene formations form a permeable and unitary aquifer.

- The aquifer with a Sarmatian free level is fed with precipitation and minor losses from irrigation systems;
- The main drainage area is the Black Sea through a system of lakes that lie along the coast and in the southern part of the City of Constanta;
- After the completion of the Carasu irrigation system (1972), the water level rose by more than 25m, with different consequences: an increase in discharge in coastal lakes (hydrological and hydrodynamic impact on Lake Techirghiol) an increase in recharge through leakage , the deep aquifer, and an increase in discharge flow index in the valleys;
- Hydrogeological parameters are: hydraulic gradient of 0.9% (in Lake Techirghiol) to 0.14% (in the south), permeability of 50 to 2000 m^2/day, with local values of 5000 m^2/day.
- Senoniana Chalk, sandstones, and the Senoniana Cenomanian-Albien sands, act as a waterproof layer, separating the two aquifers hydrodynamically;

Figure 2: Hydrogeological map of the Sarmatian aquifer (including NO_3 potential sources and RAJA's groundwater sources)

The regional aquifer system in southern Dobrogea is the most important reservoir of drinking water in Romania. It provides water supply in the rural and urban areas, important economic and social objectives, and the tourist areas of the Black Sea.

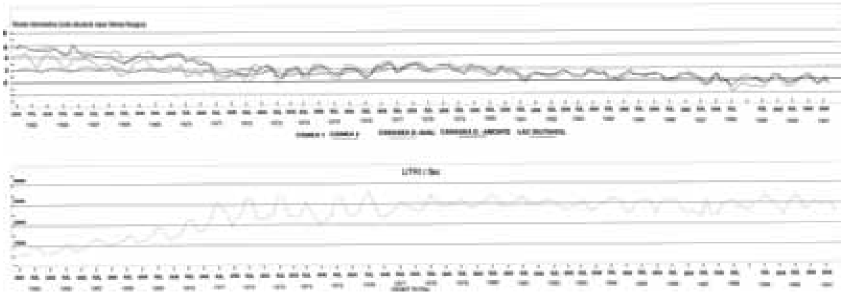
Based on chemical analyses made in the past 30 years, underground water from the aquifer system in southern Dobrogea can be characterized as follows:

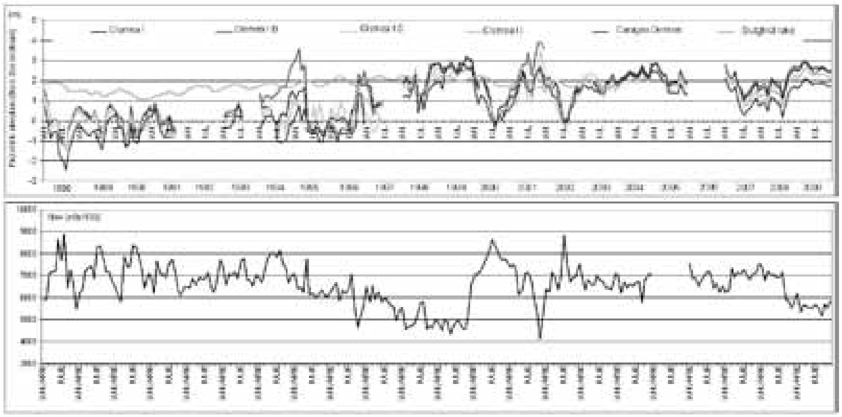
- the J-K aquifer - bicarbonate, calcium-magnesium type with temperatures 20-26°C, total mineralization varies between 300 and 1000 mg/L and total hardness is between 8-26 degrees.
- the Sm aquifer - mainly calcium bicarbonate with total mineralization of about 1 g/L. Locally, near the shore, the content of ions Cl^- and Na^+ is higher (water is of the sodium chloride type and mineralization can exceed 4 g/L). In the marshy area of Mangalia, because of the relationship with the depth aquifer, local water becomes sulfurous.

PIEZOMETRIC EVOLUTION OF THE LOWER J-K CRETACEOUS AQUIFER AND UPPER SM AQUIFER

Flow chart - bump catchments Constanta

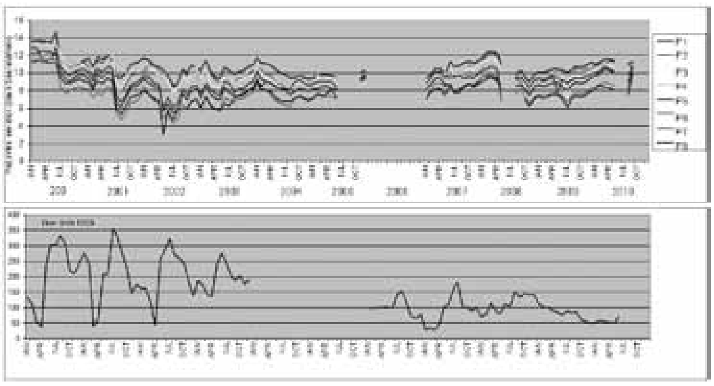
We present graphically only the evolution of the piezometric load over the past 50 years,





Flow chart - bump catchments Pecineaga

We present graphically only the evolution of the piezometric load over the past 10 years:



On 3.1. chart we see a constant piezometric evolution depending on flow statment. Also we see small changes in lake level according with piezometric level, which means we have a hydraulic connection between each.

On 3.2. chart the piezometric evolution shows a different situation. At a constant flow, the piezometric level decreases in time. This was the response of the aquifer to the lower discharge from an irrigation system that was increasingly less used in agriculture. As a result, the piezometric level of this aquifer decreased by about 4m.

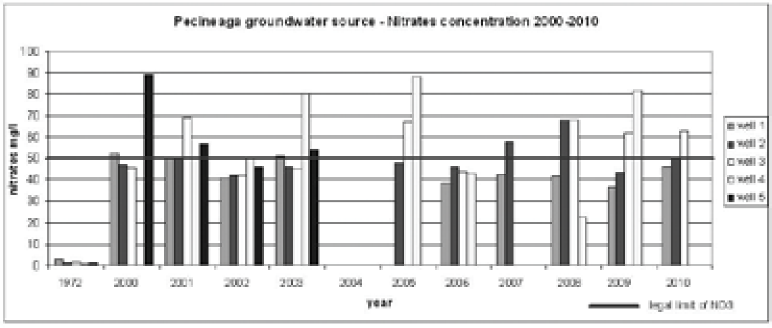
EVOLUTION OF NITRATE CONTENT IN GROUNDWATER AQUIFERS

A total of 360 chemical analyses from 160 wells of 119 catchments were processed, groundwater samples taken in the second half of 2007, some of them monitored in 2000-2010, including the nitrates situation during the execution of drilling.

The depth of water in the aquifer that feeds the Jurassic deposits and Medgidia Constanta, is low in nitrates and in over 30-40 years of operation there were no significant changes in nitrate content.

Underground water in the upper Sarmatian aquifer from the southern coast has registered an increase, sometimes significantly, in the content of nitrates for a part of wells.

A special situation presents the Sarmatian abstractions of the littoral area, which ensures water supply to the tourist areas between Eforie and Vama Veche. If in the capture of Costinesti, Tatlageac, Albesti, Vartop, there were no significant changes in nitrate content, in the captures of Techirghiol, Biruinta, Dulcesti, Pecineaga, an alarming increase in nitrate content is found in some of the wells, as shown in the chart below:



This alarming increase in the concentration of nitrate is favored by the high degree of vulnerability to pollution of the aquifer in the area studied, and generally throughout the upper aquifer area.

POLLUTION SOURCES OF THE SUPERIOR AQUIFER – SARMATIAN

Qualitative indicators of underground water values are directly dependent on a number of natural and anthropogenic factors, namely:

- Geomorphological features, geological and structural-tectonics of the area;
- Structure, lithology and hydrogeological parameters of the aquifer captures;
- Thickness, extent and lithology of the covered deposits of the aquifer captures;
- Climatic conditions of the area (temperature, precipitation, etc.), especially in the case of ground water aquifers;
- Operating regime of the captures;
- Point sources and existing disseminated pollution: zootechnical complexes, infiltrations from the sewers of the localities;
- Intense agricultural activity (excessive use of chemical fertilizers)

Nitrate concentrations that are found naturally in groundwater are generally low (below 10 mg/l). Nitrate concentrations exceeding natural levels due to human activities exclusively (agriculture, industry, rising domestic wastewater).The chart above shows that at the execution of drilling, the nitrate level was low in all cases, well below limits.

CONCLUSIONS

To keep the water quality especially in these parameter NO_3, our company has to mix different water volumes with low and high nitrate concentration so as to maintain the nitrete concentration below 50 mg/l at the end.

To keep the water quality especially in these parameter NO_3, our company has to mix different water volumes with low and high nitrate concentrations so as to maintain the nitrate concentration below 50 mg/l at the end. We have to keep in mind that the septic sewerage system must be changed with a network sewerage system to collect wastewater and treat it. This is our goal for all villages in our interest area.

To inform and insist on the Ministry of Environment to control and reduce or eliminate those other sources of contamination on which we do not have any responsibility. We mention here:

- the bigbreeder houses, with no wastewater treatment plants
- the high amount of chemical fertilizers used in agriculture.

These are the main causes of high concentration of nitrates. Unfortunately, the flow water rate of aquifer, slow and steady infiltration of nitrates and difficulty in time to eliminate all sources of nitrate pollution will cause problems for many years.

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Notes:

ECOLOGICAL ASPECT OF SUSTAINABLE DEVELOPMENT OF THE MUNICIPALITY OF LAPOVO

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Keywords: Municipality of Lapovo, ecological sustainability, urban development

INTRODUCTION

Development of most human settlements in Serbia, in the second half of the 20th century, can generally be described as industrial. This resulted in significant side effects on natural resources, mainly caused by a lack of ecological awareness when industrialization was planned, then carried out. The rise of ecological awareness in Serbia was slightly behind developed countries then. Unfortunately, it was emphasized when transition started, especially due late transition start. The Committee on Human Settlements of the Economic Commission for Europe (ECE) has established a bearing for sustainable human settlements development treating its three main aspects (Lujanen, 1996): ecological, economical and social equally (combined with the role of the so-called third sector, with integration of GIS in the human settlements sector).

ECE recommended that the ecological aspect of sustainable development was to be perceived through five components: fresh water resources, traffic, waste management, energy consumption, and green structure.

This paper illustrates how inconsistent planning and partial problem-solving can lead to a negative impact on the environment. On the other hand, this is an individual attempt to emphasize that proper data base organization is a very important step when urban management is to be performed properly. So, this paper treats all the components in sense of forming an appropriate data base. Combining provided layers is supposed to be a significant platform for sustainable municipal management planning, which is inevitable if remediation is expected/wanted.

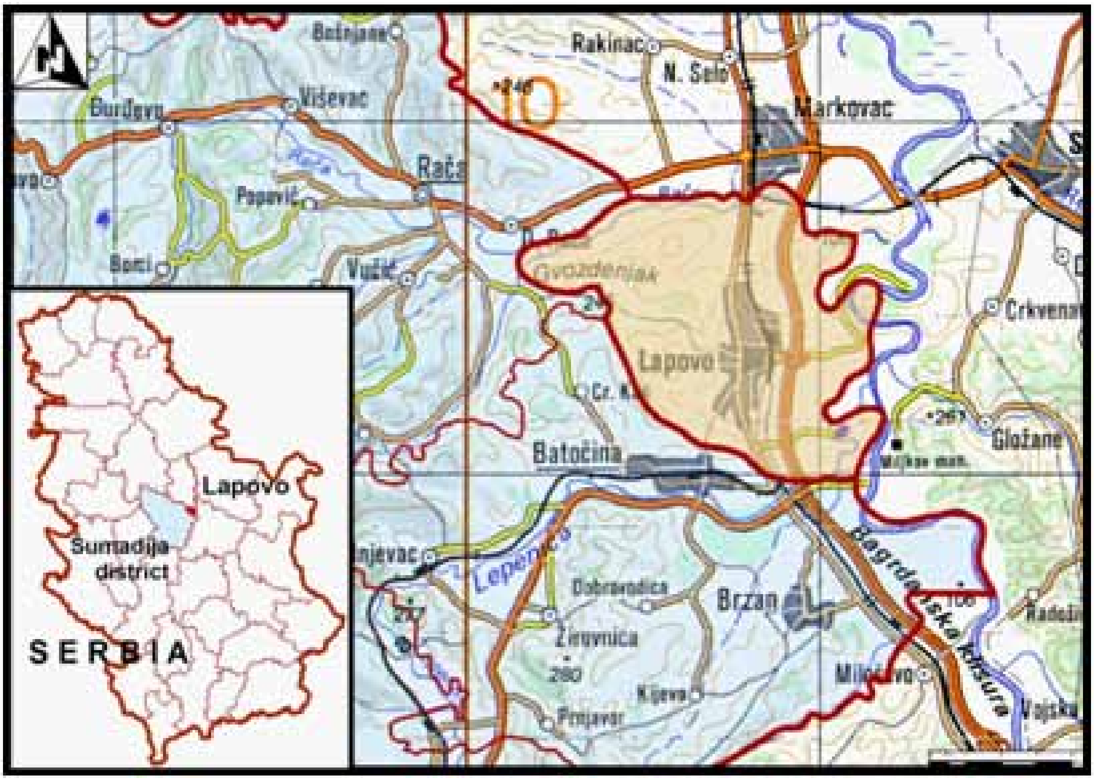

Figure 1: Location Map

RESEARCH AREA

The research area is framed in Lapovo, a municipality situated in the central part of the Republic of Serbia, in the NW part of the Šumadija District. The Velika Morava River is one of the most significant domicile rivers and Lapovo fits in the central part of its basin (Fig. 1).

Lapovo`s good position on international route E75, with a junction of the international Belgrade-Niš-Athens railway line ensures a high potential for further economic development. On the other hand, it exposes it to a threat for pollution threat.

Like all other neighboring municipalities, Lapovo has suffered from major urban management problems. As a result of anthropogenic impacts on natural resources, the standard of living deteriorated during the past two decades. Thus, among other factors, this might be the one closely linked to population decrease.

There is a general trend of population decrease in Serbian municipalities as a result of various factors. Figure 2 shows the specific population increase ($\frac{population\ difference}{time\ step}$) in Šumadija District municipalities by census year. It is apparent that other than Kragujevac and Aranđelovac, all municipalities exhibit a significant decrease, especially in the past decade.

What differentiates Lapovo from neighboring municipalities is a significantly higher mortality rate (Fig. 3), which might be the criteria for linking population decrease with the deterioration of the standard of living as a result of anthropogenic impact on the environment.

METHODS OF EVALUATION

Following ECE`s recommendations for evaluation of the five mentioned components the of ecological aspect of sustainable development, Lapovo should be described as follows:

Fresh water resources issues of the Lapovo Municipality are not supposed to be quantitative, since the water-supply source Garevina is situated in an up to 3 km wide, 5 to 15 m deep, alluvial

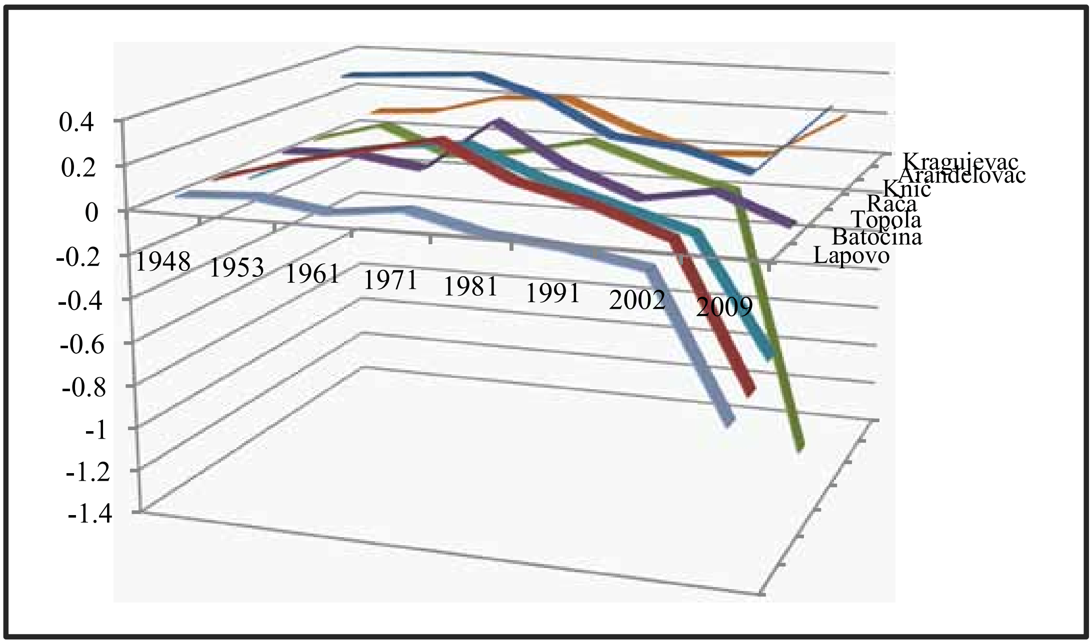

Figure 2: Municipalities of the Šumadija District – Specific Population Increase by Census Year

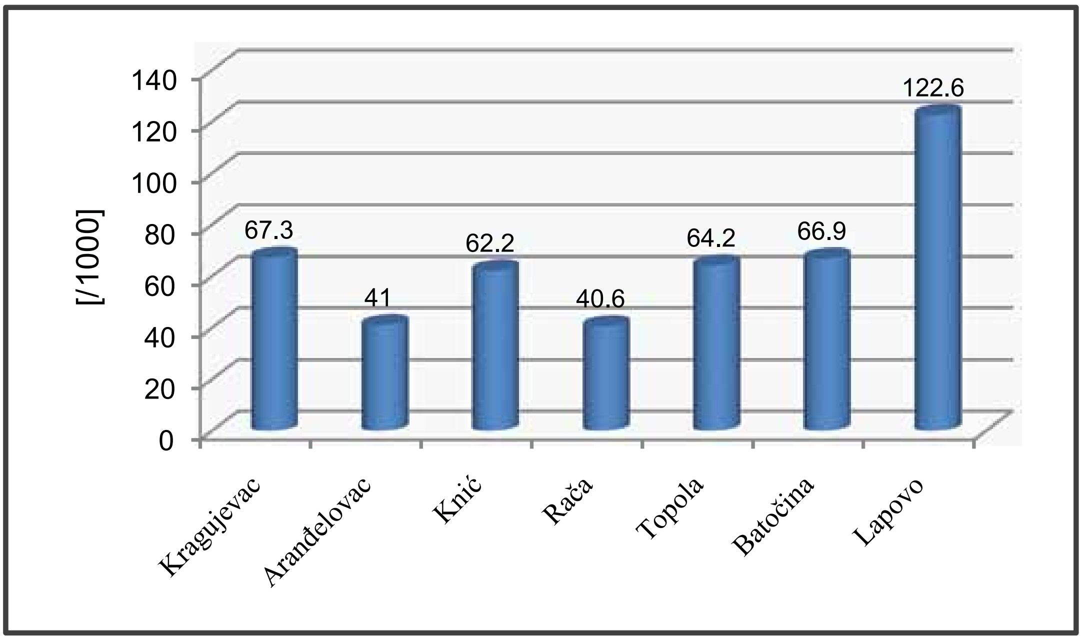

Figure 3: Šumadija District Municipalities – 2004 Mortality Rate

aquifer of the Velika Morava and Lepenica rivers, with a transmissivity ranging from 1.2 to 8.7 m^2/s. This source is comprised of10 wells, of which only two are operating and have an aggregate capacity of approximately 30 l/s. As a result, quantitative issues can reasonably be dealt with by revitalizing the existing wells and drilling several new wells. However, groundwater quality is a much larger issue. Abstracted groundwater is loaded with nitrates and nitrites, as well as with manganese (15 times exceeding quality guidelines) and iron (Fig. 4). The problem is complex and multifaceted (no organized sewage system, municipal landfill, train washing facility and agricultural activities in the infiltration zone; and illegal gravel extraction facilities which exposed the alluvial aquifer to excessive pollution).


a) b) c) d)

Figure 4: . GW sample collected from an observation well – visualization of elevated iron concentration a – Immediately upon sampling; b – 10 minutes later c – 20 minutes later (with a couple of days "old" reference sample); d – 30 minutes later (with the reference sample).

A new water supply source Skela is due to be opened. However, in the absence of responsible planning, a scenario similar to Garevina might be expected. Still, neither of the two sources is a long-term water supply solution, since the alluvial aquifer is exposed and constantly threatened by pollution.

Traffic growth is an alarming issue worldwide. It generates most of the CO, NO_x and VOC emissions and its share of emissions has rapidly increased in the past 30 years. Since Lapovo exhibits a constant population decline, road traffic in the inner municipal zone is not supposed be a threat. The biggest and most significant problem is railway traffic, since the train washing facility is situated in the infiltration area of the water supply source. Additionally, the condition of the rails is unacceptably poor. Besides passengers, the railway line is used for freight traffic so excessive pollution is a major concern. Another traffic issue is the international highway E75, running across the infiltration zone, which adds to the excessive pollution threat.

Waste management is another critical area where management did a major role. The municipal landfill is located in the alluvium and constantly contaminates the source. Additionally, no organized sewage system is in place due to a lack of funding. Only about 5% of the sewage network has been completed. Most of the households (estimated at 70%) use private substandard cesspools. It is estimated that municipal wastewater constantly "feeds" the source.

Energy consumption, as in other economies in transition, is a critical issue: it is highly inefficient and causes severe environmental problems resulting from high levels of sulphur dioxide (SO_2), nitrogen oxide (NO_x) and carbon dioxide (CO_2) emissions. The housing sector offers a high potential for energy savings. In general, short-term conservation and efficiency measures are estimated to save at least 15% in annual energy consumption (Lujanen 1996). Also, proper energy resource selection can be crucial for energy saving and help decrease the environmental impact (Harris 2009).

The green structure is receiving increasing attention lately. It is supposed to meet people`s need for recreation and to be a part of nature. Since Lapovo has not been significantly urbanized, this component of the ecological aspect of sustainable development is the least concern.

RESEARCH METHODS

For groundwater investigation purposes, a hydrodynamic model was generated using Processing Mod-Flow open-source software. The research area was schematized in steady state, as a 6.2 by 8 km orthogonal network, with 10,092 fields made up from 87 rows and 116 columns. This field setup and density were assumed to be accurate enough for the goal of the model and the scope of the work. Initial schematization was performed with a square, 100 by 100 m cell network, in 62 rows and 80 columns. Then the network was densified around the Garevina and Skela source areas, keeping in mind the variable network rule that dimensions of adjacent cells should not differ by more than 50% (Kresic, 1997).

The model's cross-section had two 2 layers. Layer thicknesses were generated in Golden Software Surfer, using the research area DEM as a basis.

Groundwater flow area was finite by impermeable environment (Fig. 5). The alluvial aquifer was modeled as a 5 to 12 m thick shelf, thickening as rambling from the rivers. The cover was represented by a layer with lower permeability, recharge and effective porosity values. The Velika Morava and Lepenica rivers were modeled as constant head boundary (ϕ=const).

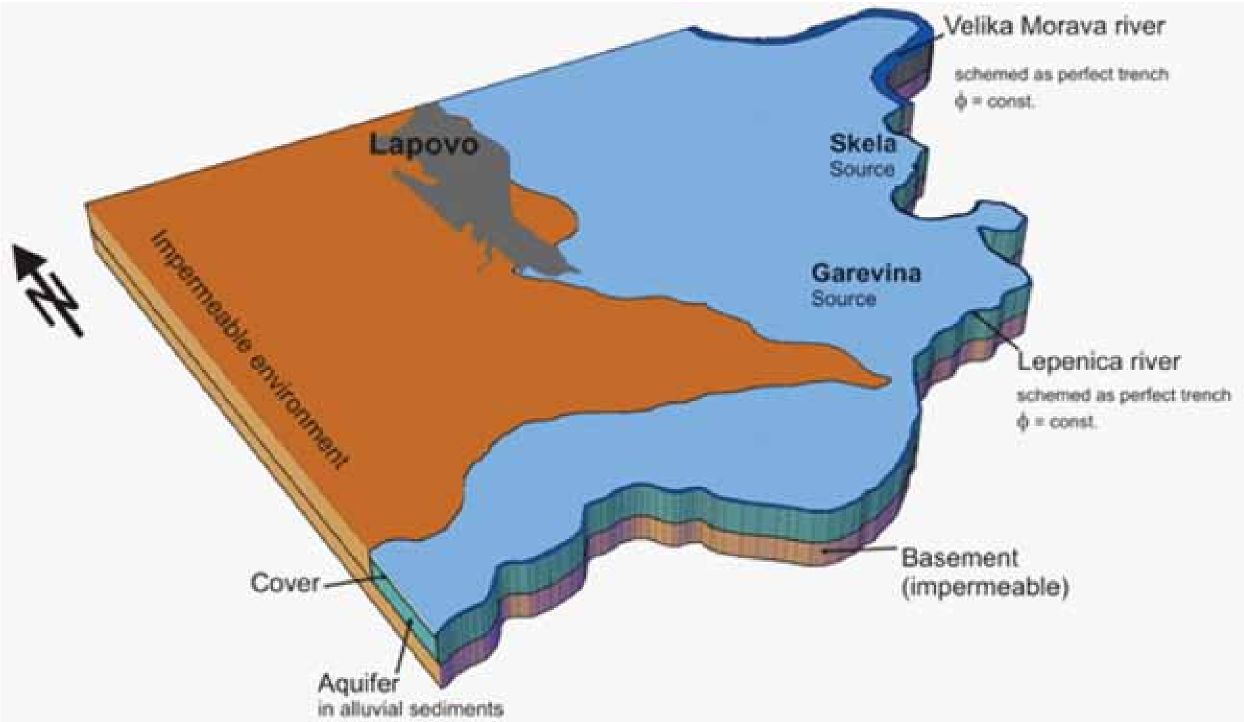

Figure 5: Conceptual Model

RESULTS

The starting point of the model was the active Garevina source (2 production wells yielding 15 l/s each). Calibration produced approx. filtration coefficient values in different areas (Tab. 1).

Table 1: Model-calibrated approx. Kf values

Area	Kf Value [m/s]
Alluvium in source areas	7.5×10^{-4}
Alluvium away from sources	4×10^{-4}
Alluvium at contact with impermeable rock	2×10^{-4}
Cover	10^{-5}

In general, calibrated values matched those obtained from testing of each well at both sources, so the model could be accepted as representative. Afterwards, it was used to compare the current (Fig. 6) with the planned abstraction situation (Fig.7), as well as to simulate two of the largest pollutant carriers in the research area: the municipal landfill and the train washing facility. The model addressed the above- mentioned pollutants because they represented the largest environmental threats. On the other hand, their locations were defined, making it possible to model them.

Pollution from the disorganized sewage system, agricultural activities in the infiltration zone and illegal gravel extraction facilities were not addressed in the model.

The planned scenario included the activation of the new source, Skela, and the shutting down of Garevina. Skela was modeled with 6 production wells yielding 15 l/s each. The planned yields are realistic regarding hydrogeological setting in the Skela source alluvium. Based on the planned configuration, there is an apparent hydraulic head change in the research area: the shutting down of Garevina caused increased groundwater flow towards Skela (Fig. 7).

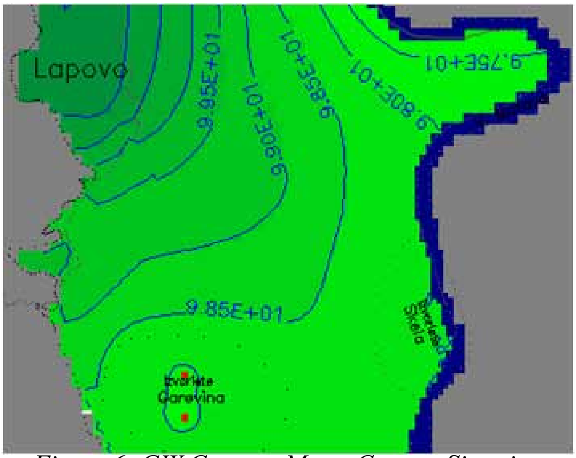

Figure 6: GW Contour Map - Current Situation

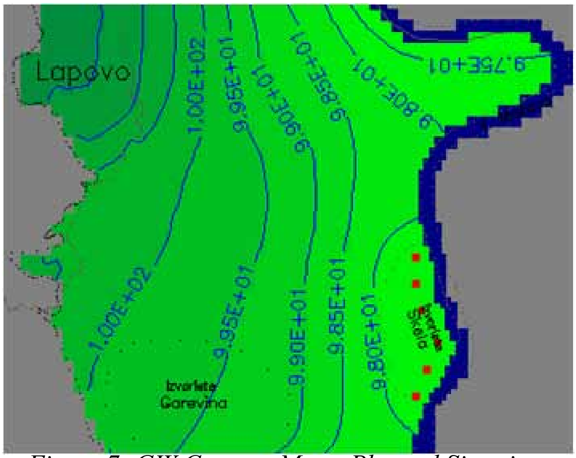

Figure 7: GW Contour Map - Planned Situation

Causally, excessive pollution risk rose up. Since pollution from the landfill and the train washing facility is constant, increased groundwater flow might affect that in certain time step it gets to the source.

The "particle tracking" application of PM-Path sub software was used to analyze excessive pollution in the research area (Guiguer 1997). To verify the model, simulation was performed first with the current abstraction situation (Garevina on / Skela off) and one year was set as the time step.

Pollution from the train washing facility reaches the source area after five time steps/years (Fig. 8). After 19 time steps, pollution from the landfill reaches the source area as well (Fig. 9). The situation shown can be accepted as realistic, since in real time the pollution has already "arrived" at the source area.

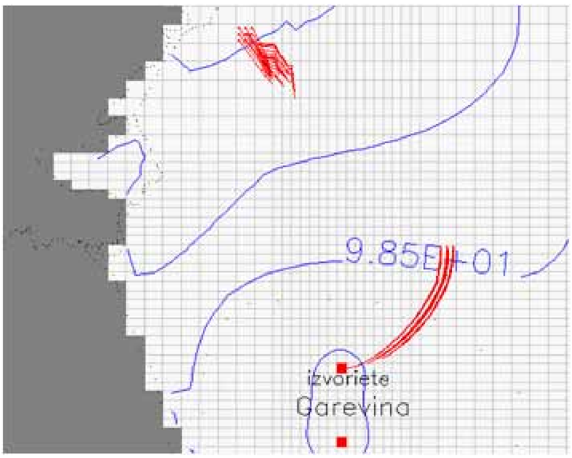

Figure 8: Particle Tracking of Pollutants
Garevina switched on / Skela switched off
After 5 Time Steps

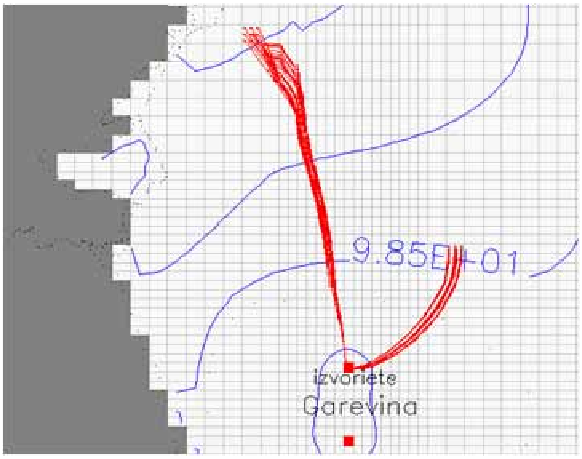

Figure 9: Particle Tracking of Pollutants
Garevina switched on / Skela switched off
After 17 Time Steps

After the current situation, the simulation of the planned situation showed that pollutants will reach the Skela source area: from the train washing facility, after 10 time steps (Fig. 10); and from the municipal landfill, after 27 time steps (Fig. 11). Apparently, the Skela source will face the same problems as Garevina has been facing for years, if the abstraction plan remains unchanged.

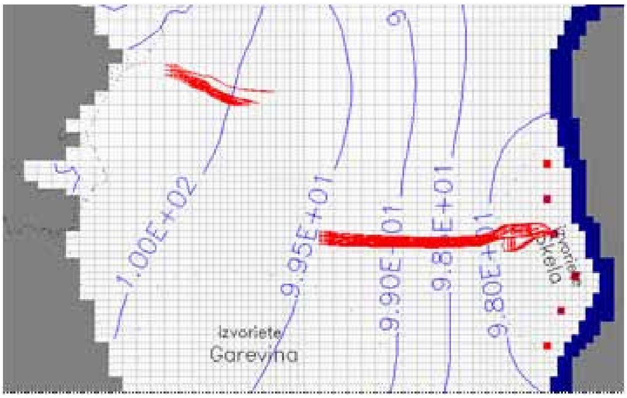

Figure 10: Particle Tracking of Pollutants Garevina switched off / Skela switched on After 10 Time Steps

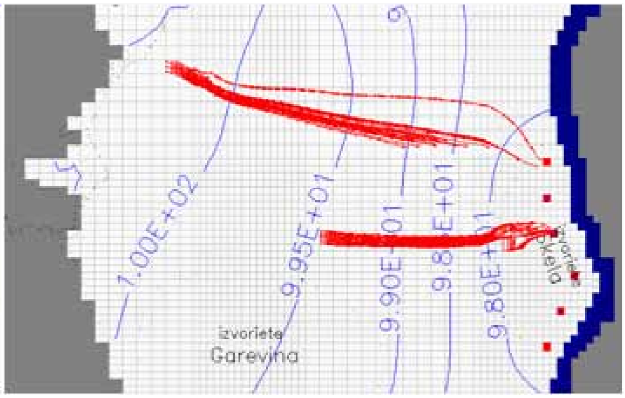

Figure 11: Particle Tracking of Pollutants Garevina switched off / Skela switched on After 27 Time Steps

The model was then used to manage research area groundwater flow conditions. The idea was to use the Garevina source to draw groundwater away from Skela, in fact to use it as a hydraulic barrier (Figs. 12 and 13).

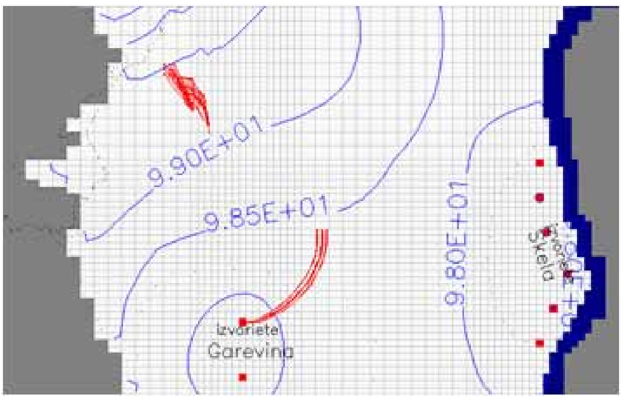

Figure 12: Particle Tracking of Pollutants Garevina switched on / Skela switched on After 6 Time Steps

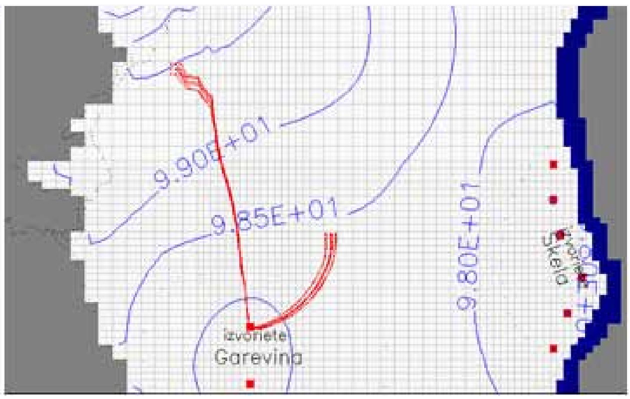

Figure 13. Particle Tracking of Pollutants Garevina switched on / Skela switched on After 19 Time Steps

The simulation showed that leaving Garevina on affected groundwater flow so pollution from train washing facility and municipal landfill did not get to the Skela source area neither after 6, 19 nor 100 years (which was set as maximum number of time steps).

CONCLUSION

The work presented in the paper was an attempt to use common hydrogeological research methods for general groundwater management. The idea of leaving the Garevina source active so that it can "defend" the Skela source from potential excessive pollution turned out to be a scientifically justified option. However, the environmental problems in the research area are slightly more complicated then represented with the model, because pollution from the disorganized sewage system, agricultural activities in the infiltration zone and illegal gravel extraction facilities were not addressed.

Investment in sewage system construction and water system revitalization would be a major burden on the budget of Lapovo. Nobody can stop agricultural activities, even in the infiltration zone. Illegal gravel extraction should be manageable.

Inconsistent planning at the time Lapovo was being developed left too many problems for the current municipal management to handle. Environmental problems should be approached then differently. The task ahead is to set a solid basis for the future, following ECE`s guidance for the ecological aspect of sustainable development, forming a proper data base for the five previously mentioned components:

- The fresh water resources data base should, besides mapping the currently used alluvial aquifer, consider other options such as an aquifer in Neogene sand, as well as limestone;
- The traffic data base should consider the international railway and highway as possible sources of excess pollution, such that zones where the road/railway track is not in a good condition could be treated as zones with a higher excessive pollution probability;
- The waste management data base should start out as a spatially-defined pollutants cadastre;
- The energy consumption data base should treat groundwater as energy;
- The green structure data base should treat soil properties for certain plants (Danijels 2009);

This would lead to the ability to combine and overlap all layers. The idea is to build a model with a well-thought-out algorithm for layer calculation in order to obtain a qualitative output as a basis for sustainable municipal planning/management (Kukurić, 1999). The model should have the ability to offer a proposal for urban development of the Lapovo Municipality, because only a multisectoral approach to problem solving can contribute to ecological sustainability (De Žarden 2006).

According to ECE, "…environmental problems cannot be dealt with merely by upgrading technology…"; public values and everyday habits need to change.

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Extended Abstract

COMPUTING WELL-DRIVEN GROUNDWATER FLOW WITH A FINITE VOLUME METHOD

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INTRODUCTION

The amount of water that can be extracted from a groundwater source trough a single drain is limited by the condition that the extraction is discontinued if the water level in the drain drops below it's bottom. Therefore, if the correlation between the hydraulic in the drain and the extraction rate is inaccurately discretized in a computational code, not only that the result will be inaccurate, but it may happen that the drain in the model runs dry due to the hydraulic head underestimation.

Peaceman model [7] sets the mesh cell size in the finite difference method such that the correlation between the hydraulic head and the extraction rate is correct. This model has been generalized in various ways in the subsequent publications [8, 1, 6, 2] and others.

In finite element codes for well-driven groundwater flow simulation, drains are represented as arrays of mesh edges (see [3, 9, 4]). Representing a drain as an array of one-dimensional cells is more appropriate in finite volumes and finite differences. Here we present a finite volume method for well-driven porous media flow which uses a computational mesh tailored for finite elements. It replaces one-dimensional elements used to model drains in the original mesh with one-dimensional cells. Special discretization of the flux between the porous medium and the drain related to Peaceman model is proposed. Unlike the original Peaceman model, our discretization can be used for unstructured meshes, and for any sufficiently large mesh size.

PROBLEM FORMULATION

Groundwater flow equation is given by

$$S\frac{\partial h}{\partial t} = \nabla \cdot (K \nabla h) \tag{1}$$

where: S - specific storage, h - hydraulic head, q - flux density, K - hydraulic conductivity. We consider boundary conditions

$$h = g_D \qquad on \qquad \Gamma_D \tag{2}$$

$$(-K\nabla h)\mathrm{n} = g_N \qquad on \qquad \Gamma_N \tag{3}$$

where n is the outward unit normal to the domain boundary $\partial\Omega=\Gamma_D \cup \Gamma_N$, $\Gamma_D \cap \Gamma_N = \emptyset$.

Either the hydraulic head or the total flux per unit of time Q is specified in each well. Initial condition is

$$h|_{t=0} = h_0 \tag{4}$$

Colmated layer is formed along the drain wall due to the drain clogging [5]. This causes an additional hydraulic resistance:

$$q \cdot n_d = \Psi(h_r - h_w) \tag{5}$$

where: h_w - hydraulic head inside the well, h_r - hydraulic head just outside the colmated layer, n_d - unit normal to the drain wall pointing inside, $\Psi= K_c/d_c$ - transfer coefficient, K_c - unknown conductivity of the colmated layer, and d_c - unknown thickness of the colmated layer.

FINITE VOLUME DISCRETIZATION

Integrating (1) over polyhedral control volume T, using the divergence theorem and implicit Euler time integration gives

$$|T|S\frac{h^{n+1} - h^n}{\Delta t} = \sum_{f \in \partial T} \chi_{T,f} Q_f^{n+1}, \qquad Q_f = \int_f q \cdot n_f ds, \tag{6}$$

where Q_f - flux through face f , n_f - unit vector normal to face f , and $c_{T,f} = 1$ if n_f points outside of T, or −1 otherwise.

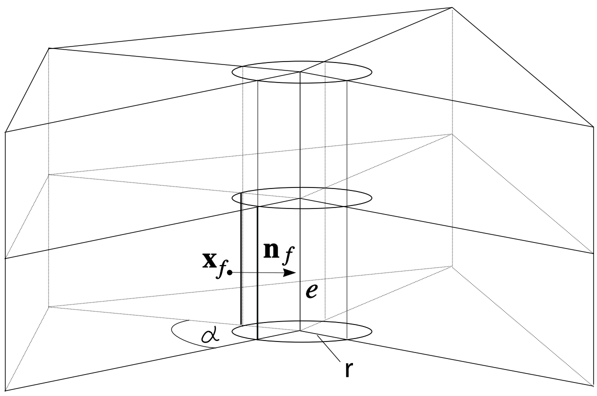

Figure 1: Drain discretization.

Flux through inner faces is approximated as

$$Q_f = -|\ f|||Kn||\frac{h_{out} - h_{in}}{||x_{out} - x_{in}||} \tag{7}$$

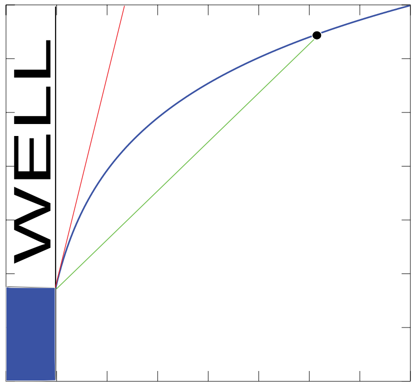

Figure 2: Well function.

Flux through a face where the conductivity is discontinuous is obtain combining onesided flux approximations

$$Q_f = -|f|\,\|K_{out}n\|\frac{h_{out}-h_f}{\|x_{out}-x_f\|}, \qquad Q_f = -|f|\,\|K_{in}n\|\frac{h_f-h_{in}}{\|x_f-x_{in}\|} \tag{8}$$

After eliminating h_f, one obtains

$$Q_f = -|f|\frac{\Psi_{in}\Psi_{out}}{\Psi_{in}+\Psi_{out}}(h_{out}-h_{in}) \tag{9}$$

$$\Psi_{in} = \frac{\|K_{in}n\|}{\|x_{in}-x_f\|}, \qquad \Psi_{out} = \frac{\|K_{out}n\|}{\|x_f-x_{out}\|} \tag{10}$$

At the interface between a 3d cell and a drain (Fig. 1), Ψ from (5) is used in (9) instead of Ψ_{out}.

EXAMPLE

Exact hydraulic head for the stationary case with a well of radius r in the center of a cylinder of radius R is:

$$h(\rho) = \frac{h_r \ln\frac{R}{\rho} + h_R \ln\frac{\rho}{r}}{\ln\frac{R}{r}} \tag{11}$$

where r is the distance from the well central axis. Total well flux is

$$Q = 2\pi KH\frac{h_R - h_r}{\ln\frac{R}{r}} \tag{12}$$

where H is the cylinder height. Axial well resistance has been neglected here.

We take R = 20m, h_R = 100m, h_r = 60m, h_w = 55m and Ψ is computed from (5) using Q from 12. The exact and the numerical fluxes are given in Table 1. If the well radius is much smaller than the mesh size, the flux is ten times smaller than it should be. The reason is that $h'(\rho)$ is very sharp at $\rho = r$, and it is not well approximated with a finite difference (Fig. 2).

Table 1: Exact and numerical fluxes for r = 0.01 and r = 0.5, with and without the proposed correction.

	Exact Q	Numerical Q	Q with correction
r = 0.5	0.06813	0.06634	0.06894
r = 0.01	0.03306	0.00322	0.03312

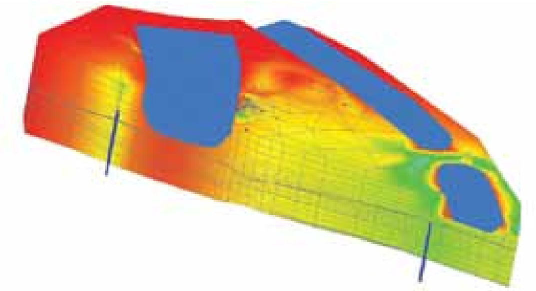

Figure 3: Realistic model of a portion of Belgrade Groundwater Source, with three water bodies and two wells visible.

CORRECTION

To allow the computation on coarse meshes, we replace R in (11) with the distance between x_{in} and the central well axis $\rho(x_{in})$, and use the derivative of this formula to obtain a replacement for the second formula in (8) for the case of a 3d-1d cell interface:

$$Q_f = -|f|\|K_{in}n\| \frac{h_r - h_{in}}{r \ln \frac{\rho(x_{in})}{r}}. \tag{13}$$

This is related to Peaceman model [7]. Results presented in the last column of Table 1 show that the total well flux computed with this correction is much more accurate.

CONCLUSION

The presented finite volume method for well-driven groundwater flow uses a computational grid tailored for a finite element method, in which well drains are represented by one-dimensional elements. In its interpretation of the grid, our method adds faces and cells that correspond to well drains with geometry that is not fully resolved in the original grid. Nodes are not added or moved.

We proposed a correction to the discretization of the flux between the 3d porous medium and a drain. Total well flux obtained with this correction is very accurate. This method was used for the computation of a realistic model shown in Fig. 3.

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Notes:

Full Paper

GROUNDWATER RECHARGE SOLUTION BY RAINWATER USING DRIED SHALLOW DUG WELLS IN WARD NO. 19, KATHMANDU, NEPAL

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Abstract: Groundwater is a major source of water contributing to water supplying system of Kathmandu City. Kathmandu is an urbanized valley filled with fluvio lacustrine Quaternary sediments. This area is situated in the core part of the ancient city. Groundwater extraction is very high in comparison to recharge in the area due to intense urbanization. The major reason for low infiltration of rainwater into the shallow aquifer of the area is due to the surface and sub-surface layers of black Kalimati clay. Sandy clay pockets exist in a perched form within the Black Kalimati clay horizon which is not exposed. However, during pit percolation test some of these sandy clay pockets are encountered at shallow depth i.e. in Shantaneshowr at the depth of 1.81m (PT4) and at North of Maruhiti at 1.82m (PT3). Hence, sub-surface groundwater recharge techniques should be the appropriate method to recharge the aquifer in this area. Dried dug wells or dead wells which are scattered rampantly in the study area, can be a viable medium to recharge groundwater because dug wells are connected to the shallow aquifer horizon. In the locations where sandy clay is encountered at the shallow depth percolation pits can be designed to recharge groundwater estimating the rainwater catchments of the area.
Keywords: Aquifer recharge, flow net, Kalimati clay, pit percolation, recharge well

INTRODUCTION

Groundwater has been a major source of water contributing to the water supply system in Kathmandu as in Ward no. 19 areas (Fig 1). Due to urbanization in the city, surface infiltration has been reduced considerably, and due to growing population the consumption of groundwater is ever rising. Hence, the water table has gone down remarkably. Over-extraction of groundwater has decreased groundwater level in shallow as well as in deep aquifers, reportedly ranging from 1m to as much as 4m since about 1984 A.D. (BGR, 1999). As so many people depend on these traditional water supply systems, it is necessary to preserve them. With no other sources, it has been necessary to turn to rainwater for recharge though not enough rainwater can be used to recharge aquifers.

LOCATION AND TOPOGRAPHY

Kathmandu is a mountain valley situated on the Lesser Himalaya of central Nepal, stretching 30 km towards East-West and 25 km in North-South holding area of about 750 sq. km. and lies between 27032'49" to 27049'11" North latitude and 85011'10" to 85031'10" East longitude surrounded by high rising mountains. The valley floor consists of recent fluvio-lacustrine deposits over the base rock of Phulchoki group rocks which falls in Kathmandu complex. The study area (Ward no: 19) lies in North-West part of the valley in Kathmandu district. The Bisnumati River lies in the West of the study area. The study area consist flat land near the Bisnumati River and the main habitation zone mounds towards East of the river.

METHODOLOGY

Water level data were acquired by measuring the water level of dug wells (n=15, Fig 2) from the ground surface. On the basis of the data, a groundwater contour map and flow net were prepared. Pit percolation tests were conducted at 4 stations (PT 1, PT 3, PT 4 and PT 5, Fig. 2). The geological information about the distribution of sediments and geological formations were obtained from the Engineering and Environmental Map of Kathmandu, DMG (1998).

GEOLOGICAL SETTING

Kathmandu is an oval-shaped intermountain valley. The geology of Kathmandu Valley can be divided into two parts, as basement rock and soft valley sediments. On the basis of a gravimetric survey, Moribayashi and Maruo (1980) tried to interpret the basement topography of Kathmandu Valley. According to them, the maximum depth of the basement is estimated to be little more than 650m from the present surface of the valley under Baneshowr. Geologically, the Kathmandu Basin lies on the rock of the Kathmandu complex (Stocklin and Bhattarai, 1977).

The geology of soft sediments of Kathmandu has recently been studied by Shrestha et al. (1998). According to Shrestha et al. (1998), the soft fluvio-lacustrine sediments of the Kathmandu Valley are divided into two series of sediments, namely Quaternary Unconsolidated Sediment and Plio-Pleistocene Slightly Consolidated Sediment. The Quaternary Unconsolidated Sediment which can be observed in the study area is comprised of:

a) Recent Alluvial Soil: It includes recent sediments of flood plains and lower alluvial terraces. It consists of clay and sand, and fine gravels can be observed near the Bisnumati River.
b) Residual Soil: It includes humic silty loam to sandy gravel whose thickness is 1-3 m in places and occurs on slopes. Can be observed in the southern part of the study area

The Plio-Pleistocene Slightly Consolidated Sediment which can be observed in the study area is:

Kalimati Formation: Among different types of Plio-Pleistocene sediments, only Kalimati clay can be observed in the study area. It consists of grey to dark silty clay and clayey silt, calcareous and phosphitic in nature. Organic clay schist boulder beds, pit layers and lignite are occasionally found. This formation has a very low groundwater potential (aquitard) and low permeability.

AQUIFER SETTING OF KATHMANDU VALLEY

Aquifers are geological formations which are permeable enough to transmit water through them to yield a sufficient quantity of water to the wells and springs. The groundwater system of the Kathmandu Valley is considered as a closed and isolated groundwater basin, with more or less interconnected smaller groundwater basins. Most of the sediments in the shallow part of the northern and northeastern area and deeper parts (>90 m.) of the central and southern provinces form good aquifer zones (BGR, 1998). In the central provinces where it is underlain by impermeable lacustrine clay, the water table occurs within these impermeable sediments of predominantly silts. The groundwater that occupies these sediments is classified as a perched aquifer (Metcalf and Eddy Inc, 1999). The occurrence, distribution, and movement of groundwater is governed by various factors such as the amount of precipitation over the catchment basin, rate of infiltration, topography, geology and the drainage network of the area. JICA, 1990 divided the deep part of the Kathmandu basin into three parts, as the Northern Groundwater District (NGWD), Central Groundwater District (CGWD) and Southern Groundwater District (SGWD) (Fig. 1). Sediments in the NGWD are composed of unconsolidated highly permeable materials of micaceous sand and gravel. The unconsolidated coarse sediments are as thick as 60m (JICA, 1990). Sediments in the CGWD consist of impermeable, very thick black Kalimati clay accompanied by some lignite and peat with a maximum depth of 200m. Unconsolidated coarse sediments of low permeability underlie this thick black clay (JICA, 1990). Sediments of SGWD are characterized by basal gravel covered by a thick impermeable clay formation. The aquifer is not well developed and is recognized along the Bagamati River between Chobhar and Pharping (JICA, 1990).

RAINWATER HARVESTING AND AQUIFER RECHARGE

Rainwater harvesting (RWH) is the collection of rainwater from where it falls for further use, especially during the dry season. RWH can be categorized under three headings as rooftop, road top and open space RWH. RWH which failed to direct storage is termed surplus water, which can be drained through the percolation zone to supplement open space rain water harvesting.

Table 1: Catchment coefficient for rainwater harvesting (Source: Pacey, Arnold and Cullis, Adrian 1989, Rainwater harvesting: The collection of rainfall and runoff in rural areas, Intermediate Technology Publications, London)

Type of catchments	Coefficient
Roof catchments	
Tiles	0.8-0.9
Corrugated metal sheets	0.7-0.9
Ground surface covering	
Concrete	0.6-0.8
Brick pavement	0.5-0.6
Untreated ground catchments	
Soil on slopes less than 10%	0.0-0.3
Rocky natural catchments	0.2-0.5
Green area	0.05-0.10

Rainwater harvesting is influenced by two factors: rainfall and catchment area characteristic. Rainfall is the most unpredictable variable, hence to determine potential rainwater supply for a given catchment reliable rainfall data are required. The number of annual rainy days also influences the need and design for RWH. If the dry period is too long, big storage tanks would be needed to store rainwater. Hence in such regions, it is more feasible to use rainwater to recharge the aquifers rather than for storage. Catchment area characteristics make a remarkable difference in quantity of rainwater which can be harvested, influenced by the runoff coefficient of the catchments. The runoff coefficient (Table 1) for any catchments is the ratio of the volume of the water that runs off the surface to the value of rainfall that falls on the surface. Rainwater harvesting (RWH) potential can be calculated from the following relation:

RWH Potential = Area of roof top or terrace × Height of rainfall × Runoff coefficient. (UN-HABITAT, 2005)

AQUIFER RECHARGE

According to structure, aquifers can be of three types: confined, unconfined (Fig 3) and perched. Unconfined and perched aquifers are close to the ground surface so water can be extracted easily and can be recharged easily. Confined aquifers are deep in nature, need deep tube wells to extract water from them, and they take a long period of time to get recharged. In this study we only deal with a shallow unconfined aquifer.

Techniques for artificial recharge of aquifers: Aquifers can get recharged in two ways: naturally and artificially. In natural recharge, rainwater and surface water get percolated into the aquifer by itself through an uncovered soil surface or fissures in the rock mass.

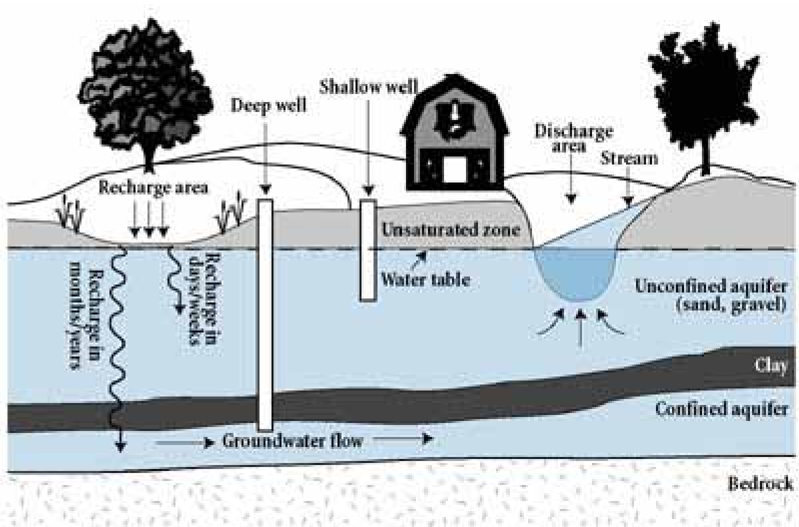

Figure 3: Confined and unconfined aquifer (Figure source: web-site)

Artificial recharge of groundwater can be defined as open space rainwater harvesting. In artificial recharge, water is percolated using different tricks and techniques, generally to recharge the shallow aquifer. The techniques of artificial recharge can be broadly categorized into two groups: surface spreading methods and sub-surface methods:

Surface spreading methods: Surface spreading methods are suitable where a large area of a basin is available and aquifers are unconfined. The rate of infiltration depends on the nature of the top soil; if the surface soil is sandy the infiltration rate will be higher than that of silty soil. The presence of a solid suspension in water used for recharge clogs the soil pores leading to reduction in infiltration rate. Types of spreading methods are:

- Flooding: This method is suitable for flat topography. The water is spread as a thin sheet. It requires a system of distribution channels for the supply of water for flooding.
- Basin and percolation tank: This is the most common method for artificial recharge. In this method, water is impounded in a series of basins or a percolation tank.
- Stream augmentation: Seepage from natural streams or rivers is one of the most important sources of recharge of the groundwater reservoir which is seasonal. When the total water

supply available in a stream/river exceeds the rate of infiltration, the excess is lost as runoff. This runoff can be arrested through check bunds or by widening the stream beds, thus a larger area is available to spread the river water increasing the infiltration.

- Ditch and furrow system: In areas with irregular topography ditches or furrows provide maximum water contact area for recharge. This technique consists of a system of shallow flat bottomed and closely spaced ditches/furrows which are used to carry water from the source like stream/canals and provide more percolation opportunity.

Figure 2: Location of studied dug wells and percolation pit

Sub-surface methods: In these methods the structure lies below the surface and recharges groundwater directly using recharge wells. Types of sub-surface methods are:

- Recharge wells: Recharge wells can be of two types: an injection well where water is injected, and a recharge well where water flows under gravity. A dug well can be used as a recharge well for the shallow aquifer.
- Pits and shafts: In areas where an impervious layer is encountered at a shallow depth, pits and shafts are suitable structures for artificial recharge. These structures are cost-effective to recharge the aquifer directly. Silt-free source water can be put into the recharge shaft/pit directly through pipes. In areas where the source water has silt, the shaft/pit should be filled with boulder at the bottom and coarse sand to the top to have inverted filter or the source water should be passed through a separate filter chamber before it enters the shaft/pit.
- Soak away or percolation pits: A soak away is a bored hole up to 30 cm diameter drilled in the ground to a depth of 3 to 10 m. The soak way can be drilled with an auger unless hard rock is

found at a shallow depth. The borehole can be left unlined if a stable soil formation like clay is present. In such cases, the soak away can be filled up with a filter media like brickbat or coarse sand. In an unstable formation like sand, it is suitable to line the soak way with a PVC pipe to prevent the collapse of vertical sides. The pipe may be slotted to promote percolation from sides.

Table 2: Percolation rate at percolation pit (mode value is considered for more accuracy)

S.N	Pit no.	Location	Co-ordinates		Percolation rate (cm/min) (mode value)
			Latitude	Longitude	
1	PT1	Sahid Nirgun Marga	27º42’23.2” N	85º18’19.2” E	0.5
2	PT3	North of Maru Hiti	27º42’17” N	85º18’19.3” E	1
3	PT4	Shantaneshowr	27º42’16.9” N	85º18’20.2” E	1.25
4	PT5	Angan Chen Chowk	27º42’16.1” N	85º18’21.8” E	0.25

Table 3: Mean groundwater level (masl) of 15 wells (from 23 July 2010 to 27 July 2010)

S.N.	Well no.	Location		Groundwater level (masl)
		Latitude	Longitude	
1	DW1	27º42’15.8”N	085º18’20.6”E	1297.3
2	DW2	27º42’15.4”N	085º18’21.2”E	1299.3
3	DW3	27º42’13.8”N	085º18’18.4”E	1296.4
4	DW4	27º42’16.7”N	085º18’20.9”E	1296.2
5	DW5	27º42’20”N	085º18’20.7”E	1298.5
6	DW6	27º42’20.7”N	085º18’18.5”E	1296.2
7	DW7	27º42’21.7” N	085º18’19.7”	1295.4
8	DW8	27º42’22.9” N	085º18’20.6” E	1297.8
9	DW9	27º42’24.3” N	085º18’18” E	1296.7
10	DW10	27º42’25.2” N	085º18’17.9” E	1297.5
11	DW11	27º42’23.9” N	085º18’13.4” E	1298.4
13	DW13	27º42’25.8” N	085º18’23.6” E	1298.7
14	DW14	27º42’24.1” N	085º18’26.6” E	1298.5
15	DW15	27º42’18” N	085º18’20.1” E	1295.9

HYDROGEOLOGY

Pit percolation: The pit percolation rate measured in the study area is presented in Table 2. During the test, sand layers were encountered at a shallow depth at Shantaneshowr, at a depth of 1.81m (PT4), and at North of Maruhiti at 1.82m (PT3). The percolation rate is also high at these locations (Table 2). Hence these locations are suitable to recharge the aquifer applying the recharge pit and recharge well method. Lots of dry wells with a promising depth are available in the sites; hence these wells can be a suitable method to recharge the aquifer.

Flow net: A groundwater contour Amsl map was drawn on the basis of groundwater levels read at 15 different dug wells from 23 July 2010 to 27 July 2010 (Table 3). A flow net (Fig. 4) was drawn on the groundwater contour Amsl map to detect the groundwater flow direction and groundwater extraction zone and recharge zone (Fig. 4). The general groundwater flow direction is almost east to west in the area, the trend changes only in northern part (i.e. Mu Gully and Sunta Gully), where groundwater flow direction is almost from north to south. Kothanani Gully and Maru Bahi are high groundwater extraction zones. The only recharge zone is near Sunta Gully.

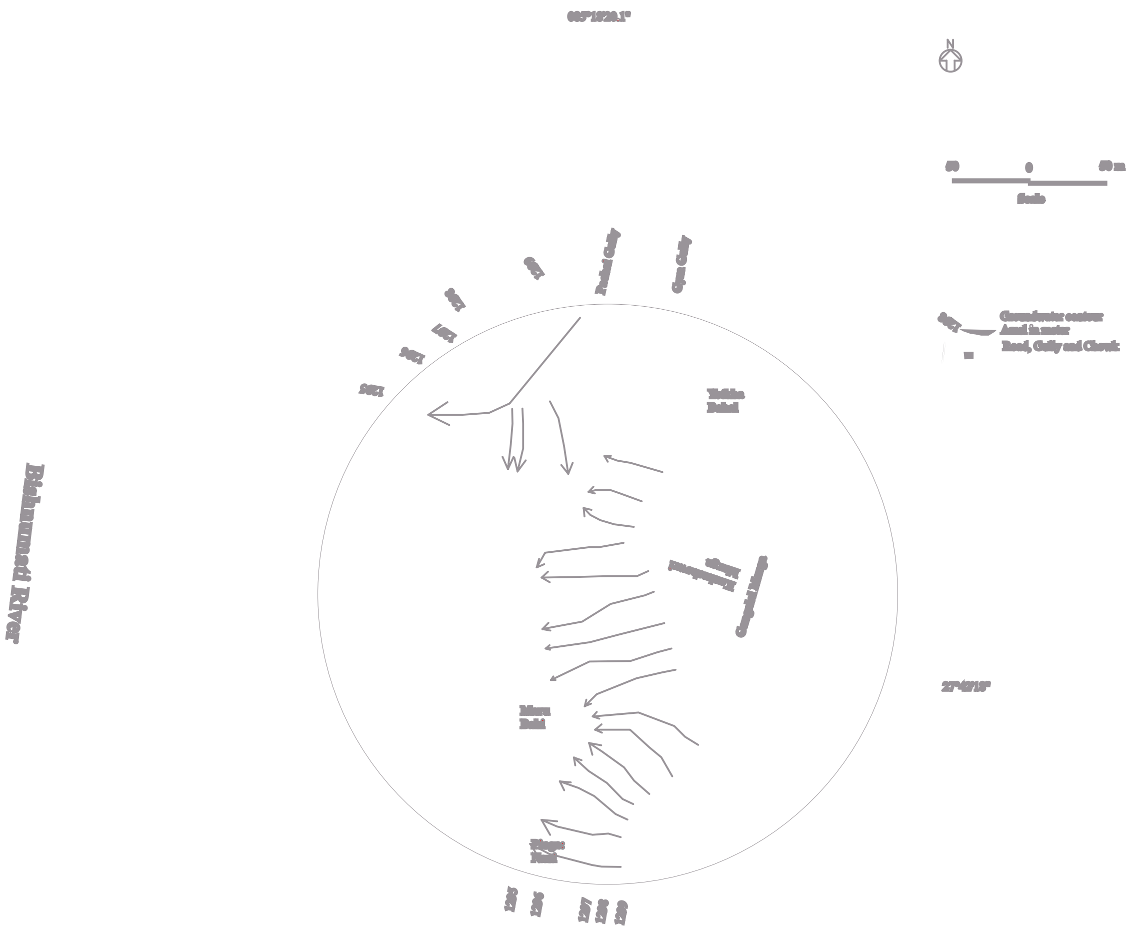

Figure 4: Groundwater contour Amsl and flow net

DISCUSSION AND CONCLUSION

Ward no. 19 is a densely populated urban zone in the core of Kathmandu, with high numbers of dug wells scattered profusely. Denizens of the locality rely upon groundwater for their daily purposes. Recently, due to high extraction and minimum recharge, the water table has been declining rapidly. So, during the dry season most of the dug wells could not provide water. Many dug wells have already dried perennially so they may be termed as dead wells.

The study area lies in the central groundwater district and comprises the black clay of the Kalimati formation with a low percolation rate, so during rainfall rainwater gets lost to runoff. So the rainwater should be captured during rainfall for recharge purposes. Rampantly scattered dead wells can be reliable and the most economic medium to capture and recharge groundwater in the area. Percolation pit methods can be another dependable method.

The groundwater flow direction of the area is nearly from east to west. The trend is different only at the northern part where the flow direction is nearly from north to south. The flow net does not show any recharge zone except at Sunta Gully, while high extraction zone are Maru, Dhoka Tol and the western part of Yetkha. During pit-percolation tests, sand layers were encountered at a very shallow depth in Shantaneshowr, at a depth of 1.81m (PT4), and at North of Maruhiti at 1.82m (PT3), and the percolation rate is also high in that area so the area can be a potential groundwater recharge zone.

Acknowledgements: I would like to acknowledge local residents of Ward no. 19 Kathmandu for their help and I would like to thanks Mr. Binod Acharya for his help during field visit and data compilation.

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THEME 2:

THE IMPORTANCE OF THE AEROBIC STATE OF GROUNDWATER, AND THE PROCESSES WHICH ARE DRIVEN BY THE LEVEL OF AEROBICITY

Extended Abstract
Invited Paper

OCCURRENCE AND FATE OF NEW PESTICIDE METABOLITES IN GROUNDWATERS IN GERMANY

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Abstract: The occurrence of pesticides and emerging pesticide metabolites in aquatic systems are of major concern in various countries, particularly in the US and Germany, respectively. The findings of desphenyl-chloridazon (DPC) and N,N-dimethylsulfamide (DMS) without the parent compounds chloridazon and tolylfluanid, respectively, in groundwater resources arises awareness for water utilities, authorities and the pesticide industry as data evaluation and assessment was unclear so far. In the meantime the Federal Environmental Agency of Germany (UBA) published a statement that the newly emerging pesticide metabolites are non-relevant substances due to minor toxic properties and must not be restricted under the EU-limit of 0.1 µg/L for pesticide compounds. At present more than 40 non-relevant pesticide metabolites are known in Germany which will be monitored in a joint research project of water suppliers and the pesticide industry.

INTRODUCTION

Pesticides are used world-wide in increasing quantities to protect plants or plant products. In many countries residues of pesticides in food and water are restricted due to health risks. For groundwater and drinking water a very low standard for pesticides and their relevant metabolites of 0.1 µg/L was set already two decades ago in the legislation of the European Union as well as in many national directives. Due to the availability of very sensitive analytical methods a lot of pesticide compounds have been found in wastewater, surface water, groundwater and drinking water, respectively. In recent years metabolites and degradates formed after application became of major concern as their concentrations found in the environment were often higher than those of the parent compounds. This paper gives an overview about the occurrence and fate of new pesticide metabolites which were not known and could not be detected in aquatic systems until now due to missing sensitive analytical methods.

METHODS AND METHOLOGY

Selection of metabolites

In 2007 and 2008, respectively, the Federal Office of Consumer Protection and Food Safety (BVL) in Germany published a list of 4 active compounds and 7 metabolites as well as a list of 14 active compounds and 33 metabolites, which proved during out-door tests that they might enter groundwater after application. At the same time, degradation products of the fungicide tolylfluanid and the herbicide chloridazon have been found in ground¬waters in Germany in concentrations even above 1 µg/L. In the present study, the occurrence of the metabolites of chloridazon, tolylfluanid, chlorothalonil, dimethachlor, metaza¬chlor and S-metolachlor in German groundwaters was investigated.

Analysis of metabolites

Analysis of the pesticide metabolites from water samples was done by solid-phase extraction of the analytes and subsequent determination by liquid-chromatography and tandem mass spectrometry coupled via an electrospray interface (HPLC-ESI-MS-MS). Due to the polar nature of the analytes sample pre-concentration was done with a volume of only 10 mL. For solid-phase extraction a polymeric material (100 mg of bondelut PPL from Varian) and an automated extraction system (Gilson, GX274 Aspec) were used. Elution was done with 6 mL of methanol. The solvent was evaporated to dryness and the dry residue was reconstituted with 100 µL methanol and 400 µL HPLC water. Then 50 µL were injected into the HPLC system. HPLC-ESI-MS-MS measurements were performed on a HPLC system 1200 SL from Agilent Technologies connected to an API 4000 Q-trap triple quadrupole mass spectrometer from Applied Biosystems/MDS Sciex Instruments using electrospray ionisation in positive and negative mode. The separation was carried out at 80°C using a Luna C18 5 µ column from Phenomenex. A methanol/HPLC water gradient with 0.1% formic acid was used as eluent. Applying this method to groundwater samples, limits of detection down to the low ng/L range could be achieved for all pesticide metabolites under investigation.

RESULTS AND DISCUSSION

Within the past 20 years the desethyl-metabolites of atrazine, simazine and terbutylazine have often been monitored together with the parent compounds in surface water, groundwater and drinking water, respectively. Particularly desethylatrazine was found more often in higher concentrations in groundwater and drinking water than the active pesticide atrazine. Although atrazine was banned since 1991, atrazine and desethylatrazine are regularly found in about 3 to 5% of groundwater samples monitored in Germany. But there is a clear tendency to lower concentrations and findings since the 20 years period. Generally the desethyl-metabolites of atrazine, simazine and terbutylazine are assessed by UBA as relevant pesticide metabolites and must not exceed the EU-limit for groundwater and drinking water in Germany.

Additionally two other pesticide metabolites 2,6-dichlorobenzamide (parent compound diclobenil) and AMPA (aminomethylphosphonic acid) (parent compound glyphosate) are monitored in water resources. In some cases 2,6-dichlorobenzamide was found in elevated concentrations (> 1µg/L) in groundwater samples, where diclobenil was applied in fruits and wine for many years. AMPA occurred primarily in surface water and not in groundwater as it regularly enters the aquatic environment via waste water effluents.

In November 2006 N,N-dimethylsulfamide (DMS) was identified as until that time unknown metabolite of the fungicide tolylfluanid.

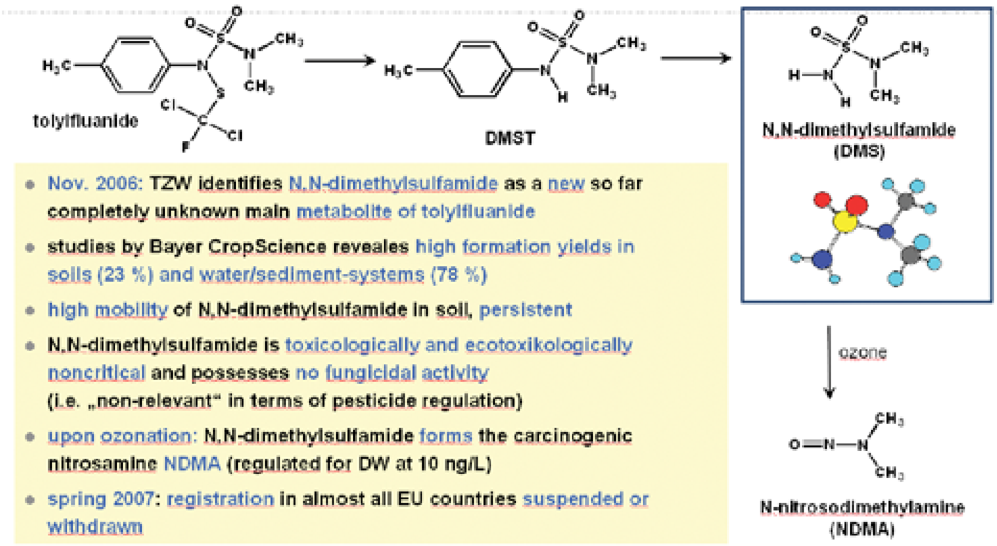

Figure 1: Fate of tolyfluanid

DMS was found to be highly mobile and persistent in aquatic systems, but not toxic to humans and aquatic microorganisms and was therefore assessed as a non-relevant pesticide metabolite. Upon ozonation (reaction of ozone with DMS in water treatment) a well-known N- nitrosamine (NDMA) can be formed for which a drinking water limit of 10 ng/L (0.01 µg/L) was set by German health agencies (Figure1).

Monitoring activities clearly proved the widespread occurrence as well as elevated concentrations of DMS in surface water, groundwater and drinking water (Figure 2).

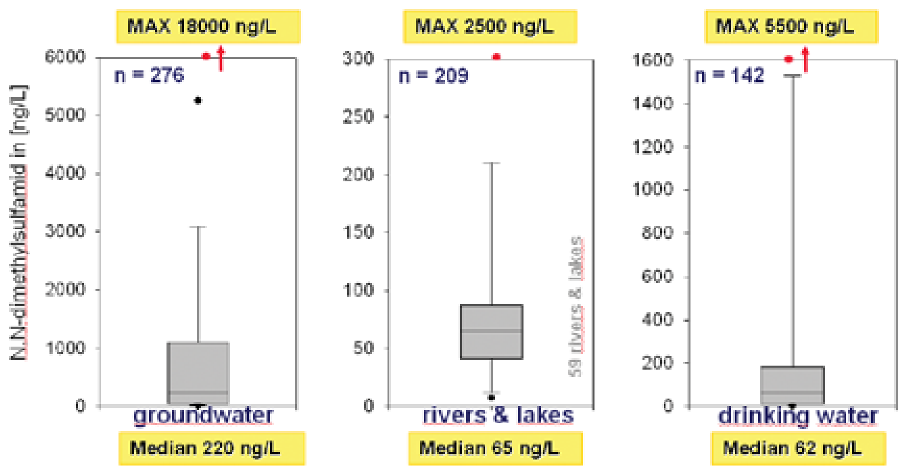

Figure 2: Occurrence of N,N-dimethylsulfamide (DMS) in the aquatic environment.

High DMS-concentrations (> 1µg/L) were often found in fruit and wine growing areas of the country Baden-Württemberg in Germany, where the fungicide tolylfluanid was used for several decades (Figure 3).

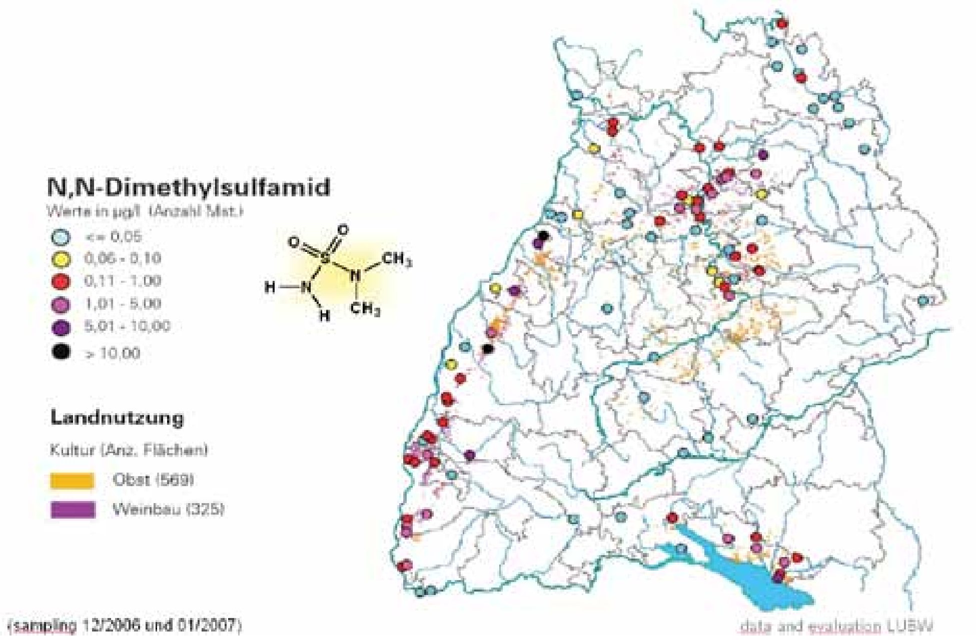

Figure 3: Distribution of N,N-dimethylsulfamide (DMS)-concentrations in fruit in wine growing areas in Baden-Württemberg, Germany

A second example for the occurrence of pesticide metabolites in groundwater resources was the fate of chloridazone (Figure 4).

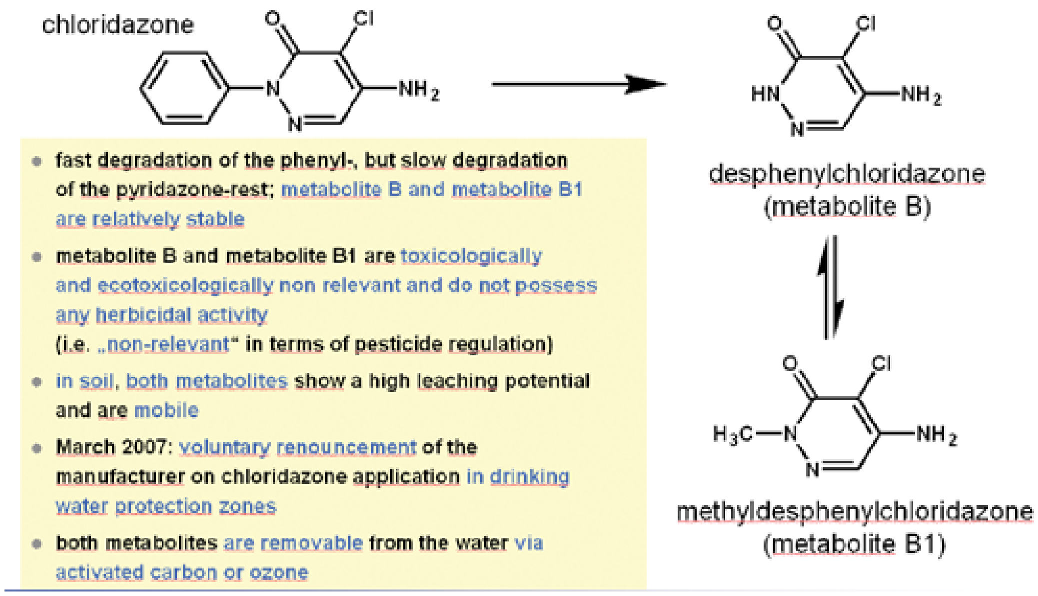

Figure 4: Fate of chloridazon

The herbizide chloridazon is readily degraded to the persistent metabolites B (desphenyl-chloridazon) and B1 (methyl-desphenyl-chloridazon). These metabolites are non-relevant compounds in terms of pesticide regulation. Although chloridazon was applied primarily in sugar beets for several decades, the active compound was not found in the aquatic environment due to a fast degradation. But the concentrations of the very mobile and persistent metabolites B and B1 are relatively high in the northern parts of Baden-Württemberg. The distribution of the concentrations measured is presented in Figure 5.

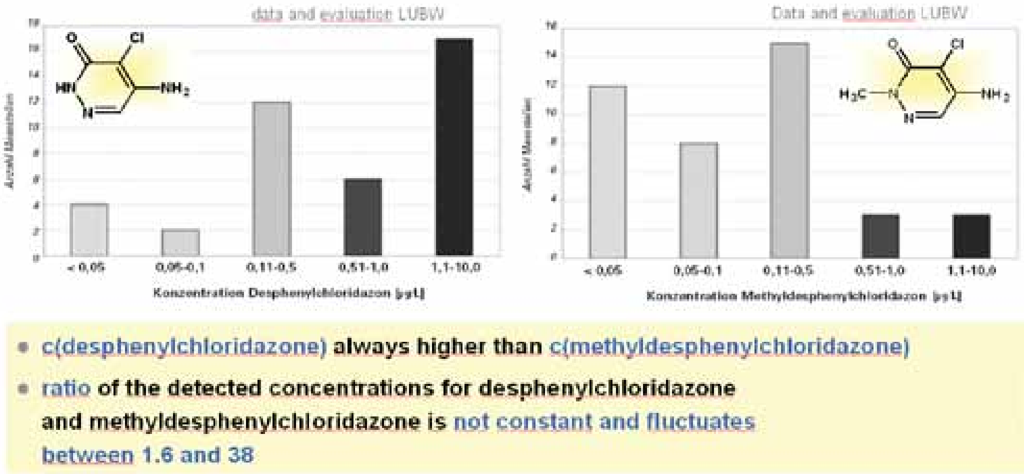

Figure 5: Distribution of concentrations for the metabolites B and B1 in Baden-Württemberg, Germany

Beside the findings of DMS and the metabolites B and B1, non-relevant metabolites of active compounds like metazachlor, S-metolachlor etc. could also be found (Table 1).

Table 1: Frequency of pesticide metabolite occurrence in German groundwaters

	Concentration level		
Pesticide/Metabolite	**> 0.01 µg/L**	**> 0.1 µg/L**	**> 1 µg/L**
Desphenylchloridazon	> 90%	86%	46%
Methyldesphenylchloridazon	77%	68%	9%
N,N-Dimethylsulfamide	88%	43%	15%
Metolachlor	2%	-	-
Metolachlor-OA	6%	1%	-
Metolachlor-ESA	24%	11%	1%
Metazachlor-OA	23%	7%	-
Metazachlor-ESA	29%	12%	1%

In most cases findings of pesticide metabolites could be clearly related to previous agricultural applications of pesticides. N,N-dimethylsulfamide (DMS) and desphenyl-chloridazon (DPC), were found in almost 90% of all groundwater samples under investigation with concentrations up to several µg/L. Metabolites of metazachlor and S-metolachlor were also frequently found whereas dimethachlor metabolites were only rarely found and metabolites of chlorothalonil were not detected at all. As a rule, sulfonic acid metabolites (-ESA) were detected more frequently and in higher concentrations than the respective carbonic acids (-OA), indicating a preferential biodegradation pathway.

CONCLUSIONS

The occurrence, evaluation and assessment of pesticide metabolites are an on-going issue for water suppliers, authorities and the pesticide industry in Germany as well as in Europe. As emerging pesticide metabolites are regarded as non-relevant compounds, immediate actions have not to be undertaken so far. But in general, pesticide metabolites are more difficult to remove in water treatment than the active compounds. Particularly the removal rate of N,N-dimethylsulfamide (DMS) is extremely low. On the point of view of drinking water supply health-based risks of emerging and non-relevant pesticide metabolites were not deserved at present but precautionary measures should be carried out to reduce and to minimize the entries of pesticide metabolites into the aquatic environment in order to protect the water resources for future generations.

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Extended Abstract

IMPACT OF WELL OPERATION ON IRON RELATED CLOGGING IN UNCONSOLIDATED QUATERNARY AQUIFERS IN BERLIN, GERMANY

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Abstract: The capacity of drinking water wells, i.e. the yield for a given drawdown, is often decreasing after a certain time of operation. This effect is called well ageing and is due to different processes related to the geology and hydrochemistry at any given well site, and to the construction and operation of these wells. The Hydrogeology Workgroup and partners investigate wells in Berlin and France in terms of their ageing behaviour with the aim to determine suitable measures helping to slow down well ageing processes and optimise strategies for well operation and maintenance.A precondition for well clogging by iron incrustations is the mixing of different groundwaters with incompatible chemical properties in the well and/or within the aquifer, and is induced by combined hydrochemical and microbiological processes.The assessment of (I) the formation of reduced/oxidized groundwater layering in the aquifer, (II) the localization of mixing zones, and (III) mixing ratios within the well was done by field and laboratory studies.The research reveals that redox conditions in the well and the surrounding aquifer are subject to short to long-termed variations. These variations are caused by operation intervals of the wells and by seasonal effects. The results permit a characterization of oxygen enrichment and transport dependent on well operation, location and design and further on an input-output balancing and modeling of incrustation rates.
Keywords: bank filtrate, iron incrustation, redox zonation, well ageing.

IMPACT OF WELL OPERATION ON IRON-RELATED CLOGGING

Approximately 40% of all water abstraction wells work inefficiently in terms of well performance or water quality according to an international survey (HOWSAM et al., 1995).

The main reason for inefficient well performance is the so-called well ageing (or clogging), i.e. the decrease in performance due to biological, chemical and/or physical processes in and around the well. This causes high costs, both for (re-)construction of new wells (capital investment) and well operation (energy consumption, maintenance needs), and a great potential for improvement.

For an assumed majority of 80 % of drinking water wells in Germany, ageing is caused by iron (and manganese) incrustations. These incrustations are mostly related to the exploitation of unconsolidated aquifers with certain iron containing geological and reducing hydrochemical properties.

The described research is embedded in the project “WELLMA”. The project is initiated and financed by the Berliner Wasserbetriebe (BWB) and Veolia Eau, and coordinated at the Berlin Centre of Competence for Water (KWB). It aims at the optimization of operation, maintenance and water quality of drinking water wells.

Well clogging by iron incrustations is induced by combined hydrochemical and microbiological processes. A precondition for these processes is the mixing of different groundwaters with incompatible chemical properties in the well and/or within the aquifer.

Due to the abstraction of both reduced iron-containing and oxidized groundwater from unconsolidated aquifers, drinking water wells of the City of Berlin (Germany) tend to extensive well ageing. The research includes investigations on groundwater, bank filtrate and artificially recharged groundwater abstracting well sites to evaluate analogies.

First analyses of Berlin wells identify wells in hydraulic unconfined settings to be more affected by ochre formation compared to those in confined settings.

A distinct knowledge of mixing processes is the basic factor to reduce well clogging by adapted operation, maintenance and design strategies. Determination of mixing conditions includes:

- formation of reduced/oxidized groundwater layering in the aquifer,
- localization of mixing zones, and
- mixing ratios within the well.

Short to long termed variations

Raw water of nearly all of the 25 investigated drinking water wells is in hydrochemical disequilibrium and is expressed by an absence of oxygen, but a coexistence of nitrate and iron concentrations. Therefore, nitrate potentially acts as an indicator where oxygen is absent.

Additionally, the hydrochemical monitoring of a well switching event at these wells, showed that abstracted well water reaches static conditions after nearly two hours of operation. But on closer examination, distinct mid-term variations after one week of constant operation were observed. Comparison of quarterly well samplings reveals most extensive differences in the hydrochemistry of the well water and represents seasonal impacts on the redox zonation.

Redox zonation and oxygen input

KOHFAHL et al. (2009) identified soil air and its entrapment due to oscillations of groundwater surface as the main source of oxygen enrichment in groundwater. Alternation of well operation states amplifies this process. This is shown by close meshed in-situ monitoring of oxygen in the proximate abstracting zone of three different well sites in Berlin (for example see Fig. 1).

The initial redox zonation in the studied aquifers varies between the different sites according to their hydrogeological settings. As shown in Fig. 2, the transition zone from oxic to anoxic can reach several meters in the aquifer. Hence, switching on the well causes a shifting of oxygen into the groundwater fluctuation zone. With increasing time of operation oxygen migrates into deeper zones of the aquifer.

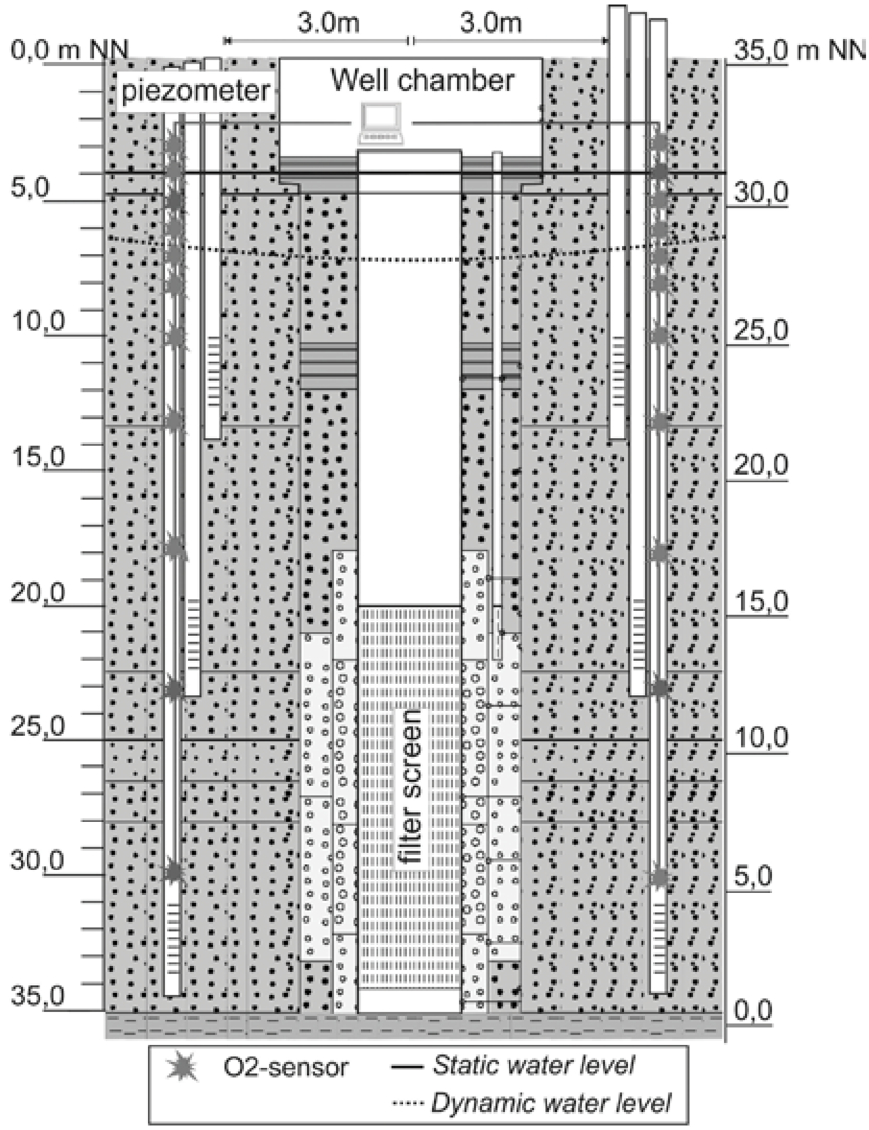

Figure 1: Scheme of a well site investigated in this study. Oxygen concentrations were measured with in situ oxygen sensors in a bidirectional monitoring network. Sensors are closer meshed in the groundwater fluctuation zone. Collateral to oxygen sensors, multi-level piezometers are installed for a hydrochemical characterization of the aquifer and a localization of redox zones. For the identification of mixing zones near to and in the production well, depth-oriented samplings in the well itself were performed.

Furthermore, the analysis of different operational schemes reveals a shifting of this oxic groundwater zone in the aquifer caused by intermittent operation of neighboured wells. This results in various changes in the flow gradient and migration of an oxic(suboxic)-anoxic front in the aquifer. Results indicate that this process is more obvious at bank filtrate sites with less reducing conditions compared to groundwater abstracting sites. At groundwater-dominated well sites, oxygen measurements show a decrease in oxygen concentration in the well near the aquifer after days of constant operation. Oxygen is retarding faster and the transition zone from oxic to anoxic is less developed.

The results permit a characterisation of oxygen enrichment and transport dependent on well operation, location and design.

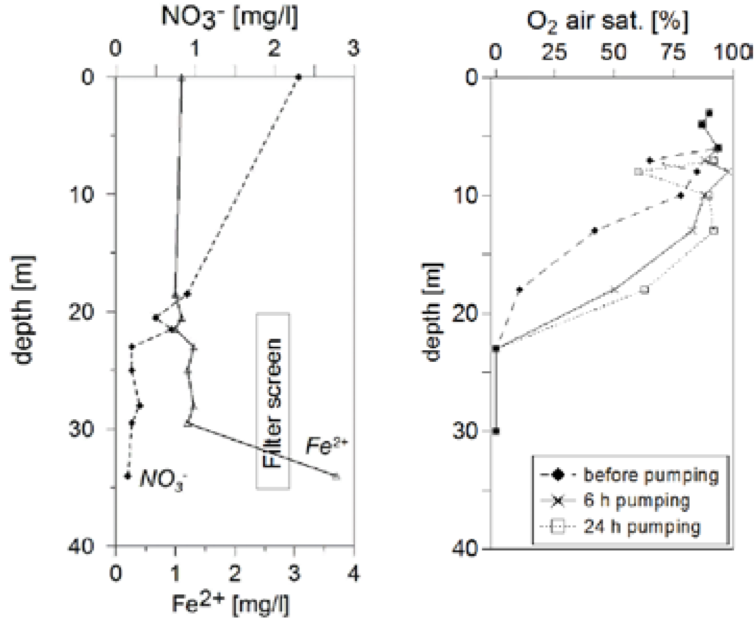

Figure 2: Depth profiles of NO_3^-, Fe^{2+} (left) and O_2 (right). O_2 saturations originate from a section in 3 meter distance to the above described well (see Fig. 1) during a 24 hour pump test. 100% O_2 air saturation equates to atmospheric concentration. NO_3^- and Fe^{2+} are sampled depth-oriented in the well, as shown in Fig. 1. Samples were taken during operation at different depths below the pump and the well head.

Mixing zones and ratios

On the basis of combined depth-orientated hydrochemical raw water samplings with influx measurements (flowmeter), mixing zones were located and mixing ratios calculated. This admits with regard to hydrochemical aquifer data an input-output balancing and further on a modeling of incrustation rates.

Figure 2 shows a representative extract of the existing results. The distinct redox zonation in the aquifer displayed by the oxygen saturations is reflected in the well. Oxygen is generally absent in all studied wells. The appearance of elevated NO_3^--concentrations in the upper filter section is probably a residue of the oxic/suboxic zone in the aquifer. In contrast, high Fe^{2+}-concentrations are limited to the lower filter section.

Adapted operation of well fields

On the basis of these monitoring strategies, processes responsible for iron-related clogging can be identified. Results provide support and recommendations for operation and design of drinking water wells to reduce well ageing.

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Extended Abstract

EFFECTS OF BOUNDARY CONDITIONS ON THE CLEANING EFFICIENCY OF RIVERBANK FILTRATION AND ARTIFICIAL GROUNDWATER RECHARGE SYSTEMS REGARDING BULK PARAMETERS AND TRACE POLLUTANTS

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Abstract: Drinking water is often produced from surface water by river bank filtration (RBF) or artificial groundwater recharge (AGR). In this study, effects of redox conditions, temperature and discharge on the cleaning efficiency of RBF and AGR were evaluated. Besides bulk parameters like DOC, organic trace pollutants like iodinated X-ray contrast media, naphthalenesulfonates, complexing agents and pharmaceuticals were analysed. At virtually all sites investigated, TOC, DOC, AOX, UVA, nitrate and turbidity turned out to be reduced significantly. Several substances were generally easily removable during river bank filtration, regardless of the site, season, discharge or redox regime. In contrast, for more refractory substances the cleaning efficiency was affected by temperature, discharge, retention time and redox conditions.

INTRODUCTION

Drinking water is often produced from surface water by river bank filtration (RBF) or artificial groundwater recharge (AGR), as examplarily presented in Figure 1. The underground passage is acting as a physical filter (depending on the grain size and distribution of the substrate), removing e.g. bacteria and algae present in the surface water. Moreover, the substrate provides surfaces for physico-chemical sorption processes and a habitat for microorganisms. Sorption and biological degradation contribute to the clean-up of the infiltrated water and many organic trace pollutants are partly or completely removed. Dilution of infiltrate with natural groundwater can either reduce pollutant concentrations from surface water (when groundwater is less contaminated) or even increase them, e.g. when nitrate is released from nearby farmland.

Depending on many factors like the availability of oxygen and nutrients (organic carbon, nitrogen species, phosphate), retention time, temperature and mineral composition and chemistry of the substrate and the water infiltrating, site specific redox milieus develop. Though at many sites certain redox conditions prevail during most of the year, seasonal changes are common. For example, aerobic and anaerobic conditions may alternate during conditions of low water and flood, causing dissolution or precipitation of e.g. manganese and iron species and oxides. Especially for AGR sites, discontinuous flooding can cause abrupt changes in the chemistry and redox milieu of a site compared to RBF sites. Moreover, even at sites characterised as generally aerobic, anaerobic redox markers like methane can be detected, indicating the co-existence of different processes (Alewell et al., 2008).

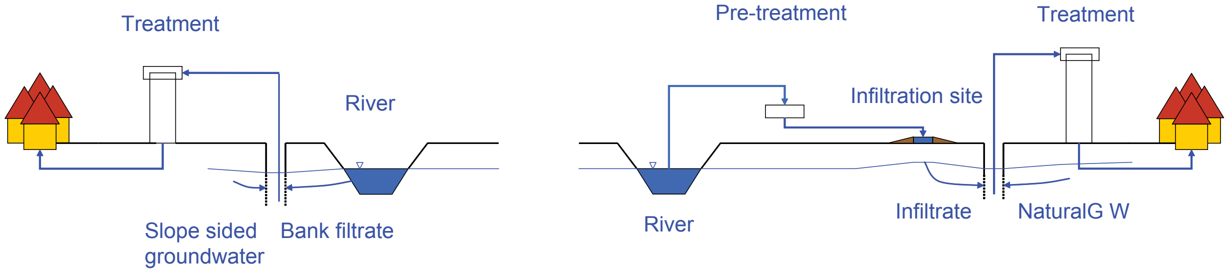

Figure 1: Production of drinking water from river bank filtration (RBF, left) and artificial groundwater recharge (AGR, right).

Surface water bodies are rather often polluted by accidental spills during the transport and storage of chemicals or hazardous substances by ship, railroad or pipelines. Even more spectacular hazards become aware to the public when chemical plants or refineries fail and chemicals or hazardous substances are released into the environment or directly into surface or groundwater. Severe examples comprise the recent red sludge accident at Kolontár (2010), the average of a tankship transporting sulfuric acid (near Loreley, 2010) or the release of pesticides during the extinction of a fire at a chemical plant in Schweizerhalle (1986). Besides accidental spills, daily pollution of streams by waste water treatment plant effluent or untreated waste water (e.g. Götz et al., 2010), or the application of agrochemicals and pesticides, occurs. The spectrum of trace pollutants detected in surface waters is thus very large.

For a safe operation of treatment facilities, operators are interested in the cleaning efficiency of both AGR and RBF systems. Therefore, parameters affecting cleaning efficiency and thus water quality like changes in redox milieu, temperature, river discharge or concentration level were evaluated in this study. Of special interest was, besides bulk parameters like DOC, the behavior of organic trace pollutants like iodinated X-ray contrast media (Figure 2), naphthalenesulfonates, complexing agents and pharmaceuticals. The aim was to identify factors reducing the removal of trace pollutants and to recognize substances being refractory under certain conditions.

SITE DESCRIPTION

Nine RBF and AGR sites in the US, Germany and Switzerland, with different redox conditions, ranging from aerobic to strictly anaerobic, retention time (1 to 150 days) and trace pollutant levels, were monitored. Sites investigated were situated at the rivers Rhine, Elbe, Ruhr, Missouri, Platte, and Great Miami. For detailed site descriptions see Storck et al. (2010) and Rüetschi (2004).

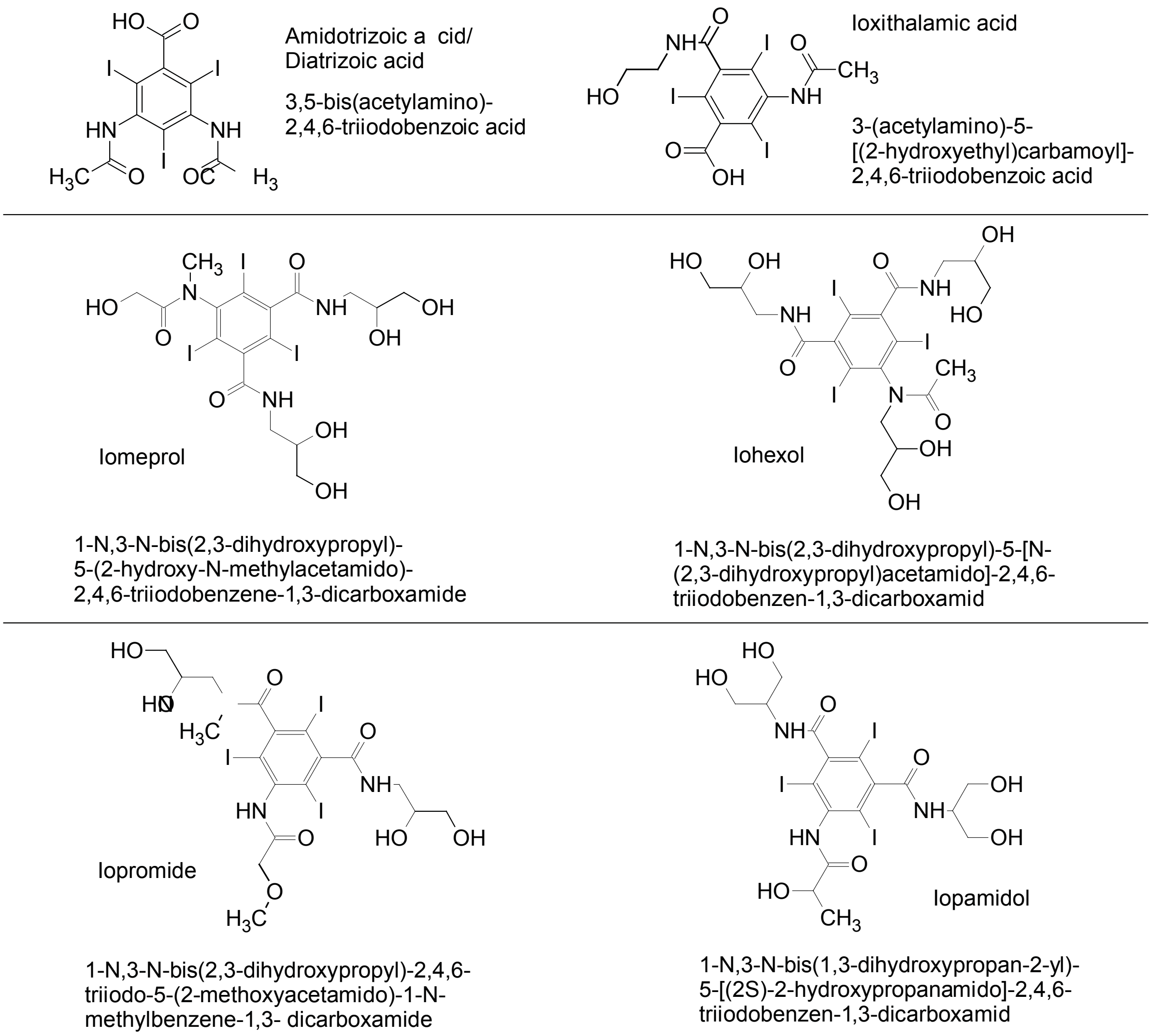

Figure 2: Trivial and chemical names and structures of some iodinated x-ray contrast media.

MATERIAL AND METHODS

Surface water and water from monitoring wells was sampled at regular intervals depending on the approximate retention time of the sites. Samples were analysed for bulk parameters like DOC, organic trace pollutants like iodinated X-ray contrast media, naphthalenesulfonates, complexing agents and pharmaceuticals. A detailed description of analytical methods applied at the RBF and of most methods applied at the AGR sites is given in Storck et al. (2010). Removal efficiency for each compound was calculated by comparing the output concentration in the monitoring well with the concentration in surface water.

RESULTS AND DISCUSSION

At virtually all sites investigated, TOC, DOC, AOX, UVA, nitrate and turbidity were reduced significantly. As an example, DOC-removal from an AGR site in Switzerland is presented (Figure 3). Though DOC concentration in the Rhine water used for infiltration often exceeded 1.5 mg/L, the concentration in the wells ranged mostly between 0.4 and 0.6 mg/L, resulting in a mean removal of 72 %. The contribution of dilution with natural groundwater to overall DOC removal was mostly negligible during running infiltration (Storck and Alewell, 2009). Long-term volumes of infiltrated and abstracted water are balanced and mean concentrations of persistent compounds like EDTA, carbamazepine, and sulfamethoxazole are similar in the Rhine and in the wells (Figure 4), underlining the small quota of dilution.

Concentration peaks of DOC in the Rhine were buffered. However, a slight tendency towards elevated DOC in winter/early spring in abstracted water was suspected. At most other sites, no significant relation of DOC removal with season was observed, but increased retention time was related to increased DOC removal within a site. Moreover, the main removal of DOC was observed closest to the infiltration zone, which is consistent with literature data (e.g. Sontheimer, 1991, Rüetschi, 2004, Rauch-Williams and Drewes, 2006, Oren et al., 2007).

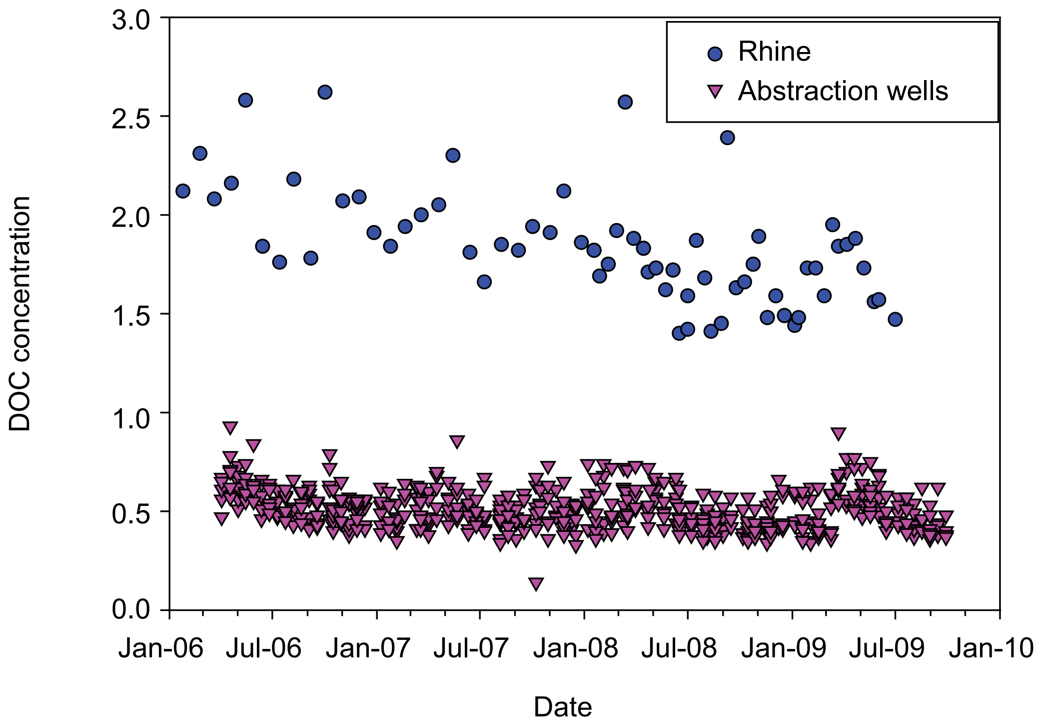

Figure 3: Long-term investigation of the DOC concentration in the Rhine (infiltrate) and in abstraction wells of an AGR system in Switzerland. Data: IWB Basel.

Several substances were generally easily removable during river bank filtration, regardless of the site investigated, season, discharge or redox regime. Some examples are iopromide, iohexol, iomeprol, caffeine, and galaxolide (Figure 4). In contrast, removal of more refractory pollutants was mainly determined by the key factor redox milieu, whereas temperature and discharge of the river were less important. Increased retention time improved in particular the removal of substances less biodegradable. A very prominent example seems to be iopamidol, being rather persistent at aerobic milieu and short retention times, while at anaerobic or more reducing milieu removal seems to be enhanced (Storck et al. 2010a,b). Interestingly, at a generally aerobic AGR site, iopamidol was removed by >76% (Figure 4). At the latter site, methanogenesis occurs on the micro-scale (Alewell et al. 2008), indicating reducing redox milieu. Thus, iopamidol may be removed due to the reducing milieu at the micro-scale.

Persistent substances at all sites were mainly EDTA, sulfamethoxazole, carbamazepine, amidotrizoic acid, 1,5-Naphtalenedisulfonate, and 1,3,5 Naphthalenetrisulfonate.

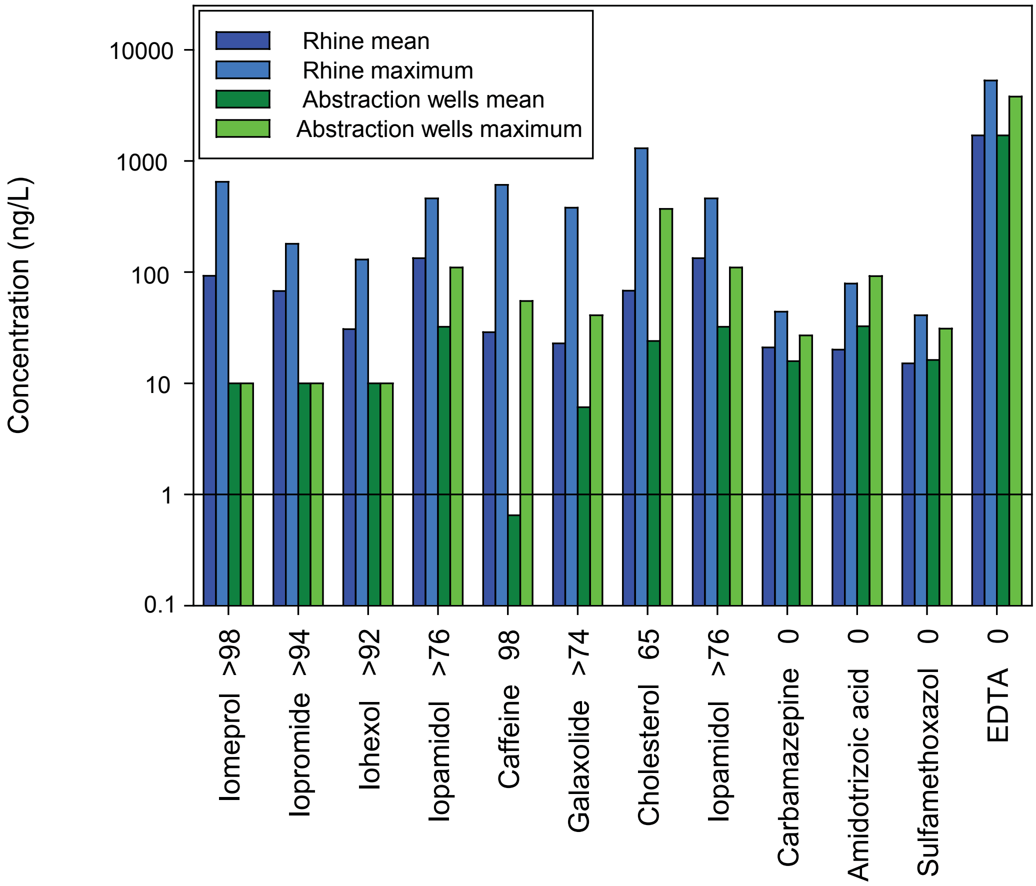

Figure 4: Concentration level of organic trace pollutants in the Rhine near Basel and in abstraction wells of an AGR site (2-4 years). At x-axis, percentage of removal during AGR is shown. ">" indicates the inclusion of values <limit of quantification in the calculation. Data: IWB Basel.

CONCLUSION

For most substances, removal efficiency was not affected by temperature and discharge, thus RBF and AGR are very robust processes. Redox conditions were identified as a key factor in the removal of certain trace pollutants. However, the role and impact of nutrient availability on redox milieu and on the biological degradation and removal of trace pollutants has to be further investigated.

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Extended Abstract

THE EFFECT OF CERTAIN BIOCHEMICAL FACTORS ON WELL CLOGGING UNDER SUBOXIC AND MILDLY ANOXIC CONDITIONS

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Keywords: groundwater, radial well, well ageing, ageing indicators, ageing rate, hydraulic resistance.

INTRODUCTION

Well clogging is a common phenomenon in alluvial media which contain iron. It can be persistent to the point of hindering normal operation and even cause a well to ultimately be shut down. Deposits on well screens generally feature organic mass of the microbial population present. Well screens are a suitable place for bacterial growth, aided by an abundant inflow of nutrients along with groundwater.

Several alluvial aquifer sites in Serbia, along the Sava, Danube, Tisa and Velika Morava rivers, were studied from 2005 to 2010 (JCI, 2010b, 2011). This paper presents some of the outcomes which shed light on the correlation between several important indicators of biochemical clogging processes (such as the redox potential and iron concentration) and the kinetics of the increase in local hydraulic resistances (KLHR) (Dimkić and Pušić, 2008; Dimkić et al. 2011a, 2011b).

There are four distinct phases of groundwater flow from the river to the wells of a drinking water supply source: flow through the river bed, flow under oxic conditions, flow under low oxic or anoxic conditions, and processes within the well screen zone.

During Phases 1 and 2, the oxygen dissolved in the river water is used for oxidation of organic substances and other oxidation processes (there is every indication that the oxidation processes involving bivalent iron present in the mineral composition of the aquifer are significant).

Phase 3 is conditional upon a high rate of oxygen consumption which leads to a low oxic, or anoxic, state. Here the iron from the mineral composition is reduced and dissolved in the groundwater.

In Phase 4, (dissolved) bivalent iron is converted, under favorable biochemical conditions, into trivalent iron (deposit), which clogs the well screen and its immediate zone.

The forms of chemical reactions depend on substance concentrations in the water, the oxic state, and the biological agent.

Investigations conducted at the Belgrade Water Source (BWS, an alluvial water source) (JCI, 2010a; Dimkić et. al, 2011a) have shown that under low oxic and initial anoxic conditions, distinct iron clogging processes take place at well screens. In such cases, criteria for the prevention, or deceleration, of clogging become more relevant than conventional criteria for mechanical clogging of the well. BWS is characterized by a relatively low oxygen concentration and low redox potential, and features varying total iron concentrations. The groundwater is borderline anaerobic/aerobic. It is relatively inert to corrosive activity and carbonate incrustation. BWS is a bank filtration-type source, comprised of 99 radial wells. A decrease in well discharge was noted at the very beginning of service.

After 2005, old well laterals were replaced at five wells (hereinafter: new wells). These wells were used to study the rate of clogging of the (new) laterals, expressed via the local hydraulic resistance (LHR) of the well, as a function of clogging indicators:

$$LHR = f\left(Fe, Eh, B\right) \tag{1}$$

where: Fe is the iron concentration in the well water, mg/l; Eh is the redox potential of the well water, mV; and B is the microbial activity expressed as the count of potentially active cells per milliliter of water, p.a.c./ml.

LHR is expressed as the quotient $\frac{\Delta S}{v}$, where ΔS is the local well drawdown (i.e., the difference in water levels between the well and a nearby piezometer), and v is the entrance velocity of groundwater at the well screen (discharge per unit area) (Dimkić and Pušić, 2008).

The variation in LHR over time may be expressed as

$$KLHR \approx \frac{\Delta(LHR)}{\Delta t} \tag{2}$$

where: KLHR is the kinetics of local hydraulic resistance variation. KLHR is an indicator of the change in the LHR rate, or the rate of well ageing. For practical purposes, KLHR is expressed as the annual variation in LHR. Local hydraulic resistances are quantified using the results of periodic well pumping tests.

Figure 1 shows plots of LHR variation over time at the new wells. The variation is depicted using a single, relative time axis (the period of operation with the new laterals is analyzed). The origin of the axis represents the time of installation of new laterals at each of the wells.

The initial LHR is the hydraulic resistance unaffected by clogging. The resistance caused by subsequent clogging differs from well to well. It corresponds to the difference in magnitude of Eh and Fe of the individual wells. Using the data shown in Figure 1 and based on Equation 2, it is simple to calculate KLHR for a given time interval. KLHR is a function of several parameters (Dimkić et al, 2011b):

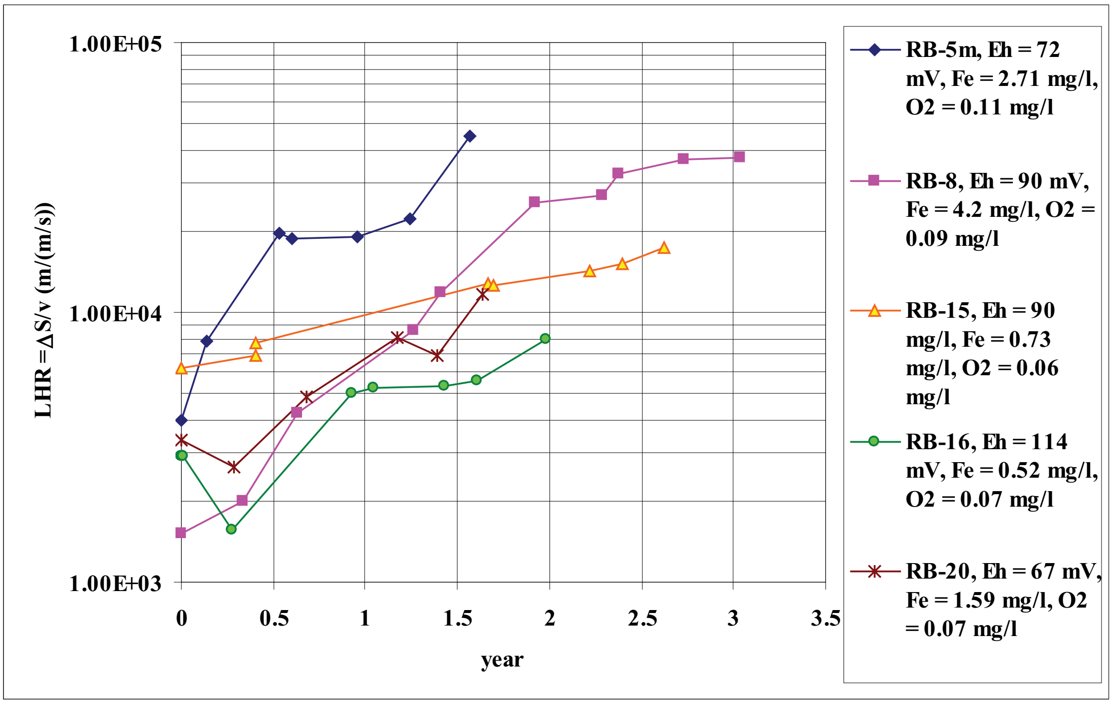

Figure 1: Variation in LHR of the selected wells, following installation of new laterals (Dimkić et al., 2011b). Average values of Eh, Fe and O_2, determined after installation of new laterals, are shown.

$$KLHR = KLHR(v, Eh, Fe, B, \Gamma, ...) \tag{3}$$

where: v - well entrance velocity, Fe – iron concentration in the well water, Eh - measured redox potential, B – a quantity which describes the intensity of bacterial growth in the well, Γ – a quantity which depends on several parameters – well screen installation method, gravel pack and aquifer grain-size distribution.

The correlation between the oxic state of the groundwater and the magnitude of KLHR was analyzed. On multiple occasions v, Eh, O_2, Fe, Mn, NO_3, NH_3, SO_4, H_2S and B were assessed at some 150 wells across Serbia. Figure 2 shows monitoring data and depicts typical chemical profiles of five wells in an anoxic environment and five wells in an oxic environment. Five of the wells are “new wells” (RB-5m, RB-8, RB-15, RB-16 and RB-20), where it was possible to define KLHR from the beginning of operation of the new laterals.

Well B-23 (BWS) is located in an oxic environment (Eh > 300 mV, O_2 = 0.5-1 mg/l, but with a relatively low iron concentration, Fe = 0.3-0.6 mg/l). Well B-21 (also at BWS) is in a suboxic environment (Eh > 200 mV, O_2 = 0.5-1 mg/l, Fe < 0.1 mg/l). It was determined with a high degree of reliability that the rate of iron clogging at these wells was relatively low.

The remaining three (vertical, tube) wells are located in distinctly oxic environments (Ključ Water Source, Morava River alluvion; and Mediana Water Source, Nišava River alluvion), where Eh > 300 mV and O_2 > 3 mg/l. The iron concentration in these aquifers is very low (Fe → 0).

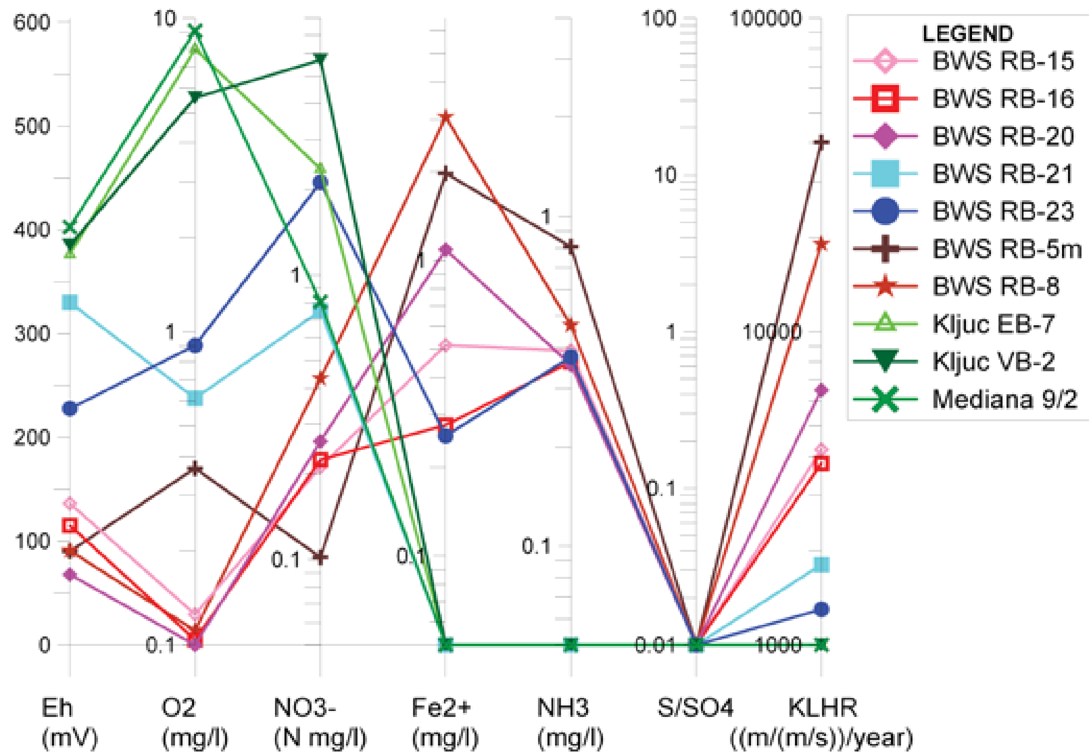

Figure 2: Graphical representation of aerobic state indicators of nine wells in alluvial media in Serbia.

Starting from Equation (3), assuming that Γ is relatively uniform and keeping in mind that there is an inter-dependency between Eh, Fe and B, it is possible to approximate:

$$KLHR = \varphi(\Gamma) f_1(v) \cdot f_2(Eh) \cdot f_3(Fe) \tag{4}$$

In the case of the five new BWS wells, as a result of simplification it is possible to construct plots of partial dependencies between KLHR and Eh, or Fe (Figure 3).

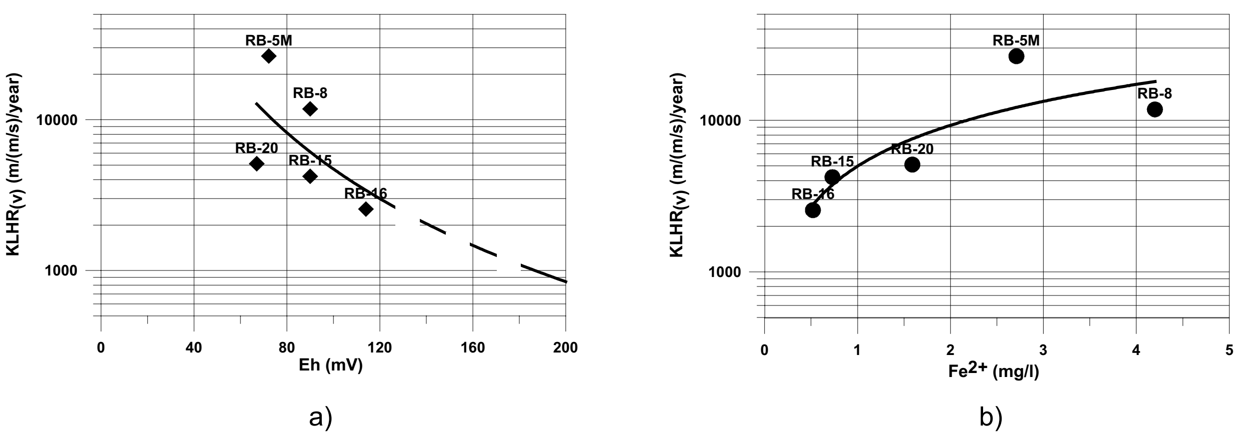

Figure 3: KLHR as a function of redox potential of well water and iron concentration.

The dashed line in Figure 3a is an extrapolation of the function KLHR = f(Eh), based on data reflecting very low, or negligible, hydraulic losses at the wells in oxic water. The following empirical expression may be written for these five wells:

$$KLHR = Const_1 \cdot v \cdot Fe^{\frac{3}{4}} \cdot e^{-Const_2 \cdot Eh} \tag{5}$$

The rate of clogging also depends on well discharge during the course of abstraction. In practice, the question of forecasting LHR may arise; it should not exceed a specified limit during a given time interval. For example, the criterion is that the annual increase in LHR should not exceed a certain value (allowed value - AV), to ensure well longevity. The following empirical expression is proposed:

$$\Delta S_{year} = v_{perm} \cdot KLHR_{year} \leq AV\ (m) \tag{6}$$

where: ΔS_{year} is the specified, limiting hydraulic resistance at the well lateral formed during one year (m), v_{perm} is the permissible entrance velocity of groundwater at the well (m/s), and $KLHR_{year}$ is the variation in LHR during the same time period (s^{-1}).

In practice to date, the concept of critical, maximum permissible entrance velocities at the well screen (v_{perm}) has been related solely to the seepage instability phenomenon of the aquifer in the vicinity of well screens (for example: Sichardt, 1928; Abramov, 1952; Kovacs and Ujfaludi, 1983). An additional criterion is introduced here – the permissible rate of well clogging, $KLHR_{year}$. Of course, both criteria need to be met. However, neither the setting of v_{perm} nor the sizing of the well screen such that the entrance velocity (v_{en}) is lower than permissible ($v_{en} < v_{perm}$), will ensure that the clogging of laterals will be fully arrested. This will only reduce the rate of clogging and allow the annual increase in LHR to stay below a specified limit.

Further, it is possible to establish a correlated between vperm and the oxic state of the groundwater, where Eh was taken as an indicator. Figure 4 is a graphical illustration of this approach. It also shows plots of permissible velocities based on the recommendations of several authors, where seepage instability was the sole criterion.

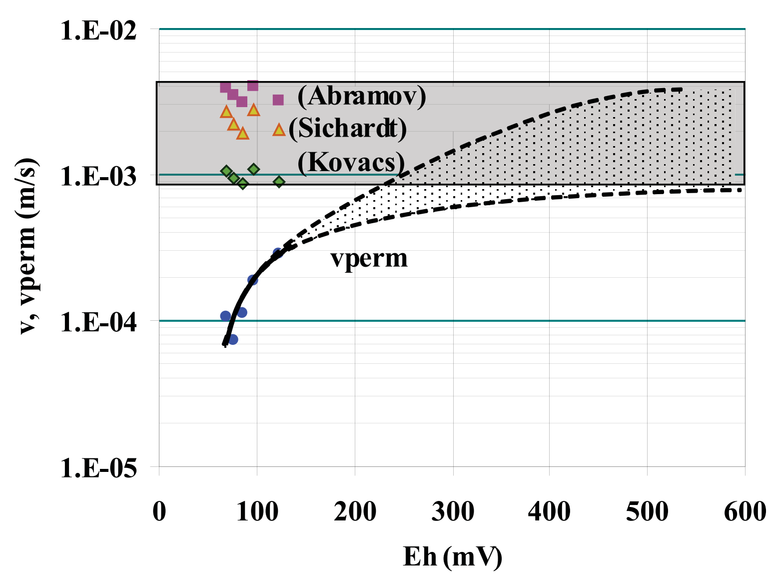

Figure 4: Illustration of well screen entrance velocities, v (conventional criteria) and vperm (limited, permissible annual well clogging), as a function of the oxic state (expressed as Eh of groundwater).

The BWS case study showed that vperm at nearly all the wells was much lower than that calculated using "classic" experimental formulas related to seepage stability in the immediate vicinity of the well screen. This particularly applies to anoxic/suboxic conditions, or in the present case to 70 mV ≤ Eh ≤ 150 - 200 mV, Fe = 0.5-6 mg/l.

With regard to groundwater source design, namely well discharge decline and well ageing, the oxic state in which biochemical processes become dominant is 50 mV ≤ Eh ≤ 200 mV. In this range of oxic conditions the critical well screen entrance velocity depends on biochemical parameters. Under high oxic conditions, biochemical clogging with iron is much less pronounced, or virtually equal to zero.

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Extended Abstract

DRINKING WATER ABSTRACTION BY BANK FILTRATION – STATE OF THE ART IN RESEARCH AND PRACTICE REVIEWED BY SYSTEMATIC LITERATURE-MATRIX

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Abstract: The use of bank filtration is an important option for water abstraction for many public water supplies. The success of bank filtration strongly depends on the prevailing conditions in the colmation layer of river beds as microbial activity and chemical transformation processes determine the quality of the bank filtrate. The overall objective of this work was a literature review on the state of the art in research and practice of drinking water abstraction by bank filtration. The main interest of this review was to obtain detailed information on important parameters and their change as a function of their spatial allocation within the infiltration path. The literature review included physical, chemical, microbiological and "other" parameters as well as black-box-models. Many "new" substances ("emerging pollutants") are gaining increasing importance for drinking water production because of their characteristics and their occurrence in the environment. A specifically structured matrix was used to organise the compilation of literature in order to facilitate an optimised access to the collected information.
Keywords: bank filtration, drinking water supply, literature review, spatial processes, water quality

INTRODUCTION

The use of bank filtration, which can occur naturally or be induced by a system of laterally or vertically connected wells, is an important option for public water supplies. The success of bank filtration strongly depends on the prevailing conditions in the colmation layer of river beds as microbial activity and chemical transformation processes there are commonly more distinctive compared to those found in surface or ground waters. The actual biogeochemical interactions determining the quality of the bank filtrate depend on numerous factors including aquifer mineralogy, shape of the aquifer, oxygen and nitrate concentrations in the surface water, types of organic matter in the surface and ground water environment, as well as land use in the local catchment area (Hiscock and Grischek, 2002). In Europe, bank filtration has been a very important technique for drinking water abstraction for over a hundred years. Especially in Germany, the technique is very common and applied at sites at the rivers Rhine and Elbe as well as at surface water around Berlin (Ray et al., 2002). According to Schmidt (2006), 13 % of the drinking water in Germany and approximately 75 % of the drinking water production in Berlin consist of water abstracted through bank filtration. Along the River Danube, there are many bank filtration sites - particularly in Vienna (Austria), near Bratislava and Gabcikovo (Slovakia), in Budapest (Hungary), and in Belgrade (Serbia). There are also bank filtration sites in the USA (e.g. Lincoln, Nebraska and Louisville, Kentucky) and in India. Along the filtration passage, the concentration of contained substances is changed by physical, chemical and biological processes. This naturally occurring process can therefore be used for water quality improvement. However, the river bank's cleaning capacity depends on the quality of the surface water being used as input water, as well as on a lot of local and structural conditions such as redox-conditions, distance, residence time in the subsoil, soil properties, quality of the landside groundwater and climatic conditions (Ziegler, 2001). Because of their characteristics and their occurrence in the environment, many 'new' substances ("emerging pollutants") are gaining increasing importance for drinking water production. Besides many others, the following substances are of specific relevance: persistent organic pollutants (POPs), pesticides with their relevant metabolites, organic complexing agents, mineral oil components (BTEX), perfluorinated compounds (PFT – perfluorinated tensides), pharmaceuticals, x-ray contrast agents and hygiene parameters.

The overall objective of this work was a literature review of the state of the art in research and practice of drinking water abstraction by bank filtration. The main interest of this review was to obtain detailed information on important parameters and their change as a function of their spatial allocation within the infiltration path. Subsequently, processes and their effects on groundwater quality could be discretised. The literature review included physical, chemical, microbiological and "other" parameters as well as black-box-models. A specifically structured matrix was used to organise the compilation of literature in order to facilitate an optimised access to the collected information.

METHODS

During the literature review in 2009, more than 224 publications were evaluated involving both international literature and literature dealing with the rivers Danube and Rhine, including detailed descriptionsof, for example, the Viennese situation. Additional information was collected during visits of Basel Waterworks (Switzerland) with their well documented artificial groundwater recharge site near the River Rhine, and TZW (Technologiezentrum Wasser) in Karlsruhe, Germany, which has substantial know-how in the field of groundwater management and emerging pollutants.

For the detailed analysis of international literature, the process of bank filtration (flow path from surface water to collection well) was spatially structured as follows:

- Surface water
- River bed, hyporheic interstitial
- Flow in the saturated zone
- Unsaturated zone of retention areas
- Collection well

International literature was assigned to the matrix according to specifically described substances, substance groups or overall parameters as well as according to described processes and their spatial allocation within the infiltration flow path. Consequently, the publications were numbered, whereby one publication can refer to one or more spatial processes, specified parameter(s) or group(s) of substances or overall parameters (Figure 1). Four separate matrices were created for physical, chemical, microbiological and "other" parameters.

In addition to this "specific" information, studies with no direct spatial allocation within the infiltration process as well as studies on pillar-experiments and aquifer storage and recovery systems (ASR), were assigned to the four matrices and categorised as "black-box" models.

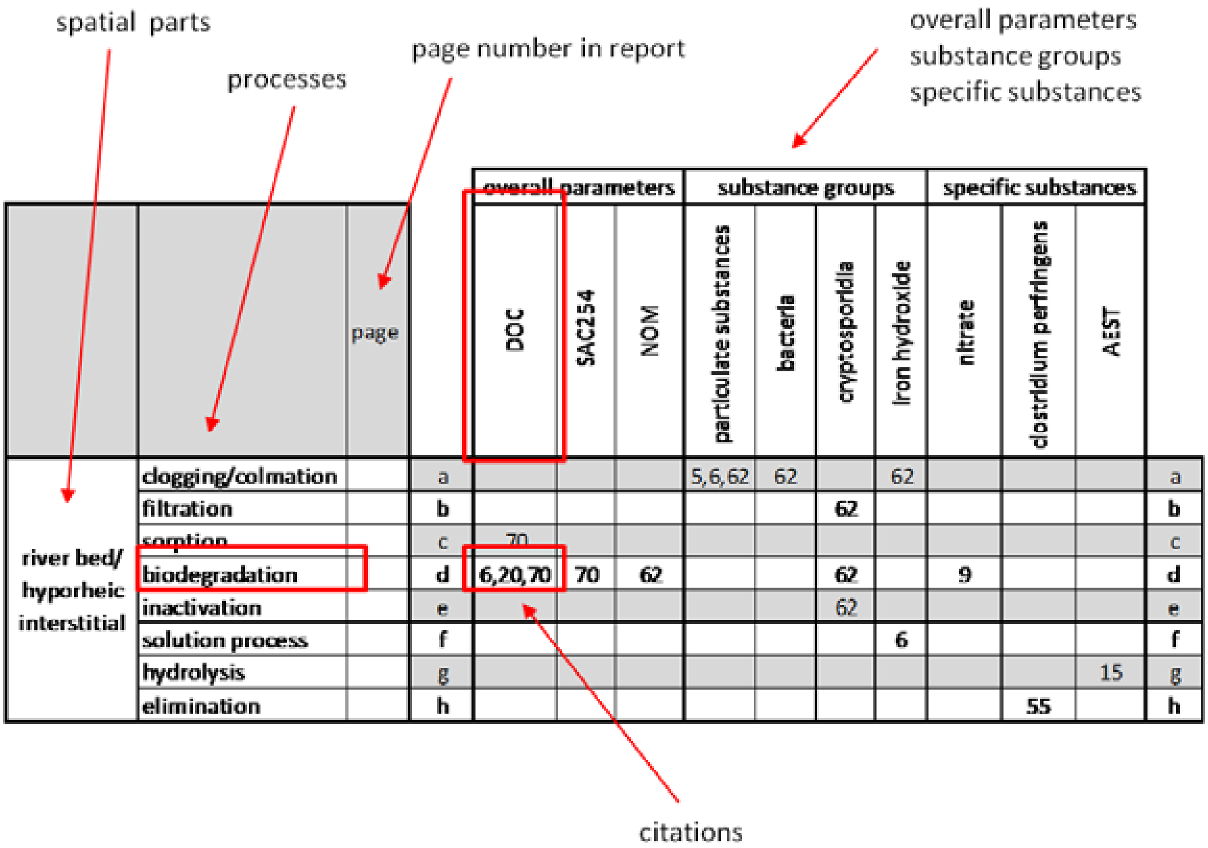

Figure 1: Parts of the literature matrix for substances, group substances and overall parameters in the area of the hyporheic interstitial (mixed from all matrices)

RESULTS AND DISCUSSION

The literature review resulted in four matrices compiling information from 70 publications. By consolidating the matrices, a reference book was elaborated, where all different parameters of relevance during bank filtration (from surface water to collection well) are dedicated to a spatial part (and appending processes like sorption, microbiological reduction etc.).

The matrix structure allows the allocation of citations of particular information from one and the same publication to more than one process or parameter in different spatial parts of the flow path. Data obtained from the different citations were thus assigned to the different processes in the different spatial parts as well as to the particular parameters/specific substances or substance groups. Most publications consider more than one parameter or process, so the particular information on each parameter or process was allocated to the matrix and the information was summarised in one specific citation. Figure 2 and 3 show examples for citations in different parts of the matrix from one and the same publication. All together, 469 citations from 70 publications were summarised and allocated in the four matrices to 81 parameters (substances, substances groups, overall parameters) at different spatial parts including black-box-models:

- Matrix for processes concerning physical parameters: 22 citations - 7 parameters
- Matrix for processes concerning chemical parameters: 330 citations - 44 parameters
- Matrix for processes concerning microbiological parameters: 111 citations - 25 parameters
- Matrix for processes concerning 'other' parameters: 6 citations - 5 parameters

All specific citations are outlined in a reference book. All numbered citations in the matrices are linked to the pagination in the reference book to get easy access to relevant information.

The specific information from each citation can refer to one specific process at a specific part of the flow path and additionally just to one specific substance, substance group or overall parameter. This basic 'filtered' information is organized in different levels of detail (Figure 4). The aggregation of information is up to the user. Figure 4 shows the different levels from parts of the chemical parameters, therein organic parameters and therein the TOC.

spatial parts	process	parameter 1	parameter 2	...
river bed - hyporheic interstitial	filtration	62		
	biodegradation	62		
	inactivation	62		
	...			

Figure 2: One publication (#62), one parameter – allocated at different processes

spatial parts	process	parameter 1	parameter 2	...
river bed - hyporheic interstitial	...			
	biodegradation	62	62	
	...			
	...			

Figure 3: One publication (#62), one process – allocated at different parameters

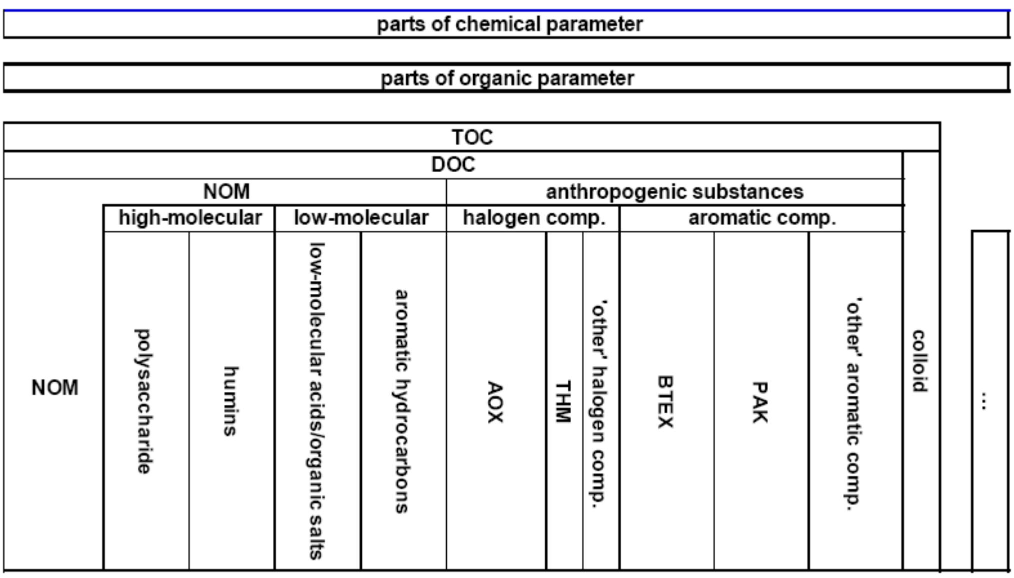

Figure 4: Parts of chemical parameters, therein organic parameters and therein the TOC

Additional substances, groups of substances or overall parameters as well as additional processes can be integrated in the matrix structure by flexible insertion of lines and columns. So the matrix gives the setting of the structure but the matrix is not closed in any direction. The overview over all citations gained through the matrix highlights topics, which are internationally reviewed in many cases (e.g. conductivity, dissolved organic carbon) in contrast to other topics, which are not worked out or considered at this moment within the flow path. Within the matrix structure it is easy to find concrete relevant information to appropriate (parts of) topics, but the conclusion about the presented information is still the task of the matrix user. However, the user's position is to configure the focus of the required information to his own needs and to his actual question as well as getting a fast overview of relevant international literature.

CONCLUSION

This mode of a literature review presents a very useful tool to get direct access to detailed information for each spatial part within the filtration flow as well as for relevant parameters for drinking water abstraction by bank filtration. We intend to continue this work to pursue the state of the art in research and practice and to provide detailed information on this important topic for drinking water supply.

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Notes:

Extended Abstract

ACCUMULATED DEPOSITS NEAR SUBSURFACE IRON REMOVAL WELLS: DO THEY CATALYZE THE FE^{2+} REMOVAL PROCESS?

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INTRODUCTION

Subsurface iron removal, or in-situ iron removal, is an established treatment technology to remove iron from groundwater. In Europe, numerous drinking water supply companies are operating (some of) their production wells with this technology (Hallberg and Martinell, 1976; Mettler, 2002; Rott et al., 2002; van Beek, 1985). The principle of subsurface iron removal is that aerated water is periodically injected into an anoxic aquifer through a tube well (Figure 1a), partially displacing the original groundwater. Based on the large surface area of iron hydroxides on the soil grains in the subsurface, it is thought that the heterogeneous reaction of Fe^{2+} oxidation on the surface of iron hydroxides is dominant during subsurface iron removal. In literature, the system's efficacy is explained by adsorptive-catalytic oxidation (Rott and Friedle 1985; van Beek, 1985), where adsorbed Fe^{2+} is oxidized to form new adsorption sites. On its way into the aquifer, the injected oxygen-rich water oxidizes adsorbed Fe^{2+}, creating a subsurface oxidation zone:

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \tag{1}$$

When heterogeneous ferrous iron oxidation is complete, the iron hydroxide surface is regenerated for adsorption of Fe^{2+} during abstraction (Figure 1b):

$$\equiv Fe(III)OH + M^{2+} \rightarrow \equiv Fe(III)OM^{+} + H^{+} \tag{2}$$

with "═" being the iron hydroxide surface and M the adsorbing iron cation. Once the iron (oxy) hydroxide surface is exhausted, no more Fe^{2+} is adsorbed and iron breakthrough is observed in the produced water. Hence, during abstraction the iron front is retarded and more iron-free water can be produced than was injected. Every period of injection-abstraction is referred to as a *cycle*, with the first injection-abstraction period being cycle 1. More water with reduced iron concentrations can be abstracted (volume V) than was injected (volume VI), i.e., this volumetric ratio (V/VI) determines the efficiency of the system.

Figure 1 Principle of subsurface iron removal (a) injection and (b) abstraction phase

Subsurface iron removal has been implemented since the 1970s in Europe (Mettler, 2002), nevertheless the technology has not yet found widespread application elsewhere. The iron removal occurs in the aquifer and is therefore not as visible as conventional above-ground rapid sand filtration, resulting in concerns regarding the long-term sustainability. Clogging of the aquifer is an issue that is raised frequently, however, in literature there is agreement that clogging of the aquifer does not pose a serious threat to subsurface iron removal (Appelo et al., 1999; Braester and Martinell, 1988; Grombach, 1985; van Beek, 1985; Mettler et al., 2001; van Halem et al., 2011). Although previous publications have not reported aquifer clogging around subsurface iron removal wells, doubts on the sustainability of this technology still limit the widespread application. However, this inexpensive technology holds great promise for the developed and developing country context, with the potential application for arsenic (van Halem et al., 2010) and manganese removal. In order to assess the sustainability of subsurface iron removal it is essential to unravel the dominant processes occurring during injection-abstraction cycle. The objective of this study was to investigate the role of accumulated deposits near a 12-year-old iron removal well on the Fe^{2+} oxidation, exchange and adsorption mechanisms. Results of column studies with drilled sediments that were operated with natural groundwater and different injection water qualities are presented in this paper.

MATERIALS AND METHODS

Composition of deposits

Bore holes (SonicMast with SonicDrill 2x7) were drilled at 5m from the injection/abstraction wells and ±50m from the wells. The borehole at 50m was considered to be outside the affected oxidation zone. 800mL samples were taken every meter at the depths from 10 to 28 meters below ground level. Classification of the drilled material (van Halem et al., 2011) showed that at approximately -12m the clay layer ended and coarse sand material (brownish) started. Greyish coarse sand was found at a depth of 22-26 m and the lower clay layer started at 26-27 m, showing that the well was into a confined aquifer. The depth of the perforated well filters was from 15 to 26 m. The soil samples were taken in September 2008, subsurface treatment started in 1996 and had been operated for 12 years at the moment of sampling.

Depending on the subsequent analyses, the samples were oven dried at 40°C or 105°C. Samples from every meter depth were analyzed in a certified laboratory with ICP-MS scan after chemical extraction with: Acid-Oxalate for amorphous iron and manganese; or, Nitric Acid for total iron and a wide range of compounds (including, Na, Mg, Al, Si, K, Ca, Mn, Sr, Ni, Sc, Ti, As). Acid-Oxalate extraction consisted of reductive dissolution of amorphous iron/manganese with an oxalate buffer solution which consisted of 0.2M ammonium oxalate and 0.2M oxalic acid (at pH=3). During digestion the sample was agitated and light was excluded.

For the column studies 3 different samples were selected, namely (A) one from within the oxidation zone, at 5m from the well; (B) one from outside the oxidation zone, at 50m from the well; and (C) one from the boundary layer below the oxidation zone. The chemical composition of these sediments is summarized in Table 1. Additionally, clean filter sand (washed for 24h with 5M HCl) was used in one of the columns as a reference.

Table 1: Chemical composition of the sediments inside (A), outside (B) and at the boundary (C) of the oxidation zone

Sediment	**depth**	**Fe**	**am-Fe**	**Mn**	**Ca**	**Na**
	m	mM/kg	mM/kg	mM/kg	mM/kg	mM/kg
A	21-22	418.9	65.1	3.1	265.2	1.8
B	21-22	240.6	19.1	1.9	177.7	1.6
C	23-24	210.3	24.3	1.8	49.5	1.8

Column studies

The experimental set-up consisted of four transparent columns with a length of 9cm and an inner diameter of 38mm. The columns were constructed out of 140mL syringes (Monoject) and filled with 100mL sediment material. During all experiments, the columns were wrapped in aluminium foil to exclude light. The experiments were executed at a drinking water treatment plant, "Vitens Loosdrecht", with natural groundwater. During the research period the groundwater had an average pH of 7.2 (±0.01), a constant temperature of 11 °C, 0.1 mmol Fe.L^{-1}, 3.3 μmol Mn.L^{-1}, 1.07 mmol Ca.L^{-1}, 0.52 mmol Na.L^{-1}, 0.28 mmol Si.L^{-1}, and 0.14 mmol SO4.L^{-1}. At the start of each experiment the columns were conditioned with the groundwater, until complete breakthrough of iron occurred, and the redox potential stabilized. In order to simulate the injection-abstraction cycles of subsurface iron removal, the flow was reversed from upflow to downflow to start an injection phase. A normal injection mode consisted of injection with drinking water originating from the same water treatment plant. However, to measure the exchangeable Fe^{2+}, injection cycles have also been performed in the absence of O_2 and/or Na^+.

The push-pull operational mode of injection-abstraction was simulated in the 1D plug-flow environment of the columns with down flow for injection and upflow abstraction (1.2 L.h^{-1} ±0.05). An injection-abstraction cycle started with 14 (±0.5) pore volumes of injection water and subsequently the influent was switched to groundwater. Electrical conductivity was used as a conservative tracer from which the pore volume could be calculated to be 0.04-0.05L, depending on the sediment type. The weight of the sediment material per column was 0.16kg and 0.17kg for filter sand and natural sediment, respectively. The flow rate in the columns (2.0-2.5 m/h) was controlled with a multi-channel pump and PVC tubing with low gas permeability. Anoxic conditions were maintained in the columns by using an airtight FESTO system (6 x 1 PUN, I.D. 4mm) with matching connectors and valves.

Fe analysis of the water samples was done with an Atomic Absorption Spectrometer (Perkin-Elmer Flame AAS 3110). In-line measurements were done for dissolved oxygen (Orbisphere and WTW Cellox 325), OR potential (WTW SenTix ORP), pH (WTW SenTix 41), and electrical conductivity (WTW TetraCon 325). Measurements were registered on a computer with Multilab Pilot v5.06 software.

RESULTS

Regular injection-abstraction cycle

Figure 2 shows the breakthrough curves for Fe in the groundwater after injection with tap water (0.28mM O_2). The Fe breakthrough is the fastest for the clean filter sand column, with a retardation to C/C0=0.5 of 7.5 pore volumes (R_{Fe}=7.5). The Fe retardation factor for the reference sample from outside the oxidation zone, sediment (B), is slightly higher at 10. The presence of iron and manganese oxides, natural organic matter and clay content will enhance the Fe removal compared to clean filter sand. The columns filled with sand from inside (A) or on the boundary of (C) the oxidation zone showed better Fe removal efficacies with retardation factors 21 and 15, respectively. The column with the highest Fe content in the sediment (A) was most effective in the retention of Fe^{2+} during a regular injection-abstraction cycle. The R_{Fe} of this column was 3 times higher than of the clean filter sand column, illustrating that the presence of (accumulated) iron hydroxides enhanced the removal of Fe. Although the Fe content in the sediment can account for the enhanced performance of column A, it does not differentiate between columns B and C; both columns have more or less the same Fe content. Between these two columns the difference can be found in the amount and type of calcium mineral. The calcium in the sediment of column B has been identified as calcite (XRPD; van Halem et al., 2011), whereas the calcium in column C was linked to the presence of calcium sulphates (SEM-EDX; van Halem et al., 2011). Column C retained more Fe^{2+} during a regular injection-abstraction cycle, indicating that it does not seem evident that the presence of high calcite concentrations catalyzed the subsurface iron removal process.

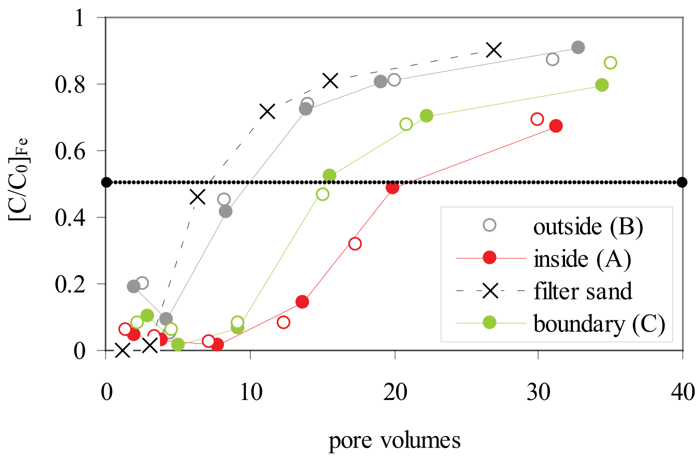

Figure 2: Fe behaviour during injection-abstraction cycle in columns containing filter sand, or sediments A, B or C.

Exchangeable Fe^{2+} exchange

The adsorptive capacity of the sediments or the exchangeable Fe^{2+} on the sediments can be measured with an injection-abstraction cycle in the absence of oxygen. The Fe^{2+} exchange on the material in the columns can be calculated from the Fe retention measurements after injection with 0.1M NaCl, in the absence of O_2. During such an injection phase, abundant Na^+ will be available to exchange with the exchangeable Fe^{2+} on the sand material. The amount of exchangeable Fe^{2+} on the sand material can be estimated either from the Fe^{2+} leaching from the columns during injection, or from the Fe^{2+} retention during abstraction. It is, however, practically almost impossible to measure the relatively short Fe^{2+} peak passing after injection of 1 pore volume. During abstraction the breakthrough process is much slower, making it feasible to accurately measure the total amount of Fe retained in the columns. Figure 3 depicts the Fe measurements during injection (negative pore volumes) and during abstraction (positive pore volumes) for column B. The retardation factor for this particular cycle was 8 and the total amount of retained Fe was calculated to be 0.04mM, corresponding to 0.22mM/kg.ds. The sites available for exchangeable Fe^{2+} on this particular sediment with this particular groundwater type can be calculated to be 0.44 meq/kg. It should be noted that the experiments were executed with natural groundwater, thus the exchangeable Fe^{2+} on the sediments are limited by the presence of other cations, such as Ca2+. An overview of the retained Fe in the other columns is given in Table 2, both for injection of O_2^- free tap water and 0.1M NaCl demineralized water. The table shows that Fe^{2+} exchange was higher in the sediment from within the oxidation zone, reaching up to 0.83 meq/kg for column A. The presence of high iron oxides is known to enhance Fe^{2+} exchange (Appelo and Postma, 2005). The presence of calcite did not have the same effect on the exchangeable Fe^{2+} fraction, as both clean sand and calcite-containing sediment (B) have the same Fe^{2+} retention in the columns. In order to differentiate between a catalytic oxidation reaction and the occurrence of cation exchange, the columns have been loaded with O_2^-containing water, either with or without 0.1M NaCl. These results will be presented in the full paper.

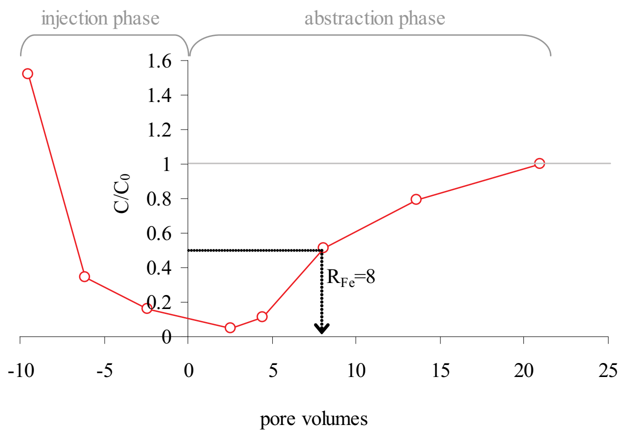

Figure 3: Fe behaviour during injection of 0.1 M NaCl and subsequent abstraction of natural groundwater in Column B

Table 2: Retardation factor, retention and exchangeable Fe^{2+} for columns containing filter sand, or sediments A, B or C

Column	Retardation factor		Fe retained		Exchangeable Fe^{2+}
	0.1M NaCl	tap	mM Fe	mM Fe/kg	meq/kg
filter sand	8	7	0.04	0.20	0.40
A	15	15	0.07	0.41	0.83
B	8	7	0.04	0.22	0.44
C	11	12	0.05	0.30	0.60

CONCLUSIONS

Sediments obtained inside the oxidation zone of a 12-year-old subsurface iron removal well showed better Fe^{2+} retention during injection-abstraction cycles in the column environment than sediments from outside the oxidation zone. The exchangeable Fe^{2+} fraction for sediments containing accumulated deposits was twice as high as for sediments that had been unaffected by subsurface iron removal, resulting in a doubling of the Fe retardation factor.

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Extended Abstract

AEROBIC DEGRADATION POTENTIAL OF THE HERBICIDES MECOPROP, DICHLORPROP AND BENTAZONE IN GROUNDWATER FROM CHALK AQUIFERS

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Abstract: The aerobic degradation potential of mecoprop, dichlorprop and bentazone was studied at a concentration of 1 µg/L in laboratory batch experiments with groundwater from chalk aquifers. Within the incubation period of 129 days, ^{14}C-mecoprop concentration decreased to 60-80% in the microcosms with groundwater collected from two monitoring wells (Wells 1 and 2). Dichlorprop degradation was neither observed under aerobic nor anaerobic conditions, while 17-27% of the initial concentration of ^{14}C-bentazone was removed. The results indicated a degradation potential of mecoprop and bentazone under aerobic conditions.
Keywords: Degradation, Drinking water, Pesticides

INTRODUCTION

Organic micro pollutants such as pesticides and degradation products are detected in an increasing number of aquifers all over the world (Barbash et al., 2001). In some countries such as Denmark, drinking water supply is based on groundwater, treated with a simple aeration and filtration process before it is distributed directly to the consumers. This requires high quality groundwater that must meet the standards in the EU Groundwater Directive with threshold limit values for pesticides and their metabolites in groundwater at 0.1 µg/L for each pesticide or metabolite and 0.5 µg/L for the sum of pesticides and metabolites (European Parliament and Council, 2006). The frequent findings of pesticides in Danish groundwater have resulted in the closure of many drinking water wells. In the period 1987-2007, a total of 2176 Danish abstraction wells were closed, 25% of these due to pesticide contamination (Miljøstyrelsen, 2009). Diffuse pesticide pollution is one of the major environmental challenges since it is difficult to remediate aquifers contaminated with trace concentrations.

The natural redox conditions of aquifers are considered to be one of the important factors governing the degradation of pesticides in groundwater (Larsen et al, 2001). In and around drinking water abstraction fields the geological structure may be complex with dual porosity which in combination with changing abstraction patterns may lead to mixing of different water types, creating steep concentration gradients and drastic redox changes. This may stimulate microbial degradation of the contaminants by addition of relatively low oxygen concentrations (Tuxen et al., 2006). Therefore, geological variations in combination with water abstraction may affect microbial degradation processes and redox conditions in aquifers (Ludvigsen et al., 1998; Janniche et al., 2011).

The present investigation focused on three pesticides; mecoprop, dichlorprop and bentazone which are some of the most frequently found and detected pesticides in Danish groundwater. The selected pesticides are all herbicides and are moderately soluble in water and include both non-polar compounds and dissociable compounds. The purpose of the study was to examine the aerobic degradation potential of three pesticides in slightly pesticide contaminated groundwater from chalk aquifers.

MATERIALS AND METHODS

Groundwater sampling

Groundwater samples were collected from two monitoring and three drinking water wells approximately 1 m above the screen in February 2010 and wells were purged three volumes before sampling. The drinking water wells were owned by the major water supply of Denmark, København Energi, KE. Oxygen, pH, temperature and electrical conductivity were measured in the field with a flow cell. Groundwater samples for pesticide mineralization experiments were collected in 1L sterilized glass bottles with overflow, in order to prevent aerobic conditions, and kept at 10°C until setting up the experiments.

Mineralization investigations

Pesticide mineralization investigations were performed with [ring-^{14}C]-mecoprop (Izotop, Budapest, Hungary, 95% radiochemical purity, 23mCi/mmol), [ring-^{14}C]-dichlorprop (Izotop, Budapest, Hungary, 99.03% radiochemical purity, 25mCi/mmol) and [ring-^{14}C]-bentazone (Izotop, Budapest, Hungary, 97.96% radiochemical purity, 44mCi/mmol). Aerobic incubations were set up for each pesticide in duplicates and incubated in the dark at 10ºC, corresponding to the aquifer temperature. Each bottle had a headspace of atmospheric air. Control incubations for biological activity, were autoclaved 20 minutes at 1.5 bars and 120°C at three times with one day intervals. For dichlorprop 6 anaerobic incubation bottles were set up in where the headspace were replaced with 80%N_2/20%CO_2-gas mixture in order to remove all oxygen.

Laboratory batch experiments contained 40g autoclaved chalk sediment and 60mL groundwater in 100 mL DURAN bottles with Teflon inlayer caps for aerobic incubations. ^{14}C-ring labelled dichlorprop, mecoprop and bentazone were added to a concentration of 1µg/L of pesticide to each of the bottles. For ^{14}C- activity measurements, 2mL water subsamples were collected at each sampling and transferred to a 20 mL polyethylene scintillation vial containing a 6 mL scintillation vial with 1 mL 0.5 M NaOH. The subsample was acidified by adding 0.1 mL 37% HCl to strip off $^{14}CO_2$. The 6 mL inner vial of this 'double vial' system served as a CO2 trap and was removed after 48 hours. Scintillation liquid was added and the ^{14}C-activity of both the 20 mL vial and the 6 mL vial was quantified by counting for 20 minutes in a liquid scintillation analyser.

RESULTS AND DISCUSSION

Groundwater characterization

The collected groundwater was in the neutral range (pH 7.1-7.4) and anaerobic, indicating reduced conditions ranging from nitrate reducing to iron reducing in all five wells (Table 1). Water from Well 1 (screened 28-30 meter below surface (mbs)) had the highest oxygen concentration and microbial activity. Well 2 had the highest concentrations of sulphate, chloride, magnesium, calcium, sodium and methane. Wells 2, 3, and 4 had the lowest concentrations of Fe (II). Well 3 had the highest concentration of nitrate, but the lowest sulphate concentration. The water samples from Wells 2-5 represented a relatively long depth interval and they were thus not as depth-specific as the water sampled from Well 1.

Table 1: Characterization of groundwater from the five sampled wells

	Well 1	Well 2	Well 3	Well 4	Well 5
Screen depth (mbs)	28-30	9-24	14-35	14-35	16.5-28.5
Temperature (°C)	4.0	9.5	9.1	9.0	9.1
pH	7.37	7.05	7.15	7.05	7.12
Conductivity (µS/cm)	420	666	540	489	599
Oxygen (mg/L)	0.35	0.06	0.11	0.22	0.03
Cl^- (mg/L)	34.1	52.7	44.0	35.1	34.3
Mg^{2+} (mg/L)	25.3	24.2	22.7	22.0	22.1
Ca^{2+} (mg/L)	120.3	183.6	136.9	142.8	160.8
Na^+ (mg/L)	20.0	21.3	18.3	15.4	15.9
K^+ (mg/L)	3.22	9.3	3.67	3.02	3.89
Mn^{2+} (mg/L)	0.034	0.053	0.039	0.034	0.059
CH_4 (mg/L)	0.257	0.007	0.019	0.012	0.010
SO_4^{2-}(mg S/L)	178	192	141	183	181
Fe^{2+} (mg/L)	2.02	0.63	0.69	0.52	2.48
NO_3^-(mg N/L)	0.08	0.04	2.17	0.44	0.02
NH_4^+ (mg N/L)	0.57	2.48	0.38	0.18	0.31
Dissolved Organic Carbon (mg/L)	1.832	2.592	1.851	1.726	1.858
ATP (pg/mL)	58.0	16.9	23.4	2.8	6.7

Mineralization potential

Mecoprop concentration in the laboratory experiments with water collected from Well 1 and Well 2 decreased to approximately 60-80% of the initial concentration under aerobic conditions, while 92-97% remained in the autoclaved controls after 129 days of incubation. After a long lag phase, significant decrease of mecoprop was noted in Well 1 (Figure 1). Mineralization was slow, but $^{14}CO_2$ production was substantially higher (2-5%) than the level in the autoclaved controls (0.0-0.5%). The observed degradation potential of mecoprop is in accordance with previous investigations involving chalk under aerobic conditions (Janniche et al., 2010, Kristensen et al., 2001), though their studies revealed slightly shorter lag phases and indicated a potential degradation under aerobic conditions.

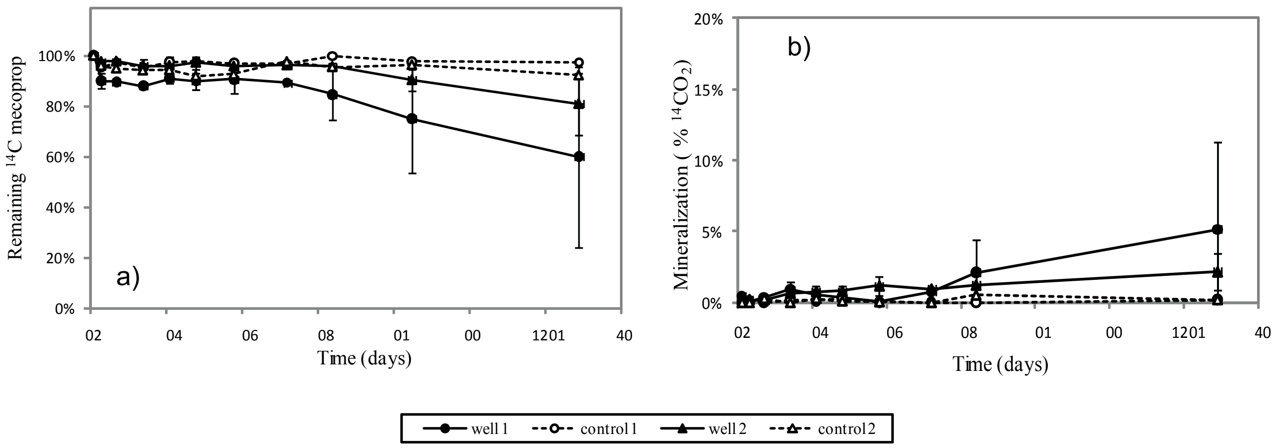

Figure 1: Degradation of mecoprop under aerobic conditions.
(a) Remaining pesticide, (b) mineralization (relative $^{14}CO_2$ production)

Dichlorprop degradation was neither observed under aerobic nor anaerobic conditions within the incubation period of 129 days. 97-104% of the initial dichlorprop concentration remained under aerobic conditions (Figure 2). Studies by Pedersen (2000) and de Lipthay et al., (2000) showed recalcitrance of dichlorprop under aerobic conditions. In contrast, degradation of dichlorprop was observed in a laboratory column experiment (Tuxen et al. 2000) and a continuous field injection experiment (Broholm et al. 2001) in an aerobic aquifer.

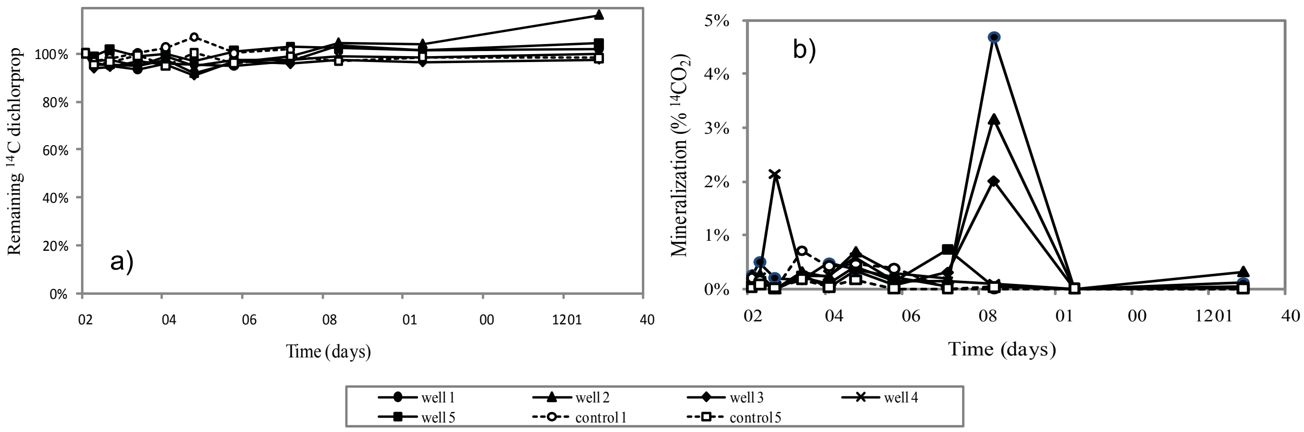

Figure 2: Degradation of dichlorprop under aerobic conditions.
(a) Remaining pesticide, (b) mineralization (relative $^{14}CO_2$ production)

For bentazone, 17-27% of the initial concentration was removed after 129 days of incubation, while only 9% was removed in the abiotic controls (Figure 3). Though bentazone is usually considered to be recalcitrant (Tuxen et al., 2002 and Broholm et al., 2001), a degradation potential for bentazone in groundwater was observed.

Tuxen et al. (2006) investigated how increasing oxygen concentrations affected the length of the lag phase and the degradation rate. Mecoprop mineralization was then higher (53 %) with high oxygen concentration compared to the one (32 %) with low oxygen concentration and the length of the lag phase was shortened 10 times in the microcosm experiments with high oxygen concentration (7.7 mg/L) compared with low oxygen concentration (<0.3 mg/L).

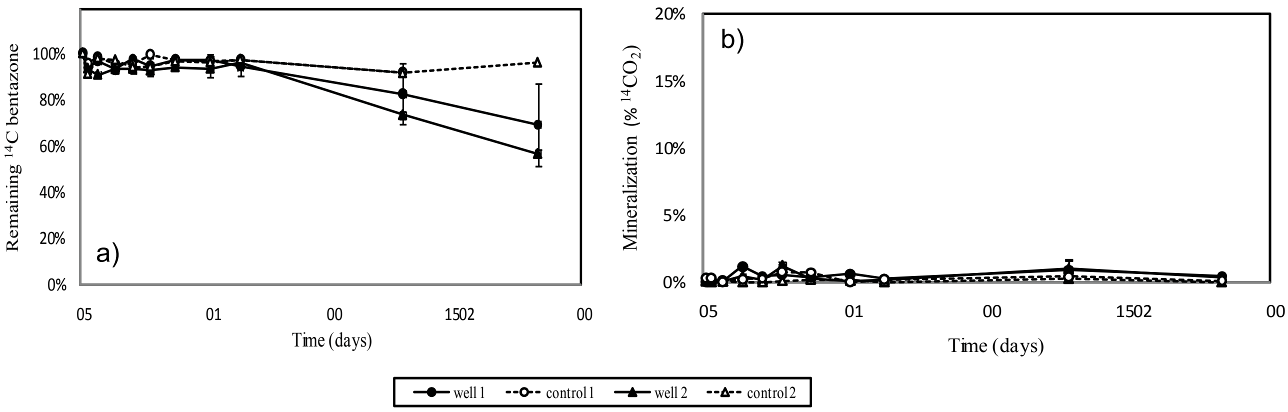

Figure 3: Degradation of bentazone under aerobic conditions.
(a) Remaining pesticide, (b) mineralization (relative $^{14}CO_2$ production)

CONCLUSION

Batch experiments with chalk material and groundwater showed the degradation potential for mecoprop and bentazone in the presence of oxygen. To our knowledge, bentazone has not been reported before to be degraded with aquifer material. In order to gain more knowledge regarding bentazone degradation in aquifer material, optimization of redox conditions from anaerobic to aerobic by adding oxygen concentration must be studied.

The study is partly funded by GOODWATER Initial Training Network under grant agreement no. 212683 which addresses the increasing global importance of biological groundwater remediation and management of sites contaminated by organic chemicals.

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Extended Abstract

EFFECT OF PHOSPHATE ON CHROMIUM REMOVAL FROM GROUNDWATER BY IRON OXIDE BASED ADSORBENTS

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Abstract: In this study, batch adsorption experiments and Rapid Small Scale Column Tests (RSSCT) were conducted using Cr(VI) containing model water, at pH values 6, 7 and 8.5. Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH) were used as adsorbents. The best Cr(VI) adsorption was observed at pH 6, and GFH showed much better removal than IOCS. With increase of PO_4^{3-} concentration in model water from 0 to 2 mg/l, at pH 6, strong decrease in Cr(VI) removal efficiency from 92.6% to 24.1% with GFH, and from 19.4% to 13.5% with IOCS was observed. Similar trends were observed at pH 7 and 8.5. An exception was for Cr(VI) removal with IOCS at pH 8.5 where there was almost no inhibition by PO_4^{3-}. Inhibition of Cr(VI) removal by PO_4^{3-} observed in batch adsorption experiments was confirmed in the RSSCT. Better Cr(VI) adsorption on GFH and IOCS, observed at lower pH values can be presumably explained with the effect of pH on the surface charge of adsorbents. The point of zero charge is reported to be between 7 and 8, and at pH 6, the surface of the adsorbent is consequently positively charged which attracted negatively charged species of Cr(VI) and PO_4^{3-}.
Keywords: Phosphate, Chromium, Groundwater, Iron oxides adsorbents

INTRODUCTION

Chromium is the twenty-first most abundant element in the Earth's crust and is used in diverse metal products and processes such as alloying, electroplating, leather-tanning, corrosion prevention etc. (Chowdhury and Yanful, 2010). As a result of inappropriate waste-disposal practices, chromium contamination of surface water and groundwater has become a significant environmental problem (Palmer and Wittbrodt, 1991). Chromium can also occur naturally as a result of dissolved minerals from weathering of chromites and other chromium-bearing minerals present in bedrock and soil (Nriagu and Nieboer, 1988).

Chromium has two oxidation states in the water system, namely Cr(VI) and Cr(III), that have different mobility and toxicity. Cr(VI) species, having mobile and strongly oxidant characters, are known as mutagen and potential carcinogen (NPT, 2007). In contrast, Cr(III), having a limited hydroxide solubility and low toxicity, is generally regarded as a no dangerous pollutant. However, current analytical methods and the variable speciation of chromium in water favor a guideline value for total chromium.

Several methods for chromium removal such as precipitation, electrochemical reduction, adsorption onto different media, ion exchange, solvent extraction, nano filtration, reverse osmosis and biological removal have been applied (Sharma et al., 2008, Mayo et al., 2007, Hu et al., 2004 and Fendorf et al. (1997)). Adsorption of chromium on different sorbents such as iron oxide, iron coated sand, iron coated activated carbon and granular ferric hydroxides (Driehaus et al., 1998) has also been investigated.

Raw water typically contains a mixture of many ions and compounds rather than a single one. These ions may enhance adsorption, may act relatively independently or may interfere with one another. This study investigated the effect of PO_4^{3-} on adsorptive removal of Cr(VI) by Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH).

EXPERIMENTAL

GFH used in this study was obtained from the manufacturer GEH Wasserchemie in Osnabruck (Germany). IOCS was obtained from the Dutch Water Company Vitens, from the water treatment plant Brucht that treats groundwater with high iron content.

Model water was prepared by mixing demineralized water with the required amount of Cr(VI) prepared from a stock solution of 100mg/L Cr(VI) in the form of $Cr_2O_7^{2-}$. 100 mg/l HCO_3^- was added to increase model water buffering capacity. Subsequently, pH was adjusted to the required values using 1M HNO_3 or NaOH solutions. PO_4^{3-} was obtained from KH_2PO_4 from Merck.

For batch adsorption experiments, acid-cleaned and closed 500 ml plastic bottles, fitted with tubes for periodic sampling, were filled with model water and 0.1g/l of pulverized IOCS and GFH (grain size< 63µm) were added. Bottles were placed on an Innova 2100 rotary shaker at 100 rpm and kept at 20 ±1oC. All samples were filtered through a 0.45 µm membrane filter using a polypropylene syringe filter.

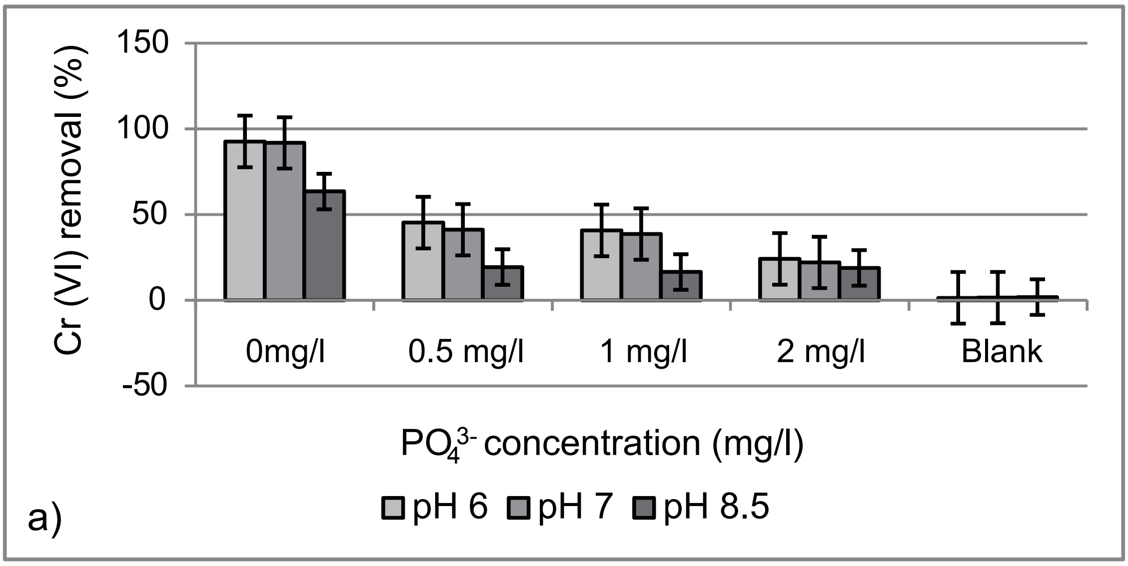
In addition to batch adsorption experiments, RSSCT were conducted assuming constant diffusivity. Glass columns with an inner diameter of 1.8 cm were packed with IOCS or GFH (356-390 µm size fraction) was used. Samples of feed water and filtrate were taken at regular time intervals of 1 hour. Columns were operated at a filtration rate of 46.6 m/hour, resulting in an empty bed contact time of 0.35 min.

Cr(VI) was analyzed with the atomic absorption spectrometer (Thermo Elemental Solaar MQZe-GF 95), with an auto-sampler and a graphite furnace used as detector (AAS-GF). For dilution acidified demineralized water was used. Nickel nitrate (50 g Ni/l) was used as a matrix modifier. Samples were passed through a 45 µm filter and acidified with HCl to pH below 2. Cr(VI) was analyzed according to the Standard Method for examination of water and waste water, 18th edition of 1992. PO_4^{3}- was measured with the ascorbic acid spectrophotometer method at 880 nm.

RESULTS AND DISCUSSION

Figure 1(a) clearly shows that the removal of Cr(VI) by GFH decreased strongly when PO_4^{3-} was added to the model water. In the absence of PO_4^{3-}, GFH removed 92%, 91% and 63% of Cr(VI) at pH 6, 7 and 8.5, respectively. The presence of 0.5 mg/l of PO_4^{3-} only decreased Cr(VI) removal by GFH to 45%, 41% and 19% at pH 6, 7 and 8.5, respectively. Cr(VI) was poorly removed by IOCS (Fig. 1b), with removal efficiency limited to approximately 20% only. The presence of ≥ 0.5 mg/l of PO_4^{3-}, at pH 6 and 7, resulted in only a slight reduction of Cr(VI) removal efficiency, while PO_4^{3-} inhibition at pH 8.5 was negligible.

PO_4^{3-} removal by GFH and IOCS also reduced with 16% and 5%, respectively, when 0.5 mg Cr(VI)/l was present in model water at pH 7. Similar to Cr(VI) removal, GFH was more effective than IOCS for PO_4^{3-} removal.



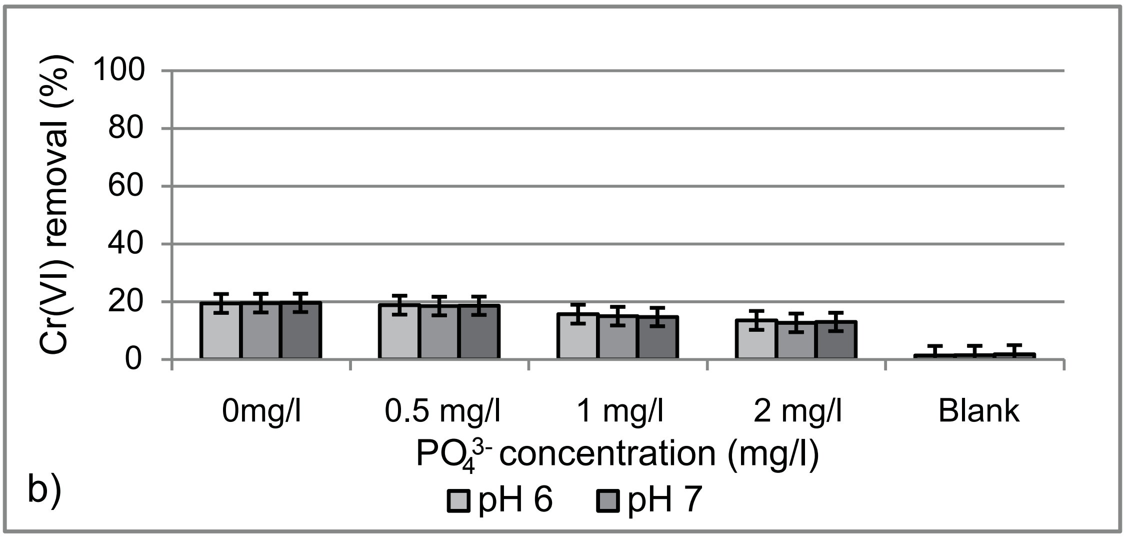


Figure 1: Effect of PO_4^{3-} and pH on Cr(VI) removal in batch adsorption experiments; Adsorbent: 0.1g/l GFH -(a), IOCS -(b); CT=24 h; Model water: initial [Cr(VI)] = 0.5 mg/l; [HCO_3^-] = 100 mg/l.

The mechanism of Cr(VI) adsorption by GFH and IOCS is likely a combination of electrostatic attraction and ligand exchange, as suggested by Hu et al. (2004) who studied the adsorption of Cr(VI) on magnetite. Chowdhury et al. (2010) and Hu et al. (2005) also suggested that electrostatic attraction is the key mechanism of chromium removal by maghemite (g-Fe_2O_3) from aqueous solutions and that the process is highly dependent on initial chromium concentration, pH and temperature.

Figure 2 shows Freundlich adsorption isotherms for Cr(VI) adsorption on GFH. The GFH adsorption capacity for Cr(VI) in order to meet the WHO guideline for Cr (50 µg/l) were 4.2 mg/g without addition of PO_4^{3-} in the model water. The adsorption capacities decreased up to 2.2 mg/g and 1mg/g, respectively, when 1 mg/l and 6 mg/l of PO_4^{3-} were separately added to the model water. This supports strongly the competitive effect of PO_4^{3-} and Cr(VI) on the surface of the adsorbent.

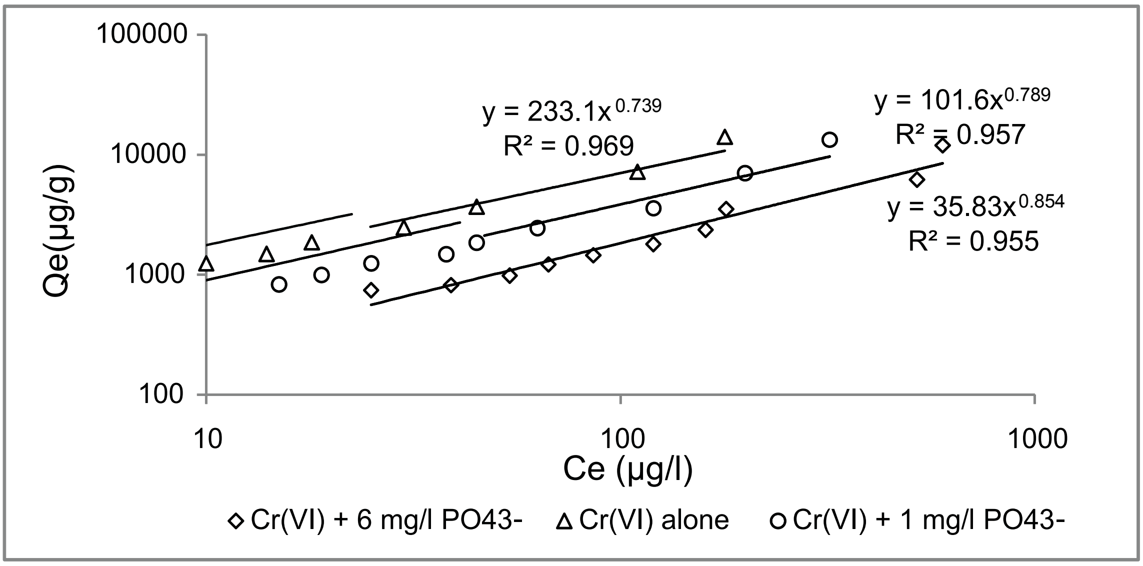


Figure 2: Freundlich adsorption isotherms for Cr(VI) adsorption on GFH at pH 7. Initial [Cr(VI)] = 3 mg/l; [HCO_3^-] = 100 mg/l, GFH dosage = 0.1- 2 g/l; Contact time = 30 days

RSSCT test confirmed that GFH adsorbs Cr(VI) much better than IOCS. After 10.000 empty bed volume (EBV) of phosphate-free model water filtered, 10% and 85% of Cr(VI) breakthrough was observed in filter columns with GFH and IOCS, respectively. The presence of 1 mg/l of phosphate in model water dramatically changed the breakthrough pattern with C/Co of 74 % for GFH after 10.000 EBV filtered. In the removal of Cr(VI) with IOCS, the breakthrough patterns with C/Co of 57% (Cr(VI) alone) and 73 % (Cr(VI) together with PO_4^{3-}) were obtained only after treatment of about 4.000 EBV. Results from RSSCT support the results from batch adsorption experiments that show much better removal of Cr(VI) with GFH. RSSCT also confirmed that GFH and IOCS Cr(VI) adsorption capacity is reduced in the presence of PO_4^{3-} (Fig. 3).

Figure 3 (b) shows that the capacity of GFH to remove phosphate was higher than the capacity of IOCS. Eighty percent of phosphate breakthrough was obtained after treatment of about 4000 EBV for IOCS while the phosphate breakthrough of ninety percent was obtained after treating approximately 8000 EBV for GFH in the model water with 0.1mg/l of Cr(VI).

According to Fendorf et al. (1997), who studied the mechanism of chromium removal by goethite by Extended X-ray absorption fine structure (EXAFS) spectroscopy, three different surface complexes exist on goethite: a monodentate complex, a bidentate-binuclear complex, and a bidentate-mononuclear complex. At low surface coverages, the monodentate complex was favored while at higher coverages the bidentate complexes were more prevalent. The bidentate-binuclear complex appears to be in the greatest proportion at these highest surface coverages.

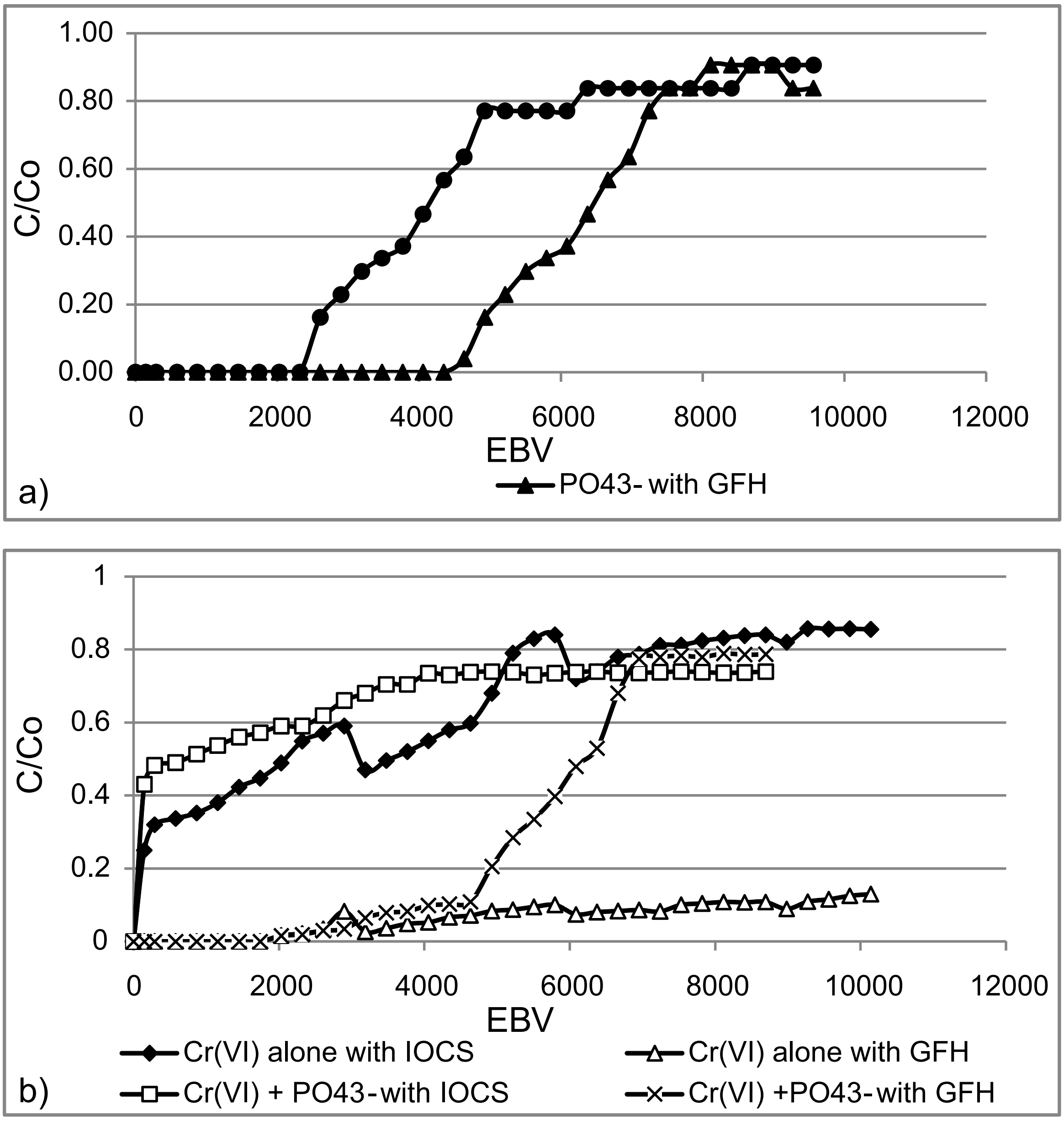


Figure 3: RSSCT breakthrough curves for Cr(VI) (a) and PO_4^{3-} (b) removal with GFH and IOCS. [Cr(VI)] = 0.1 mg/l, [PO_3^{4-}] = 1mg/l, Filtration rate = 46.6m/h, EBTC = 0.35 min, Model water: Cr(VI)=0.1 mg/l, PO_4= 0 or 1 mg/l, HCO_3^- = 100 mg/l, pH 7

Khaodhiar et al. (2000) also studied chromate adsorption and equilibrium modeling on IOCS. They found out that chromate was weakly adsorbed or formed an outer-sphere surface complex with the IOCS surface. This can probably suggest why Cr(VI) was less adsorbed by IOCS compared to GFH. Cr(VI) was adsorbed on GFH through inner-sphere surface complexes (strong complexes). This conclusion is supported by the results obtained by Hsia et al. (1993), that investigated adsorption of Cr(VI) on hydrous Iron Oxide. According to their results, an inner-sphere coordination of chromate to iron oxide surface was identified from EDAX and FTIR results. The isoelectric point of the system containing more chromate was a few pH units lower than that of the system containing less chromate or no chromate. This phenomenon was attributed to an increase in the negative charge of the iron oxide surface as a result of adsorption of chromate.

CONCLUSIONS

In this study, IOCS and GFH showed the potential to adsorb both Cr(VI) and PO_4^{3-}. GFH showed a higher adsorption capacity for both Cr(VI) and PO_4^{3-} than IOCS. The higher GFH adsorption capacity for Cr(VI) can be explained by the fact Cr(VI) and phosphate form strong inner sphere complexes with GFH, while weak outer-sphere complexes are formed on the surface of IOCS as it has been proven by previous studies.

For both adsorbents, better removal of Cr(VI) and PO_4^{3-} was observed at a low pH value (pH 6). The presence of PO_4^{3-} decreased the adsorption capacities of Cr(VI) and vice versa. Cr(VI) and PO_4^{3-}, being both negatively charged, compete for the surface adsorption sites on GFH and IOCS. Better adsorption of Cr(VI) and PO_4^{3-} at low pH could be explained by electrostatic attraction forces present at lower pH, due to positively charged adsorbent surface.

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EXTENDED ABSTRACT

CRITICAL REVIEW OF MANGANESE REMOVAL FROM GROUNDWATER: AN OVERVIEW OF 100 MANGANESE REMOVAL TREATMENT PLANTS

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Abstract: The aim of this study was to provide an overview of selected full scale groundwater treatment plants in The Netherlands, Belgium, Germany, Jordan and Serbia that comprise manganese removal through aeration and rapid sand filtration with focus on the effect of ground water quality and process design parameters on manganese removal efficiency. From this study no strong statistical correlation was found between manganese removal and water quality data or process design parameters. Yet this study suggests that some parameters are of importance for proper manganese removal. Amongst others the most important are: (1) acidity (pH) of filtrate, (2) ammonium removal, and (3) iron load (kg/m^2 filter area). Filtration rate (m/h) and Empty Bed Contact Time (EBCT) seem to have a limiting effect on manganese removal efficiency.
Keywords: groundwater quality, groundwater treatment, manganese removal, process parameters

INTRODUCTION

Groundwater is world-wide the predominant source of drinking water production (UNEP, 2000). In addition to several other impurities (e.g., iron, ammonium, methane) groundwater frequently contains elevated levels of dissolved manganese, which needs to be reduced for both, health and aesthetic reasons. The removal of manganese from groundwater is commonly done through aeration-rapid sand filtration. Such treatment approach is the most cost effective but in practice this treatment is frequently associated with several problems such as:

- very long ripening period (several months to more than a year) to achieve effective manganese removal with new filter media (Cools, 2010; Krull, 2010);
- frequent manganese breakthrough in filtrate after some years of operation (Fig. 1), which introduces the need for filter media replacement with associated long start-up and additional

costs for filter media disposal and replacement (Buamah et al.2008);
- inefficient manganese removal for some types of groundwater.

Despite the fact that a lot of research has been done on manganese removal through aeration-rapid sand filtration in the past, mechanisms controlling the process are still not fully understood. Recent research (Buamah, 2009) suggested that performance of conventional manganese removal plants could be improved by introducing manganese and/or iron (hydro)oxide rich filter media in the rapid sand filters.

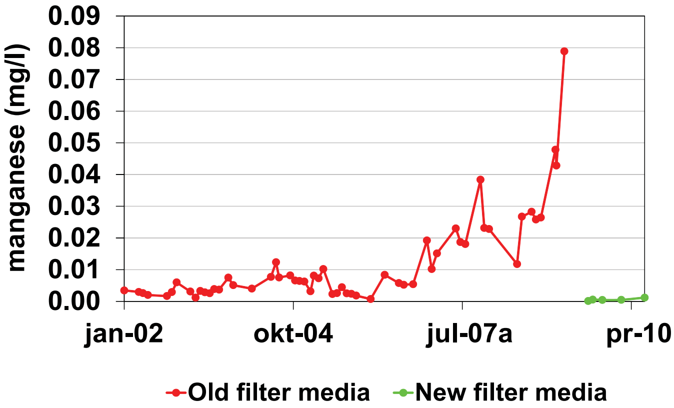

Figure 1: An example of manganese breakthrough in a groundwater treatment plant based on aeration-rapid sand filtration.

The aim of this study was to provide an overview of selected groundwater treatment plants in The Netherlands, Belgium, Germany, Jordan and Serbia that comprise manganese removal. The focus of the overview will be on treatment plants based on conventional ("wet and dry") aeration-filtration systems, including plants that incorporate a contact or sedimentation tank and/or pH correction. The overview will cover both, groundwater quality matrix (Bruins et al, 2011a), as well as process design considerations plant (i.e., type of aeration, filter media type, grain size, bed depth) (Bruins et al, 2011b) The purpose of the inventory is to provide an insight into practical experiences with manganese removal in full scale conventional plants.

METHODS

The inventory is based on information gathered by visiting groundwater treatment plants and interviewing employees of different water companies from several countries (The Netherlands, Belgium and Germany). This study also includes the practical experiences of the first author with over 20 groundwater treatment plants. Performance of full scale plants, with a focus on manganese removal, was correlated with groundwater quality matrix and plant design parameters. Furthermore the focus was particularly on the first filter stage, in which manganese removal was often combined with the removal of ammonium, iron and sometimes methane. Principle Component Analysis (PCA) was conducted with both, groundwater quality data and plant design parameters.

RESULTS AND DISCUSSION

Figure 2 illustrates a typical start up (ripening) period of a rapid sand filter with new quartz sand in a drinking water production plant in The Netherlands.

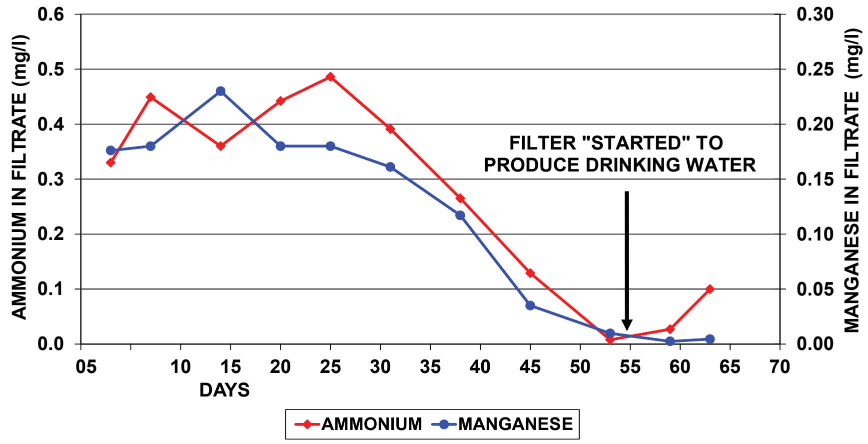

Figure 2: An example of the ripening period of a rapid sand filter with new media.

Figure 2 shows that efficient removal of ammonia and manganese in a filter with new media starts at approximately the same time. This is in agreement with suggestions of other researchers that ammonium is hindering manganese oxidation due to the low redox potential of the groundwater (Scherer and Wichmann, 2000). As a consequence, higher concentrations of ammonium (>2 mg/l NH_4) in (raw) groundwater could hinder efficient and complete manganese removal in conventional one stage aeration-filtration systems (Gouzines et al, 1998). Results emerging from this study, in general, support this conclusion. The highest concentration of ammonium in the raw groundwater treated in a single aeration filtration stage at which complete manganese removal was achieved (>99.5 % Mn removal) was 2.0 mg/l NH_4. PCA conducted with data from all the plants included in this study confirmed strong positive correlation between ammonium concentration in raw groundwater and manganese removal efficiency (Table 1).

Analysis of data collected in this study confirmed that for effective manganese removal the pH should in general be above 7.0. Collected data also show that under certain conditions (e.g. iron load of <1.5 kg Fe/m^2, rather low filtration rate of about 6 m/h, and EBCT of >20 min), very effective manganese removal could be achieved even at pH below 7.

Analysis of the data collected for this study also suggests that another limitation for proper manganese removal in practice is a high iron load on the filter media. At an iron load exceeding approximately 2.7 kg Fe/m^2 of filter media, the manganese removal efficiency was significantly reduced (Fig. 3). None of the treatment plants included in this study, with an iron load above 2.7 kg/m^2, achieved complete manganese removal.

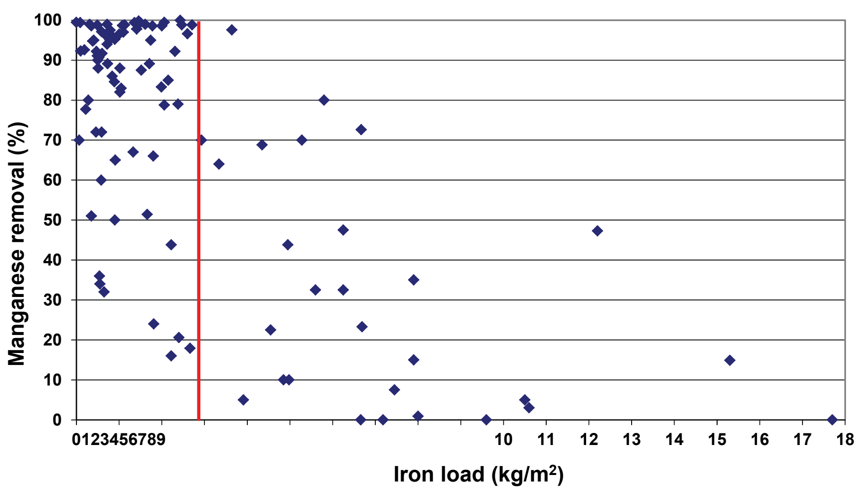

Figure 3: Effect of iron load (kg/m^2) on manganese removal efficiency (Bruins et al, 2011a).

Results from treatment plants included in this study also show that complete manganese removal was not achieved at any plant that operates at a filtration rate above 10.5 m/h. Furthermore, results collected show that an EBCT of above 11.5 minutes is required to obtain complete manganese removal. As a consequence, filter bed height of approximately 2 meters will support effective manganese removal, even though complete manganese removal was obtained at some plants having a bed height of only 1 meter. It should be mentioned that in this case other critical parameters for manganese removal were optimal (high pH, very low iron load, no or low ammonium concentration in raw water, low filtration rate and long EBCT).

In Table 1 an overview of the statistical correlation between all of the parameters involved in this study and manganese removal is given. A poor statistical correlation does not necessarily mean that a parameter has no influence on manganese removal. For example, the correlation between oxygen in filtrate and manganese removal is very poor, but manganese removal will always be negatively affected when there is no or only small concentrations (<1 mg/l) of oxygen available in the water. Lack of oxygen instigates a reducing environment and as a consequence manganese oxidation cannot take place. Moreover, already formed manganese oxides are expected to leach Mn^{2+}. For efficient manganese removal sufficient oxygen concentrations should therefore be ensured, which can be achieved by different types of aeration (e.g., spraying, tower aeration, cascade).

Table 1: Statistical correlation between manganese removal and other parameters.

Parameter			**Correlation with Mn removal**
Process conditions	Filtration rate	(m/h)	-0.5046
	Bed height	(m)	-0.2859
	EBCT	(min)	0.3349
	Fe load	(kg/m^3)	-0.6308
	Fe load	(kg/m^2)	-0.6861
Raw water	$c(Mn^{2+})$	(mg/L)	-0.0362
	$c(Fe^{2+})$	(mg/L)	-0.5527
	$c(NH_4^+)$	(mg/L)	0.0354
	$c(HCO_3^-)$	(mg/L)	0.3167
	$c(Ca^{2+})$	(mg/L)	0.3159
	$c(PO_4^{3-})$	(mg/L)	-0.2469
	$c(SiO_2)$	(mg/L)	-0.3732
	DOC/TOC	(mg/L)	0.0483
Filtrate	$c(NH_4^+)$	(mg/L)	-0.2018
	NH_4^+ removal	(%)	0.8617
	pH	(-)	0.6164

Concentration of ammonium in raw water is another example of a parameter that is statistically poorly correlated to, yet has a remarkable influence on, manganese removal. Based on the study presented no complete removal of manganese can be achieved at ammonium concentrations above 2 mg/l. If this is the case, in traditional "wet" aeration-filtration systems oxygen can become a limiting factor. If "dry" aeration-filtration is used, higher amounts of ammonium can be oxidised. In this study it was found that even more than 5 mg/l NH_4 could be oxidised in a single filter.

CONCLUSIONS

From this inventory of water treatment plants in practice it was concluded that manganese removal in (first) filter stages, combined with the removal of iron and ammonium, is influenced by several parameters. These include both, water quality matrix, as well as operational design parameters.

In general and with respect to the results emerging from this study, complete manganese removal can always be achieved in the first filter stage of a traditional aeration-filtration treatment plant by meeting all of the following conditions:

- pH filtrate : > 7;
- iron load : < 2.7 kg Fe/m^2;
- filtration rate : < 10.5 m/h;
- EBCT : > 11.5 min;
- filter media bed height : 2 m;
- NH_4 in raw water : < 2 mg/l;
- oxygen in filtrate : > 1 mg/l.

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Notes:

EXTENDED ABSTRACT

SUBSURFACE IRON AND ARSENIC REMOVAL FOR DRINKING WATER PRODUCTION: INFLUENCE OF THE MULTI-COMPONENT GROUNDWATER MATRIX

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INTRODUCTION

Subsurface iron removal, or in-situ iron removal, is an established treatment technology to remove iron from groundwater. In Europe, numerous drinking water supply companies are operating (some of) their production wells with this technology (Hallberg and Martinell, 1976; Mettler, 2002; Rott et al., 2002; van Beek, 1985). The principle of subsurface iron removal is that aerated water is periodically injected into an anoxic aquifer through a tube well (Figure 1a), partially displacing the original groundwater. Based on the large surface area of iron hydroxides on the soil grains in the subsurface, it is thought that the heterogeneous reaction of Fe^{2+} oxidation on the surface of iron hydroxides is dominant during subsurface iron removal. In literature, the system's efficacy is explained by adsorptive-catalytic oxidation (Rott and Friedle 1985; van Beek, 1985), where adsorbed Fe^{2+} is oxidized to form new adsorption sites. On its way into the aquifer, the injected oxygen-rich water oxidizes adsorbed Fe^{2+}, creating a subsurface oxidation zone:

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \tag{1}$$

When heterogeneous ferrous iron oxidation is complete, the iron hydroxide surface is regenerated for adsorption of Fe^{2+} during abstraction (Figure 1b):

$$\equiv Fe(III)OH + M^{2+} \rightarrow \equiv Fe(III)OM^+ + H^+ \tag{2}$$

With "≡" being the iron hydroxide surface and M the adsorbing iron cation. Once the iron (oxy) hydroxide surface is exhausted, no more Fe^{2+} is adsorbed and iron breakthrough is observed in the produced water. Hence, during abstraction the iron front is retarded and more iron-free water can be produced than was injected. Every period of injection-abstraction is referred to as a cycle, with the first injection-abstraction period being cycle 1. More water with reduced iron concentrations can be abstracted (volume V) than was injected (volume VI), i.e., this volumetric ratio (V/VI) determines the efficiency of the system.

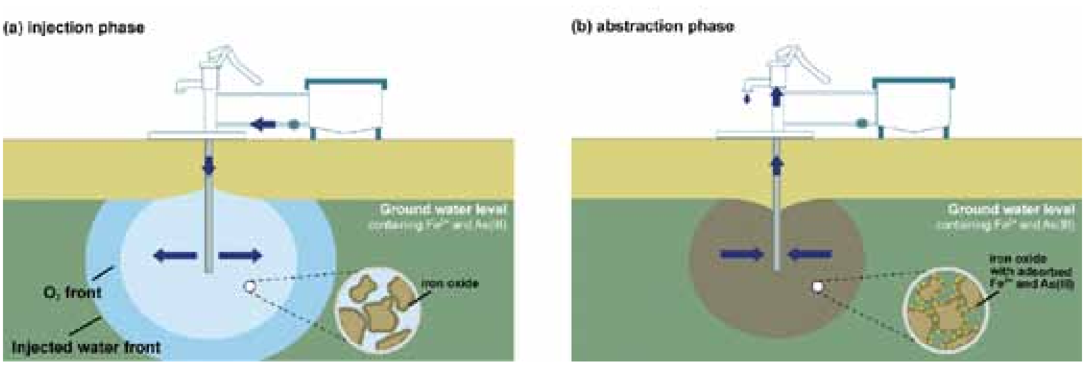

Figure 1: Principle of small-scale subsurface iron and arsenic removal (a) injection and (b) abstraction phase

In Bangladesh, elevated iron and arsenic concentrations have been found to often co-occur in anoxic and anaerobic groundwater (Nickson et al., 2000). Subsurface Arsenic Removal (SAR; van Halem et al., 2010) relies greatly on the iron removal processes, as precipitated iron hydroxides form adsorptive surfaces for the arsenic (Dixit and Hering, 2003):

As(III):
$$S-OH + H_3AsO_3 \rightarrow S-H_2AsO_3 + H_2O \quad (3)$$

As(V):
$$S-OH + H_2AsO_4^- \rightarrow S-HAsO_4^- + H_2O$$
$$S-OH + HAsO_4^{-2} \rightarrow S-AsO_4^{-2} + H_2O \quad (4a, 4b)$$

In literature, a reduction of arsenic concentrations with SAR from a maximum of 40 µg.L-1 to below the WHO guideline (10 µg.L-1) has been reported after the injection of aerated water into the aquifer (Rott et al. 2002; Appelo and De Vet, 2003). In Bangladesh, subsurface removal of higher arsenic levels was investigated by Sarkar and Rahman (2001), namely, 500 - 1300 µg.L-1. In that study concentrations as low as 10 µg.L-1 were not reached, nevertheless, more than 50% removal was observed. A similar initiative can be found on the Indian side of the border in the Bangal Delta, with reportedly removal of arsenic to below the WHO guideline at six community scale SAR plants (Sen Gupta, 2009). Although these results are promising, very little is known about the limitations of this technology in the diverse geochemical settings of Bangladesh. The objective of this study was to investigate the effect of different inorganic groundwater compounds, including phosphate, silicate, nitrate, calcium and manganese, on Fe^{2+} and As(III) removal during SIR/SAR. These commonly occurring inorganic compounds may limit or enhance Fe^{2+} or As(III) removal and greatly determine the effectiveness of SIR/SAR in site-specific geochemical conditions. In order to isolate the compounds of interest, injection-abstraction cycles of SIR/SAR were simulated in the laboratory with synthetic groundwater in sand columns.

MATERIALS AND METHODS

The experimental set-up consisted of duplicate transparent PVC columns with a length of 30cm and an inner diameter of 36mm (wall thickness 2mm). During all experiments, the columns were wrapped in aluminium foil to exclude light. The columns were filled with washed (24h with 5M HCl) filter sand (500g; grain size = 0.6-1.2mm). The push-pull operational mode of injection-abstraction was simulated in the 1D plug-flow environment of the columns with down flow for injection and up flow abstraction (1.1 L.h-1 ±0.05). An injection-abstraction cycle started with 14 (±0.5) pore volumes of injection water, to allow for complete breakthrough of dissolved O_2. Subsequently the influent was switched to groundwater to allow retention of Fe^{2+} and As(III). The abstraction phase consisted of synthetic groundwater with pH 6.9 (±0.02), a temperature of 20°C (±0.1), 0.1mM Fe^{2+}, 2.7uM As(III), pH buffer (5mM $NaHCO_3$), ionic strength buffer (1.6mM NaCl) and additionally the inorganic compound of interest (phosphate, silicate, nitrate, calcium or manganese). The chemicals (reagent grade, Sigma-Alldrich) were dosed as $FeSO_4.7H_2O$, $FeCl_2$, $NaAsO_2$, $NaHCO_3$, NaCl, Na_2PO_4, $Na_2SO_3.5H_2O$, $NaNO_3$, $Ca(NO_3)_2.4H_2O$ and $MnSO_4.H_2O$. The synthetic groundwater was produced by sprinkling demineralized water on a 6m O_2 stripping column containing stainless steel Pall Rings. From the bottom, pure N_2 was blown into the stripping column to sparge out all O2. Before entering the sand columns, the water was checked for O_2 with the Orbisphere (HACH Lange; M1100 Sensor; 410 Analyser) to ensure concentrations below 0.05mg.L-1. Addition of stock solutions was done with a dosing pump followed by a static mixer. pH correction was achieved by addition of HCl or NaOH and all stock solutions were sparged with N_2 in order to ensure the absence of O_2. Iron analysis of the water samples was done with an Atomic Absorption Spectrometer (Perkin-Elmer Flame AAS 3110). Arsenic analysis was performed with Graphite Furnace Atomic Absorption Spectrometer (Perkin-Elmer 5100PC) with an electrode discharge lamp (EDL) and a $Ni(NO_3)_2.6H_2O$ matrix modifier. In-line measurements were done for dissolved oxygen (Orbisphere and WTW Cellox 325), Eh potential (WTW SenTix ORP), pH (WTW SenTix 41), and electrical conductivity (WTW TetraCon 325). Measurements were registered on a computer with Multilab Pilot v5.06 software.

RESULTS

Fe^{2+}-As(III) O_2 system

The measurements in Figure 2a illustrate that once abstraction has started, first the tracer passed the column (electrical conductivity), with a C/C0 at 1 pore volume. The initial oxygen concentration of 0.28mM was pushed out of the column and reached <0.01mM after 5.5 pore volumes. The retardation of Fe breakthrough compared to the tracer simulates the delay of Fe front arrival at the well compared to the injection water front. In the experiments, Fe^{2+} is allowed to breakthrough, in order to calculate the dimensionless retardation factor R. R_{Fe} is calculated from a Vi corresponding to the pore volume when the tracer (electrical conductivity) is C/C_0 = 0.5, and V is the number of pore volumes that can be abstracted with iron concentrations below $[C/C_0]$Fe=0.5. The reference injection-abstraction cycles in Figure 2a show a R_{Fe} of 43, meaning that 43 times more water with [Fe]<0.5C0 can be abstracted than was injected. Figure 2b shows that if no Fe^{2+} was present in the groundwater and column, the As(III) removal was limited to several pore volumes (R_{As}=2-3). In the presence of Fe^{2+}, the As(III) removal is much larger, with an As retardation factor of 30. Clearly, the presence of Fe^{2+} in the changing redox conditions in the column improved As(III) retention through processes of Fe^{2+} oxidation-precipitation and adsorption.

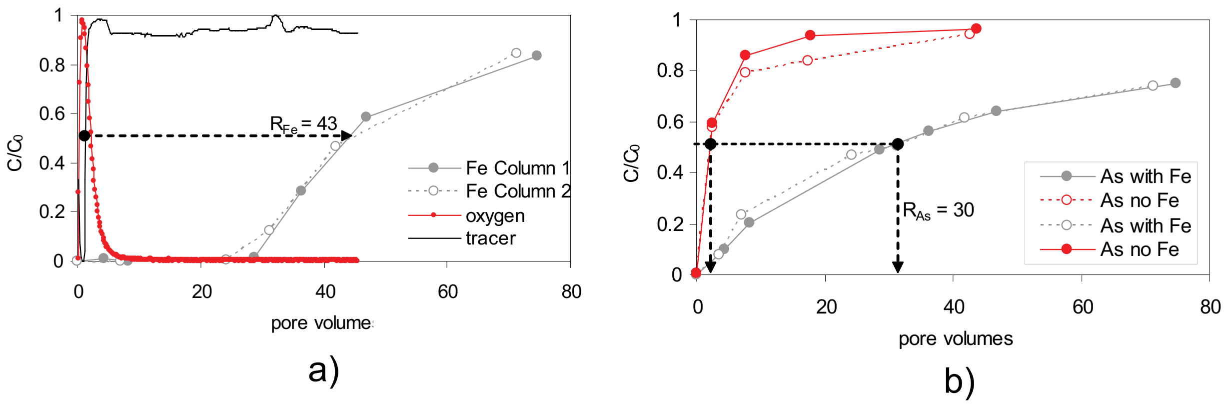

Figure 2: (a) Behavior of O_2, tracer and Fe^{2+} during the reference injection-abstraction cycles, and (b) Behavior of As(III) during the reference injection-abstraction cycles with and without 0.1mM Fe^{2+}

Addition of other inorganic compounds

The effect of phosphate on the removal of As(III) during subsurface arsenic removal is two-fold, namely through (i) Fe^{2+} oxidation-precipitation and (ii) competitive adsorption. Competitive adsorption between As(III) and PO_4 onto iron oxides has been studied in detail (Ciardelli et al., 2008; Stachowicz, 2007), making PO_4 the most important competing anion for arsenic. As(III) behaviour during oxidation and precipitation of soluble Fe^{2+} was studied by Ciardelli et al. (2008), reporting a As(III) removal reduction from 73% to 63% in the presence of 2 mg PO_4-P/L at pH 7.2. The combination of its ability to occupy the same adsorption sites as arsenic and its elevated concentrations compared to trace amount of arsenic makes PO4 a strong competitor in natural waters. This observation correlates well with the results from the column experiments (Figure 3), showing that As retardation was reduced from 30 to 6 in the presence of 0.01 mM PO_4. The effect of silicate, nitrate, calcium and manganese on Fe and As retardation during injection-abstraction cycles are summarized in Figure 3 and will be discussed in detail in the full paper.

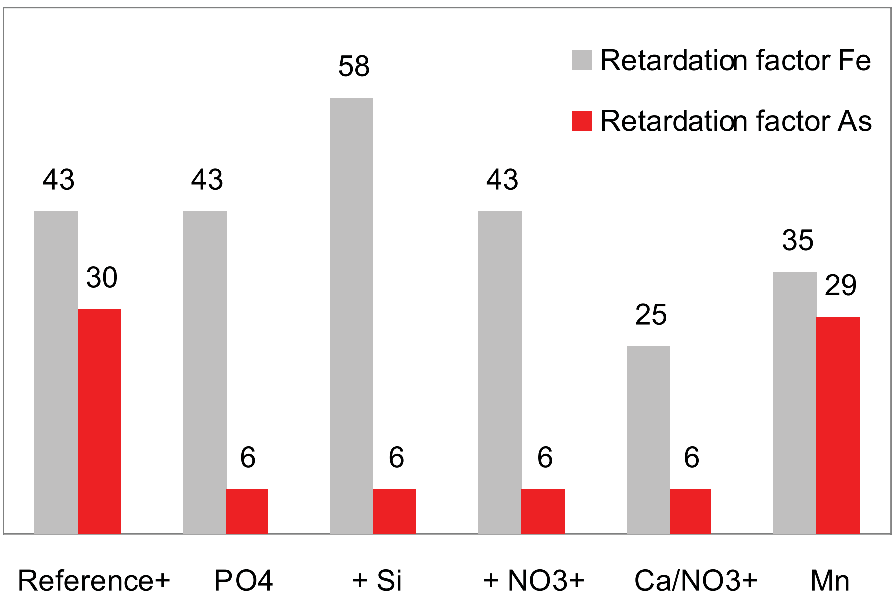

Figure 3: As and Fe retardation factors for the reference cycles and after addition of phosphate, silicate, nitrate, calcium or manganese

CONCLUSIONS

It was found that during injection-abstraction cycles in the Fe2+-As(III)-O2 column system it was possible to reach very effective iron and arsenic retardation, though arsenic breakthrough started immediately upon abstraction. Arsenic removal was found to be seriously inhibited by the presence of phosphate, silicate, and nitrate, illustrating the vulnerability of this Subsurface Arsenic Removal in diverse geochemical settings. Subsurface Iron Removal was found not be as sensitive to other inorganic groundwater compounds, though iron retardation was slightly limited by calcium and manganese.

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Notes:

Extended Abstract

FLUORIDE OCCURRENCE IN GROUNDWATER IN THE NORTHERN REGION OF GHANA

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Keywords: Groundwater, Fluoride, Ghana, Piper classification diagram, Principal component analysis, Geochemistry.

INTRODUCTION

Due to its many advantages, groundwater has become the major source for potable water supply in rural communities in Ghana. Consequently, over 90% of rural domestic water requirements in the Northern Region of Ghana is met from groundwater sources (Gyau-Boakye and Dapaah-Siakwan, 2000; CWAS-NR, 2007). The presence of fluoride in groundwater beyond the 1.5mg/L WHO guideline value has, however, resulted in the closure of many otherwise successful boreholes for consumption in the region, in order to avoid the incidence of fluorosis (WHO, 2008).

Fluoride is known to have both beneficial and detrimental effects on human health (Fawell et al., 2006; Karro et al., 2006; Gao et al., 2007; Biswsa et al. 2007; Chae et al., 2007; WHO, 2008). Ingestion of low concentrations of fluoride (about 1mg/L) in drinking water can prevent the incidence of dental caries. Intake of excess fluoride for long periods can, however, result in the incidence of dental and skeletal fluorosis, as well as other adverse health effects including growth retardation, changes in DNA structure, lowering of IQ of children and even death when doses reach very high levels (about 250mg/L) (Apambire et al., 1997; Shormer et al., 2004; Brunt et al., 2004; Fawell el al., 2006; Meenakshi et al., 2006; Reddy et al., 2010; Currell at al., 2011).

A limited fluorosis survey conducted in six selected communities in the eastern corridor of the Northern Region of Ghana, where the presence of high fluoride in groundwater is most prominent, revealed the incidence of dental fluorosis (Ayugane, 2008). The prevalence rate in some of the communities was found to be as high as 61%. The severe type of dental fluorosis and the possible emergence of skeletal fluorosis were also observed.

Fluoride occurs practically in almost all natural groundwaters, in varying concentrations from trace to as high as 2800mg/L in environments such as the Soda Lakes of the East African Rift System. The dominant factors that control the concentration of fluoride in natural groundwater include: the geological settings and types of rocks/minerals traversed by groundwater, the solubility of fluorine-bearing minerals in the aquifer matrix and the amount of leachable fluorine they contain, the anion exchange capacity of aquifer materials (OH- for F-), the chemical composition of the traversing water and its contact time or reaction time with fluorine-bearing materials. The climatic conditions of an area of interest also have an influence on the fluoride concentration of the groundwater (Apambire et al., 1997; Hurtado et al., 2000; Brunt et al., 2004; Biswas et al., 2007).

Several minerals (over 150) are known to contain fluorine. The most common include fluorite (CaF_2), fluoroapatite ($Ca_{10}(PO_4)_6F_2$), villianmite (NaF), the micas including muscovite ($KAl_2(Si_{23}AlK(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$) and biotite ($K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$), the amphiboles such as hornblende ($NaCa_2(Mg,Fe)O_{10}(OH,F)_2$ and also rock phosphate. Clay minerals such as illite, chlorite and smectites also represent excellent anion exchange media that can contribute to fluoride enrichment of groundwater (Frencken et al., 1992; Apambire et al.,1997; Brunt et al., 2004; Weinstein & Davison, 2004). Due to its favorable dissolution properties, fluorite seems to be the main mineral that predominantly controls aqueous fluoride geochemistry in most environments (Apambire et al., 1998; Weinstein & Davison, 2004; Mamatha et al., 2010). Fluoride contamination of groundwater could also result from anthropogenic sources such as application of phosphatic fertilizers, processing of phosphatic raw materials and use of clays in ceramic industries (Frencken, 1992; Brunt et al., 2004; Naani et al., 2008).

Even though groundwater remains the most important source for rural water supply in the Northern Region of Ghana, little is known about the natural and/or anthropogenic factors that control the groundwater chemistry, hence the groundwater quality and fluoride contamination. The aim of this paper is to study the groundwater chemistry in the region with focus on the occurrence and genesis of high fluoride waters in the eastern corridor of the region. The Piper graphical classification and principal component analysis (PCA) were used as approaches to gain an insight into the groundwater chemical composition and the dominant mechanisms influencing the occurrence of high fluoride waters. PCA allows large amounts of multidimensional groundwater quality data to be condensed into a lower dimensional format, and can provide valuable insight into the underlying hydrogeochemical and/or anthropogenic processes influencing the ground water quality within an aquifer system. In hydrochemical applications, principal components (PCs) resulting from the PCA technique can be interpreted in terms of geochemical processes such as water-rock interactions, by examining the loadings of the original chemical parameters on each of the PCs (Vlassopoulos, 2009).

MATERIALS AND METHODS

The study area: The eastern corridor of the Northern Region of Ghana, the study area, is located between latitudes 9° 0″ and 10° 30″ N and longitudes 1°0W and 1°0″ E. It comprises eleven administrative districts (West Mamprusi, East Mamprusi, Bunkpurugu-Yunyo, Gushegu,Karaga, Saboba/Cheriponi, Zabzugu Tatale, Yendi, Nanumba North and Nanumba South) and covers an area of about 27,900 km^2 with a population of some 1,150,000. The climate of the area is classified as semi-arid (Asiamah et al., 1997; WRC, 2006).

The area is underlain by Neoproterozoic to Palaeozoic sedimentary rocks, locally referred to as the Voltain sedimentary formation. The Voltain sediments consist mainly of sandstones but also include shale, mudstone, arkoses, grey wackes and siltstones. Some limestone, conglomerates and evaporates also occur in the formation. The sediments originated mainly from a glacial event followed by prolonged marine incursions (Junner and Hirst, 1946; Kesse, 1985; Acheampong and Hess,1998; WRC, 2006). The mineralogy of the Voltain sediments is found to include sodic plagioclase feldspars, quartz with minor chlorite, calcite, talc, K-feldspar, ziolite, saponite, some micas and clay minerals such as Na-montmorillonite (Acheampong and Hess,1998; WRC, 2006; Yidana, 2010). The main minerals found in the limestones and dolomites are Ca- and Mg-carbonates. These carbonate minerals are also found in sandstones and clays, either as accessory minerals or as cement around the inert grains (Freeze and Cherry, 1997; Appelo and Potmas, 2005). Groundwater occurrence and flow in the formation is mainly controlled by the presence of secondary permeability and along bedding plains, due to the loss of primary porosity (Gill, 1969; WRC, 2006; Yidana, 2011).

Methods: More than 350 groundwater samples taken from boreholes drilled in about 300 villages in the study area, were analysed for Na, K, Ca, Mg, SO_4, pH, Temp (0C), electrical conductivity (EC), total dissolved solids (TDS), HCO_3, Cl, NO_3, F and total hardness, using standard methods. Unstable hydrochemical parameters such as EC, pH, and alkalinity were measured in situ immediately after collection of samples. At each borehole site, groundwater was pumped for more than 10 minutes prior to sampling in order to get a representative sample. The statistical software package SPSS 18.0 was used for calculation of basic descriptive statistics and for multivariate (PCA) statistical analysis. The number of PCs considered from the PCA were determined on the basis of the Kaiser criterion of the eigen values greater than or equal to 1(Kaiser, 1960) and from a Cattel scree plot (Cattel, 1966). The variamax orthogonal rotation was used in order to facilitate the PCA interpretation. The ground water samples were plotted on the Piper diagram for classification using the GW Chart software.

RESULTS AND DISCUSSIONS

Table 1 shows the mean concentrations of the major groundwater constituents, as well as pH, TDS, temp and F. The concentration of fluoride in samples ranged from 0.0 to 11.6 mg/L with a mean value of 1.2 mg/L. About 23% of the samples were found to have fluoride concentrations exceeding 1.5 mg/L, the WHO guideline for drinking water. The percentage of the fluoride contaminated wells suggests that about 24,000 people in the study area could be at risk of the incidence of fluorosis, if water from the affected boreholes is used for human consumption. About 52% were within the acceptable limit of 0.5-1.5 mg/L while 25% were found to have fluoride concentrations below the minimum standard of 0.5mg/L, which is required for the prevention of dental caries. The total dissolved solids (TDS) of the groundwater samples in the area also ranged from 8.0 mg/L to 3373 mg/l, with a mean value of 396 mg/L. Ninety six percent of groundwater samples were found to be fresh (TDS <1000mg/L) and 4% were found to be brackish water (1000 mg/L > TDS < 10,000 mg/L)(Hounslow, 1995). The groundwater temperature ranged from 30ºC to 34ºC, with a mean value of 31ºC.

Table 1: Mean concentrations of major constituents in groundwater samples from the Northern Region.

Parameter	pH	TDS	Temp	F	HCO_3	Ca	Mg	Na	K	Cl	SO_4
Mean concentration(mg/L)	7.8	395	31	1.2	349	319	15	1218	3	498	42
	±.55	±286	±0.8	±1.3	±181	±40.3	±18.6	±98.8	±4.5	±121	±204.9

Groundwater types

Groundwater quality data from samples taken in the study area were plotted on the Piper Trillinear diagram for classification, based on their positions on the diagram (Fig. 1) (Hounslow, 1995). The water samples were observed to plot in all the zones of the anion plot field (triangle on the right). The majority of the samples, however, clustered towards the HCO_3^- corner, indicating the predominance of the anion in the area. Similarly the samples were observed to plot in all the zones of the cation plot field (triangle on the left), with the majority clustering towards the $Na^+ + K^+$ corner.

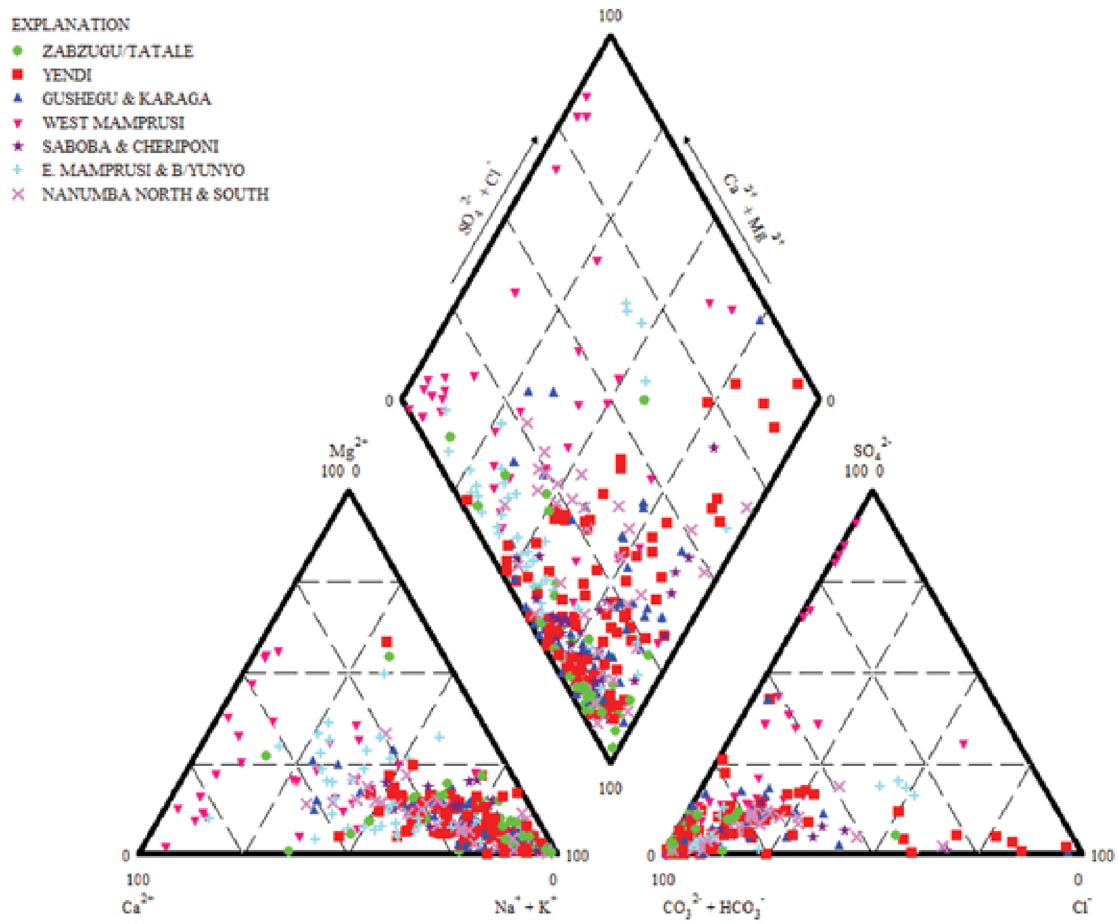

Figure 1: Piper diagram showing the chemical character of groundwater in the eastern corridor of the Northern Region of Ghana.

Based on the plots on the central diamond, the water types found in the area are: Ca-Mg-HCO_3, Ca-Mg-SO_4, Na-Cl, Na-SO_4, Na-HCO_3 and mixed water type (that is groundwaters in which none of the ions is dominant).

Principal components

In this study, PCA performed on the groundwater quality data reduced the dimensionality from the 13 original physico-chemical parameters determined in more than 350 groundwater samples, to 4 principal components, which cumulatively explained 72% of the data variability. Table 1 shows the principal components (PCs), the loadings (weightings) and the percentage variance explained by each PC.

Looking at the loadings within the individual components (Table 1), it is observed that the first component (PC1) shows strong relationships with Mg, Ca, SO_4 and total hardness. The dominance of these chemical parameters may be a reflection of the dissolutions of gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$) and dolomite ($CaMg(CO_3)_2$ found in the sediments in the study area with evaporate deposits. The second component (PC2) is mainly dominated by high positive loadings for EC, TDS, Na and Cl. PC2 likely represents a combination of processes, including the dissolution of halite (NaCl), found in the evaporates and high rates of evapo-transpiration typical of arid climates, which concentrates groundwater constituents, resulting in increased TDS.

Table 3: Principal components, loadings and percentage variance explained

Groundwater chemical parameter	Principal components			
	PC1	PC2	PC3	PC4
pH	-.235	.113	**.393**	**.612**
EC	.436	**.847**	.158	.072
TDS	.476	**.826**	.145	.048
Tot.hard.	**.937**	.098	.059	-.071
NO_3	-.068	-.086	**-.618**	.214
HCO_3	.111	.102	**.753**	.112
Ca	**.737**	.197	.000	-.091
Mg	**.898**	-.023	.118	.015
Na	.217	**.827**	**.310**	.164
K	.103	.011	-.336	**.785**
Cl	-.030	**.850**	-.323	-.050
SO_4	**.863**	.154	.018	.069
F	**-.229**	**.475**	**.227**	-.038
% Variance explained	**28**	**24**	**12**	**6**
Cumulative % of variance explained	**28**	**52**	**63**	**72**

PC3 is also characterized by positive loadings of Na, HCO_3 and pH, and a negative loading for NO_3. The chemical parameters dominating this component suggest dissolution reactions involving carbonate and silicate minerals, cation exchange processes involving Na-montmorillonite, as well as evapo-transpiration processes. The dissolution of carbonate minerals such as calcite and dolomite may result in the predominance of calcium, magnesium and bi-carbonate ions. The replacement of calcium and magnesium ions in the water by sodium ions from the aquifer matrix through cation exchange processes, may result in increased sodium ion concentration in the groundwater (Freeze and Cherry, 1979; Adams et al., 2001; Guo et al., 2007; Reddy, 2010; Mamatha, 2010). The dissolution of sodic plagioclase feldspars that occurs in the Voltain sediments, may also be a mechanism contributing to the sodium ions in the groundwater (Freeze and Cherry, 1979; Hounslow, 1995; Acheampong and Hess, 1998; Reddy, 2010). The positive loading of pH on PC3 may be a reflection of the consumption of protons in the mineral dissolution reactions and the loss of CO_2 from the groundwater due to the evapo-transpiration processes, both processes contributing to increased pH. The negative loading for NO_3 possibly indicates an absence of contamination of the groundwater from anthropogenic activities. The fourth component (PC4) is mainly influenced by K and pH. The predominant processes represented by PC4 , may be a reflection of the importance of weathering reactions involving silicate minerals, possibly K-feldspar which is reported as occurring in the Voltain sediments (Acheampong and Hess, 1998), as well as degassing of CO_2 from the groundwater due to evapo-transpiration processes. These processes results in increased potassium ions concentration and pH.

Genesis of high fluoride groundwaters in the eastern corridor of the Northern Region.

The presence of fluoride ions up to a concentration of 11.6 mg/L in the groundwater samples suggests that favorable conditions exist for the dissolution of fluorine- bearing minerals present in the study area, as well as other processes which contribute to fluoride enrichment. Typical sedimentary rocks including sandstones, shales, clays, limestone and evaporates, such as those underlying the study area, are known to contain fluorine in the range of 50 to 1000mg/L. The fluorine may be present as fluorite (CaF_2) in the carbonate rocks and evaporates may also be found in micas in the clays (Frencken et al., 1992; Brunt et al., 2004; Mamatha, 2010). A review of the PCA results highlights the following with regards to fluoride loading on the PCs:

1. fluoride has positive loadings on PC2 and PC3 which are dominated by Na, Cl, HCO_3 and pH;
2. fluoride shows a negative relationship with PC1 which is characterized by calcium and magnesium ions;
3. fluoride shows an opposite relationship with NO_3 as indicated by the opposite loadings of these two chemical parameters on PC3.

These observations suggest that the geochemical processes contributing to the concentration of the parameters associated with PC2 and PC3 may also be the processes influencing the enrichment of fluoride in the study area. These include mineral dissolution reactions, ion exchange processes and evapotranspiration processes. Both calcite and fluorite contain calcium, and therefore their solubilities are interdependent. As a result conditions or processes that result in calcite precipitation and the removal of calcium from solution, promote the dissolution of fluorite and the enrichment of fluoride in solution (Appelo and Potmas, 2005; Rafique, 2009; Mamatha, 2010). Thus the processes which result in the predominance of bicarbonate ions and increase in pH, possibly result in the attainment of the saturation limit of calcite and therefore its precipitation, which favors the dissolution of fluorite and fluoride enrichment. Moreover, the Na^+/Ca^{2+} cation exchange processes that may be contributing to the Na^+ concentrations also depletes the Ca^{2+} concentration in the groundwater, which promotes the dissolution of fluorite and a mechanism for F^- mobilization in the area (Brunt et al., 2004; Weinstein & Davison, 2004; Appelo and Potmas, 2005; Mamatha, 2010). The positive loading of fluoride on PC3 also suggests the release of fluoride from mineral surfaces under high pH groundwater conditions (high OH^- content), probably through F^-/OH^+ anion exchange, contributing to the elevated fluoride concentrations in the eastern corridor of the Northern Region of Ghana.

In addition to the interactions between groundwater and fluoride-rich minerals, evapo-transpiration may be another important factor contributing to the occurrence of high fluoride groundwater in the study area. The evapo-transpiration process contributes to an increase in the concentration of calcite ($CaCO_3$) as a consequence of the removal of water from the groundwater system in the process. This may facilitate the attainment of the calcite saturation limit and subsequent precipitation, promoting the dissolution of fluorite and fluoride enrichment of the groundwater. Similarly, the evapo-transpiration process also directly concentrates the fluoride ions due to the loss of water from the groundwater system, resulting in elevated fluoride concentrations. There is probably no contribution from anthropogenic activities to the fluoride enrichment, considering the opposite relationship between fluoride and NO_3 as indicated by the opposite loadings of these two chemical parameters on PC3.

CONCLUSIONS

Groundwater samples from the eastern corridor of the Northern Region of Ghana contained fluoride ions up to a high concentration of 11.6 mg/L. About 23% of the samples were found to have fluoride concentrations exceeding 1.5mg/L, the WHO guideline for drinking water, and can result in the incidence of dental fluorosis if consumed. About 52% were within the acceptable limit of 0.5-1.5 mg/L while 25% were found to have fluoride concentrations below the minimum standard of 0.5mg/L, which is required for the prevention of dental caries. The geochemical processes that control the overall groundwater chemistry in the study area possibly also promote fluoride enrichment of the groundwater. These processes include mineral dissolution reactions, ion exchange processes and evapotranspiration. The predominant mechanisms controlling the fluoride enrichment probably include: calcite precipitation and Na/Ca exchange processes, both of which deplete Ca from the groundwater and promote the dissolution of fluorite, F^-/OH^- anion processes, as well as evapo-transpiration processes which concentrate the fluoride ions and increase their concentration. The results of the current study may help in the planning of strategies for the provision of safe drinking water in both cases of excessive and insufficient fluoride content in the groundwater in the study area.

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Full Paper

FATE OF EMERGING POLLUTANTS IN LLOBREGAT RIVER WATER UNDER CONTROLLED REDOX CONDITIONS: RESULTS OF BATCH EXPERIMENTS AND FIRST RESULTS IN FIELD TEST SITE

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Abstract: Soil Aquifer Treatment (SAT) is a known technique for improving recharge water quality in Managed Aquifer Recharge (MAR) systems. The fate of organic contaminants through SAT is largely controlled by the redox state. The efficiency of these systems regarding the degradation of organic micropollutants was studied in two working scales. Batch experiments including aquifer material were assembled to study the degradation of 9 emerging compounds of the Llobregat river water under different redox isolated conditions. Results for atenolol and carbamazepine are presented in this work as representative examples of all the evaluated compounds. Field scale experimentation is being performed in the Sant Vicenç dels Horts (Barcelona, NE Spain) test site (Barcelona, Spain). First results at the test site show similar removal trends for atenolol and carbamazepine than observed in the laboratory experiments. The recharge system was recently completed with the installation of a horizontal reactive layer (made up of compost, clay and iron oxide) at the surface of the infiltration pond, which is expected to enhance the degradation of selected micropollutants in the coming months.
Keywords: Llobregat river, aquifer artificial recharge, batch experiments, emerging organic micropollutants, reclaimed water, redox conditions, Soil Aquifer Treatment (SAT).

INTRODUCTION

Managed Aquifer Recharge (MAR) is widely used as a technique to increase groundwater resources. Moreover, it has been demonstrated that the unsaturated zone reduces chemical pollution of the recharge water due to physicochemical and biological processes occurring in the vadose zone, with large retention times and chemical changing conditions. All these processes are identified as Soil Aquifer Treatment (SAT) (Dillon, 2005). In the area of the Llobregat Delta Aquifer (Barcelona, NE Spain), different techniques of MAR have been applied, including infiltration ponds (Hernández et al, 2011).

The recent development of analytical techniques has allowed detecting the presence of the so-called "emerging organic micropollutants" in water and soils. Such compounds may affect the living organisms even at ng/L or microg/L concentrations. In wastewater and drinking water plants, a remarkable removal of these chemicals from water can be obtained only by using advanced and costly treatments. Nevertheless, a number of studies are demonstrating that the physical, chemical and biological processes associated with water movement within the subsoil represent a natural alternative treatment to reduce the presence of these contaminants too. Among other factors, the redox conditions of the system seem to affect to a great extent the behaviour and removal of organic contaminants (Lyngkilde and Christensen, 1992). In real aquifer systems, the redox state is usually regulated by the oxidation of a mixture of organic compounds. Cometabolism is likely to control the degradation of the contaminant.

In this context, during 2009 a set of laboratory batch experiments were assembled in order to reproduce biogeochemical conditions present during aquifer recharge and to assess the behaviour and fate of organic micropollutants under different redox conditions. Such knowledge would allow a correct interpretation of field scale results as well as proper design for real field applications. The second phase of this study consists of field experimentation, using a well-known and instrumented recharge site in the Llobregat Delta Aquifer (Barcelona, NE Spain), where micropollutant occurrence and geochemical evolution have been monitored since 2009.

LAB-SCALE EXPERIMENTS: ISOLATION OF REDOX STATES

Methodology

Experimental procedure: Nine organic compounds, which are representative of the main chemical families occurring in the Llobregat river basin waters (Castillo et al., 2000; Céspedes et al., 2005; Muñoz et al., 2009; Rodriguez-Mozaz et al., 2004), were selected for experimentation. Selected pharmaceuticals were diclofenac and ibuprofen (both anti-inflammatory), carbamazepine (antiepileptic), gemfibrozil (lows lipid levels), atenolol (beta blocker drug) and sulfamethoxazole (sulfonamide bacteriostatic antibiotic). Moreover, the two pesticides diuron and simazine were included, as well as estrone, representing the group of estrogens that causes estrogenic activity along the river.

The experimental set up included various sets of microcosms, each one containing natural sediments and synthetic water spiked with the selected organic micropollutants. Sediments were collected from a pit excavated in the bottom of the infiltration pond in Sant Vicenç dels Horts (Barcelona, NE Spain), and were sieved through 1mm sieve. X-ray diffraction (XRD) of powdered samples was used in an attempt to identify the minerals present in the sediment. Results shown presence of quarz, calcite, microcline, albite, dolomite, clinochlore and illite in the aquifer. The synthetic water was prepared based on the chemical composition of the recharge water (Llobregat river water) at the test site.

One different redox state was promoted in each set of batches by developing one specific step of the natural redox sequence for organic matter degradation. To this end, easily degradable organic compounds (sodium acetate and methanol) were provided as electron donors and, depending on the target redox condition, oxygen, NO_3^-, Mn(III/IV), Fe(III) or SO_4^{2-} was added as a specific electron acceptor. Figure 1 shows the reactions promoted in each set of microcosms according to the electron acceptor added. Nitrate and sulphate were added as magnesium nitrate hexahydrate and sodium sulphate, respectively. Mn(III/IV) and Fe(III) oxide-hydroxides were incorporated into the sediment as finely ground natural psilomelane and mixed ferrihydrite/goethite, respectively (Barbieri et al., 2011). To achieve aerobic conditions in the aerobic experiment, O_2(g) was continuously bubbled in the bottles and the concentration of dissolved oxygen was measured in each disassembled bottle using an O_2(g) electrode. In order to ensure the absence of oxygen in the remaining sets of batches, the bottles were assembled in a glove box with Ar atmosphere. Figure 2 shows the scheme of the general assemblage of each bottle. The total amount of electron acceptor was added in excess to complete the mineralization of the organic substrate according to the stoichiometric reactions.

Moreover, an experiment representing the evolution of the system under natural conditions was also carried out. It was assembled without either sodium acetate or any additional specific electron acceptor. As a reference for biological degradation of micropollutants, an abiotic set of experiments was also conducted, adding mercury chloride to the water as a biocide.

		Redox potential
1a 1b	$CH_3OH + 1.5\ O_2(g) \rightarrow CO_{2)}(g) + 2H_2O$ $CH_3COO^- + 2O_2(g) + H^+ \rightarrow 2CO_2(g) + 2H_2O$	**Aerobic respiration**
2a 2b	$CH_3OH + 1.2\ NO_3^- + 0.2\ H^+ \rightarrow HCO_3^- + 0.6\ N_2(g) + 1.6\ H_2O$ $CH_3COO^- + 1.6\ NO_3^- + 0.6\ H^+ \rightarrow 2HCO_3^- + 0.8\ N_2 + 0.8\ H_2O$	**Nitrate Reduction**
3.1a 3.1b 3.2a 3.2b	$CH_3OH + 3\ MnO_2(s) + 5\ H^+ \rightarrow HCO_3^- + 3\ Mn^{2+} + 4\ H_2O$ $CH_3COO^- + 4\ MnO_2(s) + 7\ H^+ \rightarrow 2HCO_3^- + 4\ Mn^{2+} + 4\ H_2O$ $CH_3OH + 6\ MnOOH(s) + 11\ H^+ \rightarrow HCO_3^- + 6\ Mn^{2+} + 10\ H_2O$ $CH_3COO^- + 4\ MnOOH(s) + 15\ H^+ \rightarrow 2HCO_3^- + 8\ Mn^{2+} + 12\ H_2O$	**Mn Reduction**
4a 4b	$CH_3OH + 6\ Fe(OH)_3(s) + 11\ H^+ \rightarrow HCO_3^- + 6\ Fe^{2+} + 16\ H_2O$ $CH_3COO^- + 8\ Fe(OH)_{3)}(s) + 15\ H^+ \rightarrow 2HCO_3^- + 8\ Fe^{2+} + 20\ H_2O$	**Fe Reduction**
5a 5b	$CH_3OH + 0.75\ SO_4^{2-} \rightarrow HCO_3^- + 0.75\ S^{2-} + H_2O + H^+$ $CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	**Sulphate Reduction**

Figure 1: Redox reactions considering CH_3COO^- and CH_3OH as organic substrate.

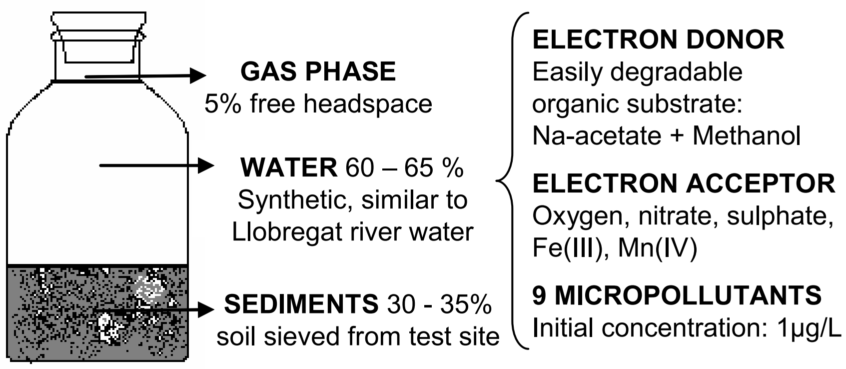

Figure 2: Scheme of the set-up of the microcosms involving synthetic water, natural sediments, electron donor and acceptor, and selected organic micropollutants.

The number of assembled bottles was calculated according to the sampling schedules. Duplicate bottles were sacrificed at each sampling time. Sampling schedules were defined according to the expected degradation rates reported in the literature and estimated from preliminary experiments. Some sampling times were set equal for different experiments to facilitate comparison among them.

Analytical techniques: To have a proper assessment of the hydrogeochemical behaviour of each microcosm, anions (Cl^-, NO_3^-, NO_2^- SO_4^{2-}, PO_4^{3-}, F^-, NH_4^+) were analysed by ion chromatography. Samples for Fe and Mn, Ca, Mg, Na, K and minor elements were analysed by inductively coupled plasma atomic emission spectrometry (IPC-AES). DOC (Dissolved Organic Carbon) was analysed by 680 °C combustion catalytic oxidation/NDIR method using a TOC-V CSH instrument and COD (Chemical Oxygen Demand) was analyzed by colorimetry with the spectrophotometer Spectroquant Nova 60. Target micropollutants were analysed using on-line solid phase extraction-liquid chromatography-tandem mass spectrometry in the CSIC-IDAEA facilities (Barcelona). Quantification was performed by the internal standard method using the corresponding deuterated compounds as surrogate standards.

Results

The analysis of redox sensitive species along the experiments evidenced an overall correct isolation of each redox state. Figure 3A shows the achievement of nitrate-reducing conditions in the respective set of microcosms according to eq. 2a and 2b in Figure 1, corroborated by the concomitant consumption of nitrate and DOC. A peak of intermediate nitrite appeared with a maximum in day 5, but it was totally consumed on the following days. The development of Fe-reduction and Mn-reduction conditions in the respective sets of microcosms were confirmed by an increase of Fe and Mn concentrations accompanied by a consumption of DOC (Figures 3B and 3C) according to eq 3a, 3b, 4a and 4b shown in Figure 1. In fact, in the Fe-reducing experiment the slow dissolution of the natural source of Fe(III) represented the rate limiting mechanism for Fe reduction. Thus, concomitant Fe(III)- and SO_4^-reduction and iron sulphide precipitation (confirmed by the dark colour of the sediments at disassembling) occurred simultaneously during the first 42 days of the experiment. Then, after SO_4 depletion, Fe(III) reducing conditions were likely to be dominating the system. Finally, the achievement of sulphate-reducing conditions according to eq 1 in Figure 1 was corroborated by the decrease of sulphate concentration coupled to a decrease in DOC (Figure 3D). In all experiments a latent period before the beginning of DOC mineralization could be observed, corresponding to the acclimatazion of the microorganisms in each redox state.

Results of atenolol and carbamazepine are presented as representative examples of the nine micropollutants monitored within this study. Figure 4 shows the evolution of atenolol and carbamazepine over time under the different redox conditions. As can be seen, atenolol was successfully removed under all redox states. The initial 50% removal of atenolol occurring within the first 7-10 days in all experiments could be attributed to some abiotic processes, most likely sorption on the sediment grains. By then, some microbial processes were responsible for the remaining 50% removal of atenolol (Barbieri, 2011). Different trends could be observed depending on the experiment. The nitrate reducing experiment was not long enough to compare nitrate reducing conditions with the more reducing systems. Yet, among the rest of experiments, faster atenolol biotic removal was observed under sulphate reduction and natural conditions.

The most effective conditions at removing carbamazepine (with percentage removals around 35%) were SO_4^-reduction and river blank microcosms, for which a quick decrease in the first samplings was observed (Figure 4 Right).According to previous studies (Schmidt et al., 2005), the maximum elimination of carbamazepine in bank filtration occurs in anaerobic conditions, while in aerobic condition the reported elimination was around 0%.

The analysis of some other micropollutants showed complex behaviour. A great variability of degradation trends was observed among the studied organic compounds as well as for the same micropollutant under different redox conditions. However, a common trend was detected: at the end of the experiments, the percentage of removal in blank experiments (natural conditions) overcame the removal for each of the isolated redox conditions. Such results have encouraged further work in field experimentation, presenting SAT as a potential efficient technique for the reduction of the concentration of emerging micropollutants.

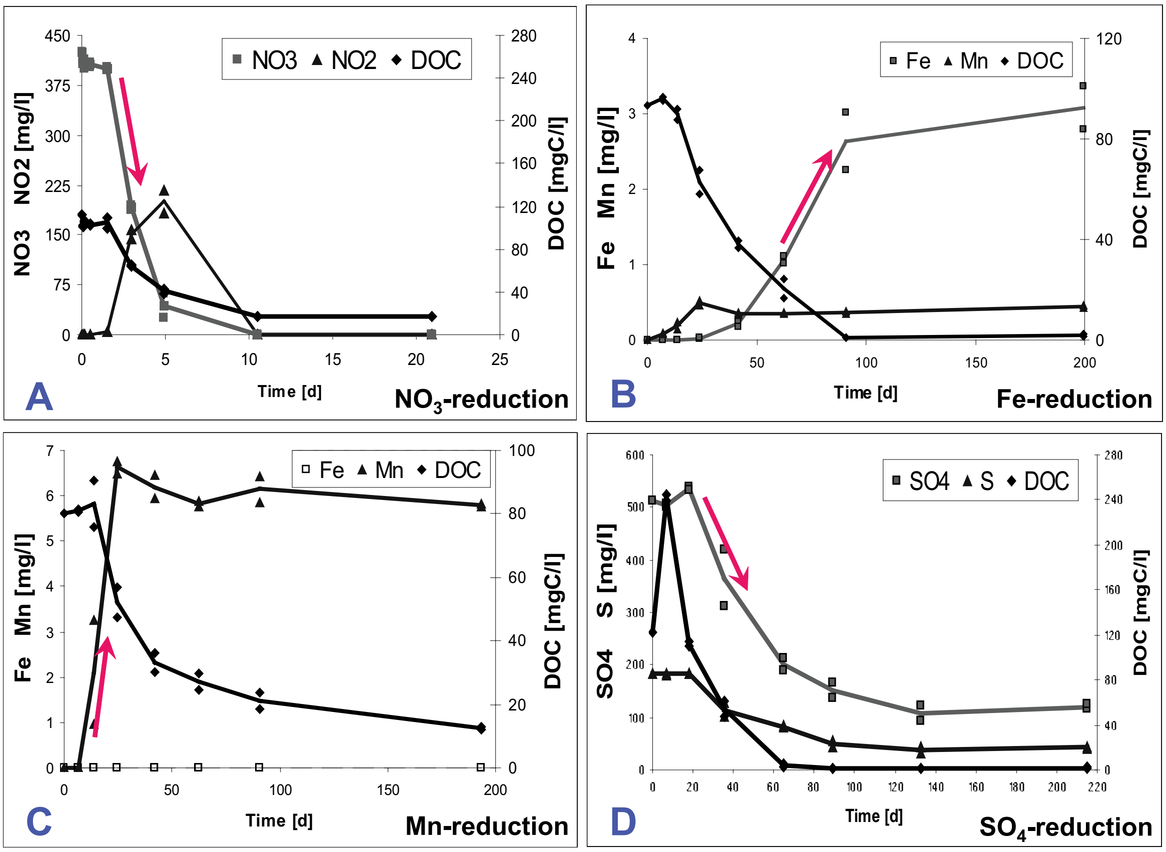

Figure 3: Evolution with time of the redox sensitive species in the nitrate (A), iron (B), manganese (C) and sulphate (D) reducing experiments.

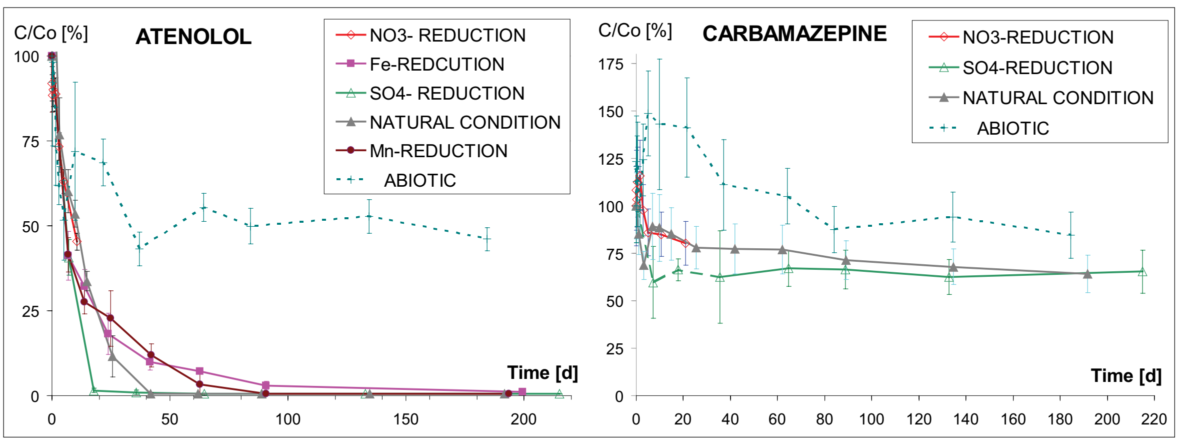

Figure 4: Removal trends for atenolol (A) and carbamazepine (B) under several redox conditions.

FIELD-SCALE EXPERIMENTATION: THE ENSAT PROJECT

Methodology

Experimental site characterisation: The Sant Vicenç dels Horts recharge system (Barcelona, NE Spain) was constructed in 2007. Since then, different research projects have been carried out improving the hydrogeological characterisation of the test site. It consists mainly of one infiltration pond (5,600 m^2) receiving raw water from the Llobregat River. There is simple pre-treatment of decantation in an excavated pond (4,000 m^2), with an estimated residence time of 3 days. The infiltration rate is around 1 m^3/m^2/day, and the unsaturated zone varies between 4 and 10 meters. Organic micropollutants, inorganic chemical compounds and general parameters have been monitored at the site since February 2009.

In 2008 the infiltration pond was equipped with a network of piezometers. Moreover, two instrumented islands were constructed inside the infiltration pond. These concrete structures allow getting water samples from the unsaturated zone below the pond (porous cups are buried 1, 2 and 5 meters deep from the bottom of the pond). Also tensiometers and humidity sensors are continuously monitored to study the response of the system regarding changes in saturation. In 2010 the monitoring network was completed with the drilling of 6 new piezometers and a third island closer to the entry of water into the infiltration pond.

Enhancement of Soil Aquifer Treatment in the Llobregat Delta Aquifer: The ENSAT project (LIFE08 ENV7E00017) aims at the enhancement of the natural remediation behaviour of the infiltration pond in Sant Vicenç dels Horts (Barcelona, NE Spain), with the installation of an organic layer. This layer is intended to provide an extra amount of DOC to the recharge water locally and to promote the development of different redox states along the travel time through the unsaturated zone and in the aquifer.

Analytical methods: Target micropollutants are also analysed using on-line solid phase extraction-liquid chromatography-tandem mass spectrometry in the CSIC-IDAEA facilities (Barcelona). Quantification is performed by the internal standard method using the corresponding deuterated compounds as surrogate standards.

Results

Selection and design of reactive layer: Leaching and column tests were performed during 2010 by CSIC-IDAEA to select the proper substrate to be applied in the field. Finally, a mixture of vegetal compost and natural soil was installed. The layer was enriched with 1% of clay (mixed with the compost before installation) and 0.1% of iron oxide (speeded in the surface of the reactive layer). Both red clay and iron oxide are expected to enhance micropollutant removal through sorption processes.

First results of micropollutants under natural conditions. The selected micropollutants to be studied in the field phase included the same 9 compounds analysed in the previous laboratory phase plus three additional degradation products of some of them (hydroxy simazine, deisopropilatrazine and epoxi carbamazepine).

Preliminary field results confirmed the easy degradation of atenolol and the recalcitrant behaviour of carbamazepine observed in previous laboratory assays.

With regard to atenolol, its concentration was found to decrease as long as recharged water infiltrated down through the subsoil to the aquifer, from an initial concentration between 40 and 50 ng/L in the unsaturated zone (1 and 2 m depth) to 10-30 ng/L in the saturated zone (20 m depth).

In the saturated zone, atenolol was only detected in the piezometers drilled inside the infiltration pond or very close to it downstream. In contrast, carbamazepine was detected in the majority of the sampled points (including several points located upstream of the infiltration pond). The concentration of carbamazepine in the aquifer and vadose zone is very stable, between 15 – 35 ng/L, and the concentration in the river water is in the same range.

Future work

The reactive layer was successfully installed in March 2011, and the infiltration period started in May 2011. Since then, sampling campaigns are being carried out to yield a complete assessment of the hydrochemical changes in the system and check the expected improvement of the removal of the selected organic micropollutants.

The instrumentation of the zone has been improved recently, and the ENSAT project has the objective of enhancing the knowledge of the attenuation processes of these compounds through SAT. The effort should be done in the interpretation of the results that will be obtained in the framework of this project in future months.

CONCLUSIONS

According to the results, the desired redox states were quite successfully created and sustained in each set of laboratory experiments. The outcome of these experiments is the characterisation of the behaviour of the emergent pollutants as a function of the isolated redox condition. The analysis of micropollutants showed a complex behaviour. However, a common trend has been detected: at the end of the experiments, the percentage of removal in blank experiments (natural conditions) overcomes the removal for each of the isolated redox conditions. Such results have encouraged further work in field experimentation, presenting SAT as a potentially efficient technique to remove emerging contaminants.

First results of atenolol and carbamazepine look very promising, because in the experimental site in Sant Vicenç dels Horts (Barcelona, NE Spain) they show similar trends of removal than in the assembled experiments in the laboratory.

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FULL PAPER

WATER QUALITY AS AN INDICATOR OF HYDROGEOLOGICAL CONDITIONS: A CASE STUDY OF THE BELGRADE WATER SOURCE (SAVA/DANUBE CONFLUENCE AREA)

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Abstract: The City of Belgrade receives most of its drinking water supply from the alluvial aquifer of the Sava River. The wells are radial, placed in the lower part of the aquifer, so they partly run below the Sava riverbed. However, the groundwater quality of the wells in one part of the source (near the confluence of the Sava and Danube rivers) was found to differ somewhat from the groundwater quality of the other wells. This gave rise to additional investigations. The results revealed the existence of a deeper, limestone aquifer which is isolated from upper alluvial sediments by a thick layer of clay in most of the terrain. The naturally potential hydraulic contact of the two aquifers was additionally maintained by well operation in this part of the source. According to multiple analyses of groundwater flow using a hydrodynamic mathematical model, a hydrogeological and hydraulic system of groundwater flow was defined in this part of the source. Although the wells are situated adjacent to the river, and some well laterals are below the riverbed, most of the groundwater that flows to the wells is partly from the wider zone of the alluvial aquifer, and partly from the deeper aquifer. At first, the results of hydrochemical investigations showed an unexpected, inverse oxic character of the groundwater in these two aquifers.
Keywords: hydrochemistry, alluvial aquifer, limestone aquifer, geology, Belgrade

INTRODUCTION

The City of Belgrade is situated at the confluence of the Sava and Danube rivers. Drinking water supply is provided by 99 radial wells, from the alluvial aquifer of the Sava River. The entire Belgrade source is characterized by the following hydrochemical parameters: oxygen concentrations about 0.3 mg/L, iron ions about 2 mg/L, oxidation/reduction potential about 110 mV, and ammonium ions about 0.6 mg/L. This represents a poor aerobic to poor anaerobic environment, with low oxygen concentrations and increased iron and ammonium ion concentrations (Dimkić et al., 2011).

However, it was determined that the well water quality in one part of the source (near the confluence of the Sava and Danube rivers) differs from the water quality of the alluvial aquifer. Exploratory boring revealed the existence of limestone sediments below the alluvial aquifer. These two series of sediments are separated by an impermeable clay layer (Fig.1).

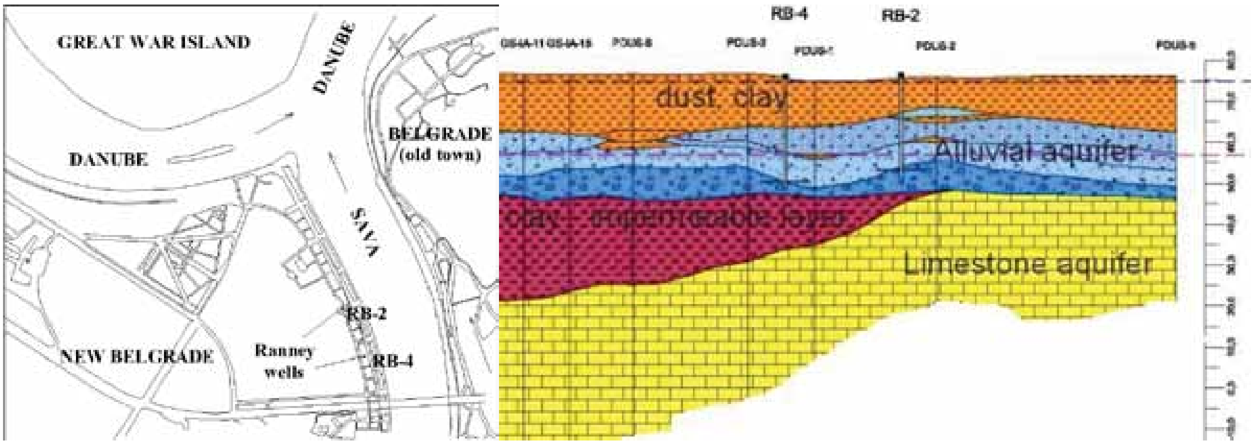

Figure 1: a) A part of the Belgrade source – Sava/ Danube confluence;
b) Lithological section along the left bank of the Sava River.

Contrary to the left bank, limestone sediments are exposed on the ground surface along the right bank of the Sava River ("Old Town" in Fig.1a) and from that point they extend eastward. This area represents the main recharge area for the limestone aquifer.

The role of the Sava River is very interesting in groundwater abstraction in this part of the source. Although the well laterals are placed directly below the riverbed, the results of hydrodynamic investigations and well water quality tests show that the water in the wells does not predominantly originate from the river. Further investigations showed that the well water was a blend of groundwaters from two aquifers.

GEOLOGY AND HYDROGEOLOGY

The geology in the area of the Sava's mouth consists of several members:

- Tertiary sediments, noted on the right bank (limestone, clay and marl). The limestone is of a riverbank nature, cracked and with a characteristic spongy porosity.
- Quaternary sediments, whose lower zone is made up of lacustrine-fluvial formations (gravel, gravel-sandy sediments, clayed in the bottom part), and whose upper zone is represented by alluvial sediments of the Sava River (a sandy-gravel complex with clay lenses).
- The final member is represented by dusty sand and sandy-marsh clay, with occasional peat. Their role is of extreme importance for defining the aerobic character of the alluvial aquifer, because they prevent the ingress of atmospheric oxygen, except in the narrow well zone, where groundwater levels are much lower.

In the hydrogeological sense, in the area along the left and right banks of the Sava River there are two types of aquifers: an aquifer within the alluvial sediments and an aquifer formed in limestone (Geozavod, 2003).

HYDRODYNAMIC MODEL INVESTIGATIONS

A hydrodynamic simulation of groundwater flow in the wider area of this part of the source was used for analysis of the groundwater flow mechanism, and also of the hydrodynamic relationship of these two aquifers. The model, consisting of six schematized layers (Fig.2), represents a complicated mechanism of groundwater flow in this part of the Belgrade source. The two aquifers, each with its own features, are in indirect hydraulic contact and form one hydrodynamic unit. The Sava River, in this part of its course, flows over a fault zone whose hydraulic role in groundwater flow remains unknown for the time being. Based on model tests, it was assumed that some of the river water is in contact with the alluvial aquifer, partly by infiltration through the (considerably) colmated riverbed, and partly through limestone on the right bank, at the very point of the confluence (lacking a clayey interlayer of alluvial and limestone sediments).

Measurements of groundwater levels during operational monitoring of the source and occasional well tests indicated an indisputable hydraulic contact between the two aquifers (Pušić, 2003).

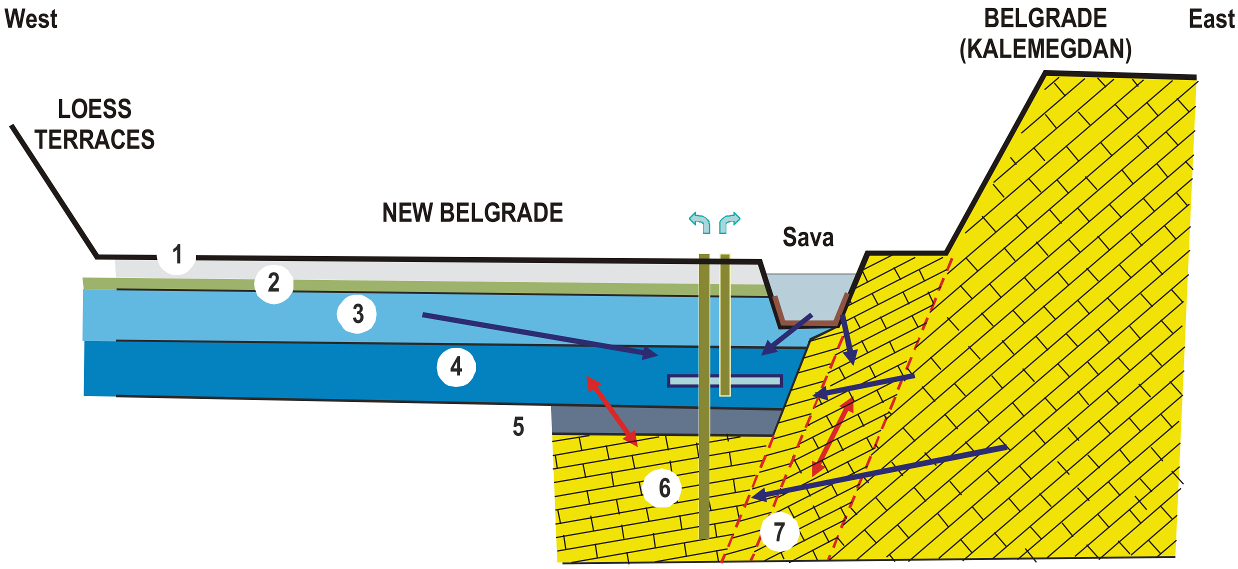

Figure 2: Modeled groundwater flow directions and aquifer layers at the Sava's mouth; Key: 1 – roof, impermeable layer, 2-4 – alluvial aquifer, 5 – clayey interlayer, 6 – limestone aquifer, 7 – fault zone.

Additionally, the results of model tests showed with a high degree of reliability that the aquifer within the limestone sediments extends beyond the riparian zone to the west. This fact is especially favorable given that the limestone in this area is covered by a thick layer of clay and thus very well protected from potential pollution from the ground surface. These results are important because of the possibility to provide additional amounts of groundwater if the city's water demand increases.

GEOCHEMISTRY

The presence of heavy metals in samples of rock material from the alluvion and limestone was determined by geochemical analyses, in order to assess the possibility of transfer of certain toxic elements into the groundwater under favorable oxidation-reduction and acid-base conditions. The analyses encompassed As, Zn, Cd, Al, Fe, Mn, Cr, Pb, Ni, Mo and Sb. The results of these analyses did not reveal an unusual load of toxic chemical elements (As, Cd, Cr, Pb, Ni, Mo, Sb). Characteristic of alluvial sediments in this part of the source were iron (0.42 to 2.58 %) and manganese (105 to 1800 ppm), such that elevated concentrations of these elements may be expected in the groundwater, especially under favorable anaerobic conditions. The concentrations of all toxic elements were much lower in the limestone samples than in the alluvial sediments.

HYDROCHEMISTRY

Hydrochemical investigations encompassed the determination of physical features and chemical and microbiological compositions of both groundwater and river water (Table 1) (Papić and Rakić, 2003). The gray areas in Table 1 show characteristic hydrochemical parameters of the given aquifer. Based on a large number of analyses of groundwater sampled from the alluvial sediments in the area of the Sava's mouth, the water was found to be poorly mineralized (TDS about 450 mg/L) and exhibited slight alkalinity (pH about 7.4). The cation content was dominated by calcium ions, followed by magnesium and potassium. The hydrogeochemical genetic coefficient Ca/Mg (meq) was 1.5 to 2.5, indicating the existence of calcite and dolomite in the sediments. X-ray tests of the alluvial sediments confirmed the presence of dolomite, quartz, calcite and feldspar. Hydrochemical tests (calcium-magnesium type of water) showed the possible presence of dolomite in the alluvial sediments. According to the anion composition, the water is of the hydrocarbonate type, followed by chlorides, characterized by low sulfate and nitrate ion concentrations. As a consequence, the oxidation/reduction potential is low (Eh~40 mV), characterizing a poorly reducing environment, and the concentration of dissolved oxygen is also low. Still, it should be noted that iron (3 to 6.5 mg/L) and manganese (0.56 to 0.9 mg/L) ions occur in high concentrations. This means that the Fe(II)/Fe(III) system determines oxidation/reduction conditions, due to the high concentrations of these elements in the sediments, as already mentioned. Based on the ions of the so-called nitrate triad, the groundwater of this aquifer is characterized by high concentrations of the ammonium ion (5 to 10 mg/L) of organogenic origin, and low concentrations of nitrate ions (1.7 to 4.5 mg/L). Concerning other elements, groundwater sampled from piezometers contained a high concentration of zinc (up to 14.5 mg/L), as a result of the construction material (galvanized pipes). This was not the case with the wells, since they are made of steel. In summary, the investigated groundwater from the alluvial sediments is of the hydrocarbonate-calcium, magnesium type, characterized by elevated concentrations of ammonium, iron and manganese ions, and an increased organic matter content ($KMnO_4$ above 12 mg O_2/L), which occur naturally in these sediments. The selected group of hydrochemical parameters indicates, as in many other water sources in alluvial sediments, the presence of elements-followers (Fe-Mn-NH_4^+) and organic substances. Microbiological analyses determined the presence of Bacillus sp.

Table 1: Selected hydrochemical parameters of groundwater and river water

Aquifer / Parameter	Alluvial		Limestone		Radial well	River
	Piezometer	Well	Piezometer	Well		
TºC	17	13.5	15.7	17	15	
pH	7.4	7.4	8	7.2	7.3	7.5
Eh ,mV	36	38	244	275	188	
O_2, mg/l	0.1	1.5	5.2	3	0.8	5.5
TDS, mg/l	450	400	550	535	430	280
$KMnO_4$, mg/l	14	12.8	6	2	4	5-25
NH_4^+, mg/l	10	5.5	0.1	0.01	0.6-1	0.3-1
NO_2^-, mg/l	0.01	0.01	0.8	0.02	0.02	0.01-0.05

Aquifer / Parameter	Alluvial		Limestone		Radial well	River
	Piezometer	Well	Piezometer	Well		
NO_3^-, mg/l	1.7	4.5	40	40	3 - 25	10
SO_4^{2-} ,mg/l	1.5	2	40	55	25	20
Fe , mg/l	3.1	6.5	0.05	0.02	0.55	0.04
Mn, mg/l	0.56	0.9	0.03	0.01	0.27	0.001
As, mg/l	0.007	0.05	0.002	0.002	0.01	0.006
Sr, mg/l	0.4	0.4	0.8	0.9		
Zn, mg/l	14.5	0.01	0.3	0.02		
Ca/Mg, meq	2.3	1.6	1.6	1.55	1.6	
Bacteriology[1]	1	1	2	2	1 , 2	3

[1] *1 – Bacillus sp.; 2 – E. coli; 3 – Enterobacter sp., Aeromonas sp.*

Hydrochemical investigations of the limestone groundwater showed that, based on physical properties, the temperature was somewhat elevated, up to 17°C. The groundwater was found to be poorly mineralized, with a TDS level of about 500 mg/L, which was somewhat higher than for the alluvial groundwater. The oxidation/reduction potential ranged from 218 to 345 mV, which was indicative of an oxidation medium, and oxygen concentrations varied from 3 to 6 mg/L. Calcium, magnesium and potassium ions dominated the macro-component content. The genetic coefficient Ca/Mg (meq) of about 1.5 suggested that the water originated from limestone, even parts of dolomitic limestone. This type of aquifer is characterized by elevated sulfate (about 40 mg/L) and nitrate (about 40 mg/L) concentrations. Regarding the ions of the nitrate triad, the concentrations of ammonium ions (0.01 mg/L) and nitrate ions (0.02 mg/L) were low. Organic content determined as $KMnO_4$ demand was about 2 mg O_2/L, and significantly lower than in the alluvial groundwater. Regarding other elements, elevated concentrations of strontium (up to 1 mg/L) were detected, which are a consequence of its presence in carbonate rocks (strontianite). The concentrations of iron (0.02 mg/L) and manganese (0.01 mg/L) were low, regardless of the presence of these elements in the limestone and the oxidation environment within them. Microbiological analyses detected the presence of coliform bacteria.

The water quality of the radial wells in this part of the source was characterized as poorly mineralized (TDS about 430 mg/L), with temperatures around 15°C and an oxidation/reduction potential of about 190 mV, which are somewhat lower than in the case of the limestone groundwater. Oxygen concentrations were about 1 mg/L, iron concentrations 0.5 mg/L, and manganese concentrations 0.27 mg/L. The water is of the hydrocarbonate-calcium, magnesium type, and the concentrations of sulfate (25 to 37 mg/L) and nitrate (3 to 25 mg/L) are elevated. Ammonium ions are present in concentrations up to 1 mg/L, and KMnO4 demand is about 4 mg O_2/L. The genetic coefficient Ca/Mg (meq) of about 1.6 indicated that the water is genetically bound to limestone and dolomitic limestone. This groundwater occasionally revealed the presence of Enterobacter sp., Aeromonas sp., and other bacterial species.

Based on sediment quality test results, a comparative analysis of surface water and groundwater within the alluvial and limestone sediments allowed for an assessment of the conditions under which the chemical composition and hydrochemical conditions were formed in this part of the Belgrade source. The software used for geochemical calculations of the hydrochemical component included SOLMINEQ.GW (Kharaka et al., 1999) and PHREEQC (Parkhurst et al., 1999) (Table 2).

Table 2: Saturation index values (SI) of selected minerals

Mineral phase \ Aquifer	Alluvial		Limestone		Radial well
	Piezometer	Well	Piezometer	Well	
Calcite	0.42	0.36	0.35	0.38	0.28
Dolomite	0.01	0.03	0.04	0.12	-0.17
$Fe(OH)_3$	1.5	1.61	-0.36	-0.69	1.19
Magnesite	-0.48	-0.41	-0.39	-0.34	-0.52
Quartz	0.27	0.46	0.3	0.16	-
Rhodochrosite-Mn	0.06	0.23	-1.29	-1.76	-0.26
Siderite-Fe	-0.26	0.03	-2.1	-2.5	-0.76
Smithsonite-Zn	0.71	-2.51	-1.07	-2.2	-
Strontianite-Sr	-0.02	-0.03	0.19	0.24	-

According to thermodynamic stability calculations of the investigated groundwater in relation to mineral phases, separate conditions were noted within alluvial sediments and limestone in this part of the Belgrade source. The groundwater of the alluvial sediments was found to be in balance with dolomite, siderite and strontianite. The values of the saturation index (SI) were higher from the balanced for the minerals calcite, $Fe(OH)_3$, quartz and rhodochrosite. Mineralogical and petrographical analyses confirmed, among other things, the presence of so-called plated grains. These are grains that are petrogenic (quartz, carbonates and others), covered with iron and manganese oxides. This was reflected in the chemical composition of the groundwater, which is of the hydrocarbonate-calcium and magnesium type, with elevated concentrations of iron and manganese favored by a reducing medium with low Eh values. Besides this, concentrations of ammonium ions were elevated as a consequence of the presence of organic matter in the sediments ($KMnO_4$ higher than 12 mg/L). A possible answer to the question regarding the origin of the calcium and magnesium composition of the groundwater in the alluvial sediments could lie in aquifer drainage into the Sava limestone and gravel, where the limestone complex is below the river deposits.

The groundwater within the limestone sediments was over-saturated in relation to calcite, dolomite, quartz and strontianite. The water is of the hydrocarbon-calcium, magnesium type, with strontium (about 1 mg/L) which is also present in strontianite in limestone. The groundwater was found to be unsaturated in relation to siderite, $Fe(OH)_3$, and rhodochrosite, and the concentrations of iron and manganese were low.

The water tapped by the radial wells was unsaturated in related to dolomite, siderite and rhodochrosite, and over-saturated in relation to calcite and $Fe(OH)_3$, and with groundwater from the alluvial sediments. Based on the chemical composition, the water was found to be of the hydrocarbonate-calcium, magnesium type.

What do the results of analytical determinations and thermodynamic calculations indicate? The schematic of the hydrochemical conditions which characterize the groundwaters within the alluvial sediments and limestones, presented in Figure 3, clearly shows the influence of the limestone on the chemical composition of the water tapped by the radial wells.

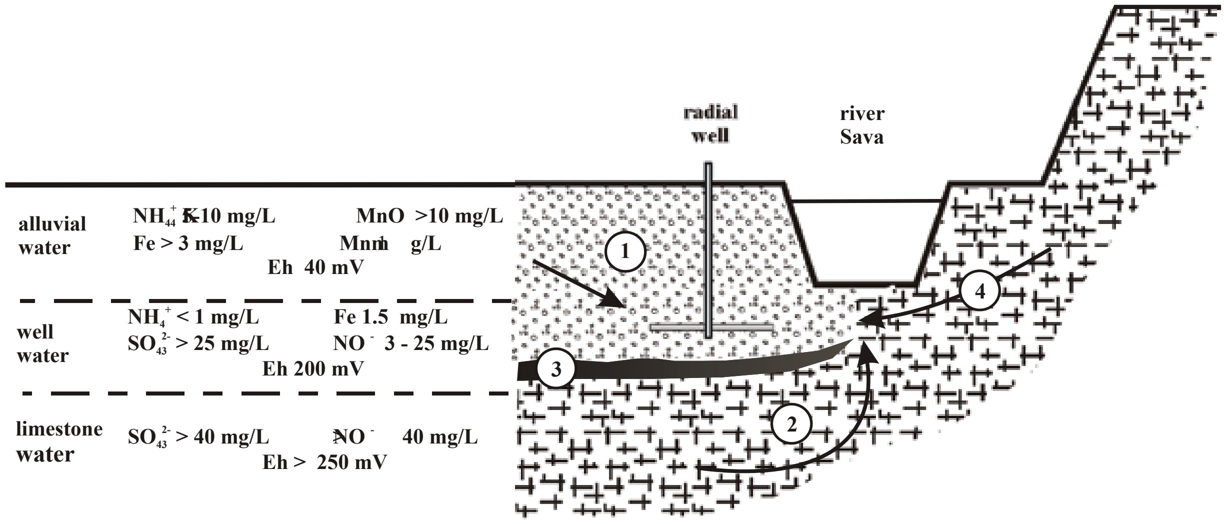

Figure 3: Schematic of hydrochemical conditions and groundwater flow.
Key: 1 – alluvial sediments, 2 – limestone; 3 –impermeable interlayer; 4 – groundwater flow directions.

The zone tapped by the radial wells is characterized by the following hydrochemical parameters of the alluvial and limestone groundwaters: Eh about 200 mV, iron less than 1.5 m/L, manganese about 0.3 mg/L, and ammonium ion about 1 mg/L. Elevated concentrations of sulfates and nitrates are also indicative of a large similarity with the composition of the limestone groundwater. During abstraction, potassium and chloride ion concentrations slightly increase, which is attributable to their presence in the deeper reaches of the limestone sediments, assuming that there is a fault that allows the two types of aquifers, alluvial and limestone, to come in contact.

CONCLUSION

The investigations undertaken in one part of the Belgrade water source, in the zone of the Sava's mouth, indicated a special character of the well water drawn from the alluvial aquifer. The groundwater quality was used as an indicator of hydrogeological relationships in this part of the source. Hydrochemical investigations and calculations showed that the groundwater tapped from the alluvion was loaded with ammonium, iron and manganese ions and organic matter, with low oxygen concentrations and a low oxidation/reduction potential, which are characteristic of a poorly reducing medium. The limestone groundwater exhibited characteristic elevated sulfate and nitrate concentrations, with an increased oxidation/reduction potential which defines an aerobic environment. Based on the oxidation/reduction conditions, it can be concluded that there is an inverse aerobic feature in this part of the Belgrade source, as the shallow alluvial groundwater is less aerobic (Eh about 40 mV) than the deeper groundwater in the limestone aquifer (Eh greater than 250 mV). The water tapped by the radial wells, with regard to its chemical composition and aerobic state, is under the influence of both the alluvial and the limestone aquifer, i.e. it is a blend of these waters (Eh about 200 mV, elevated concentrations of sulfate and nitrates).

Hydrodynamic model tests confirmed previous assumptions and indicated the direction in which the limestone aquifer extends beyond the study area.

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PHARMACEUTICAL RESIDUES IN THE DANUBE RIVER BASIN IN SERBIA – A TWO-YEAR SURVEY

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Pharmaceutical residues in the environment have been recognized as one of the emerging research areas in the environmental chemistry. Pharmaceuticals are used in human and veterinary medicine and can be excreted either as an unchanged parent compound or in the form of metabolites. They are released to the environment mainly from urban and hospital effluents, manufacturing processes, concentrated animal feeding operations, land application of manure, and improper disposal. The most significant entry routes of drugs in the environment are related to the release from wastewater treatment plants (WWTPs) and the animal excreta.

Many studies have reported that elimination of drugs in conventional wastewater treatment is incomplete for the most of the pharmaceutical substances. To obtain high-quality treated effluents, the implementation of advanced treatment technologies are required. Special attention is being paid to pharmaceutical amounts in the aquatic environment, due to continuous input that may lead to long-term adverse effects on aquatic and terrestrial organisms. Also, due to their high water solubility, pharmaceuticals can pass through all natural filtrations and reach ground water, and ultimately drinking water.

While most of European WWTPs perform tertiary wastewater treatment, in Serbia only primary and secondary treatments are performed. It should be emphasized that only 12% of urban wastewater and about 3% of industrial wastewater in Serbia is treated before being discharged into environment.

The purpose of this study was to employ a previously developed multiresidual method for quantification and confirmation of thirteen pharmaceuticals and two metamizole metabolites in monitoring of contamination of the Danube River in urban and agricultural areas in Serbia. Some of the most frequently used pharmaceuticals in Serbia were chosen for the study: ampicillin, amoxicillin (penicillin antibiotics); sulfamethoxazole (sulfonamide antibiotic) and trimethoprim; erythromycin, azithromycin (macrolide antibiotics); doxycycline (tetracycline antibiotics); diazepam, bromazepam, lorazepam (benzodiazepines); carbamazepine (antiepileptic); paracetamol, diclofenac (analgoantipyretics). Also, two metamizole (dipyrone) metabolites (4-formylaminoantipyrine, 4-FAA and 4-acetylaminoantipyrin, 4-AAA), that can be used as indicators of sewage contamination and markers for detection and quantification of natural waters pollution with wastewater, were selected for the study. The analytical method will be based on solid-phase extraction (SPE) as the sample preparation method, followed by liquid chromatography–tandem mass spectrometry (LC–MS2) analysis of the obtained extracts.

The Danube is the second longest river in Europe (the first being the Volga) and one of the Europe's most important waterway. It flows about 2850 km from the Black Forest in Germany to the Black Sea, and is affected by seventeen European countries and about 165 millions of people. In Serbia, the Danube flows through numerous industrial and urban centers (Apatin, Bačka Palanka, Novi Sad, Belgrade, Smederevo, Donji Milanovac, Kladovo) and receives significant amount of pollution. It is a recipient of urban and industrial waste, as well as agricultural land runoff. The cities of Belgrade and Novi Sad are the most significant urban pollution sources in Serbia and neither of them have wastewater treatment plants. As for industrial wastewater, the quantity of treated wastewater in Serbia has decreased from 11% (in 2000) to 3% (in 2004). Agricultural areas in Serbia extend over 5.7 million hectares, of which 4.8 million hectares is arable land. Therefore, it is important to constantly monitor contamination of the Danube River basin in Serbia, especially taking into account that this water is also used for production of drinking water.

In the present study, a total of 35 grab surface water samples were collected at 15 selected sites of the Danube River basin in Serbia, during seven sampling campaigns performed in July and October of 2009, and February, April, May/June, September and October/November of 2010. The first 11 sampling sites (SW 1–SW 11) are located on the Danube, and other four sites (SW 12–SW 15) are positioned on its tributaries Sava, Tisa and Velika Morava, near their confluence into the Danube.

Out of fifteen monitored compounds, five were found to be present in one or more samples from the Danube River and its tributaries. Carbamazepine and 4-AAA were the most frequently detected drugs, found at 60% of the sampling sites. The residues of carbamazepine were detected in the concentration range 13–94 ng L^{-1}. The frequency of its detection can be explained by low sorption, resistance to biodegradation and low removal rate in WWTPs, as well as high administered doses of this antiepileptic drug.

As for metamizole, its both metabolites were frequently detected in the study, indicating widespread sewage contamination of the natural waters. The concentrations of 4-AAA were in the range 67–354 ng l^{-1}, and the levels of 4-FAA were in the range 9–213 ng l^{-1}. Although metamizole has been banned in some countries (USA, UK), it is still one of the most popular analgesic and antipyretic drug in Germany, Italy, Spain and Serbia. Its metabolites are present in environment in high concentrations due to spontaneous hydrolysis of metamizole into the main metabolite, 4-methylaminoantipyrine (4-MAA), which is subsequently metabolized into a variety of compounds, the most important being 4-FAA and 4-AAA.

Trimethoprim was found in five surface water samples, in the concentration range 4–223 ng l^{-1}. It is used in combination with sulfametoxazole, frequently used antibiotic in Serbia. Additionally, sedative lorazepam was found in a single sample at the concentration of 34 ng l^{-1}.

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Extended Abstract

PHOTOCATALYTIC DEGRADATION STUDY OF THE INSECTICIDE METHOMYL IN AQUEOUS SUSPENSION OF TiO_2

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Abstract: The photocatalytic degradation of the insecticide methomyl in water using TiO_2 (Merck) under Osram ultra-vitalux® lamp light was studied. The effect of several operational parameters on degradation kinetics was investigated. The optimal concentration of the catalyst was found to be 2.0 g/L. Based on the Langmuir-Hinshelwood mechanism, a pseudo first-order kinetic model was illustrated. The presence of Cl^- ions significantly affect the photodegradation of the pollutant. The rate of photodecomposition of methomyl was measured using UV spectroscopy and HPLC, while its mineralization was followed using ion chromatography (IC) and a total organic carbon (TOC) analyzer.
Keywords: methomyl, photocatalytic degradation, titanium dioxide, water remediation

INTRODUCTION

Methomyl (IUPAC name S-methyl N-(methylcarbamocyloxy)thioacetimidane, CAS No. 16752-77-5) is an insecticide/acaricide widely used in agriculture. Methomyl was included in Annex I to Council Directive 91/414/EEC from 01/09/2009 (Reg. 2009/115/EC) for a period of ten years. It belongs to carbamate pesticides and was introduced by Du Pont in 1966 as a broad spectrum insecticide. Methomyl is effective in two ways: as a contact insecticide and as a systemic insecticide. In Serbia, methomyl has been used for many years (now), but there is no data relating to the applied quantity.

Methomyl is a pesticide of very high toxicity. Its mode of action is by reversible inhibition acetyl cholinesterase, an essential enzyme for proper functioning of the nervous system. It is non-cumulative and rapidly metabolized in both plants and animals to substances of lower toxicity. Considering the methomyl toxicity characteristics it was concluded that 0.0025 mg/kg of body weight per day (ADI) will not cause adverse effect in humans by any route of exposure. The results also indicated a potentially high risk for bees and aquatic organisms (EFSA, 2008).

After application methomyl will remain to some extent in agricultural soils. Also, it can contaminate surface water as a result of spray drift during application or by runoff from treated soils. Under normal environmental conditions microbial degradation in soil to carbon dioxide is the common way of degradation of the pesticide (Figure 1). The identical pathway was observed under aerobic and anaerobic conditions. There are no major metabolites formed, but methomyl oxime was identified as a minor soil metabolite. Methomyl is moderately stable to aerobic soil metabolism, but degrades more rapidly under anaerobic conditions.

In laboratory studies, methomyl does not readily absorb to soil and has the potential to be very mobile. Field studies show varying dissipation rates of the chemical in soils. Reported half lives of methomyl in soil vary from a few days to more than fifty days. Dissipation rates were related primarily to differences in soil moisture content, which may affect microbial activity, and rainfall/ irrigation, which could influence leaching. Low soil temperatures may also slow downs methomyl degradation, but no effects of pH was observed. In the photolytic study performed with methomyl, degradation of methomyl was significantly faster under irradiated conditions than in the dark control, but slower that in the standard aerobic degradation test.

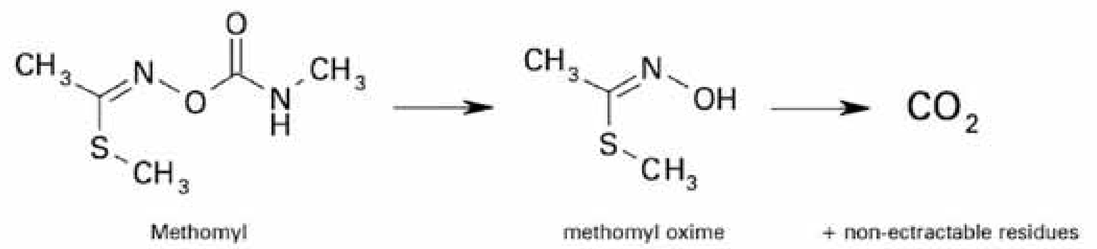

Figure 1: Degradation pathway of methomyl in soil.

Neither hydrolysis nor photolysis is expected to contribute significantly to the degradation of methomyl in water. Methomyl is not ready biodegradable. Methomyl is relatively stable to hydrolysis under neutral and acidic conditions, but has a hydrolysis DT_{50} value of 36 days at pH 9, 25oC. Methomyl has water solubility of 55.0 g/L at 25oC. Its soil adsorption is low, with a soil adsorption coefficient (Koc) of 13.3-42.8 cm^3/g (EFSA, 2008). Methomyl's low Koc value, high water solubility, and long hydrolysis DT50 value indicate that methomyl could potentially be carried by field runoff into surface water. Methomyl has been detected in surface and ground waters across Europe and America, not only during actual application but also after a long period for use (Strathmann and Stone, 2001). Therefore, in order to meet the stringent pesticide standard of water bodies and protect human health, it is deemed that remediation technologies for contaminated water are more and more required.

There are different methods for removing pesticides from water (Chang et al., 2008; Mervat, 2009; Dimkic et al., 2011), but we would focus on a method based on photodegradation. Advanced Oxidation Processes (AOPs) include catalytic and photochemical methods which use H_2O_2, O_3 or O_2 as the oxidant. The principal active species in these systems is the hydroxyl radical $^{\bullet}OH$, which is an extremely reactive and non-selective oxidant for organic contaminants (Legrini et al., 1993). The main advantage of these processes is a complete mineralization of many organic pollutants (Andreozzi et al., 1999). Several catalysts have been used (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) and among them TiO_2 is one of the most effective (Malato et al., 2002).

Methomyl has been photodegraded using AOPs. Different catalysts have been used, mostly TiO_2 (Malato et al., 2002; Tamimi et al., 2006; Tomašević et al., 2010a), as well as photo-Fenton reaction (Malato et al., 2002; Tomašević at al., 2010b). The aim of the present work is to study the photocatalytic degradation of the insecticide methomyl in water using TiO_2 (Merck) under a 315-400 nm light source. The effect of parameters such as the initial concentration of the catalyst, initial methomyl concentration, pH and initial salt concentration (NaCl) were studied.

METHODS

All chemicals used in the investigation were of reagent grade and were used without further purification. Analytical standard of methomyl (99.8%) was received as a present from Du Pont de Nemours, USA. TiO_2-Merck Eusolex® T (anatase modification) was used as received. The photodegradation of methomyl was studied by preparing a solution containing 16.22 mg/L of methomyl and a certain amount of catalyst. Both, photodegradation and analytical procedures were reported elsewhere (Tomašević et al., 2010a).

RESULTS AND DISCUSSION

Effect of catalyst amount

The degradation curves {normalized concentration (C/Co, where C is the concentration of methomyl at irradiation time t and Co is the initial concentration of methomyl) vs. time} shown in Figure 2, represents the effect of the TiO_2 concentration on the photodegradation of methomyl. As the concentration of TiO_2 increased, the reaction rate also increased. The highest reaction rate was observed when 2.0 g/L of TiO_2 was used. Above this concentration, light scattering and coagulation of catalyst particles decreased the reaction rate (Daneshvar et al., 2004).

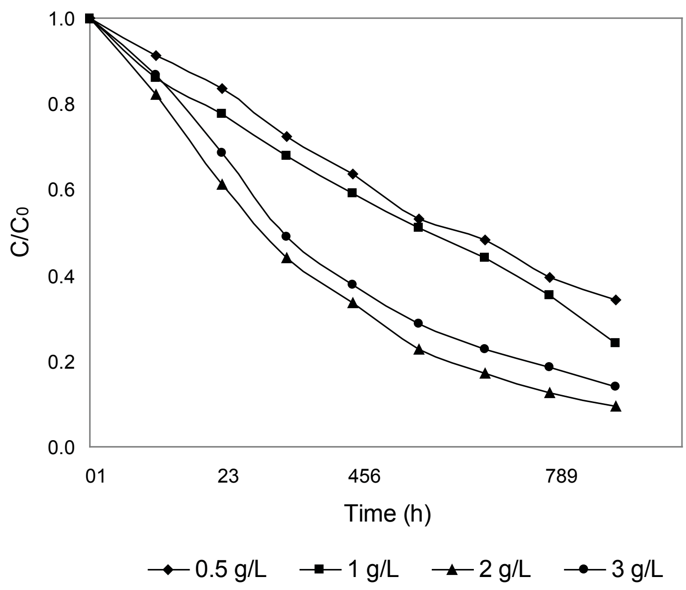

Figure 2: Effect of the initial concentration of TiO_2 on the photodegradation of methomyl.

Effect of initial methomyl concentration

In addition, the effect of the initial methomyl concentration on the photodegradation was studied and the obtained results are presented in Table 1. According to many researchers, a heterogeneous photocatalytic reaction can be successfully analyzed using the modified Langmuir-Hinshelwood (L-H) kinetic expression (Evgenidou et al., 2005; Daneshvar et al., 2008). It was possible to calculate the pseudo-first order constant and the half time of the reaction, when different initial concentrations of methomyl were used. Our results show that an increase in the initial methomyl concentration leads to a lower photodegradation rate. Here, more and more methomyl molecules were adsorbed on the surface of TiO_2 as the methomyl concentration increased, which contributed to the inhibition effect of the reaction of methomyl molecules with holes or hydroxyl radicals, due to the lack of any direct contact between them (Daneshvar et al., 2008).

Table 1: Kinetics of methomyl degradation under Osram lamp (TiO_2 concentration = 2 g/L)

Co (mg/L)	k (min^{-1})	1/k (min)	R
16.22	0.0047	212.77	0.9998
12.15	0.0051	196.08	0.9851
8.10	0.0070	142.86	0.9771
4.05	0.0077	129.87	0.9620

Effect of pH

It is known that the pH value has an influence on the photodegradation of some organic compounds in photocatalytic processes (Gupta and Tanaka, 1995; Wu et al., 2001). The photodegradation of methomyl was studied at four different pH values (2.0, 3.5, 5.6 and 9.0). The third value is the pH of a pure methomyl solution in deionized water. The pH of the solution was adjusted before irradiation by the addition of HCl or NaOH. The amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst. Above the zero point charge the TiO_2 surface is predominantly negatively charged. As the pH decreases, the functional groups are protonated, and the proportion of the positively charged surface increases (Evgenidou et al., 2005). It was found that the initial photodegradation rate decreased as the value of pH increased (Figure 3).

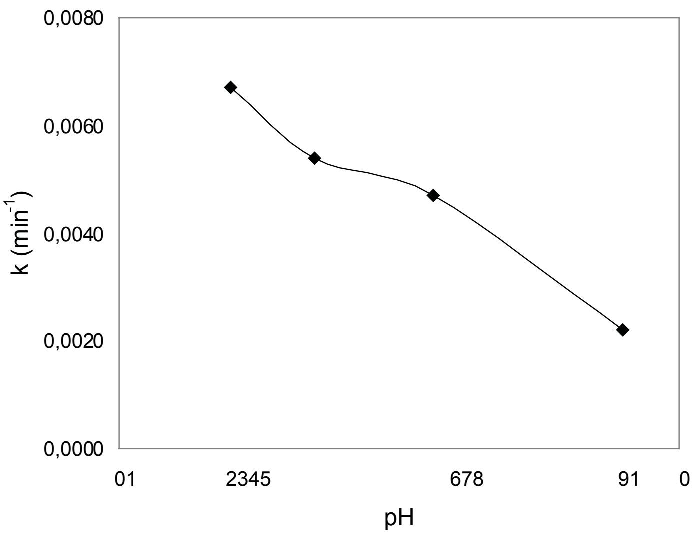

Figure 3: pH influence on methomyl photodegradation rate (TiO_2 concentration = 2 g/L).

Salt effect

The salt effect on the photodegradation of methomyl was studied using sodium chloride. The influence of different concentrations of salt (0, 1.0 and 5.0%) on the photodegradation of methomyl is presented in Figure 4. The observed decrease of photodegradation of methomyl in the presence of chloride ions can be explained by competitive adsorption (Guettai and Ait Amar, 2005; Neppolian et al., 2002) or by the hole scavenging properties of chloride ions (Neppolian at al., 2002; Chen et al., 1997). While chlorine radicals are formed slowly, they are converted into chloride anions instantly. The surface sites normally available at the TiO_2/methomyl solution interface for adsorption and electron transfer from methomyl can be blocked by anions, such as chloride anions, which are not oxidizable and are effective inhibitors of the detoxification process (Neppolian et al., 2002).

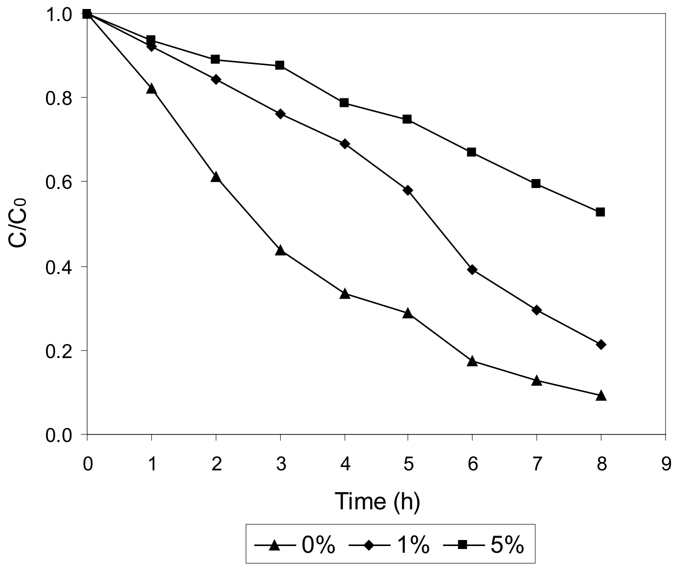

Figure 4: Salt effect on the photodegradation of methomyl (TiO_2 concentration = 2 g/L).

Mineralization study of methomyl

The ion chromatography results showed that mineralization led to the formation of sulfate, nitrate and ammonium ions during the process (Tomašević et al., 2010a). Mineralization of sulfur atoms into sulfate ions was almost complete and the maximum expected values for sulfate ions (around 9.60 mg/L) was obtained. The maximum detected value for nitrate and ammonium ions were 1.05 mg/L and 1.09 mg/L, respectively. The nitrogen mass balance was therefore incomplete at the end of the treatment (around 50% of the inorganic nitrogen expected in the process). Mineralization of organic carbon was incomplete and about 80% of the initial TOC had disappeared after 8 hours. These results are in accordance with those of other researchers (Oller et al., 2006).

CONCLUSIONS

A water solution containing 16.22 mg/L of methomyl can be efficiently photodegraded under an Osram ultra-vitalux® lamp using 2.0 g/L of TiO_2. The reaction rate depends on the initial concentration of the catalyst, initial methomyl concentration, pH and initial NaCl concentration. According to the experiments a pseudo first-order kinetic model was illustrated and sulfate, nitrate and ammonium ions were formed during the remediation process.

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METHODS FOR MONITORING OF PESTICIDE RESIDUES IN WATER: CURRENT STATUS AND RECENT TRENDS

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Contamination of water resources by pesticide residues, as a consequence of their extensive use in agricultural practice, is one of the major challenges for the preservation and sustainability of the environment. For the protection of human health and the environment, pesticide residues are routinely monitored in food, water, soil, and tissue samples. The analysis of pesticide residues in environmental samples is faced with identification and quantification of hundreds of compounds with different physicochemical properties. The use of ultra-sensitive analytical methods is mandatory since the water tolerable limits for most of the pesticides are in low levels of μg L^{-1} and, in some cases, ng L^{-1}.

Due to the low detection levels of pesticides required by regulatory bodies and the complexity of the environmental water samples, preconcentration and clean-up of the samples, prior to chemical analysis, is usually required. The preconcentration is achieved through phase transfer, most often by the use of solid-phase extraction (SPE), which enables simultaneous clean-up as well. Compatibility of reversed-phase (RP) liquid chromatography (LC) with aqueous samples allows on-line coupling of SPE with the analytical system. On-line SPE offers the possibility of reducing the sample volume compared to the off-line procedures, without loss in sensitivity, also minimizing the sample manipulation and the use of organic solvents. It has the advantage of being easily automated, facilitating its application in the monitoring programs. Modern trends in trace analysis are aimed at simplification and miniaturization of the sample preparation, as well as the minimization of the organic solvent used. In view of this aspect, there is growth in significance of solventless and microextraction techniques, such as solid-phase microextraction, stir bar sorptive extraction, single-drop microextraction and membrane liquid-phase microextraction. Application of new materials, for example carbon nanotubes or molecularly imprinted polymers, as sorbent materials in SPE has also been one of the hot research topics in the last years.

The analysis of pesticide residues is a demanding task, since pesticides belong to more than 100 substance classes, with a broad range of polarity and acid-base characteristics. In respect to their diversity, as well as highly sensitive and highly selective method requirements, the complementary use of gas chromatography (GC) and LC, both coupled to mass spectrometry (MS), is essential in pesticide residue analysis. GC–MS has been the major adopted analytical technique to perform multi-residue analysis of non-polar, volatile pesticides, such as organochlorines. For more polar, less or non-GC-amenable pesticides, LC coupled to tandem mass spectrometry (LC–MS^2) is the preferred analytical technique. LC–MS^2 has shown to be better than GC–MS or exclusively suited for many pesticide classes, such as sulfonyl or benzoyl ureas, carbamates, and triazines. Recently, ultra performance liquid chromatography (UPLC) has been developed as a powerful separation technique based on the use of stationary phases with particle size smaller than in conventional LC. UPLC coupled to tandem mass spectrometry (UPLC–MS^2) has been shown as an excellent analytical tool for multi-class analysis of compounds such as pharmaceuticals, toxins, or pesticides in water.

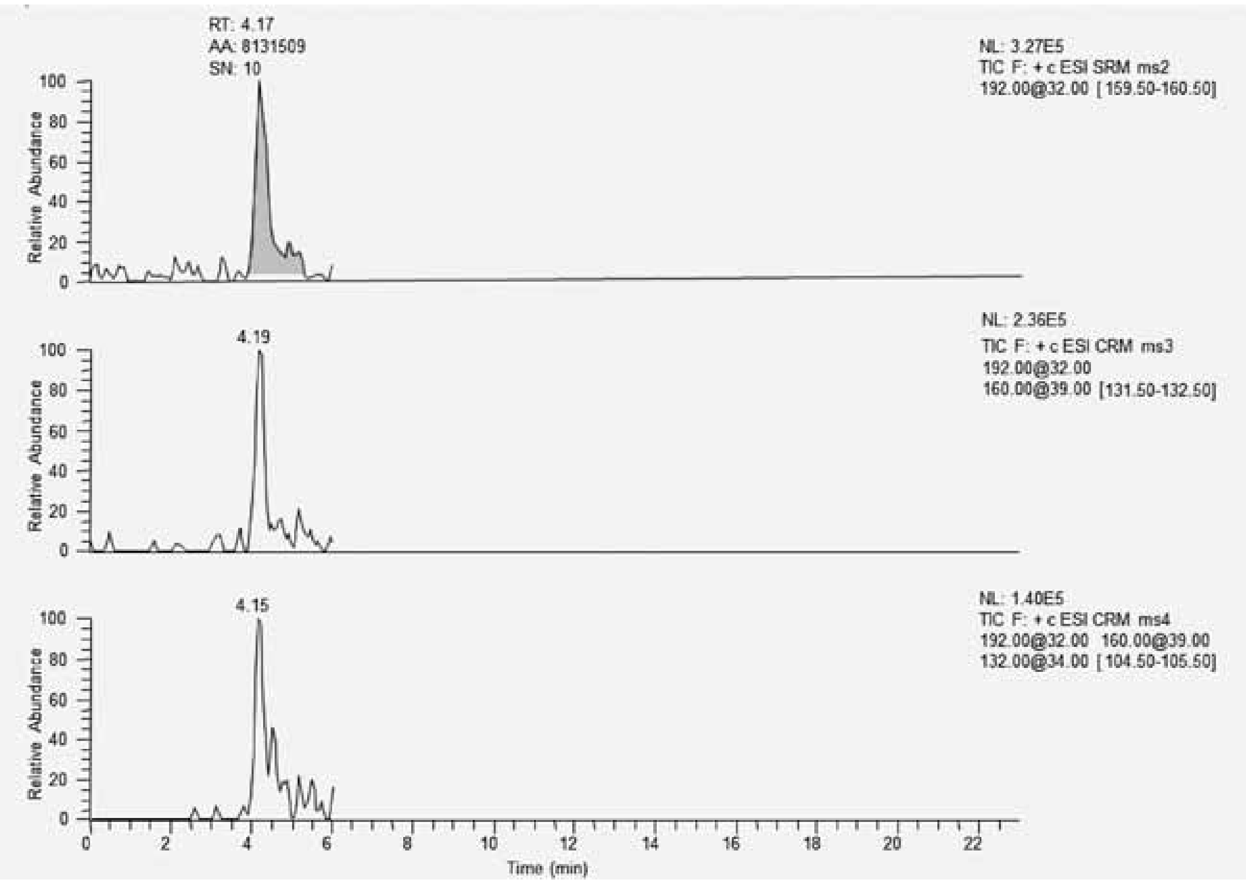

Figure 1: LC–MS^n chromatograms confirming carbendazime residue in surface water sample

Different strategies could be applied for monitoring of pesticides in water depending on the objectives of the study (whether target or non-target analysis is required). Both types of analysis have the need for different analytical approaches and may require different instrumentation. An example of target analysis is the inspection of pesticide residues in surface water according to the environmental quality standards (EQS). The relevant analytes are preselected by the residue definition given in the regulation (Directive 2008/105/EC). In contrast, the EU regulation on residues in drinking water does not contain detailed residue definitions (Directive 98/83/EC). Monitoring and identifying of pesticide degradation products, which is considered to be crucial for complete environmental risk assessment, also requires a non-target analysis. For target analyte determination the triple quadrupole analyzers proved to be the best option because of their high sensitivity and selectivity and comparatively low cost. For non-target analysis, instruments must be able to generate sufficient information for elucidation of residues, such as accurate mass from which empirical formulae can be deduced. Recently, one of the hottest trends in water contaminant analysis has been the use of time-of-flight (TOF) analyzers and quadrupole-TOF hybrids, which proved to be suitable for non-target analysis. TOF provides the selectivity and sensitivity required for an efficient and wide-scope screening, because it combines high full spectral sensitivity with high mass resolution. Furthermore, LC–TOF is the selected technique for the determination of pesticide degradation products in environmental, biological and food matrices. Another novel system already applied in the field of pesticides analysis is the hybrid linear ion trap–orbitrap. Such system combines high sensitivity with high resolution (up to 150 000) and accurate mass (2–5 ppm) measurement.

The analytical method requirements will differ depending on whether the objective is simply to detect (screening method), to quantify (determinative method) or to confirm (confirmatory method) the presence of a possible residue. Increasing concern about confirmation of positive data favored the development of different criteria to assure data quality and to avoid the reporting of false positives. The European Commission had proposed a system of identification points (IPs), where at least three IPs are required (four in the case of banned compounds) to confirm a positive finding (Decision 2002/657/EC). Different approaches could be used in order to reach the number of IPs required to confirm positive findings, depending basically on the instrument available. Figure 1 illustrates confirmatory analysis of pesticide residues found in surface water, obtained by the use of LC with multiple stage MS (LC–MSn). In this example, MS2 transition is used for quantification, while MS3 and MS4 transitions are used for confirmatory purposes.

Notes:

Full Paper

BACTERIAL POPULATIONS OF WATER AT WATER COOLER OUTLETS AS A FUNCTION OF CONSUMPTION PARAMETERS

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Abstract: In recent years, the use of water coolers has been increasing rapidly. However, due to inadequate handling and sporadic sanitation of these appliances, contamination is likely to occur. The objective of this research was to examine the bacterial populations in the water sampled at the outlets of 20 water coolers at different locations in Novi Sad, as a function of consumption parameters. Sampling was conducted in three repeated campaigns. For each sample, microbiological analyses comprised of basic testing were conducted according to current legislation and separated isolates were identified on a Vitek 2 Compact unit. The presence of coliform bacteria, Enterococcus sp., and sulphite-reducing Clostridia was not detected in any of the tested samples, but Pseudomonas sp. was detected in three samples. No direct correlation between the water level height and the microbiological profile of the water was determined (even though its influence is not to be disregarded), while a direct dependency between the frequency of water bottle replacement and disinfection was established. Based on the results presented below, nine out of the 20 tested water coolers did not comply with water quality legislation, the water was not safe for consummation, and the water coolers required regular maintenance to ensure high water quality and safety.
Keywords: Aerobic mesophilic bacteria, Bacillus spp., disinfection, drinking water, Pseudomonas aeruginosa, water cooler

INTRODUCTION

Today, with increasing concern about the state of watercourses due to uncontrolled human activity, providing microbiologically safe drinking water has become a pressing issue. Only 1% of the world's fresh water is accessible, and half of that is contaminated, such that there are sufficient water reserves on Earth but insufficient drinking water.

Drinking water quality issues in large cities throughout the world, and national water supply concepts, have created the need for the availability of microbiologically and chemically compliant drinking water. Water coolers have responded to this need, and modern devices momentarily provide both hot and cold water. Water coolers are now found in many public institutions, offices, and even households.

In developed countries, agencies responsible for water coolers have recommended a minimum of four sanitations of water coolers per year, based on many years of testing. This water cooler hygiene regime has become a part of the European Code of Practice established by EBWA, including EPDWA guidelines (Good and Steur, 2006).

The use of water coolers in Serbia is not regulated, such that there is no adequate control of the microbiological safety of the water dispensed by these devices. Additionally, there is sparse literature on the topic. The use of water coolers in Serbia follows the global expansion trend, but there is insufficient awareness of the quality of the water consumed in this manner.

The goal of this research was to examine bacterial populations of water sampled at the outlets of 20 water coolers at different locations in Novi Sad, depending on consumption parameters (water level height, frequency of water bottle replacement, disinfections), and to obtain a realistic picture of the microbiological quality of water that is increasingly consumed in this manner. For bacterial microbiotas, the counts of aerobic mesophilic bacteria, and the presence of indicator microorganisms (like coliform bacteria, sulphite-reducing Clostridia, Enterococcus sp. and Pseudomonas aeruginosa), were determined.

MATERIAL AND METHODS

For microbiological tests, samples of water were collected at the outlets of water coolers made by four different manufactures. Water was sampled at 20 different locations, in three repeated campaigns, during three months: April to June. The water samples were taken from the cold water tap of the water coolers, whose water bottle volume was 18.9 liters.

The samples were collected in the manner prescribed by the Serbian Code of Practice on Drinking Water Sampling and Laboratory Analysis (Official Gazette of the SFRY no. 33/87).

The criteria which define the bacteriological profile of the water samples were selected in accordance with the Serbian Code of Practice on the Quality and Other Requirements Pertaining to Natural Mineral Water, Natural Spring Water and Processed Water (Official Gazette of SaM no 53/2005), i.e. 250 ml samples were used for the various indicators.

The methods applied to determine aerobic mesophilic bacteria counts and detect the presence of Enterococcus sp. and sulphite-reducing Clostridia, were selected from standard methods used for drinking water health safety tests as defined in the Manual of Methods (Škunca-Milovanović et al., 1990).

The methods used to confirm the presence of thermotolerant coliform and total coliform bacteria, and the presence of Pseudomonas aeruginosa, were as described in ISO Standards (EN ISO 9308-1:2000; ISO 16266:2000).

The cultured colonies, which were (a)typical of colonies of thermotolerant coliform and other coliform bacteria and Pseudomonas aeruginosa, from membranes incubated on Chromocult Coliform agar and Cetrimid agar during 48 hours at 37°C, were re-grown on nutritious inclined agar and kept at a temperature from 4 to 8°C until the time of refreshment, which was not later than three months. Every isolate was purified applying the exhaustion method until the dominant pure culture was obtained. The macromorphological and micromorphological features (Gram-staining, sporulation) of isolated pure cultures were described (Markov and Vrbaški, 1992). For purposes of identification of isolated pure cultures, three physiological tests were conducted: catalase, oxidase and oxidase-fermentation glucose tests. The pure cultures were identified by Vitek 2 Compact (bioMérieux, France).

RESULTS AND DISCUSSION

Although there were some preliminary positives, the presence of thermotolerant coliform and total coliform bacteria was not confirmed in any of the tested samples. Growth of Enterococcus sp. and sulphite-reducing Clostridia colonies was not detected in any of the samples. Based on the results obtained for these four groups of bacteria, all the tested samples of water sampled from water cooler outlets complied with Serbian national regulations (Official Gazette of SaM no. 53/2005).

The presence of Pseudomonas aeruginosa was detected in the water sampled from the outlet of water cooler no. 1, in the second series of samples. Following disinfection of that water cooler, this microorganism was not detected in the third series of samples. Hence, it was assumed that the biofilm composed of Pseudomonas aeruginosa was either completely removed or, if it was only partially removed, the remaining biofilm did not contain these bacteria. Additionally, the preliminary test for the presence of P. aeruginosa was positive for two other samples, but when these samples were tested on Vitek 2 Compact, the presence of P. Stutzeri and Stenotrophomonas maltophilia was detected.

Based on the results, only one sample in the entire study, or more precisely a second-series sample of water from water cooler no. 1, was not suitable for consumption, according to Serbian national regulations (Official Gazette of SaM no. 53/2005).

The presence of aerobic bacterial populations, which formed colonies at temperatures of 37°C and 22°C on nutrient agar, was confirmed. The microorganism count at the water cooler outlet, at a temperature of 37°C, was from 0 to 2800 CFU/ml, while at 22°C it was from 8 to 4000 CFU/ml. Due to the lack of a comprehensive code of practice for water coolers, which would define bacterial counts at temperatures of incubation of 37°C and 22°C in water that is on the market, regardless of origin and treatment method, it was necessary to combine two codes of practice (Official Gazette of the FRY nos. 42/98 and 44/99; and Official Gazette of SaM no. 53/2005) to compare the results with regulated limit values. According to Serbian national regulations per Official Gazette of the FRY nos. 42/98 and 44/99, in bottled natural water which is on the market longer than 12 hours after bottling, the allowed number of aerobic mesophilic bacteria is up to 50 CFU/ml, while the Serbian national regulations per Official Gazette of SaM no. 53/2005 define the aerobic mesophilic bacterial count but in the time interval of up to 12 hours after bottling. Therefore, the criterion for the aerobic mesophilic bacterial count as defined in Serbian national regulations per Official Gazette of the FRY nos. 42/98 and 44/99 was used.

Figure 1 shows the proportions of water samples, by sampling campaign, which comply with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99). It is apparent that the lowest percentage of microbiologically compliant water samples is attributed to the first sampling campaign (15%), that there is a slight increase in the number of microbiologically compliant water samples in the second sampling campaign (20%), and that the largest share of microbiologically compliant water samples were recorded in the third sampling campaign (55%). The increased number of microbiologically compliant water samples between the first and second sampling campaigns is almost insignificant and is probably the result of better handling of the water coolers, or is attributable to other influences which were not addressed in this research. The significant increase in the number of microbiologically compliant water samples between the second and third sampling campaigns is due to disinfection of some water coolers just before the third sampling campaign, resulting in a significant increase in the number of microbiologically compliant water samples, from 20% to 55%.

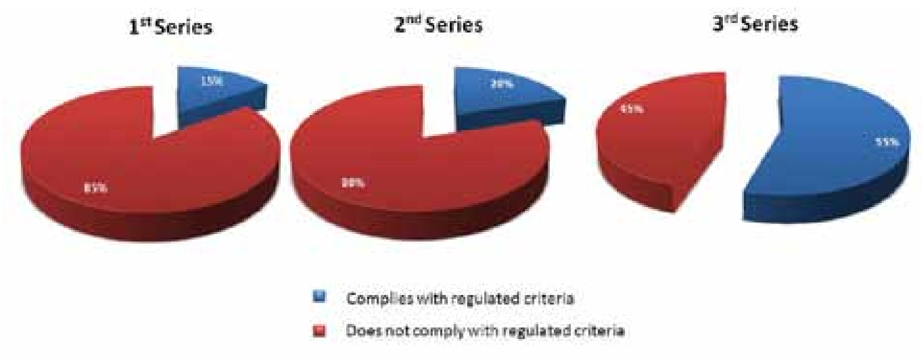

Figure 1: Proportions of water samples collected from water coolers by sample series, which comply with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99).

In this research, the dependency of bacterial populations on consumption parameters (water level height, frequency of water bottle replacement, disinfections) was examined. The water consumption parameters for the three repeated sampling campaigns and all 20 sampling locations are shown in Table 1. The bottled water was produced by four different companies (marked 1-4), and the water coolers were supplied by three different distributors. Two water producers declared their product as "non-carbonated natural water with a low mineral content" (1 and 2), while the products of the remaining producers (3 and 4) were declared as "non-carbonated natural water with a low content of soluble mineral matter and a low content of sodium".

Table 1: Water consumption parameters at sampling locations

Location of sampling	Water level height in bottle			Average frequency of bottle replacement	Producer of water bottles[2]
	1st series (cm)	2nd series (cm)	3rd series (cm)		
Unit 1	30, (3/4)[3]	19, (1/2) [3]	39, (1/1) [3]	3 days	1
Unit 2	19, (1/2)	10, (1/4)	11, (1/4)	2 days	3
Unit 3	18, (1/2)	29, (3/4)	28, (3/4)	1 day	1
Unit 4	22, (1/2)	38, (1/1)	36, (1/1)	4 days	1
Unit 5	17, (1/2)	8, (1/4)	35, (1/1)	1 day	1
Unit 6	20, (1/2)	30, (3/4)	39, (1/1)	2 days	1
Unit 7	18, (1/2)	7, (1/4)	8, (1/4)	7 days	2
Unit 8	13, (1/3)	20, (1/2)	38, (1/1)	2 days	3
Unit 9	29, (3/4)	37, (1/1)	10, (1/4)	4 days	2
Unit 10	9, (1/4)	37, (1/1)	22, (1/2)	3 days	4
Unit 11	21, (1/2)	38, (1/1)	39, (3/4)	2 days	4
Unit 12	10, (1/4)	20, (1/2)	31, (3/4)	5 days	3
Unit 13	32, (3/4)	37, (1/1)	38, (1/1)	3 days	3
Unit 14	9, (1/4)	20, (1/2)	39, (1/1)	7 days	3
Unit 15	19, (1/2)	37, (1/1)	38, (1/1)	7 days	3
Unit 16	12, (1/3)	22, (3/4)	21, (3/4)	1 day	3
Unit 17	19, (1/2)	37, (1/1)	37, (1/1)	1 day	3
Unit 18	13, (1/3)	8, (1/4)	29, (3/4)	6 days	3
Unit 19	39, (1/1)	39, (1/1)	28, (3/4)	1 day	3
Unit 20	30, (3/4)	17, (1/2)	14, (1/3)	2 days	3

1 Total water bottle height was 39 cm.

2 Water bottle suppliers identified as 1 to 4.

3 Ratio of water level height to total height of water bottle.

The height of the water level in the water bottle indicates the current volume ratio of water to air in the bottle of the water cooler. Considering that the air that enters the bottle of the water cooler and replaces the equivalent volume of water first flows through an air micro-filter whose function is to prevent contamination of the water in the bottle, the microbiological profile of the water in the water cooler should not be affected by the water level height.

Figure 2 shows the proportions of water samples that comply with the requirements defined by Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; and Official Gazette of SaM no. 53/2005), as a function of water level height, for all three sampling campaigns presented in Figure 1.

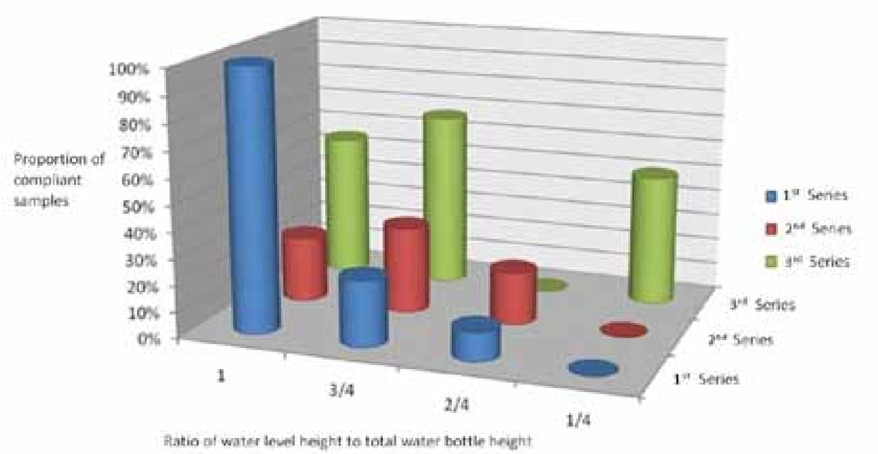

Figure 2: Proportions of compliant water samples (Official Gazette of the FRY nos. 42/98 and 44/99) as a function of water level height for all three sampling campaigns.

A comparison of aerobic coliform bacterial counts with water level heights in the bottles of the water coolers in the first sampling campaign shows that there is a correlation between the water level height in the bottle and the microbiological profile of the water. Higher water levels in the bottles corresponded to larger numbers of compliant samples (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005).

Based on aerobic coliform bacterial counts compared to water level heights in the second series of samples, no direct dependency of the microbiological profile of the water in the water coolers on the water level height could be established. However, it is apparent that the proportion of compliant water samples at 1 and ¾ water level heights was greater that the proportion of compliant samples at water level heights of ½ and ¼. This indicates an indirect dependency of the microbiological profile of the water on the water level height in the bottle.

The third sampling campaign revealed the same indirect dependency as the second campaign.

The frequency of water bottle replacement is shown in Table 1, including information about the water residence time in the bottle and the possibility of water contamination.

Figure 3 shows the total number of bacteria incubated at 37°C, in samples collected from all 20 water coolers during the three sampling campaigns, identifying the water coolers which will be discussed below.

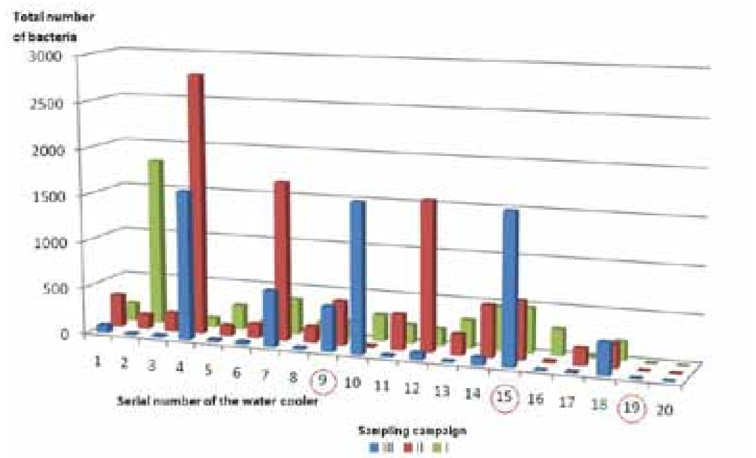

Figure 3: Total number of bacteria incubated at 37°C in water samples collected from all 20 water coolers during all three sampling campaigns.

- The frequency of water bottle replacement in Unit 19 was one day and water samples collected at the outlet of that water cooler, in all three sampling campaigns, complied with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005).
- The frequency of water bottle replacement in Units 9 and 15 was four days and seven days, respectively, and the water samples collected at the outlets of these water coolers, in all three sampling campaigns, failed to meet Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005).

Based on these results, a direct correlation between the frequency of water bottle replacement and the microbiological profile of the water sampled from the water coolers can be established, i.e. a higher frequency of water bottle replacement results in a greater number of microbiologically compliant samples of water collected from the water coolers.

During this research, several water coolers were disinfected prior to the third sampling campaign, as shown in Figure 4 (red circle).

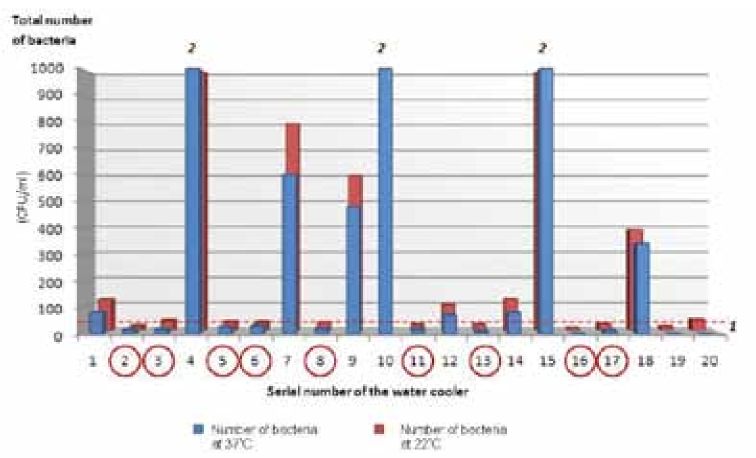

Figure 4: Microbiological profiles of water samples from water coolers (third sampling campaign).
1 Regulated bacterial count limit; 2 Bacterial counts for Units 4, 10 and 15 are beyond the range of the graphic.

The microbiological profiles of nine water coolers which were disinfected prior to sampling complied with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005) (Units 2, 3, 5, 6, 8, 11, 13, 16, 17). The water samples from Units 19 and 20 were microbiologically non-compliant in all three sampling campaigns, as shown in Figure 3, although these units were not disinfected during the course of the three sampling campaigns. The units had been installed recently (according to their users), so the compliant microbiological profile of the water sampled from these water coolers can be attributed to primary disinfection before first use, which resulted in a compliant microbiological profile of the water during all sampling campaigns, or over a period of three months. The water sampled from Units 1, 4, 7, 9, 10, 12, 14, 15, and 18 did not comply with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005), and this is attributable to the fact that they were not disinfected during the time of the three sampling campaigns.

Figure 5 shows the proportions of dominant bacterial cultures present in the water samples collected at water cooler outlets during all three sampling campaigns.

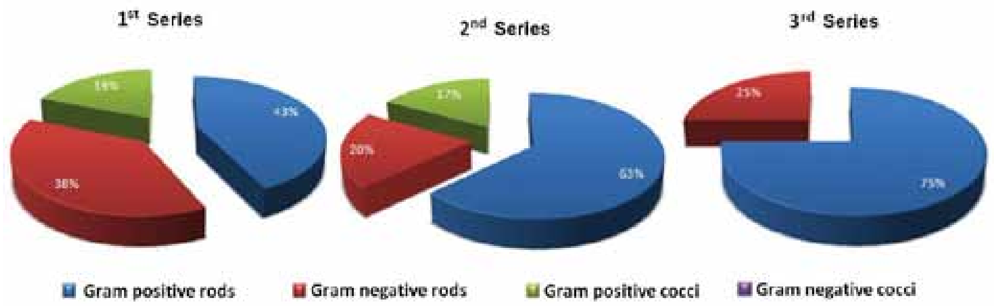

Figure 5: Proportions of dominant bacterial cultures present in water samples collected at water cooler outlets

Mostly Gram-positive rods were isolated (43% in the 1st, 63% in the 2nd and 75% in the 3rd campaign) from 60 tested water samples collected from 20 different locations during all three sampling campaigns, and their proportions increased during the course of the sampling campaigns. Gram-negative rods, in all three campaigns, exhibited the second largest share (38 in the 1st, 20% in the 2nd and 25% in the 3rd campaign). Their proportions decreased during the course of sampling. Gram-positive cocci were present in a relatively small number of the tested samples, and were undetectable in the third series of samples. In the first series, Gram-positive cocci were present in 19% of the samples, and in the second series in 17% of the samples. The presence of Gram-negative cocci was not detected in any series.

The dominant representatives of the isolated Gram-positive and Gram-negative bacteria were identified using Vitek 2 Compact. Gram-positive spore rods were of the genus Bacillus, and the isolated species were: B. cereus, B. thuringiensis and B. mycoides, while the identified species of Gram-positive cocci were Kocuria sp: K. kristinae and K. varians.

The presence of Rhizobium radiobacter was detected in the water sampled at the outlet of Unit 11 in the second sampling campaign. Following disinfection of the unit, these bacteria were not detected in the third series of samples.

CONCLUSION

Based on this research of microbiological profiles of water samples collected at water cooler outlets, the following can be concluded:

- In all three series of samples, a direct or indirect dependency between the water level height in the water bottle of the water cooler and the microbiological profile of the water could be established. This dependency is difficult to monitor due to constantly changing parameters which affect the microbiological profile of the water in the water coolers;
- A direct dependency could be established between the frequency of water bottle replacement and the microbiological profile of the water coolers. A higher water bottle replacement frequency resulted in a higher number of microbiologically compliant test samples of water from the water coolers;
- The microbiological profiles of the water sampled at the outlets of disinfected water coolers complied with Serbian national regulations (Official Gazette of the FRY nos. 42/98 and 44/99; Official Gazette of SaM no. 53/2005);
- The results of the first sampling campaign indicated an extremely poor microbiological profile of the water sampled at the outlets of the water coolers, and a lack of awareness of the water consumers about water quality and the need for water-cooler hygiene maintenance;
- During the three months of sampling and as a result of direct contacts with the users of these water coolers, a partial breakthrough was made in the understanding of the need for proper handling and regular and correct disinfection of the units, resulting in mass disinfection of the water coolers before the third sampling campaign;
- The use of water coolers is not adequately supported by regular microbiological analyses of water samples, especially in public places like schools and hospitals, where water from these water coolers can be a source of infection. Because of this risk, it is necessary for water cooler users to become personally involved in the maintenance of microbiological safety, by sanitizing the water coolers with commercial disinfectants or household cleaners like chlorine-based bleaches or acetic acid, regardless of the regulated maintenance frequency.

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Poster Presentation

PESTICIDE RESIDUES IN THE DANUBE RIVER BASIN IN SERBIA

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Pesticides are a group of substances used to fight pests and to improve agricultural production. These substances are one of the most hazardous groups of contaminants and pose a great threat to human health, fauna and environment in general. Their widespread use for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices. In surface and ground water pesticides can enter from point (localized) and non-point (diffuse) sources.

In Europe, pesticides are considered hazardous substances in accordance with current legislation regarding water. The European Union (EU) adopted the Directive establishing a framework for Community action in the field of water policy. This Directive which represents the basis for water management in EU has been approved in October 2000 with the objective to improve, protect and prevent further deterioration of water quality across Europe by the year 2015. The Directive 2008/105/EC on the protection of inland and other surface waters against pollution has set environmental quality standards (EQS), both annual average (AA) and maximum allowable concentrations (MAC), for a number of pesticides and other contaminants.

The Danube River is the second longest European river (after the Volga). It originates in the Black Forest in Germany and flows southeastward for a distance of some 2850 km passing through Central and Eastern European capitals, before emptying into the Black Sea. In Serbia the Danube has a length of 588 km or 20.6 % of its total length.

The Danube River basin in Serbia consists of the Tisa, Sava and Morava river sub-basins. The sub-basin of the Tisa River is the largest in the Danube River Basin (157,186 km^2). The Tisa is the longest tributary (966 km) of the Danube, but only 5% (164 km) of its catchments area lies in Serbia. The Sava River is the second largest tributary of the Danube and represents one of the most significant basins in the region (95,419 km^2). The lower reach of the river (206 km) flows through Serbia. The Morava River is 185 km long, with a basin area of 6126 km^2.

In this work a total of 41 pesticide residues were monitored in the Danube River Basin in 2009 and 2010. Selection of pesticides was based on current regulations and the extent of their use. The analysis of the selected analytes was performed using procedures based on solid-phase extraction–liquid chromatography–electrospray-tandem mass spectrometry (SPE–LC–ESI-MS/MS) and liquid-solid extraction followed by capillary column gas chromatography-mass spectrometry (LSE–GC–MS).

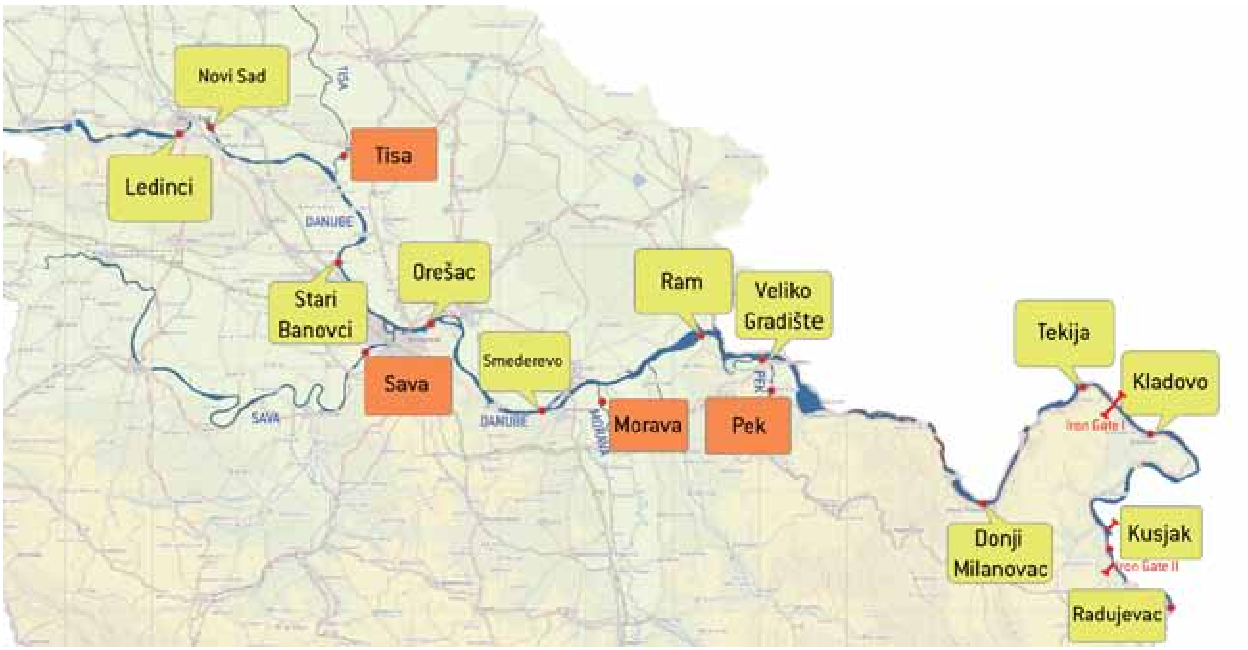

Figure 1: Map of the Danube River basin with sampling sites

Monitoring was conducted at twelve sampling sites. In total, a 410 km length of the Danube River was assessed (Figure 1). Four sampling sites, downstream from Smederevo (Ram, Veliko Gradiste, Donji Milanovac and Tekje) are within the Iron Gate 1 reservoir, two sampling sites (Kladovo and Kusjak) are in the Iron Gate 2 reservoir and one sampling site (Radujevac) is downstream from Iron Gate 2. Sampling sites in the upstream sections of the Iron Gate 1 reservoir were as follows: Ledinci, Novi Sad, Satri Banovci and Orešac. Monitoring was also conducted in the confluence zones of the Danube's major tributaries: Tisa, Sava, Morava and Pek. The water samples were collected in seven sampling campaigns in July and October of 2009 and in February, April, May-June, September, October-November of 2010.

In general, low pesticide levels were found, except for the samples collected during the May-June 2010 sampling campaign. This period is quite typical for pesticide application. On three sampling sites the concentrations found were about ten orders of magnitude higher than pesticide concentrations detected during the other sampling campaigns. At the sampling site Smederevo (Danube River), high concentrations were found for metalochlor (150 ng L^{-1}) and terbuthylazine (200 ng L^{-1}). In the Morava tributary, high concentrations were found for pesticides atrazine (188 ng L^{-1}), terbuthylazine (180 ng L^{-1}) and acetochlor (110 ng L^{-1}), while in the Tisa tributary only elevated concentrations of terbuthylazine (130 ng L^{-1}) were found. During other sampling campaigns, pesticides, if found, were present at low concentrations. Among monitored pesticides the most frequently detected was carbendazim. In the Sava and Pek, no detectable pesticide residues were found.

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THEME 3:

CLIMATE CHANGE AND ITS IMPACT ON GROUNDWATER

Invited Paper

THE NEED FOR NEW CONCEPTS IN URBAN HYDROLOGY IN THE CONTEXT OF "CLIMATE CHANGE"

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Abstract: In recent years, environmental conditions, including climate, have been very important to the operation of centralized water supply (CWS) and the sewage – wastewater treatment (SWT) in cities. Also, the technological, economical and management performance required from these systems is more demanding than expected at the beginning of their operation.Consequently, Romania has initiated the changes needed in the design, implementation and operation of CWS and SWT, focusing on systems that have groundwater as the main source.The paper highlights these changes, their possible effects and possible responses, focused on various components that may contribute to updating in relation to current requirements and demands of functionality and operation of those systems with application to groundwater bodies.
Keywords: water, sewage, sludge, adaptation, exploitation, climate change, groundwater.

INTRODUCTION

The report on "European Environment: Status and Perspective", in 2010, published by the European Environment Agency emphasizes that the environmental pressures on water systems in Europe are closely related to land use patterns and related human activities in river basins. The main pressures are: diffuse pollution, water abstraction and hydro-morphological changes and are related to hydropower generation, drainage and sanitation. The problem of soil erosion and loss especially in water reserve capacity is also relevant to how we manage water resources.

Much of Europe is affected by water scarcity and drought, while other regions are more exposed to severe flooding. Over the recent decades, in Europe there have been over 165 major floods, causing deaths, moving large population and generating economic losses. It is expected that future climate changes will worsen this situation.

The Water Framework Directive (WFD) is the key policy approach aimed at these challenges. It establishes the ecological limits of water use and management. In addition, it obliges EU Member States and regional authorities to take coordinated measures concerning, for example: agriculture, energy, transport and housing construction in the rural and urban planning context, taking also into account the conservation of biodiversity.

For the WFD to be successful, integrated river basin management is crucial, involving relevant stakeholders in identifying and implementing space differentiated measures - often involving compromise between different interests. Flood risk management, particularly the relocation of dikes and flood restoration, requires integrated urban planning and landscaping for the same purpose. Also the periods of drought should be taken into account.

GROUNDWATER ISSUES IN URBAN AREAS IN ROMANIA

Groundwater supply for the inhabitants of urban areas in Romania is typically conducted through a centralized water supply system (CWSS), consisting of the following components: the extraction front - pumping - transportation - drinking water treatment - storage - distribution network.

Stormwater and wastewater are handled similarly, through a centralized sewage collection and treatment system (CSCTS), comprising the following components: collection network - pumping stations - sewage plants - discharge into the natural environment. Of course, these general flows may, under certain conditions, be made more complex and, in some cases, easier.

For a long time the two systems were designed, constructed and operated in a separate concept. There are villages today with no water supply or sewage system, or those that only have a CWSS, without a CSCTS being properly promoted.

This situation has been surpassed. Both centralized systems should be considered as two subsystems of a single water–sewage system (WSS). This system, in turn, should be integrated into the Hydrographic Basin to which it belongs. Such an approach, based on the scheme presented in Figure 1, allows an analysis of:

- Changes in water quality, starting with the water quality at the source (considered as raw water for the water supply subsystem - WSSs), becoming drinking water, wastewater and further treated waste water that is finally discharged into the environment as a result of the sewage treatment subsystem STSs;
- Identify the legislation which must correspond to each category of water;
- The quantities of each section of the circulating water system to accommodate each beneficiary, first looking into the water quantity and quality needed for sustenance, and on the other hand into the ability to retrieve and evacuate, the environmental conditions, and the quantity and quality of water by type of user;
- Changes in production costs and costs of water for each section characteristic of the system, to promote concepts such as economic management, allowing recovery of expenses, but also respect the carrying capacity of all categories of beneficiaries, according to the average income family.

Such a concept, in Romania, is required also by the socio-economic dynamism over the past 20 years, manifested by:

- Changes in legislative requirements;
- Changes in socio-economic conditions of urban and rural areas;
- Changes in environmental requirements and climate conditions;
- Changes in the institutional/administrative system;
- Changes in human resource management;
- Changes in managerial concepts of WSS.

Ruling standards		Law no. 458/2002 amended and completed my Law no. 311/2004		NTPA 002 - 2005		NTPA 001 2005	
Types of water	Raw water	Drinking water		Waste water		Treated waste water	Raw water
Quantity	Q	0,95 Q	0,76 Q	0,69 Q + Rain water	0,69 Q		
Costs	300 lei/m^3	10000 lei/m^3		2000 lei/m^3			20 lei/m^3

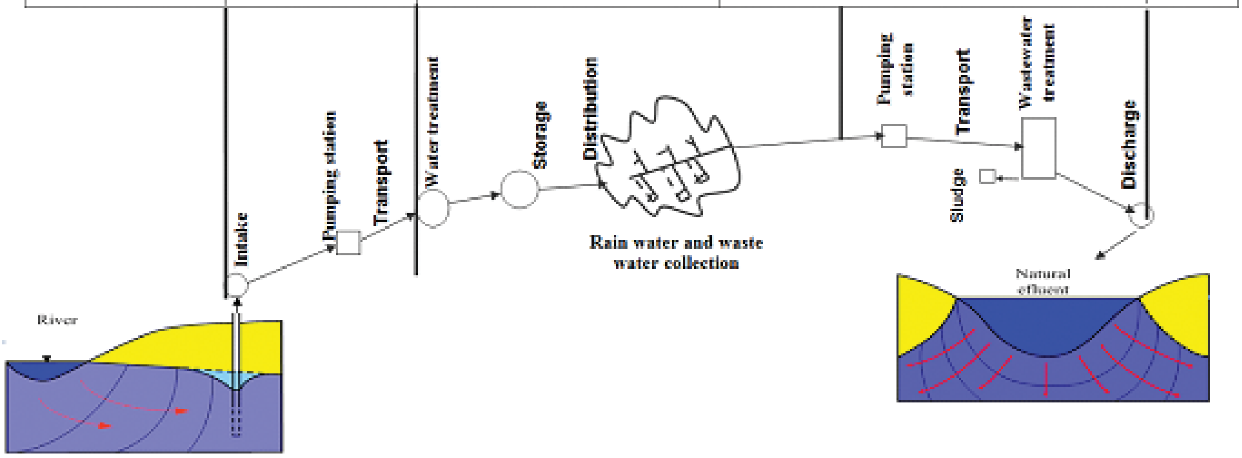

Figure 1: An integrated approach to water supply system and sewerage

Regarding changes in the legislative requirements, they follow in particular the responsibilities that Romania assumed by signing the EU accession treaty, and the Water Framework Directive no. 60/2000. Based on Government Decision no. 352/2005, Romania declared all of its territory as a sensitive area, which requires that all cities of more than 10,000 population equivalent introduce advanced wastewater treatment. Also, by the same legislative documents, the water infrastructure of settlements will be completed and considerably expanded, so that in 2013 all the towns larger than 10,000 population equivalent have a sewerage network and treatment, and by 2018 villages having between 2000 to 10,000 population equivalent should have similar facilities. Legislative changes concerning not only the development of facilities, technology and performance need to be made. Thus, through NTPA 001 “pollutant load limit values of urban and industrial wastewater discharged into natural effluents”, the NTPA 002 “indicators of quality of wastewater discharged into the town’s sewerage systems” and NTPA 011 “Requirements for discharges from urban wastewater treatment plants”, water and sewer service companies are required to promote good management in order to ensure treatment efficiency of 80-90% or more, figures which are not common today at the existing treatment plants.

A careful analysis of urban and rural realities attests to major changes in the socio-economic sphere and the water infrastructure has to adapt to these changes. Explosive development of new residential areas, especially around big cities, the emergence of housing projects, tourism, leisure, and large farms in remote areas pose problems or expansion of water distribution and sewerage networks or the achievement of local individual systems to ensure the performance already mentioned. A major issue raises the effect of introducing costs of water metering and the recovery of actual costs.

We can observe a drastic reduction in public water consumption, reducing the quantity and quality of wastewater. Under these conditions, Water Sewage System sizing is very difficult and companies have problems in managing technological and economic performance.

The same problems are also the changes in requirements due to new environmental or climate conditions. The whole European Union environmental legislation, almost entirely transposed into Romanian legislation, promoting new dimensions of environmental conditions, must be met by any socio-economic activity.

Thus, increasing the share of environmental performance in relation to the performance of process technology, and investment in environmental protection systems, have almost the same weight in the case of highly polluting activities, as the basic investment. Current climate conditions, which are expected to have a time horizon of greater openness, characterized by extreme events (drought / high intensity rains, flash floods) raise the question of a review, on the one hand, of the concepts of accumulation and restrictions during drought and, secondly, of new analytical methods for rain intensity, frequency and duration for rain calculating of urban pipe systems. Linked to the issues referred to, the analysis requires further development of sewerage systems and the structure of taking clean water generated by conventional high-intensity rain or torrential ones, to avoid phenomena of urban flooding, such as those manifested in the summer of 2005. The entire transport, distribution and collection should be reconsidered either in terms of operation at very low flow rates, with stationary water phenomena, with a deterioration in the quality of supplied water or alteration of wastewater characteristics, or at flow rates well above those taken under consideration when designing the system and that bring incalculable harm to the sewer system and adjacent urban area.

CLIMATE CHANGE COMBINED WITH THE BI-UNIVOCAL INFLUENCE OF WATER-SUPPLY AND DRAINAGE SYSTEMS AND THE NATURAL ENVIRONMENT

The issues mentioned above raise the question of reliability and risk analysis or the centralized water/sewerage system, including groundwater abstraction.

It is known that the reliability of a process, system or facility is a component of quality and it is carried throughout the life of a water/sewerage system. It should be taken under consideration during the different stages of conception, design, implementation and operation.

One of the goals of reliability assessment is establishing the operational safety and security of the system in normal conditions and in extreme situations (flood or drought). This also applies to ground water sources.

Flooding

In case of flooding, according to the experience of Romania, the extraction of underground water can be affected by:

- Loss of power supply;
- Flooding of the drilling wells;
- Decommissioning due to flooding of pumping stations;
- Moving/migration of the riverbeds, especially if “bank filtration” is used;
- Significant changes in water quality;
- Damage of the measuring and testing equipment, including any automated system.

Quantified, they represent significant losses. Of course, lack of drinking water for the population is the most important aspect.

Drought

Climate change is also manifested by the appearance of serious water shortages.

In certain areas, based on statistical data specific to Romania, the effect of water scarcity manifests itself in the abstraction of groundwater by:

- Drastic reduction of water level and available extraction flow;
- Increasing salt concentration leads to a worsening in the quality of the extracted water;
- Long term compromising of the drilling.

MEASURES / ACTIVITIES

To adapt the groundwater resources system to these cases, we should consider a series of measures and actions that are part of the Management Plan of the water supply and sanitation company, in the "Management in risk situations and environmental emergencies" chapter. First it is necessary to establish a "feasibility study and adaptation of the system to emergencies" which will be a scientific and technical basis of the set of measures. This set corresponds to the conceptual scheme in Figure 2.

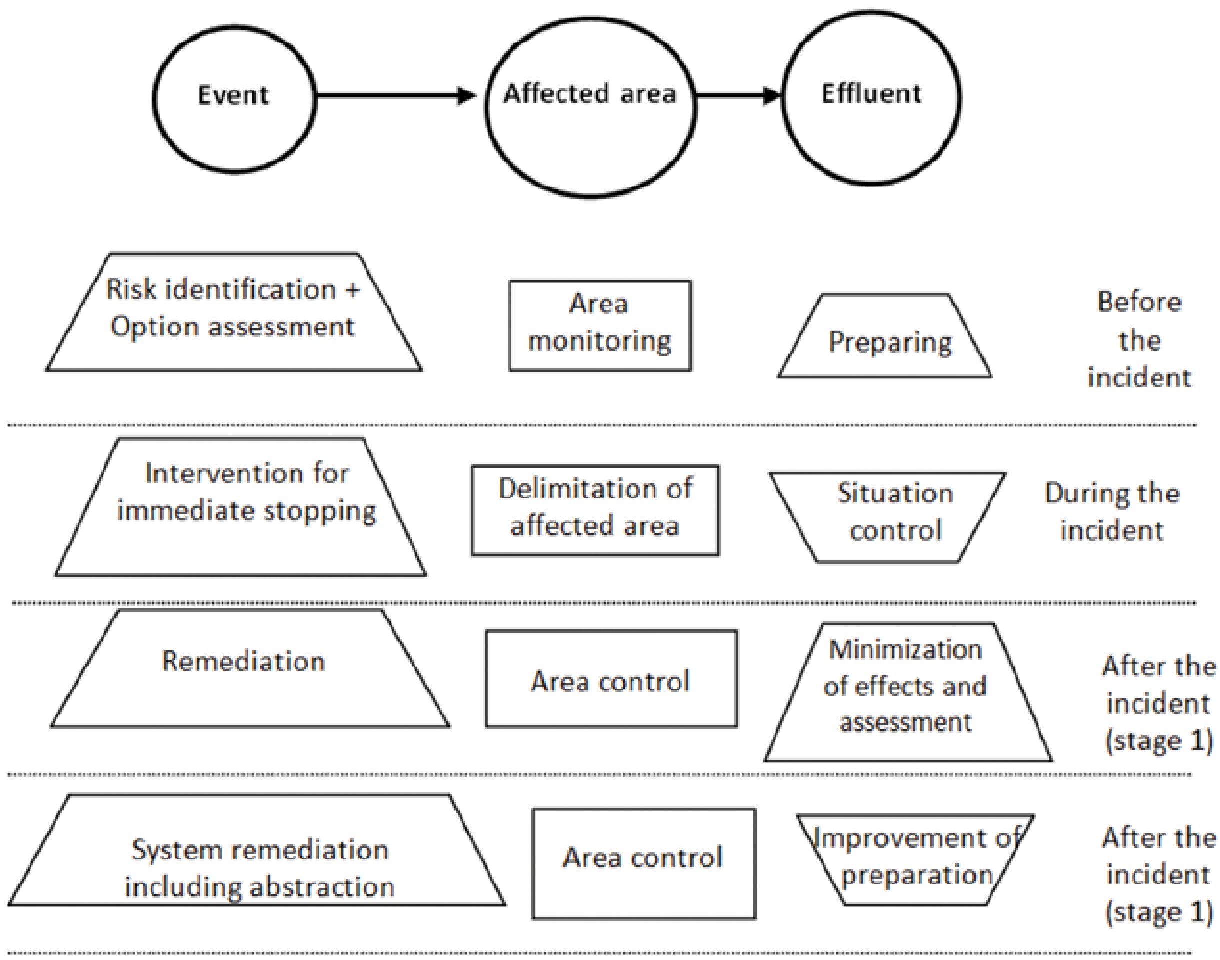

Figure 2: Operating model in case of extreme weather situations

We can highlight a preparatory step for the water supply and sanitation company and for the local government in risk situations:

- Finding alternative sources;
- Organization of storage capabilities with reserves of potable water for distribution to the population;
- Ensure the functioning of the monitoring system for alarm in the event of flooding;
- Training of intervention teams and the general public.

For the design and specialized investments, the following will be considered:

- Power supply from two different directions and independent power generators;
- Protection of wells and water supply objectives of the system against floods by specific works;
- Provision of mobile stations of low capacity of potable water, which for a short period of time will cope with the emergency situation;

All these actions/activities are subject to an analysis during the construction stages and will be updated in light of gained experience.

Other types of changes occur at the institutional/administrative level. After 2007, Romania's domestic market was open to public services of general interest, including water/sewage companies. In these circumstances, local companies face strong competition from those coming from countries with tradition in the field. Also, the need to adjust the operation of the WSS by integrating the operation of water resource management at basin level updates several forgotten concepts: application and update of specific water norms, water reuse and recycling. It requires a new concept to guide various types of water sources: groundwater sources must be dedicated primarily to public drinking water sources and surface water sources intended primarily for industrial and agricultural use. The multiple requirements mentioned above, the conditions of extreme difficulty in operating the companies, especially in small cities, without economic power, a population with low incomes, require water/sewage companies to reorganize at a regional level, perhaps in the current watersheds, and therefore possibly facilitate the connection with the work and portfolio of activities and tasks of the current branches of the "Romanian Waters" National Administration.

Recent assessments indicate that in order to achieve all the objectives that Romania has engaged in law enforcement in the water sector, the investment needed is about 20 billion euro by 2018. Such a budget is expected to be provided largely by funds from the European Union, the central budget and local budgets or loans from banks. But a significant proportion can and must come from local private capital through public private partnerships. Local administrations may draw investments in infrastructure from local private capital through specific strategies, providing certain facility, in the "win-win situation" concept.

Another category of changes occur in human resource management. As mentioned, the importance of water quality issues is increasing. Under these conditions the importance of analytical laboratory work is increasing in order to achieve compliance with that legislation. It also increases the weight of biological and bacteriological indicators in assessing the various categories of water quality, and performance of sewage treatment facilities as components of the WSS. As a result of these factors, new categories of specialists should be integrated in this activity, increasing the professional level of all categories of employees, finding new forms of motivation for employment stability and attractiveness of the water sector under a strong and competitive labor market.

Bridging some of those changes leads to changes in concepts and management of a WSS. Companies should consider to be certified according to ISO 9001 "Quality Management Systems" and ISO 14001 "Environmental Management Systems". This certification must be the result of a process of bringing in practices, procedures and a change in the organization of companies according to concepts provided by these standards. In the future, companies must be prepared for the implementation of Integrated Management Systems, which include also occupational health and safety management systems.

CONCLUSIONS

As a conclusion, the elements mentioned above are generating, at both central and local levels, the following:

- Changes in the components of what we call "urban hydrology" by taking into account the synergism of natural hydro-meteorological phenomena with the standard of living in human settlements;
- Changes in the provisions of regulations, standards, designs and operating instructions;
- Changes in water tariffs in the towns, with a focus on increasing the charge for sewage water;
- Changes in design concepts of technologies used in the WSS, but mostly from wastewater treatment plants (achievement of a 90-95% performance) or in the composition of distribution and collection networks;
- Discussing at river basin level of the orientation of different categories of water sources by type of beneficiaries.

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Notes:

Invited Paper

CLIMATE CHANGE AND WATER SUPPLY: CONSEQUENCES OF CLIMATE CHANGE AND POTENTIAL ADAPTATION STRATEGIES

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INTRODUCTION

Climate change and its impacts have been in the focus of public attention for many years. In the last year alone, the UN World Water Development Report and the World Water Forum have drawn worldwide attention to the questions of how climate change will affect the availability and quality of water and how human beings may adapt to this challenge. The European Commission's White Paper on "Adapting to Climate Change" and the report by the European Environmental Agency on the dangers of water scarcity and droughts have addressed these issues at the European level.

According to present knowledge climate change impacts in Central Europe are likely to be moderate compared to other parts of the world. Nevertheless, it will affect water supply directly, i.e. in terms of raw water availability and quality as well as with respect to the operation of the supply infrastructure.

Given that water suppliers are used to long-term planning and investment periods and know how to cope with changing parameters, they should (in cooperation with researchers, politicians and other stakeholders) be expected to succeed in adapting to the consequences of climate change.

In the following the focus is on climate change impacts and ways and means to adapt to these changes. The water supply industry is nevertheless fully aware of its responsibility for climate change mitigation, i.e. to reduce greenhouse gas emissions from water supply.

CLIMATE CHANGE IN GERMANY

Across Germany, annual average temperatures will go up, resulting in warmer and drier summers and milder and wetter winters. There are, however, large regional differences within Germany and in some areas contrary to the general trends observed across the country. As seasonal and spatial climate variabilities increase, the reliability of projections on future water management parameters decreases. Extreme weather events such as hurricanes, rain storms, and dry periods are generally more likely to occur. These, in a nutshell, are the climate changes most studies expect to occur until the end of the 21st century. However, regional projections for concrete quantitative parameters are still uncertain and can be made only within relatively wide boundaries. The degree of uncertainty is higher still if we want to determine on the basis of various climate factors (e.g. precipitation, temperature, evaporation) the changes of parameters like, for instance, groundwater recharge or runoff regimes in river catchments.

Climate change may also affect some of the familiar, fixed parameters that serve as a basis for planning and investment decisions, since the parameters derived from long-term time series that describe the availability of resources have ceased to be a reliable basis for infor-mation helping to assess future conditions. Increasing climate variability creates a wider range of potential weather conditions and may be part of future climate conditions. This requires precise analyses and monitoring of the development of all climate-related conditions that are relevant for water utilities in order to facilitate an early response to emerging trends. Long-term operating and investment decisions should take into account the expected range of climate changes which may impact the operation of water supply facilities and networks.

IMPACTS ON WATER SUPPLY

Climate change may result in the more frequent or intense occurrence of familiar phenomena that may also spread to other regions. This may include more frequent or intense periods of drought, heat waves or rain storms in regions that so far have been affected by these phenomena either not at all or only rarely. In other words, the water supply industry will not be confronted with vague unknowns but in general with phenomena it is experienced in coping with. This is not supposed to be construed as an all-clear but rather meant to encourage a proactive and unemotional discussion of the effects brought about by climate change.

Quantitative and qualitative aspects of changed water availability

While precipitation and total runoffs that increase on a multi-year average may definitely improve the water supply situation in some regions, the water industry will nevertheless have to adapt to a seasonally or intermittently diminished availability of water. Whether or not a permanent or temporary reduction in water availability will lead to a critical situation for a water supply system depends on a multitude of local factors such as, for instance,

- the existence or non-existence of alternative water sources and sufficiently flexible local water abstraction facilities enabling utilities to respond to a (temporary) loss of individual abstraction types/catchment areas;
- the existence of competing water uses and their increasing significance, if applicable (especially agricultural irrigation); and
- the expected development of water use.

The following consequences of changes in water resources availability loom ahead:

Groundwater

Permanently declining and seasonally diminished or absent groundwater recharge entails a concurrent sinking of the water table. The water resources availability situation will deteriorate particularly where (seasonally) diminished groundwater recharge affects comparatively small groundwater systems which are less capable to buffer precipitation variabilities. Springs fed by small or near-surface aquifers are especially sensitive to changes of water resources availability.

In contrast, in regions where groundwater recharge takes place almost exclusively during winters and where winters are getting wetter, average groundwater levels are expected to rise. This may cause water logging and damage to buildings, especially when increasing recharge is accompanied by a lower water demand.

Changes in water resources availability may also result in major groundwater quality changes, e.g. a non-dilution of contaminated groundwater may lead to higher pollutant concentrations in the raw water. Lower back pressures caused by sinking groundwater levels will lead to deep-well pump cavitation problems and may cause wells to run dry in extreme cases.

In coastal regions, the expected sea level rise may result in salt water intrusion into coastal aquifers. A permanently improved water resources availability is expected for regions with increasing groundwater recharges and larger groundwater resources.

Lakes and reservoirs

Seasonally and intermittently sinking levels of lakes and reservoirs will generally diminish raw water availability exactly during peak demands. This may result in smaller depths of the storage volumes suitable for raw water withdrawal, a smaller portion of cold deep water (hypolimnion) and in decreasing back pressures at withdrawal points. Beyond this, the capacities to buffer polluted inflows and water withdrawal con-trol options may be compromised.

Rains storms may adversely affect raw water quality as they may cause erosive runoffs and an increase in spillovers from separate and combined sewerage systems, entailing increased inputs of sediment- and particle-bound contaminants and microorganisms. Climatic changes will more severely affect the quality of small and shallow waters and waters with a higher trophic level than that of deep and oligotrophic waters.

Watercourses

The risk of flooding increases with the rising frequency of rain storms. Floods may adversely affect groundwater quality and mobilise dangerous substances e.g. from industrial brown-fields. Extremely high water levels may submerge bank filtration systems and thus directly pollute raw water. During extremely low flows water withdrawals from rivers might need to be reduced or even ceased.

Lower river flows may lead to higher concentration of pollutants and adversely affect raw water quality. This is relevant also when river water is used for artificial groundwater recharge or bank filtration. The polluter-pays principle is particularly significant against this backdrop.

Rain storms may adversely affect raw water quality as they may cause erosive runoffs and an increase in spillovers from separate and combined sewerage systems, entailing increased inputs of sediment- and particle-bound contaminants and microorganisms. Rain storms, floods and persisting periods of drought may interfere with utility operation and, in some exceptional cases, result in a temporary water supply cut-off.

Rising air and water temperatures

Higher air temperatures increase the vertical temperature gradient in lakes and reservoirs. Thermal stratification tends to become more stable; full circulation (required for the renewal and oxygen supply of the hypolimnion, which is generally crucial for raw water abstraction), occurs more rarely, decreases in length and may even stay away for good in isolated cases. Moreover, prolonged periods of heat will result in deeper epilimnion strata, thus reducing the depth of the hypolimnion. Increasingly insufficient deep mixing with ensuing deep water replenishment has already been observed in Lake Constance in winter times.

Higher temperatures generally accelerate biological and chemical processes in water bodies. This tends to adversely affect raw water quality; the extent of the impact however also depends on other parameters such as the availability of nutrients and oxygen. These may foster the growth of algae, for instance, so that algal blooms and a concurrent formation of odours and flavours as well as a release of bacterial exo- and endotoxins may ensue. Another consequence may be delayed phyto- and zoo-plankton growth, resulting in the degeneration of today's food chains within aquatic communities.

Higher air and soil temperatures may also lead to higher drinking water temperatures in distribution networks. Whether higher temperatures increase the risk of microbial growth and contamination depends very much on the general condition and operation of the supply system. In networks with a given tendency towards microbial recontamination, this tendency will be fortified by higher temperatures.

Higher air and water temperatures tend to favour the proliferation of a variety of waterborne pathogens. Any impairment of drinking water is possible only in exceptional cases. In general, the monitoring and treatment of raw waters potentially at risk (surface water, near-surface groundwater and spring water) is already focusing on the presence of pathogens.

Indirect consequences

Higher soil temperatures promote conversion and mineralisation processes in soils and, consequently, the pollution of seepage water. These processes depend on sufficient soil moisture. The trend towards drier summers increase seasonal topsoil desiccation which inhibits mineralisation processes. The conversion and displacement of the accumulating substances is delayed until infiltration of the vadose zone occurs in autumn, which may result in a considerable mobilisation of substances (e.g. of nitrate) and subsequent pollution of seepage water.

Intensification of agriculture with growing demand for irrigation, fertiliser and pesticide use triggered by the cultivation of energy crops for biofuel production, the extension of the vegetation period, and decreasing precipitation during that period.

Extreme weather events like rain storms, hailstorms or droughts may lead to crop failures or even ruin the entire standing growth, causing plants not to absorb fertilisers and/or the fertilisers to remain in the plant residues, which may result in massive nitrate pollution of groundwater.

Conflicts about the use of locally or regionally available water resources: locally and temporarily, water resources may not suffice to satisfy the demand of all users (i.e. water suppliers, households, farmers, commerce and industries) in a region.

Peak demand increases: the dry summer of 2003, for instance, demonstrated that water consumption increases during dry and hot periods. As a result the gap between average and peak water demands grows. The situation becomes even worse in regions with decreasing average water demand caused by e.g. a population decrease, a change in industrial consumption etc. Under such circumstances water suppliers face new challenges for the design, construction, and operation of water supply systems.

As extreme weather events and flood events are likely to increase in frequency and intensity, dam and reservoir management will have to focus more on flood protection, which in turn may result in reduced storage capacities for raw water abstraction.

ADAPTATION OPTIONS FOR WATER SUPPLIERS

Adapting to climate change is basically concerns society as a whole. This is true also for the adaption in drinking water supply, although water suppliers play a key role in this regard.

In order to identify suitable adaptation measures, water suppliers should analyse their individual situation comprehensively, focusing on the following questions, for example:

- Which impacts and consequences will affect a supply system?
- Which assets and processes of a supply system are particularly sensitive to the expected impacts?
- Which adaptation options do the ongoing operation schemes and the established management tools offer?
- What needs to be considered with regard to future investments?

A continuous integration of the findings thus obtained into all planning and decision-making processes of the operation is crucial.

The following provides an overview of adaptation options for water suppliers:

Management and protection of water resources
- Trend analyses and drawing up of long-term water availability projections
- Area-specific adaptation of monitoring networks and programmes enabling staff to knowledgeably assess potential quality changes.
- Integrated water resources management taking into account aspects of both quality and quantity
- Securing drinking water supply through official spatial planning and water resources planning and approval procedures.

Abstraction, treatment and network operation
- Redundant abstraction systems allow for a flexible combination of different types of raw water resources and abstraction technologies. This may be achieved by creating networks (developing additional proprietary raw water sources, integrating adjacent local direct supplies, connecting to regional water supply systems).
- Adapting wells and pumping facilities to changing parameters (e.g. permanent or temporary phreatic decline or falling reservoir water levels)
- Adapting water treatment to expected new or changed raw water qualities
- Creating disinfection facilities in storage and distribution systems.
- Creating larger storage capacities in water works and networks to ensure that supplies meet growing peak demands
- Adaptation of network inspection and flushing schemes
- Keeping water losses permanently low

Organisation and management
- Adapting organisational structures and management processes to the expected changes so as to be able to manage risks and crises

WHAT CAN POLITICIANS, SCIENTISTS AND WATER SUPPLIERS DO TO ADAPT TO THE CONSEQUENCES OF CLIMATE CHANGE?

There is no panacea and no one-size-fits-all solution for climate change adaptation. Regional differences of climate change impacts on water abstraction, treatment and distribution are huge. Impacts and vulnerabilities differ between catchments or even within a supply system. The need for adaptation and the scope for action are always predicated on the prevailing natural conditions, the technical structure of a supply system, interaction with other factors such as societal and economic development or the concurrent industrial and agricultural water uses. The adaptive latitude of a water supplier is also defined by general legal and political parameters. And ultimately, a lot depends on a utility's willingness to actively address climate change issues and to rely on both its own and external know-how. In particular the uncertainties of projections and the knowledge about the increasing variability of climatic conditions need to be systematically analysed and considered in the management of resources as well as in the operation and design of supply infrastructures. In this context, all societal stakeholders need to be repeatedly made aware of the fact that the protection and sustainable management of water resources is an interdisciplinary task to which the water supply industry can contribute its share but which it can by no means accomplish on its own.

Against this backdrop, it deems necessary that policy-makers, scientists and water suppliers actively support the following framework conditions:

- Granting priority to drinking water supply before and above all other uses of water resources within catchments
- Securing drinking water supply through official spatial planning and water resources planning and approval procedures.
- Procuring sufficient water rights to meet peak demands
- Granting priority to public water supply in the case of uncertain power supply
- Including water supply facilities into official flood protection programmes and schemes
- Providing basic data from supra-regional (climate) models for regional (hydrological) models (e.g. groundwater models) for water resources management purposes
- Limiting agricultural irrigation needs by developing drought-resistant crops and crop rotations and making their use mandatory
- Optimising safety of water supply, i.e. through the development of integrated supply systems

The DVGW homepage provides a platform with information about climate change adaptation, about the activities pursued by the Federal and Länder governments as well as about relevant research projects and plans related to water supply. Beyond this, it offers some examples that illustrate the practical work of water utilities:

- www.dvgw.de/water/ressourcenmanagement/klimawandel/

Invited Paper

GROUNDWATER RESOURCES UNDER STRESS CAUSED BY GLOBAL CHANGE

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Abstract: Groundwater has very important social, environmental and economic values essential for sustainable development. It is the primary source of drinking water for more than 1.5 billion people worldwide. In this paper groundwater problems caused by global change (climate change and/or variability and anthropogenic interventions) in urban and karst areas are discussed. Groundwater has become an increasingly crucial issue facing many cities around on the planet today. Rapid population growth followed by uncontrolled spreading of urbanized areas leads to growing pressure on quantity and quality of groundwater resources. Abrupt changes of local, regional and maybe global natural and human induced hydrological and hydrogeological processes deeply and dangerously affect associated ecosystems. Essential element of sustainable groundwater management is differentiating between climate change and human impacts on groundwater quality and quantity. It seems that human interventions on the groundwater resources are likely to be more important than climate change in the foreseeable future.
Keywords: groundwater, climate change, anthropogenic influence, city, karst

INTRODUCTION

Planetary water resources are under severe stress. They are significantly affected by global change, which involves more than climate change. The major drivers of global change are: population growth, climate change and/or variability, uncontrolled and unsustainable urbanization and industrialization, expansion of infrastructure, land use change, massive pollution, unsustainable water resources management (especially groundwater overpumping), massive deforestation, wetland drying up and many other reasons. Groundwater as one of the most important part of planetary water resources is under especially vigorous pressure. In this paper groundwater problems in extremely valuable and vulnerable urban and karst environments will be discussed.

Global change affects groundwater recharge and discharge rates and its quality. It increases the uncertainty associated with the future availability and variability of groundwater resources.

Current knowledge of groundwater recharge in different environments is poor. In order to better understand the future impact of global change on groundwater resources and associated ecosystems strong research efforts are needed.

Water for all purposes is extracted from the hydrological cycle. "Blue water" is rainwater converted to runoff in rivers and groundwater in aquifers. "Deep blue water" is the part of the rainfall that forms renewable groundwater resources. The both kind of blue waters are used in most day to day livelihood activities. "Green water" is a component that infiltrates into the soil to replenish the root zone. "White water" is the rainfall component that evaporates.

Figure 1 schematically represents all previously explained elements of the hydrological cycle. Table 1 presents the water budget components for three environments given in percents of precipitation. Attention should be paid to the last row where quantity of "deep blue water" or "deep percolation" component is given in red and bold numbers. This component recharges groundwater. From the assessment given in Table 1 it is obvious that decreasing of precipitation possibly caused by climate change and urbanization as human intervention can abruptly and dangerously decreases groundwater recharge. Of crucial scientific as well as practical importance is to understand and control consequences of human intervention and climate change on the groundwater quantity and quality.

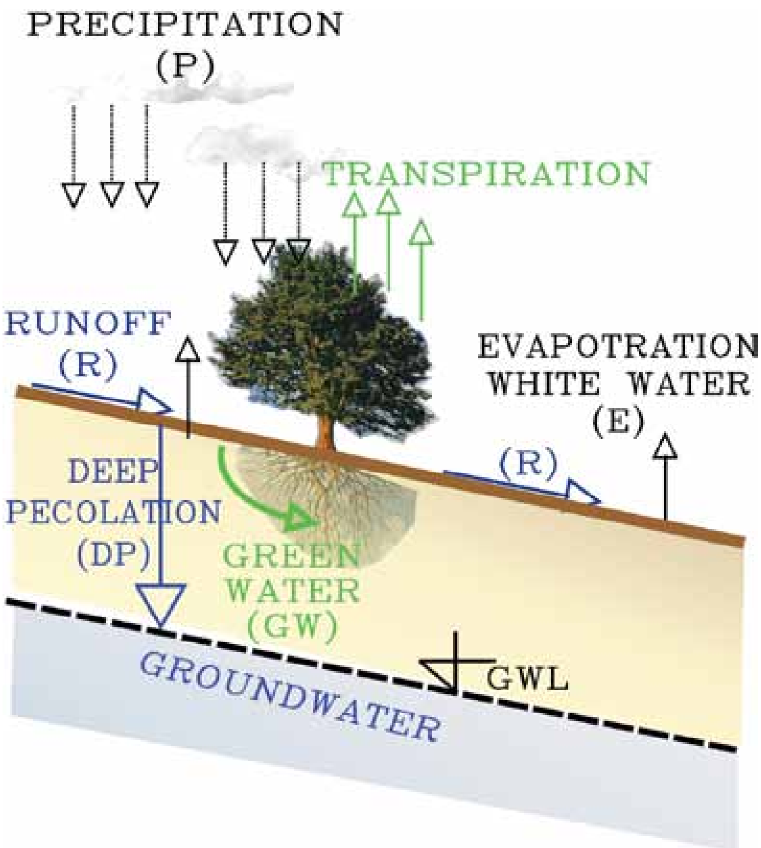

Figure 1: Schematic presentation of the water budget components of the hydrological cycle

Table 1: Water budget components for three different environments given in percentage of precipitation

Environment	Precipation	Runoff	Evaporation	Transpiration	Deep Percolation
Agricultural Landscape	100	10-25	30-50	15-30	10-30
Karst Area	100	0-15	5-10	0-10	50-70
Urban Area	100	40-80	20-60	0-5	5-10

CLIMATE CHANGE OR VARIABILITY

IPCC (2007) establishes the increase of approximately 0.8±0.1 ºC in the average global temperature near Earth's surface since 1900, and strongly connects it with anthropogenic influences of "greenhouse gasses". The American Geophysical Union (AGU, 2003) position statement on human impacts on climate is: "The complexity of the climate system makes it difficult to predict some aspects of human induced climate change, exactly how fast it will occur, exactly how much it will change, and exactly where those changes will take place". Ma et al. (2004) as well as many other scientists consider that global warming during the 20th century is caused mainly by increasing greenhouse gas concentration especially since late 1980s. Scafetta and West (2008) suggest that the current anthropogenic contribution to global warming is significantly overestimated. They estimate that the Sun could account for as much as 69 % of the increase in the Earth's average temperature.

Leroux (2005) considers that the idea of "climate change" has become widely synonymous with that of "global warming". He considers that this is paradoxically, construed in a very negative way as inevitably catastrophic, even in "cold" countries. For the detailed and unbiased analysis of this great global problem one of the obstacles is that the science of climate change is inextricably mixed up with politics and media. Galvin (2008) concludes that for this all the fuss about global warming is grossly exaggerated.

Popper (1963) declares that falsifiability is an essential element of science. The crucial problem of the General Circulation Models (GCMs) is that they may be not falsifiable or verifiable at present. Koutsoyiannis et al. (2008) consider that as falsifiability is an essential element of science, the scientific basis of climatic predictions using GCMs is under question. Their argument is that scientists need to wait several decades before know how reliable the predictions will be.

Bonacci (2010, 2011) reported that in the Western Balkans region warming started in period between 1987 and 1997, mostly in 1988. Differences of average mean annual air temperatures before and after warming are about 0.81 ºC. Before 1987, during 20th Century, increasing trend did not notice. Strong air temperature increases in the last twenty years should be explained by detailed interdisciplinary analysis. On the bases of available data it seems that during 1943-1952 mean annual air temperatures in this region were higher than average and in some stations higher than in the last twenty years. Levi (2008) stresses that scientists studying the time series of many climate-related variables had been noticing a rather sudden change around the mid 1980s. A similar conclusion about the existence of a statistically significant shift (mainly jump) in the air temperature time series, i.e. the beginning of warming in last twenty years is reported in several papers.

In the open letter to Canadian Prime Minister signed by 61 prominent international scientists in 2006 is written: "Observational evidence does not support today's computer climate models, so there is little reason to trust model prediction of the future. While the confident pronouncements of scientifically unqualified environmental group may provide for sensational headlines, they are no basis for mature policy formulation. The policy of global climate change is, as you have said, an emerging science, one that is perhaps the most complex ever tackled. It may be many years yet before we properly understand the Earth's climate system. We need to continue intensive research into the real causes of climate change and help our most vulnerable citizens adopt to whatever nature throws at as next" (www.friendsofscience.org/index.php?id=113).

GROUNDWATER IN URBAN AREAS

Cities are the world's economic power engine. Their long term sustainability strongly depends on the adequate water supply. More than 50 % of the world's population currently lives in the cities. It is estimated that in 2050 about 70 % of humanity will live in urban areas. A large part of the world's urban population use groundwater for its drinking water. Great problem is that historically, the vital role that groundwater plays in the urban water cycle has been severely neglected (Pokrajac and Howard, 2010). Groundwater degradation due to pollution and overexploitation are the most serious problems in these extremely vulnerable and valuable areas.

One of the most obvious consequences of urbanization is land use change. Changes in surface patterns can have significant implications on the urban hydrological cycle. Urbanization largely and in short time increases impermeable surface, which consequence is increasing of the surface runoff and reduction of infiltration (groundwater recharge). Result of this is decreasing of groundwater availability. Due to this reason natural groundwater recharge can be dangerously and unsustainably transformed and urban floods hazard can be extremely magnify. It should be stressed that these abrupt changes of local and regional hydrological and hydrogeological processes can deeply and dangerously influenced on surface and underground ecological processes.

Urbanization causes among others, the formation of urban heat islands. It is increased temperature field in a metropolitan urban area where the land surface is modified by urban development and waste heat generated by heating in buildings. This phenomenon therefore leads to increased water use.

The main and generally everywhere present problem is that urban groundwater resources are being exploited in an unsustainable way. For example in relatively short period of only 13 years (1987-2001) due to overpumping average annual groundwater level near Chinese capital Beijing had been decreased about 23 m. Figure 2 present a time series of mean annual groundwater level with polynomial trend line measured in one piezometer in the suburb of Zagreb town (Croatia) during the 1972-2010 period. Gradually long term decreasing of the groundwater level is mainly caused by urbanization (land use change from pervious agricultural to impervious urban landscape) as well as regulation of the Sava River, which feed this aquifer.

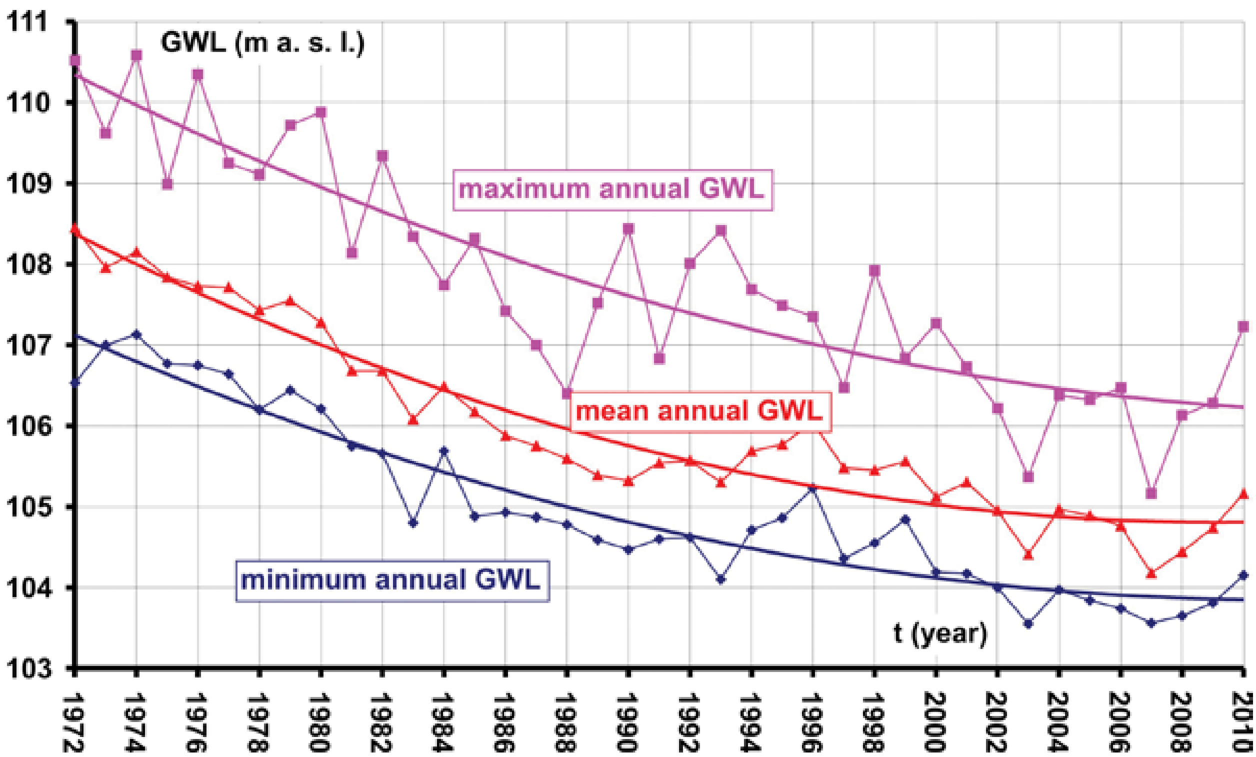

Figure 2: Time series of mean annual groundwater level with polynomial trend line measured in one piezometer in the suburb of Zagreb town (Croatia) during the 1972-2010 period

GROUNDWATER IN KARST AREAS

Karst is the type of landscape which covers about 25 % of the Earth surface. It is defined as a terrain, generally underlain by limestone or dolomite, in which the topography is chiefly formed by the dissolving of rock, and which is characterised by sinkholes, sinking streams, closed depressions, subterranean drainage and caves (Field, 2002). A wide range of closed surface depressions, a well-developed underground drainage system, and a strong interaction between circulation of surface water and groundwater typify the karst. Due to the very fast infiltration rates overland flow and permanent open stream flows in karst terrains are rare. This is the main reason why groundwater recharge in karst areas is much more effective than in non-karst areas.

Karst aquifers are generally continuous. However, numerous subsurface morphologic features in karst (caves, jamas, fractures, faults, impermeable layers, karst conduits) strongly influence the continuity of the aquifer, so that an aquifer commonly does not function as a continuum in a catchment especially during periods of abrupt groundwater rise. One of the most important characteristics of karst aquifers is the high degree of heterogeneity in their hydraulic properties. Karst aquifers can be very deep (hundreds of meters) with endless cracks, fractures, joints, bedding plains, and conduits serving as groundwater pathways. The highly heterogeneous nature of karst aquifers leads to the inability to predict groundwater flow direction and travel times. For karst aquifers' investigation special challenge represent existence of concurrent fast turbulent flow through large karst conduits and slow, diffuse laminar flow through small karst fissures, joints, cracks and bedding plains. In order to define exactly the hydrologic catchment boundaries, it is necessary to carry out extensive geologic, hydrologic and hydrogeologic investigations. Delimitations based on geological considerations could not be reliable.

Karst aquifers as well as karst underground are extremely susceptible to contamination. The surface and especially subterranean environment in karst provide a range of habitats with different chemical and biological processes. Karst ecosystems are sensitive to environmental changes. Karst species are extremely endangered because of the extreme vulnerability of karst terrains and due to fact that populations are small.

Humanity's interventions in karst are numerous (Drew and Hötzl, 1999; Bonacci, 2004; Milanović, 2004). They can be categorized as follows: 1) water storage in surface and underground reservoirs; 2) increase or decrease in the capacity of outlet structures; 3) construction on the karst surface (urbanisation, industrialisation, construction of railways and motorways, dams and reservoirs, irrigation and drainage, river regulation, etc.) ; 4) construction in the karst underground (drilling tunnels and other underground engineering construction); 5) actions to the groundwater (mainly massive pumping, rarely recharging, pollution); 6) use of the karst spring water (special problem represents development of the brackish coastal karst springs); 7) interbasin water transfer; 8) quarrying; 9) grouting; 10) massive tourism; and 11) deforestation and land use changes, which can have end in "rocky desertification".

The most common damages caused by them are: 1) collapse of surface and underground structures (Waltham et al., 2005); 2) pollution of groundwater; 3) increasing risk of flooding; 4) decrease in karst springs outflow capacity (even their draying up) and the intrusion of the sea water; 5) changes in local and regional hydrological and hydrogeological regimes; and 6) the massive destruction of surface, and especially underground, habitats and species (Bonacci et al., 2009). The worse consequence of the sea level rise, caused by global warming, will be intrusion of saline water in the coastal aquifers.

A high degree of parcelling, physically delimited by a very developed network of dry stonewalls, represents the most important feature of the many karst region landscape, especially in the Mediterranean area. Dry stonewalls are of fundamental importance as a habitat for diverse flora and fauna. They retain moisture during the hot summer period, create shade and serve as shelter for many species. Hand-built dry stonewall terraces permitted agricultural production on slopes of up to 70%. Terracing by using dry stonewalls prevents overland flow, increases groundwater recharge and serves as a very effective measure against erosion and the spreading of wildfire. Massive stone clearings mean the entire disappearance of stonewalls. This process could be very dangerous from ecological and hydrogeological points of view. The process of massive stone clearing started at the second half of the 20th century and strongly intensified at the beginning of the 21st century.

Current studies on the impact of massive stone clearing in Italian karst indicate that agricultural activities have important consequences on groundwater quality, which vary with the season and the trend of precipitation. Direct observation of the stone cleared surfaces evidences a net loss of the fine soil component, so farmers are obliged to add new soil. A great part of the lost soil reaches the sea during the frequent floods. Soil loss is the closest precursor of the desertification of the concerned areas (Conora et al., 2008). Karst ecosystems have been resilient and resistant to the lengthy but slow human pressure, especially land use changes the main activity of which was “primitive stone clearing”. This kind of coexistence between human beings and nature resulted in a sustainable functionality and balance of vulnerable karst ecosystems. It seems that present-day pressure on the karst ecosystems does not ensure their sustainable development as well as the preservation of their biological diversity.

In last about hundred years and especially in recent time anthropogenic influences created new and very fast redistribution of surface water and groundwater in karst areas, which had caused changes of connections between aquifers of neighbouring (in some cases distant) karst springs (Bonacci, 2004). For this reason technical and environmental damage in some cases has exceeded the benefits. Groundwater pollution, destruction of habitats, threatening of karst subterranean ecosystems, which can cause the disappearance of endangered species most of which are endemic, are very often negative consequences of anthropogenic activities in karst regions.

It can be concluded with high degree of probability that human interventions on the karst groundwater resources are and will be more important and dangerous than climate change in the foreseeable future.

CONCLUSIONS

The growing world population, the commensurate increase in demand on limited groundwater resources, the anthropogenic interventions and the potential impacts of climate change and/or variability on groundwater resources and ecosystems depended of them are the main reasons for necessity of interdisciplinary scientific co-operation in their management and protection. Protection and sustainable management of the groundwater resources is of crucial importance. The world needs to adopt to global change pressure in groundwater management without delay. Improving complex and continuous monitoring network of different climatological, hydrological, hydrogeological and ecological parameters as well as access to them is critical for assessment, prediction and adaptation to global change. It is highly important to understand the interaction of groundwater and surface water in karst and their influence on surface and underground biological processes.

To obtain a harmonious, reliable and sustainable development, it is necessary to take the complex, interactive, technical, social, economic, environmental and cultural aspects of groundwater resources management into account in decision-making. In the case of the transboundary karst groundwater resources management it is especially hard and dubious task. Karst catchments and aquifers display the extreme heterogeneity, variability and vulnerability of their hydrologic, hydrogeologic, hydraulic, ecological and other characteristics in time and space.

Of special importance is the establishment of firm network of contacts with leading independent scientists, who promote new ideas and concepts independently of mainstream directions. Transfer of information across spatial and/or temporal scales is one of the most fundamental issues in the groundwater hazard and risk management investigation. Science will give more certainty in groundwater resources management, but will never be enough knowledge. In order to better solve or mitigate future groundwater problems, there is an urgent need to improve strategies, approaches and solutions that will lead towards holistic, more effective and sustainable management.

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Notes:

Full Paper

CLIMATE CHANGES AND WATER SUPPLY IN SOUTHEASTERN EUROPE – THE PROJECT CC-WATERS

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Abstract: "Climate Changes and Impacts on Water Supply" is a large 3-year project under implementation since 2009. The project is being carried out by 18 partners from 9 countries from southeastern Europe. The main objective is to ensure for several decades water availability and safety for a sustainable water supply for citizens in different regions under the influence of climate changes also causing land-use changes. The project consists of seven working packages. Five of them are purely technical and closely linked. In total, 25 test areas with different climate, morphological, hydrological and geological settings are selected for the application of a jointly elaborated methodology. Estimated climate changes and, consequently, water availability and future land use patterns are considered as a valuable base for the proposal of adequate response measures in the water management sectors and to mitigate negative impacts on water supply.
Keywords: climate change, water resources, groundwater, water supply, land use, southeastern Europe

INTRODUCTION

CC-WaterS is an acronym of the 3-year project "Climate Changes and Impacts on Water Supply" under implementation since May, 2009. It is being implemented under the Southeast Europe programme (European Territorial Cooperation, ETC-SEE), funded by the European Regional Development Fund (ERDF) and the Instrument for Pre-Accession Assistance (IPA) for non-EU member states.

The project CCWaters has the objective to assess possible impacts of climate change and land use induced changes on water supply schemes in the SEE. There are 18 project partners from 9 countries involved in this project (Austria, Italy, Slovenia, Hungary, Romania, Bulgaria, Greece, Croatia and Serbia). The leading partner is the Municipality of the City of Vienna - Waterworks, Austria. The partners are from different sectors: governmental bodies, water suppliers and research institutions. They are working together and their complementary knowledge and findings should be implemented jointly in the water/land use practice to reduce the vulnerability of water intake areas. Adjustment of water management strategies should help to achieve water supply tasks under climate and regional changes. Project activities are supported and supervised by the Steering Committee and the Scientific Advisory Board (one representative from each country).

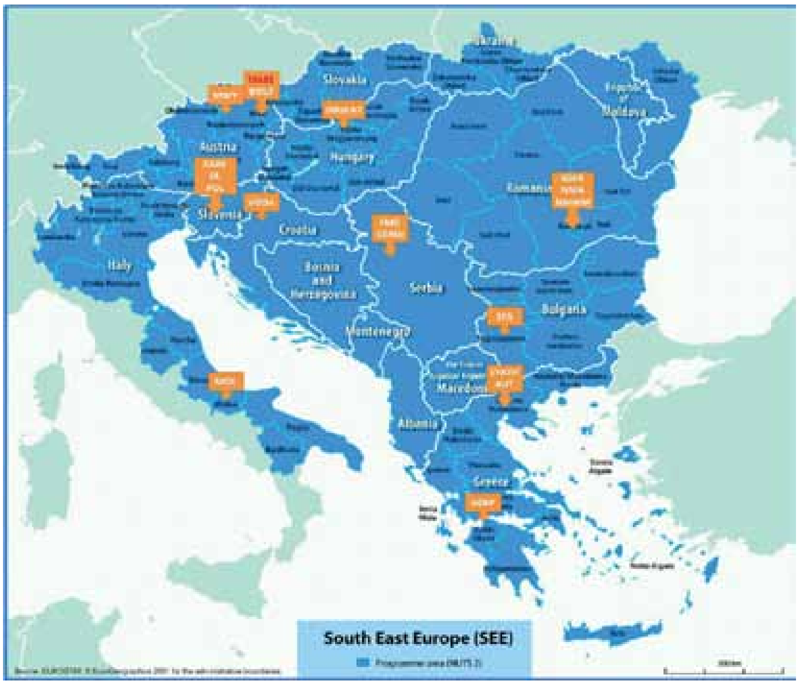

Figure 1: Study area and countries and institutions involved (acronyms)

The project consists of seven working packages (WP). Among them five deal with technical issues: Climate Change, Water Resources Availability, Land Uses and Water Safety, Socio-economic Evaluation, and Water Supply Management Measures; the remaining two, Management and Coordination, and Communication and Dissemination, are more organizational.

The five technical WPs are strongly linked. Climate Change provides input for the next parallel operating packages: Water Resources Availability and Land Uses. The results of the work of all three are the basis for Socio-economic Analyses: any changes in the water availability and safety of the public water supply result in economic losses or benefits. Therefore, climate change with its impact on water resources and land use may also have impact on the technical requirements and the organization of public water supply. Finally, adaptation of Management Measures should be a logical consequence of findings and conclusions from previously completed WPs.

In addition to preparation of the jointly developed Monograph, wider promotion of the project results is planned through numerous scientific and popular articles, brochures, and movies. The Monograph as a comprehensive document would cover the background problems of the project, the challenges, methodology and achievements regarding climate change, and the mitigation of its impacts on water supply.

During the preparation of this paper the CCWaterS project continues; some of its results are completed, others are still under evaluation and reporting. Thus a complete presentation of the project's achievements is not possible at this stage: more emphasis has put on climate change and methodology of water resources assessment, while the parts related to socio-economic analyses, management principles and proposed measures are under work in progress.

PROJECT OBJECTIVES

The main objective of CC-WaterS is to safeguard water availability and safety for a sustainable water supply for several decades for citizens in different European regions under the influence of CC provoking land-use changes.

Climate change (CC) affects fresh water resources and may have significant influence on the ability to provide safe and sustainable drinking water. The region of southeast Europe is also facing the challenge of ensuring water supply in a changing climate. Under these circumstances the policy makers and water suppliers are required to develop sustainable management practices for water resources. Land use activities will also change and it is crucial to assess their impact on water resources. In order to mitigate possible negative impacts of CC and implement alternative solutions in the most efficient way, joint transnational action with a multisectoral and multilevel approach is required. This goal oriented the CC-WaterS project and its activities directly, aiming:

- to assess the possible range of impact of CC on the water resources used for drinking water supply;
- to identify and evaluate the resulting impact on the availability and safety of public drinking water supply for several future decades;
- to delineate critical areas where measures are needed.

One of the main project targets is to develop methods and instruments to predict the magnitude and effects of land use changes and their impacts on water supply. Measures to adapt water supply management to these changes will be proposed in the final stage of the project. These measures would focus on optimization of water extraction, land use restrictions, and socio-economic consequences in three geographical units shared by the SEE countries: the Alps, Danube Middle and Lower Plains, and coastal areas, representing different climates and topography characteristics.

TEST AREAS

Each of the countries involved identified test areas where established methodology is going to be applied: Estimated climate changes (at the end of 21 Ct.) → Water and land use situation about one century from now: Water resources availability ↔ Land use changes.

In total, there are 25 test areas (from 1 to 5 per country); different climates, morphologies, geological settings and water availability are well represented. In some of the areas water is already scarce and these areas are facing different problems such as water shortage due to limited recharge, inappropriate land use, water pollution, and salt water intrusion. Some other partners proposed test areas which are rich in water, representing current or very promising sources for future water supply.

A majority of the sites includes groundwater sources utilized by local waterworks. This is quite logical given the prevalence of groundwater supply for drinking purposes over surface water use in SEE. In the entire region, 65-70% of the population is covering its demand from groundwater.

Test areas also represent well different aquifer systems with different recharge processes, patterns and discharge conditions. For instance, the karstic aquifer systems are being evaluated within the Eastern Alps (Rax-Schneeberg Mts.), the Apennines (Matese Mt.), the Horst-mountains of the Pannonian basin (Bükk Mt.), the Carpathian Mountains (Stara Planina), the Peloponnesus

(Panachaiko) or coastal Dinaric system as in the case of Croatian islands (Cres, Korčula). Alluvial aquifer systems are being studied along the Struma, Sava, Nišava, and Pek Rivers. Sub-artesian aquifers of deeper structure are selected in the Pannonian depression (Banat) or in Oltenia. Specific hydrogeological structures such as terrace and aeolian hills are also considered as in the case of Nyirseg (near Nyíregyháza). The size of waterworks has also been chosen to represent large and, for management, more complex systems, such as those of Vienna, Thessaloniki, Ljubljana or Belgrade, along with numerous smaller operational utilities.

CLIMATE CHANGE

This basic WP consists of three sub-packages:

- Establishment of transnational climate data base,
- Development, calibration and validation of an intra-project-downscaling methodology,
- Generation of future climate data and estimation of associated uncertainties.

Global Circulation Models (GCMs) are the primary tool used to simulate the global climate system and provide reliable projections of future climate change in the climate perturbed by various greenhouse gas emission scenarios. The most comprehensive overview of state of the art GCMs is presented in the last IPCC report (IPCC, 2007).

The downscaling approaches in CCWaterS which were based on RCMs and subsequent local downscaling were validated with the help of homogeneous data sets of test areas in the entire SEE region. Meteorological data from observations and simulations are merged in a transnational climate data base. The first task of the partners was to agree on one or several climate models and scenarios to be further applied for the entire region and for each test area (Fig. 2). Common understanding of the correction methods of the raw model data was an important part of this task.

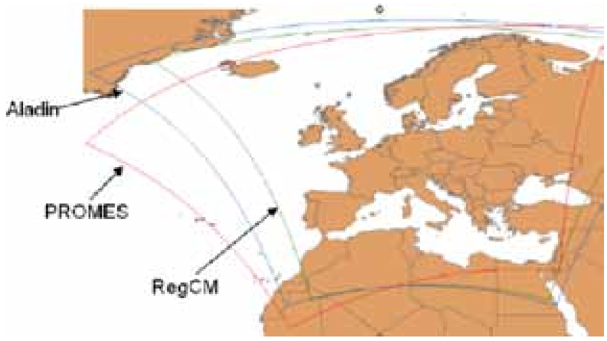

Figure 2: Spatial extent of the selected models Aladin, PROMES and RegCM used in CCWaterS

Regarding the green house emission scenario, the A1B scenario was selected as the common scenario for all analyses (IPCC, 2007). The most important reason for using just one scenario was that data by several RCM using this scenario are available from the ENSEMBLES project. As the driving GCM was considered to have a larger influence than the emission scenario, especially in the first decades of the 21st century, it was decided to use three RCMs with three different driving GCMs. The three selected RCMs from ENSEMBLES were RCM Aladin driven by GCM ARPEGE, RCM PROMES driven by GCM HadCM3Q0, and RCM RegCM driven by GCM ECHAM5-r3 (Fig. 2).

The models have a 25x25 km resolution and their A1B scenario runs are available for the entire 21st century (2000-2100) with the exception of PROMES, which is available only for 2000-2050. A comparison of three models for the period 2021-2050 and of two models for 2071-2100 was considered sufficient for an estimation of the uncertainties related to the choice of the climate model.

As RCM simulations for control runs still show considerable errors when compared with observations, the raw model data was bias corrected with a quantile mapping approach. The observational datasets used as the base of the bias correction were the E-OBS dataset developed in ENSEMBLES, which provided daily temperature and precipitation fields on a 0.25°x0.25° grid for the whole of Europe and the period 1950 – 2009. Within the Alpine region a gridded precipitation data-set by Frei and Schär was used, which has a higher spatial resolution (10') and includes many more observation stations.

For the provision of climate data with a higher resolution than 25km and for the investigation of uncertainties related to the choice of the downscaling method, three statistical downscaling approaches were applied in three areas of different climatic influences. In an Alpine test area in Austria, a statistical downscaling method (SDM) based on weather classification was tested, in Romanian areas with Continental influence a Canonical Correlation Analysis (CCA) was applied and in Mediterranean Greece an Artificial Neural Network (ANN) approach was adopted.
The two characteristic examples of the outputs of the climate model are as follows:

1. For Austrian test sites in Eastern Alps, the RCMs showed no apparent changes in temperature seasonality and variance but did show a clear increase in the mean of between 1.1 to 2.2 °C in the reference period 1961-1990 and 2021-2050 and of approximately 3.3 °C until 2071-2100. In the late period, the summer extreme temperature increased more than the given mean values. As the increase in temperature plays a major role in impacts on the hydrological cycle in Alpine areas, this clear signal will lead to clear trends in subsequent impact modeling despite high uncertainties regarding precipitation.
2. In the Serbian Carpathians, over the entire 2001-2100 period the most intense increase in air temperature and the most significant decrease in precipitation can be expected during summer. Compared to the period of 1961-1990, the air temperatures will successively rise, while the precipitation amount will fall in the periods 2021-2050 and 2071-2100 (Aladin) or rise in the period 2021-2050 and then fall in period of 2071-2100 (RegCM).

However, the results of WP Climate Change show the various uncertainties associated with the generation of climate change information for impact assessment studies. Future scenarios for precipitation also show no clear trend in many areas, as in Austria, Hungary, Romania and Croatia. In Romania only for summer, in Croatia for spring and summer, consistent results indicate decreasing precipitation. In Greece, consistent trends of decreasing precipitation in all seasons were detected. For temperature, there are rather consistent predictions of an increase of between 3 and 3.6°C in the annual mean towards the end of the 21st century. Especially in the countries in the south of the region, the highest temperature increase is expected for summer periods.

The data provided from this WP have facilitated impact modeling in the subsequent work packages and contributed to the understanding of climate change in the SEE region.

WATER RESOURCES AVAILABILITY

The three sub-packages of this WP are as follows:

- Establishment of a transnational hydrological and water management database,
- Assessment of the present conditions of water resources,
- Evaluation of climate change-induced changes in available water resources.

The expected main negative impacts of climate changes on water availability are: (i) decreasing runoff or recharge due to the negative change of the difference between precipitation and potential evapotranspiration, and (ii) increasing frequency of droughts due to the more frequent extreme events. The extent and importance of these impacts will vary by region and by type of resources. The water availability is assessed in the test areas in order to give a general picture and to highlight the sensitive regions. A common methodology has been set up for determining available water resources, based on the principle of the EU Water Framework Directive: to promote sustainable water use, the abstraction cannot exceed the renewable water resources minus the water demand of the ecosystems (Fig. 3).

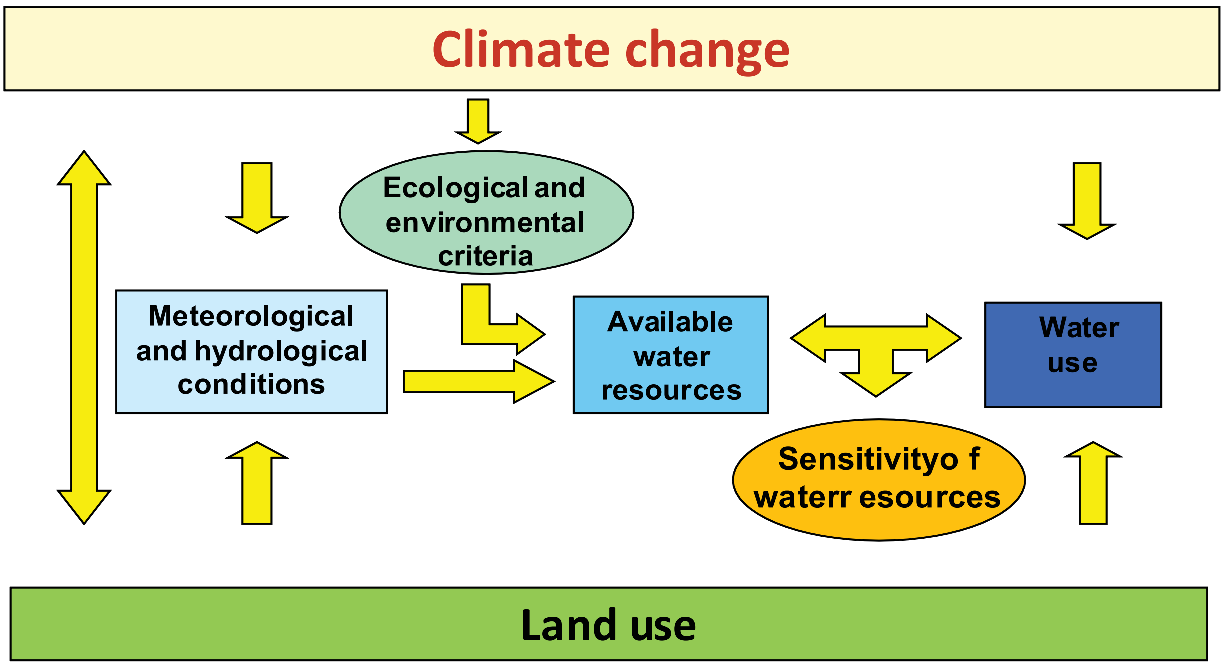

Figure 3: The main elements of the methodology for available water resources assessment

The methodology has a modular structure, including (i) setup of meteorological input (precipitation and temperature) based on datasets of climate modeling, (ii) water balance modeling, (iii) additional groundwater flow modeling if needed, (iv) consideration of ecological criteria, (v) impact of the changing land use on water availability, (vi) assessment as determination of available water resources and comparison with actual water use. The modular methodology aims to ensure similar results allowing comparative evaluation, rather than using uniform models. The applied methodology is general and can be proposed for similar assessments as well.

The water balance models are the essential part of the methodology providing the amount of renewable water resources in the long-term and at a seasonal basis. Its form depends on the type of resources and the results can be daily or monthly time series (in the case of surface water resources and springs) or long-term averages (in the case of groundwater resources from porous intergranular aquifers). In certain test areas redistribution of the recharge among baseflow, spring flow and outflow to neighbouring aquifers demands for additional – usually steady state – groundwater flow models. The ecological criteria can be expressed as minimum flow to be left in the creeks or rivers, minimum water levels in reservoirs, groundwater levels or minimum baseflow and evapotranspiration from groundwater. All these options occur in the test areas.

Results of the assessment of the climate-induced changes in land use are incorporated in the models through the parameters depending on the land use (e.g. evapotranspiration, run-off coefficient etc.). The models are calibrated and validated for different periods according to the available data, but the simulation for the comparative evaluation is carried out for the same periods: 1961-90 as baseline and 2021-2050 and 2071-2100 for assessing the variation of water reserves under climate changes. The impact of the climate is going to be finally presented as changes in the available water resources between the baseline period and future periods for all test areas. Besides the test areas with considerable changes, areas sensitive to water shortages will also be selected by comparing the calculated available water resources with the present water use.

As an example, the stochastic model applied in the case of karst springs in the Carpathian Mts. of Serbia shows that as a result of climate variations the annual average discharge of some springs will decrease from 6-23% by the end of 21Ct. Moreover, seasonal variation shows a strong depletion of the reserves during the dry period of the year (even 40% less), while an increase during winter months is expected (up to +25%). The exceptions are ascending siphonal springs with accumulated large geological groundwater reserves and they would not be seriously affected by reduced rainfalls during the summer/autumn periods (longer residence time).

LAND USES AND WATER RESOURCES SAFETY

The three sub-packages are as follows:

- Impact of existing land uses on water quantity and quality under climate change conditions,
- Evaluation of climate-change induced land use changes,
- Evaluation of the climate change impact and other pressures on future water quality.

Works of this WP mostly focus on the analyses of actual land use in test areas, current and forecasted water quality data, and expected changes in the environment as a result of climate changes.

One of the main tools used for these analyses was DPSIR (Driving Force – Presure – State – Impact – Response) (Giupponi C. 2002), which was also proposed by the European Environmental Agency (http://ec.europa.eu) (Fig. 4). The essential question that would have to be responded to for each test area is: Does climate change drive towards land use change in a test area? In the case of a positive answer the following question is to be responded to: Are these changes compatible with sustainable development of groundwater and various hydrogeological and water extraction scenarios? Analysis of relationships between actual land uses and future climate scenarios is therefore one of the essential steps towards preparation of mitigation measures (“responses”) in case of their incompatibility.

The three main land uses were studied, such as forestry and pasture in mountainous areas and agriculture in alluvial plains and karst poljes. In case of forestry, forest management practices should be changed in the water protection zones. In case of agriculture increased average temperature leads to higher mineralization of organic matter. Besides, increased rainfall will increase leaching, which extent for wetter areas is much higher than in drier areas.

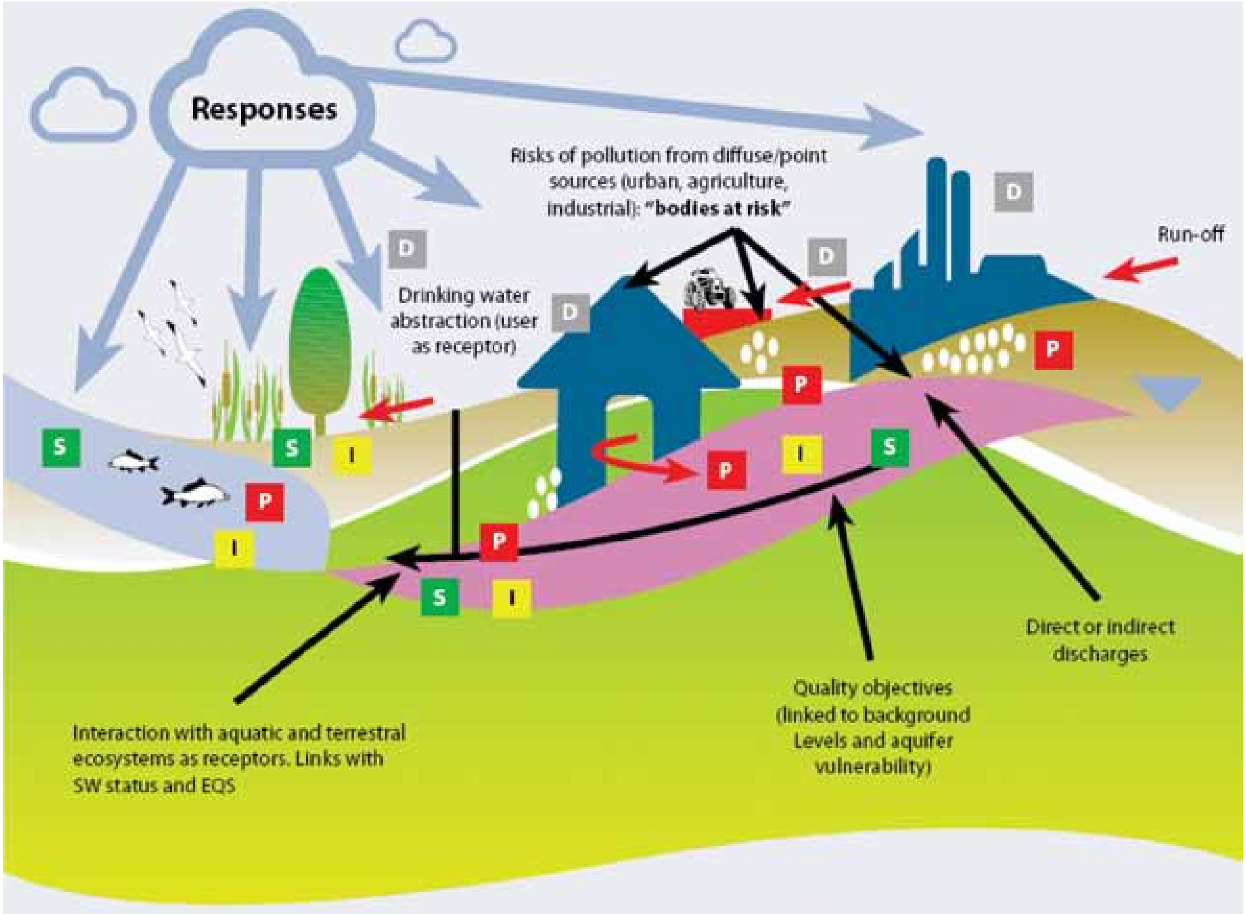

Figure 4: Scheme of DPSIR mechanism
(source: http://ec.europa.eu/environment/water/water-framework/groundwater/brochure/en.pdf)

SOCIO-ECONOMIC EVALUATION

- The following aspects (sub-packages) are considered in this WP:
- Future water availability for public water supply,
- Estimation of economic consequences of future water availability and safety,
- Estimation of emerging imbalances between different demands,
- Environmental aspects in water pricing.

Regional development leads to conflicts between competing sectors and demands for safe water resources. The main target of this WP is merging demographic forecast data and water demands with future water availability and estimation of the emerging consequences and costs of water supply. An economic analysis of water management and land use changes for different scenarios should provide better information to the water managers and help to orient their decisions towards more sustainable solutions in water utilization.

A better understanding of the socio-economic and institutional aspects of vulnerability and adaptation, including costs and benefits, is therefore found to be one of the very important demands of the project.

WATER SUPPLY MANAGEMENT MEASURES

- This WP includes work on the following subjects:
- Proposal of strategy change in spatial planning,
- Promotion of (new) legislative rules and guidelines,
- Adaptation of water supply management system,
- Feedback cycle.

The objective of current and future water supply management adaptation measures is managing the risks associated with future climate change impacts. Adaptation measures occur primarily at transnational (e.g. river catchments), sub-national and local levels and therefore involve many levels of the institutional sector being involved in decision making. It is a cross-sectoral issue requiring comprehensive integrated approaches. Objectives of this WP are:

- development of appropriate technical measures, and
- preparation of a legislative basis to mitigate possible negative effects of climate and land use changes on water supply management.

Applying well-prepared adaptation measures will serve to solve conflicts between competing sectors and demands. Measures should be integrated in the water supply management system (WSMS) of the region.

The following water supply management options under different climate conditions would be considered and evaluated in WSMS:

- land use: managing supply and possible loads,
- legislation: changing environmental standards, restriction of land uses, enlargement of protected areas,
- managing the demand: water pricing and prioritization and competitiveness (management of imbalances) by using outcomes of WP Socio-economic evaluation,
- alternative supplies: identification of new resources, alternative recharge, regulate-managing the flow (including ranking criteria for evaluation of alternatives),
- managing water supply.

CONCLUSION

Transnational action is needed to prepare SEE for the challenge of ensuring water supply for society for several decades. Policy makers and water suppliers must develop sustainable management practices for safe drinking water supply, considering existing and future CC influences of the changing climate. Therefore the on-going project CC-WaterS is identifying and evaluating impacts on the availability and safety of public drinking water supply for several future decades. Elaborated adaptation measures build the ground for an optimization a WSMS regarding water extraction, land use restrictions, and socio-economic consequences under climate change scenarios for water suppliers in SEE. The joint actions to produce WSMS on a transnational level in the different areas with specific characteristics of the climate, topography and water resources availability would be the result of performed analyses.

In CC-WaterS, SEE governmental bodies, water suppliers and research institutions work together and implement jointly developed solutions, to be applied on a regional or local level. Capitalizing on already existing knowledge and data from EU-funded scientific projects and eliminating parallel investigations, CC-WaterS will make information applicable for concrete solutions, develop tools and instruments for public water supply and implement safeguarding measures. An accessory dissemination strategy will ensure that durable results of the CC-WaterS are transferred to the relevant users.

Acknowledgements: CC-WaterS project is under implementation since 2009 under the South East Europe programme (European Territorial Cooperation, ETC-SEE). It is funded by the European Regional Development Fund (ERDF) and the Instrument for Pre-Accession Assistance (IPA). The SEE programme supports projects within four Priority Axes: Innovation, Environment, Accessibility, and Sustainable Growth Areas - in line with the Lisbon and Gothenburg strategies, and is contributing to the integration process of non-EU member states.

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MANAGEMENT OF COASTAL AQUIFERS UNDER CLIMATE CHANGE SCENARIO, OUTLINE OF REMEDIATION ACTIONS TO CONTROL SALT INTRUSION

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Keywords: salt intrusion, climate change, groundwater modelling, integrated river basin modelling, groundwater management, coastal aquifer.

INTRODUCTION

Many coastal zones are characterized by high density of population. Due to the increasing concentration of human settlements, agriculture developments and economic activities, the shortage of fresh groundwater for domestic, agricultural and industrial uses is becoming more and more evident. It is estimated that one third of world fresh water use comes from groundwater and this fraction is continually increasing due to rising of population and loss of surface water availability caused by pollution. Increasing over exploitation of groundwater from human activities together with land reclamation are threatening coastal lowlands. Moreover climatic changing with different rainfall regimes and increasing sea level can further influence the salinization process.

The major objective of the EU LIFE SALT project is to contribute to the efficient use of coastal aquifers in order to mitigate the effect of saline intrusion in the potable water exploitation.

STUDY AREA

The project is developed in the Esino River Basin flowing to the Adriatic Sea in central Italy near the city of Ancona. The Esino River watershed surface, represented in Figure 1, is 1.203 Km^2 with an annual average flow of 15 m^3/s. Its environmental condition, especially in the lower part, is poor due to intensive agricultural and industrial activities and uncontrolled pollution loads from untreated discharge and combined sewer overflows.

The continuous urban development, together with the excessive use of water resources are leading to adverse environmental consequences, like pollution increasing and seawater intrusion. Currently a wells field in the lower part of the watershed is used for the supply of drinking water to the surrounding municipalities. This water amount (1.4 million m^3 each year) is a strategic resource since it contributes to integrate the drinking water that comes from a mountain spring. Moreover, droughts in recent years have also caused an alarming decline of the mountain spring freshwater used for drinking supply, and consequently it has been necessary to pump a greater amount of groundwater from the aforementioned wells to satisfy potable water demand.

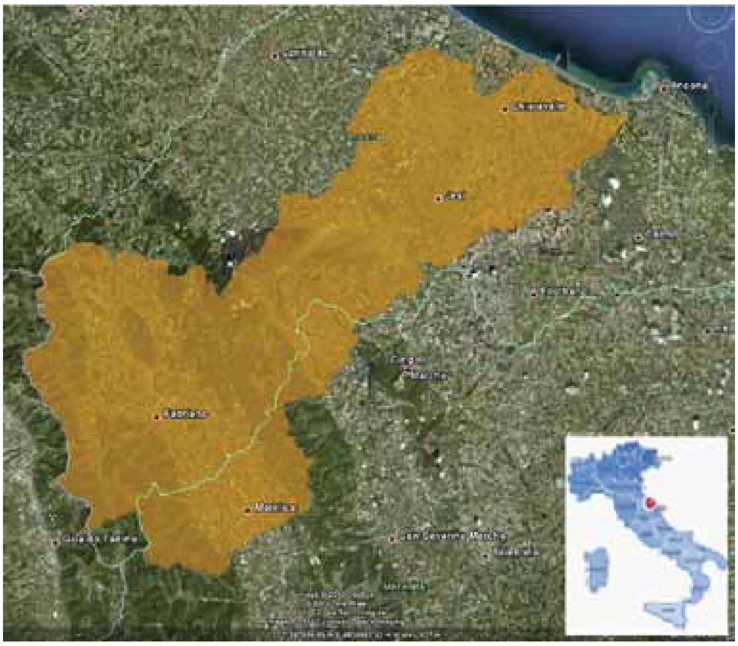

Figure 1: Esino River watershed surface.

MODELLING OF THE AQUIFER

The overall objective of the SALT project is to increase the knowledge of aquifer dynamics in order to define the most effective strategy to control and prevent saline intrusion. In order to meet this objective, the project uses advanced modelling tools to predict the climatic variability and the subsequent impact on water resources. For the modelling of salt intrusion FEFLOW from DHI WASI has been used. Feflow is a 3D finite element subsurface model flow and transport simulation system which is particularly suitable for salt intrusion analysis being able to simulate density dependent flow.

The project work plan defines the following main tasks:

- Data collection, monitoring campaign and GIS implementation;
- Construction and calibration of the hydrogeological model (aquifer and river watershed);
- Simulation of salt intrusion under present and future scenarios considering climate change;
- Definition of remediation actions.

Figure 2: Alluvial aquifer, Esino River (135 Km²).

Several monitoring campaigns have been carried out in order to characterize hydraulic and hydrogeological condition of the watershed:

- continuous flow hydrographs along the Esino River in N° 3 cross sections (see Fig. 3),
- spot flow measurement in different river sections aimed at the calculation of the average flow transmission from the river to the aquifer,
- topographic survey, water level and profile of electric conductivity in selected wells, using multiparametric probes.

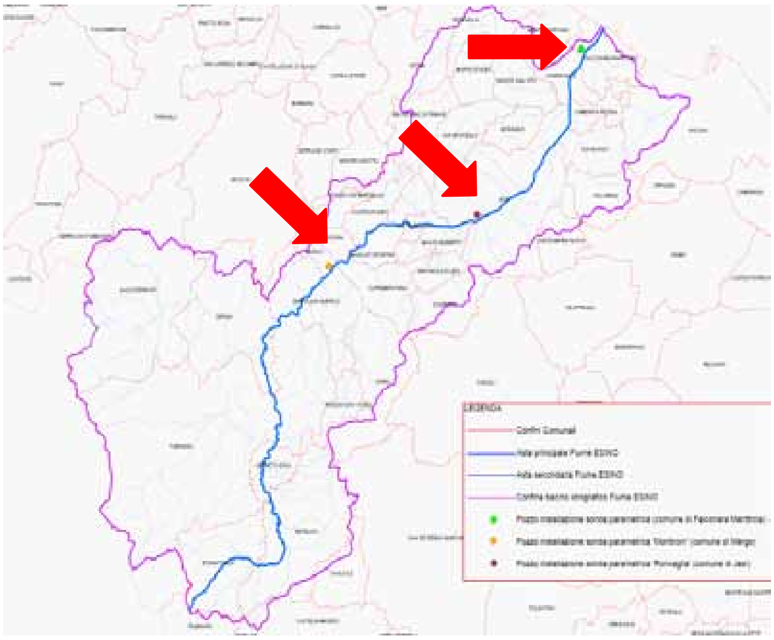

Figure 3 - Map of the river watershed with selected cross sections where continuous flow is recorded.

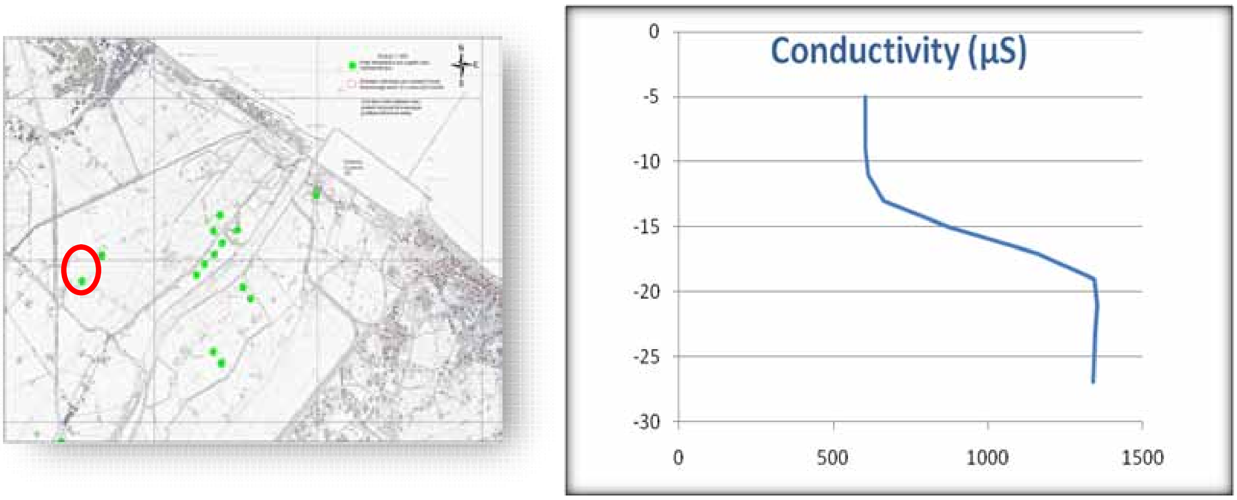

Figure 4 - Conductivity parameter measured in well field used for potable supply

The Esino River, that recharges the aquifer from the surface, has been simulated using HEC-HMS for precipitation runoff processes and HEC-RAS for the river hydraulics. The hydrological of the Esino River model has been calibrated considering some individual rainfall-runoff events from a historical database (see Fig. 5).

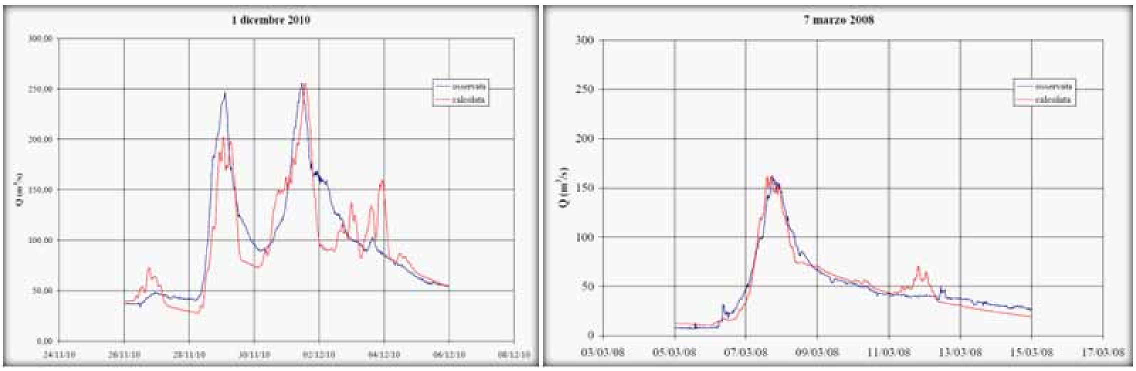

Figure 5 - Calibration of the HEC-HMS rainfall-runoff model

The aquifer model domain was built using data from a DTM (Digital Terrain Model) to define the topography of the study area.

From the available data of stratigraphy taken from more than a hundred wells, an average characterization of the model vertical domain has been done. Four geological units have been identified and reported in the Feflow 3D: gravel-clay, clay-sand, gravel-sand and the impermeable acquiclude. The figure below shows the three dimensional conceptual model of the Esino alluvial aquifer with the calculation mesh, the river bed and the four geological units.

Specific value of Conductivity K and Drain/fillable porosity parameters was initially assigned to each geological layer that describes vertical model scheme and then adjusted in relation to pumping test results. In order to consider the flow transmission between the river and the aquifer, the dynamic river level from HEC-RAS simulations has been allocated to the correspondent elements in Feflow.

The base scenario of flux model implemented with Feflow represents the hydrogeological balance of the model and accordingly the analysis and evaluation of groundwater resources availability considering:

- daily rain time series (mm/d) from 2003-2010 in the meteorological stations of Matelica, Iesi and Agugliano,
- historical GW levels in selected wells (some spot between 2005 and 2010),
- GW water level continues time series from October 2010 to date in three selected wells.

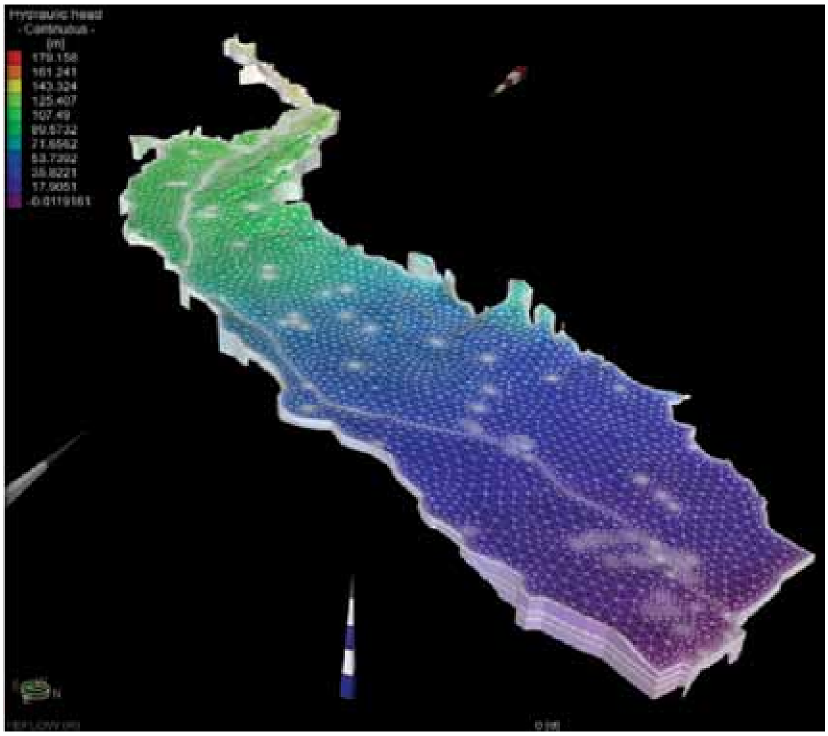

Figure 6 - Mesh model of alluvial Esino aquifer implemented in Feflow.

Several difficulties have been encountered in the calibration process due to the lack of complete historical data and the very short period of coverage. Moreover, for some of the available wells only 2-3 years of spot measurement twice per year were available.

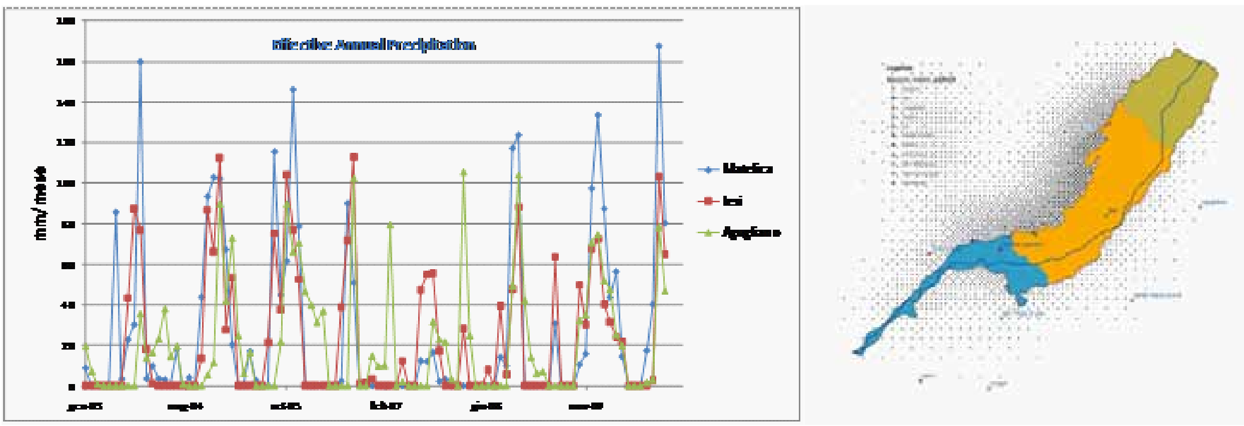

Figure 7 - Pluviometric data and distribution of Matelica, Iesi and Agugliano meteorological stations.

In order to obtain a reliable hydrogeological water balance it was necessary to simulate all the known wells. Due to the lack of detailed flow hydrographs, average pumped flow from main industrial wells has been considered.

The flow from the domestic wells has been uniformly allocated to the model area. Boundary conditions considered for the simulation are: sea level downstream and groundwater level at the upper planimetric limits of the domain.

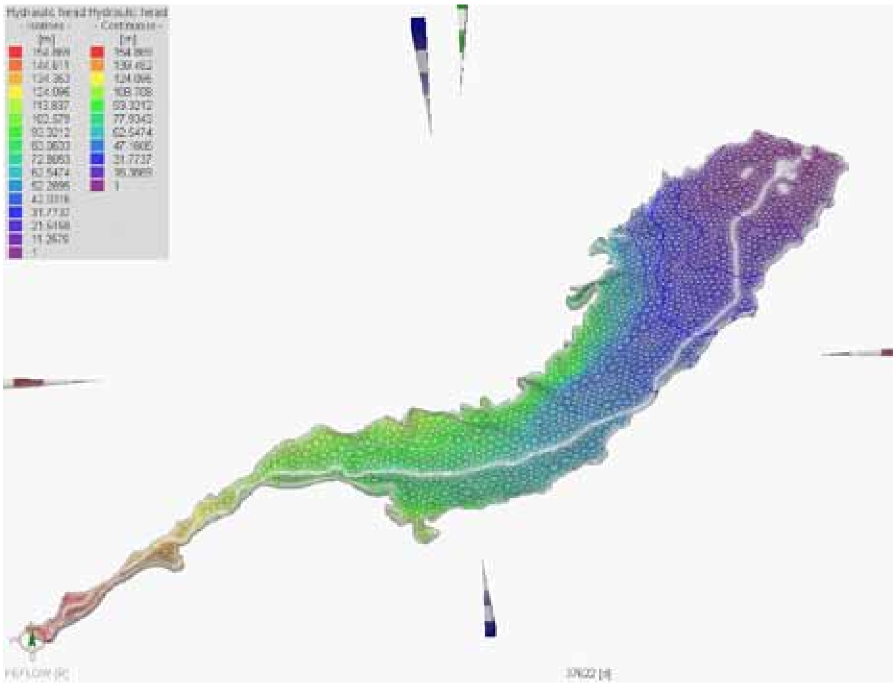

Figure 8 - Initial head elevation in Feflow groundwater model.

HYDROLOGICAL WATER BALANCE

The water balance is often used as a preliminary instrument to program the management of water resources. To estimate the resources that are actually available in a basin, it is essential to know all the various factors entering the equation of system balance within a certain temporal interval (i.e. hydrological year). To verify the consistency of result obtained from the Feflow model simulation, a preliminary budget of the water volume expected has been calculated (see Fig. 9).

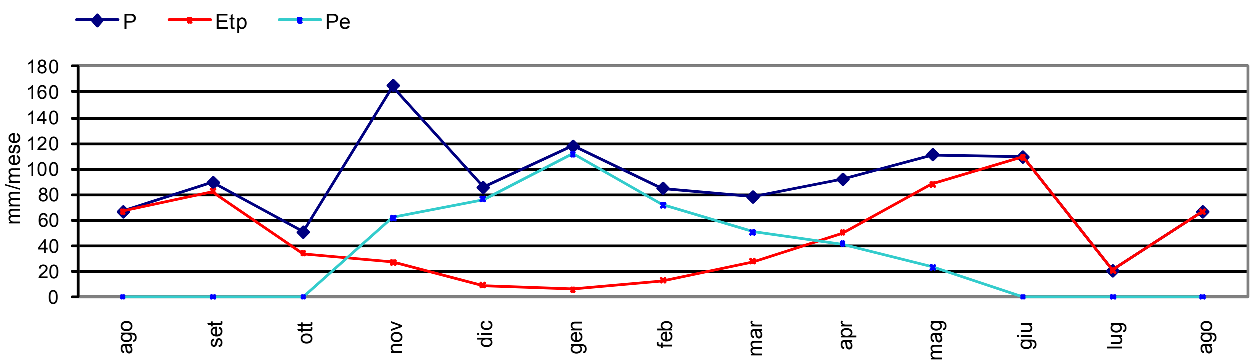

Figure 9 - Graph of average measured precipitation P, average calculated evapotranspiration ETP and effective calculated precipitation Pe in year 2010.

Once established that the model has provided a proper balance of water volumes, the simulated groundwater level has been compared with historical data. In the figure below an example of a detailed output time series obtained in a control point, located 13 Km from the sea, is reported.

The model, as an average, seems to represent correctly the water level in the aquifer. Looking at the water level trend, it seems that the aquifer, in this location, is not overexploited.

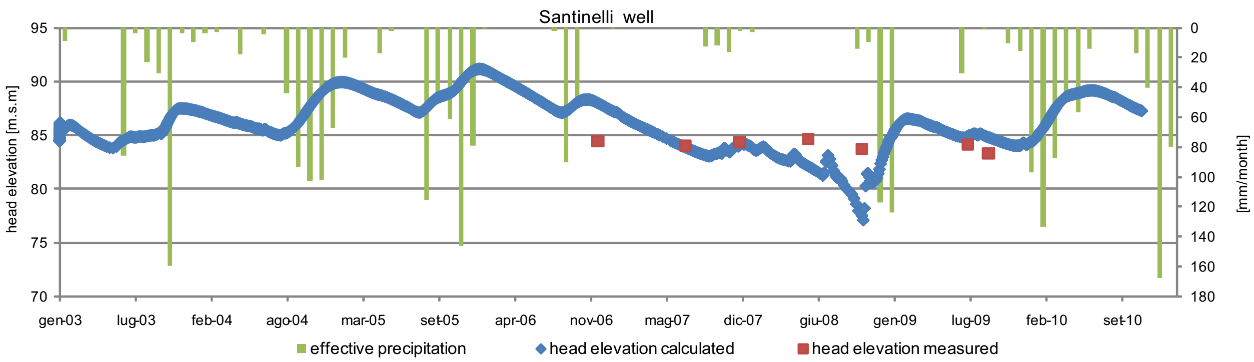

Figure 10 - Graph of trend precipitation (green line), head elevation calculated during simulation (blu line) and head elevation measured (red points) in observation point "Sadam well".

CONCLUSIONS - NEXT STEPS

From the field measurement carried out and the analysis of previous publications and historical data, the origin of salt intrusion in the Esino alluvial aquifer is not only related to the influence of the sea, but also to the rise, in some areas, of salty pliocenic water from fracture zones (Nanni 1985).

The calibrated aquifer model will be used for the simulation of the salt intrusion in the present scenario using as control point the vertical spot profile of electric conductivity in several wells distributed in the model domain.

Further simulations will determine the effect of climate change scenario in the groundwater salinity taking into account the current withdrawal regime (more than 7,800,000 m^3/y only from main wells).For this purpose the future projections of precipitation and sea level for the period 2011 - 2030 will used as boundary conditions for the climate change scenario. These projections come from the CMCC-MED model, driven by the IPCC's greenhouse gas emissions scenarios downscaled in order to reach a spatial resolution suitable to for the Esino area. The Feflow-HMS-RAS integrated model will then be used to evaluate remediation actions aimed to control salt intrusion in the long term considering for example the effect of groundwater artificial recharge and/or reduction of withdrawals.

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NOTES:

Extended Abstract

HYDROLOGICAL TRENDS OF RIVERS IN CENTRAL AND EASTERN SERBIA AS THE FIRST INDICATOR OF POTENTIAL FUTURE CAPACITIES OF CERTAIN ALLUVIAL WATER SOURCES

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Keywords: Temperature, precipitation, climate change, average discharge, low discharge.

INTRODUCTION

The difference between the present and the future capacity of an alluvial water source (ALWS) depends on a series of factors: the number of groundwater abstraction wells, changes in river morphology, changes in riverbed colmation, well ageing, variation in river water levels and discharges, varying inflow from the upland, variation in precipitation and evapotranspiration levels, and the like. The causes of these changes may be sought among human activities, natural processes, and climate change (irrespective of whether climate change is a result of natural processes or human activity). A study of the Pek River [5] addresses only the impact of climate change; it was assumed that all other conditions at the ALWS site remain unchanged (except for temperature, precipitation, river discharge, and upland boundary conditions). The derived hydrological trend of the river is equal to or slightly higher that the ALWS trend in the catchment area (C.A.) of this river. Expressed in numerical terms, (Trend Q_{ALWS}) / (Trend Q_{RIVER}) ≈ 80 ÷ 100 %. Although this relationship depends on a number of factors, it is to be expected that for the majority of ALWSs this relationship will be 60 ÷ 120%. In other words, for a river whose long-term hydrological trend is -40%/100 years, the ALWS capacity trend is -32 ÷ -40 % / 100y, or, if extended, -24 ÷ -48 % /100y (with ALWS site conditions remaining unchanged).

The Velika Morava is the largest river in central Serbia. Its long-term discharge is about 250 m^3/s, while minimum discharges during hydrologically adverse years are as low as 40 m^3/s or less. The surface area of this river's C.A. is about 50,000 km^2. It is home to some 4 million inhabitants who largely receive their water supply from ALWSs. The drinking water demand is in the order of 10 m^3/s, or roughly 1/4 of the discharge of the Velika Morava during low-flow periods. In addition to the Velika Morava and its tributaries, noteworthy are the rivers in eastern Serbia, the tributaries of the Danube, especially its major tributaries: the Mlava, the Pek and the Timok. With regard to future drinking water supply security, considerable pressures are expected in central and eastern Serbia, given the imminent increase in water demand and decrease in discharge (to a greater or lesser extent) of all rivers in the region. The topic of this paper is an assessment of the decline in average annual and monthly river discharges during low-flow periods, and their correlation with derived temperature and precipitation trends. Additionally, an initial, rough estimate of ALWS capacity under altered climate conditions (and unchanged ALWS site conditions) is derived via a tentative correlation between the hydrologic trend and the ALWS capacity trend.

The period selected for analysis is from 1949 to 2006. This period is convenient because it is relatively long (58 years), data are available from numerous monitoring stations, and they exhibit a close similarity to estimated long-term temperature and precipitation trends, and particularly river discharge trends in Serbia [6], [7].

TEMPERATURE AND PRECIPITATION TRENDS IN SERBIA

All global and regional climate models predict an increase in temperature, and most also predict a decrease in precipitation in Serbia. The average annual temperature increase is expected to range from 1°C to as much as 6°C/100 years, largely depending on the selected scenario and to a much lesser extent on the analyst [1], [2], [3], [4], [5]. Annual precipitation predictions range from current levels (trend = 0) to -25%/100 years. However, only a few of these models offer spatial (within Serbia) and temporal (yearlong) distributions. Each prediction is sensitive to assumption uncertainties and calculation imperfections. They need to be examined and critically assessed. The quality of a prediction grows with increasing validation by recorded data and especially by trends. To assess past climate trends, 26 temperature stations and 34 precipitation stations were selected [6]. The annual average temperature trend in Serbia was found to be about 0.6°C/100 years, while the precipitation trend was around zero; the spatial distribution is shown in Figure 1 [6], [8].

The distribution of certain monthly temperature trends is questionable: the highest upward trends have always been predicted for the months of July, August and September. They are considerably higher than the predicted annual trend (often double the annual trend or more, under the given scenario), while the actual trends for July and August in all of Serbia were higher than the annual average (which is about 1°C/100 years, not far from the predicted correlation: double the annual trend), but September, along with November and December, was the only month with a distinct negative temperature trend (in the order of -1.4°C/100 years). Table 1 shows recorded monthly trends based on 26 temperature stations in Serbia for the 1949-2006 period.

Table 1: Registered 1949-2006 trends by month and annual averages

Type of station	Station	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Aver
Temperature (°C/100years)	Average of 26 stations	1.9	1.3	3.2	-0.1	1.7	1.1	1.1	0.8	-1.4	1.2	-1.9	-2.2	0.6
Precipitation (%/100years)	Average of 34 stations	-16.0	-21.7	-12.4	35.7	-43.7	-6.6	11.5	43.1	70.9	6.3	-41.4	-17.9	-0.3

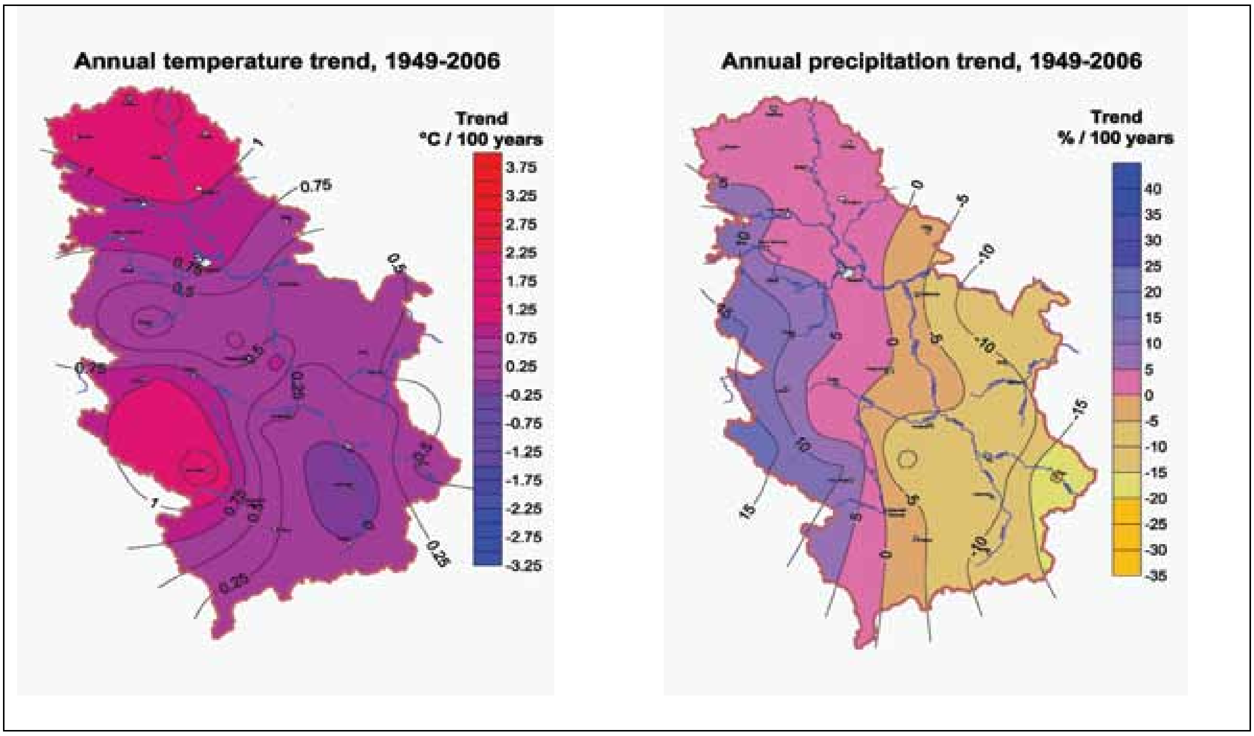

Figure 1: Recorded annual temperature and precipitation trends in Serbia (1949-2006).

The distribution of certain monthly precipitation trends is especially questionable: the highest downward trend was almost always predicted for the months of July, August and September (often in the order of -50%/100 years), which is inferior to the predicted annual trend, while the actual trends in July, August and September in Serbia were in the order of +10, +40 and +70%/100 years, respectively. September is at the same time the month with the highest and most consistent positive precipitation trend in all of Serbia. Table 1 shows recorded monthly trends based on 34 precipitation stations in Serbia for the 1949-2006 period. The months from November to February exhibit a downward precipitation trend, August and September exhibit an upward precipitation trend, and the other months vary.

PAST AVERAGE ANNUAL HYDROLOGIC TRENDS IN CENTRAL AND EASTERN SERBIA

Serbia, especially its eastern part, experiences a downward river discharge trend (expressed as a percentage of the discharge per 100 years). However, contrary to climate parameters, it is difficult to spatially generalize because several factors affect these trends. The most important factors are:

1. The size of the river,
2. The transfer of water, if any, between catchments upstream form a given hydrological station,
3. The volume of water used by man in a given C.A.,
4. The presence or absence of river reservoir(s) in the C.A.,
5. Any land use changes in the C.A., and
6. Climate change (including differences associated with geographical locations within Serbia).

1. Small rivers are much more stochastic in nature and sensitive to water withdrawal for human consumption, while large international rivers (the Danube, the Sava and the Tisa) often do not adequately reflect what happens within Serbia. As such, medium-size rivers (C.A. 5,000-50,000 km^2) are the most reliable representatives of the overall trend in a particular area (including climate change and human activity), provided that Factor 2 – water transfer between catchments – is not significant.

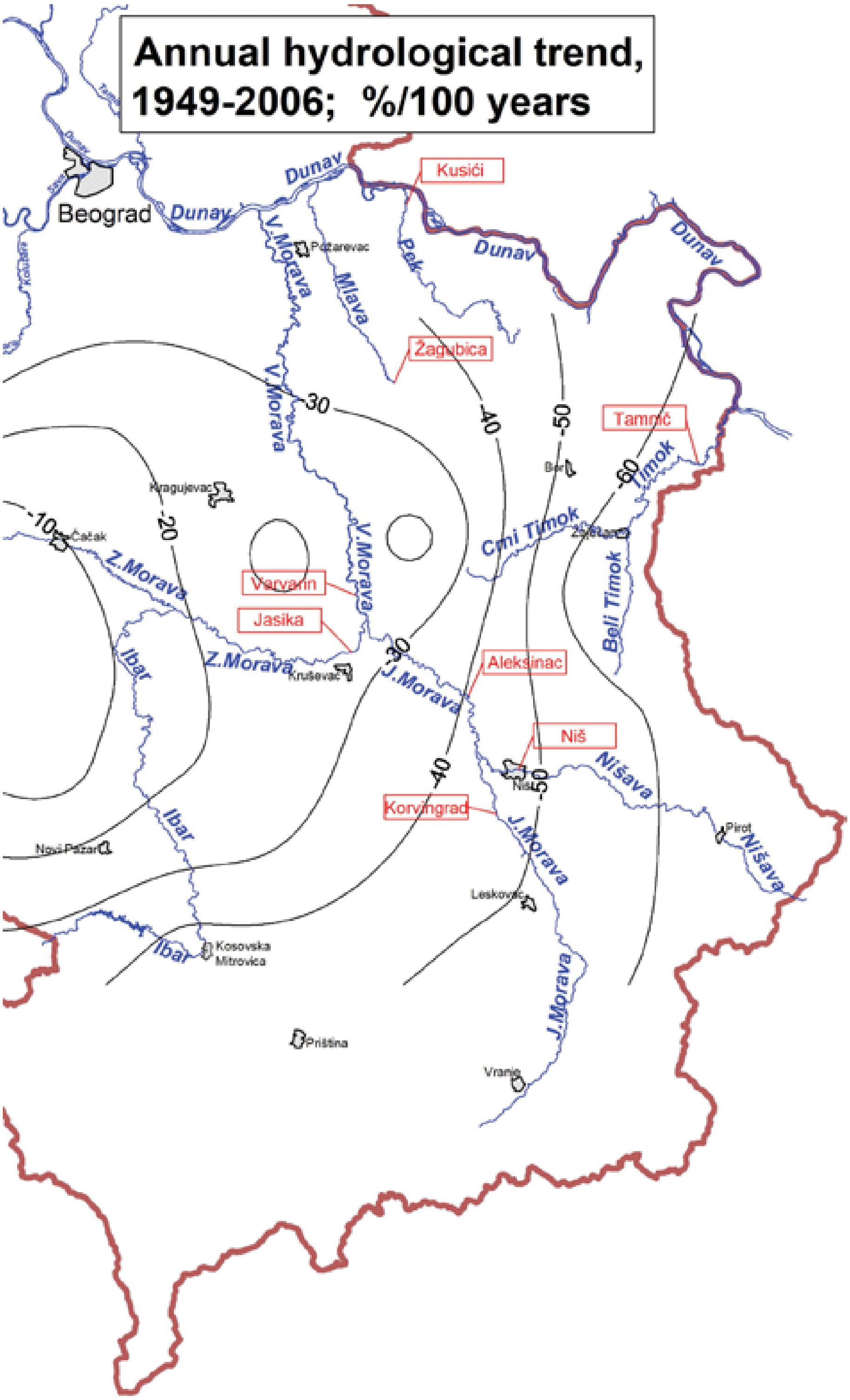

Figure 2: Isolines of the downward average annual river discharge trend.

2. Factor 2 is dominant at many hydrological stations and such stations need to be excluded from analyses (otherwise they require comprehensive calculations for which reliable data are generally unavailable), in order to derive relevant results.
3. Factor 3 is significant, and the degree of significance ranges from negligible (small volumes of water withdrawn from large rivers) to dominant (large volumes withdrawn from small rivers), within the framework of the recorded trend. A favorable circumstance from a trend analysis perspective is that much more water is used in Serbia for drinking water supply (where relatively accurate data are available), than irrigation (where there are only rough estimates).
4. The existence of a river reservoir upstream of a given hydrological station is generally a negligible or small addend to the overall hydrological trend. Exceptions are small rivers, or large river reservoirs relative to the surface area of the C.A.
5. Land use changes are relatively rare in Serbia but there is a slight arable land shrinkage trend.
6. Climate change is often the most important contributor to the overall hydrological trend. Climate change has to date had the greatest impact and resulted in the most distinct recorded downward precipitation and river discharge trends in eastern Serbia [6]. Conversely, only minor change has been noted in southwestern Serbia, where many rivers exhibit near-zero trends as a result of an upward precipitation trend, but also an upward evapotranspiration trend due to a slightly higher temperature increase in that region (Figure 1).

An approximate geographical distribution of the downward average annual river discharge trends for central and eastern Serbia is shown in Figure 2. It should be noted that within all river discharge trend isolines there are rivers and monitoring stations which often exhibit significant trend variations (both up and down), as a result of Factors 1, 3, 4 and especially 2. Figure 2 was compiled based on the trends recorded at 18 selected river monitoring stations across Serbia, where Factors 3 and 4 were assessed as having an acceptable degree of impact, and where Factor 2 was either absent or negligible.

WHAT CHARACTERIZES LOW DISCHARGE TRENDS IN SERBIA?

The average intra-annual distribution of the hydrological trends recorded at 18 stations across Serbia, and at 8 individual stations most typical of central and eastern Serbia (Fig. 2), is shown in Table 2. A significantly lower trend (very near zero) was noted during the months of low flow (July to October), as a result of an upward precipitation trend during these months and, additionally, often due to the presence of a river reservoir upstream from a given station, which equalizes annual discharges. However, in the future, especially if the temperature trend would be more than 2ºC/100 years, a downward trend of low flows is also to be expected (albeit less pronounced than in the case of average annual flows), particularly if there are no upstream river reservoirs.

Table 2: Registered 1949-2006 trends by month and annual average (%/100/years)

River - Hydrological Station	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Aver
Average of 18 stations	-12	-55	-22	-20	-70	-31	-27	-7	19	-22	-76	-68	-36.7
V. Morava - Varvarin	-15.7	-93.9	-52.3	-35.6	-97.0	-21.9	-10.0	8.2	9.4	-2.4	-34.3	-51.0	-33.0
Z. Morava - Jasika	10.3	-63.0	4.2	8.7	-94.7	-18.8	-7.7	6.8	21.6	-0.3	-30.2	-29.5	-16.0
J. Morava - Aleksinac	-62.2	-129.1	-94.1	-49.0	-91.2	-33.4	-23.1	6.2	-10.9	-9.9	-50.4	-72.8	-51.7
Nišava - Niš	-72.4	-119.0	-100.4	-111.9	-123.8	-53.2	-50.2	-0.4	-10.9	2.8	-46.2	-85.6	-64.3
J. Morava - Korvingrad	-52.9	-98.3	-98.6	-20.1	-89.1	-21.7	-1.3	12.7	-2.6	-16.7	-47.1	-74.9	-42.5
Mlava - Žagubica	-31.4	-79.4	32.0	46.4	-26.1	-27.7	-51.7	-14.4	-8.0	-20.2	-86.8	-77.8	-28.8
Pek - Kusići	-35.8	-62.4	-22.9	-40.6	-91.6	-124.4	-25.7	-1.6	2.5	1.4	-67.7	-53.5	-43.5
Timok - Tamnič	-48.2	-127.3	-251.4	-142.2	-94.7	-18.7	-12.3	2.5	-4.5	-9.3	-48.7	-74.4	-69.1

WHAT IS TO BE EXPECTED IN THE FUTURE?

The full-length paper contains a discussion of this subject, as well as general conclusions.

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FULL PAPER

CLIMATE CHANGE IMPACTS ON ALLUVIAL WATER SOURCES IN THE PEK RIVER CATCHMENT AREA

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Keywords: Temperature, precipitation, river discharge, climate change, alluvial water source.

INTRODUCTION AND PRESENT STATE

Within the scope of the international project “Climate Change and Impacts on Water Supply in South East Europe” (CC Waters), the task of the Jaroslav Černi Institute for the Development of Water Resources was to assess the impact of climate change on the capacity of alluvial water sources. One of the pilot areas, which is addressed in this paper, is the catchment area (C.A.) of the Pek River and two of its alluvial water sources (ALWSs): Jelak (providing drinking water supply for the City of Veliko Gradište) and Mlaka (servicing the City of Kučevo). These two ALWSs were selected because they face similar water quantity issues regarding river flow, but with possibly different impacts on the water sources and water management.

Figure 1: Pek River C.A.

The Pek River C.A. is situated in central-eastern Serbia (Fig. 1). The altitudinal range is from 72 to 1066 m above sea level. The Pek River is a tributary of the Danube, and their confluence is at the City of Veliko Gradište (V. Gradište). The surface area of the Pek River C.A. is 1230 km^2, with a population of approximately 45,000. The majority of the population lives in three cities: Majdanpek (the most upstream city), Kučevo, and V. Gradište at the mouth of the river. Population growth has been recorded only in V. Gradište, while the other cities and particularly villages report a decline.

The mean annual temperature and precipitation are about 11.1°C and 643 mm/y at V. Gradište, and 10.9°C and 672 mm/y at Kučevo. The approximate average rates of abstraction for urban drinking water supply are: Majdanpek 70 l/s, Kučevo 25 l/s, and V. Gradište 40 l/s. During the summer, drinking water demand increases significantly in V. Gradište (the only tourist destination in the area, albeit not major), but not as much in Kučevo. There is no treatment except for chlorination. Agriculture near the cities has remained at about the same level for many years, while it has declined in the villages. In recent years, the water supply system (WSS) of V. Gradište has been experiencing water shortages during the hot months of hydrologically dry or even average years. The Kučevo WSS does not currently face drinking water deficit issues, but they are likely to occur in the future.

Table 1 shows recorded temperature, precipitation and discharge trends at several stations in the Pek C.A. for the 1949-2006 period. This period is convenient because it is relatively long (58 years) and exhibits a close similarity to estimated long-term temperature and precipitation trends, and particularly discharge trends in Serbia [3].

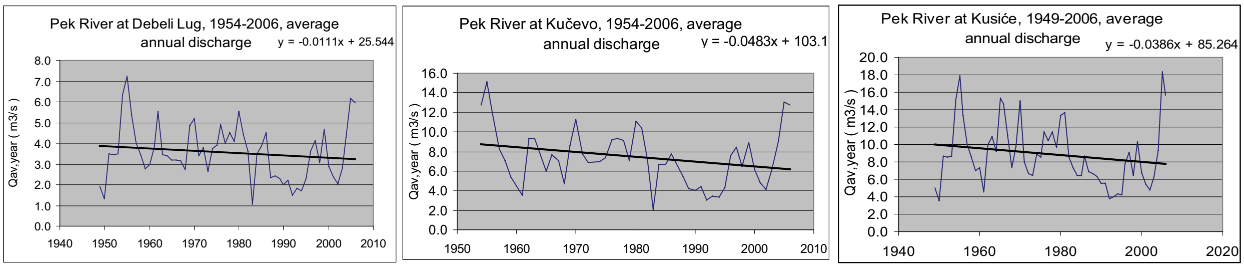
Table 1: Registered 1949-2006 trends by month and annual averages

Type of station	**Station**	**JAN**	**FEB**	**MAR**	**APR**	**MAY**	**JUN**	**JUL**	**AUG**	**SEP**	**OCT**	**NOV**	**DEC**	**Aver**
Temperature (°C/100y)	Veliko Gradište	1.3	1.0	2.2	-0.7	1.1	0.5	0.6	0.5	-2.1	0.0	-1.8	-2.9	0.0[1]
Precipitation (%/100y)	Braničevo (near VG)	-50.3	-39.4	-47.0	76.1	-106.7	-23.0	4.3	63.0	98.6	36.2	-78.2	-39.8	-10.5[2]
Precipitation (%/100y)	Voluja (near KU)	-22.9	-70.1	9.2	58.2	-54.8	-76.7	-76.6	21.8	7.0	13.1	-93.0	-45.5	-31.0[2]
Precipitation (%/100y)	Vlaole (near MA)	-66.3	-54.0	-49.7	1.0	-76.0	-24.8	-30.9	56.6	64.5	-50.9	-96.4	-43.1	-33.6[2]
Pek discharge (%/100y)	Kusići (V. Gradište)	-35.2	-38.6	-10.9	-19.3	-71.8	-123.6	-50.6	-4.5	9.6	3.5	-122.0	-64.6	-43.5[3]

1 The estimated present average annual temperature trend for this region is about +0.4 °C/100 years [3].
2 The estimated present average annual precipitation trend for this region is about -10 %/100 years [3].
3 Very close to the present average annual river discharge trend for the region in which the Pek C.A. is located [3].

The months of August and September, followed by July and October, are of particular interest when the impact of climate change on water resources is assessed because they exhibit the most critical relationship between the availability of water resources and water demand. The low flow trend in August, September and October is about "0" – there is no trend, and this is considerably more favorable than the annual average as a result of an upward precipitation trend in August and September, and in the case of the Pek C.A., also due to the presence of the Pustinjac Reservoir which provides drinking water supply to the most upstream city – Majdanpek.

There are three hydrological stations on the Pek River: an upstream station at Debeli Lug (near Majdanpek), a central station at Kučevo, and a downstream station at Kusiće (near V. Gradište). The longest existing time series for these stations, including the trends observed during the indicated period, is shown in Figure 2. A significant decrease in discharge is apparent. Several national studies indicate that the registered long-term trend for the Pek River is about -40% ÷ -45%/100years (of this value, about 2/3 ÷ 3/4 are attributed to climate change [3]).



Trend= -0.0111x10000/3.561= -31.2%/100 y. Trend = -0.0483 x10000 /7.414 = -65.2 %/100 y. Trend= -0.0386x10000/8.877= -43.5 %/100 y.

Figure 2: Observed annual trends at the three hydrological stations on the Pek River.

METHODOLOGY

Figure 3 shows the general methodology (GM, or needed steps) followed to assess climate change impacts on ALWSs in the Pek Test Area. Each step has been assigned a number and is addressed later in the text. Simplifications and assumptions:

- Each ALWS can be upgraded (new wells, artificial recharge, and the like). Additionally, all wells exhibit signs of declining discharge, to a greater or lesser extent, due to clogging. Such possibilities and processes are not taken into account in the assessment of climate change impacts on the ALWSs (i.e., the ALWSs are modeled as being the same today and in the future). The ALWS setting is the same today and in the future (no erosion, no siltation, and no morphological changes in the immediate environment). The assessment does not examine whether the capacity of a particular ALWS is adequate or not for the area it services.
- The groundwater model calibration time step is one week (GM, Steps 1 and 2), September-December 2010 (Jelak-V. Gradište) and March-June 1997 (Mlaka-Kučevo), while the calculation time step is one month, consistent with available data (GM, Step 9).
- Climate forecast parameters (temperature and precipitation) were obtained from other CC Waters partners (GM, Step 3). The climatic scenario used was A1B.
- Land use within the C.A. will not change significantly in the future and, as such, will not result in any runoff coefficient or water balance variation in the upstream portion of the C.A. (GM, Step 4).
- The water balance was not assessed using the conventional hydrologic method. Instead, the multiple non-linear correlation method (VNC) was used, as the dependency of discharge on temperature and precipitation, with corrections for additional water demand and possibly additional evapotranspiration. Changes in the rates of water abstraction for future irrigation and drinking water supply needs upstream from a given river discharge are taken into account, under optimistic (minimum), moderate (plausible) and pessimistic (maximum) scenarios. The additional evapotranspiration was also looked into under three scenarios (optimistic, moderate and pessimistic). Following discharge calculations, the river boundary condition for the HD model was determined based on the established correlation between river discharge and water level, via a large number of recorded data points: discharge-water level pairs (GM, Step 5).
- The time periods considered were: 1961-1990 (base period), and 2021-2050 and 2071-2100 (future periods). Based on recorded hydrologic data and estimated future climatic and hydrologic data, selected critical years are: V. Gradište – 1962 (past), and 2035 and 2096 (future); and Kučevo - 1961 (past), and 2035 and 2096 (future). Critical months were always July through October, such that the HD models were run through the March-October period (GM, Step 6).

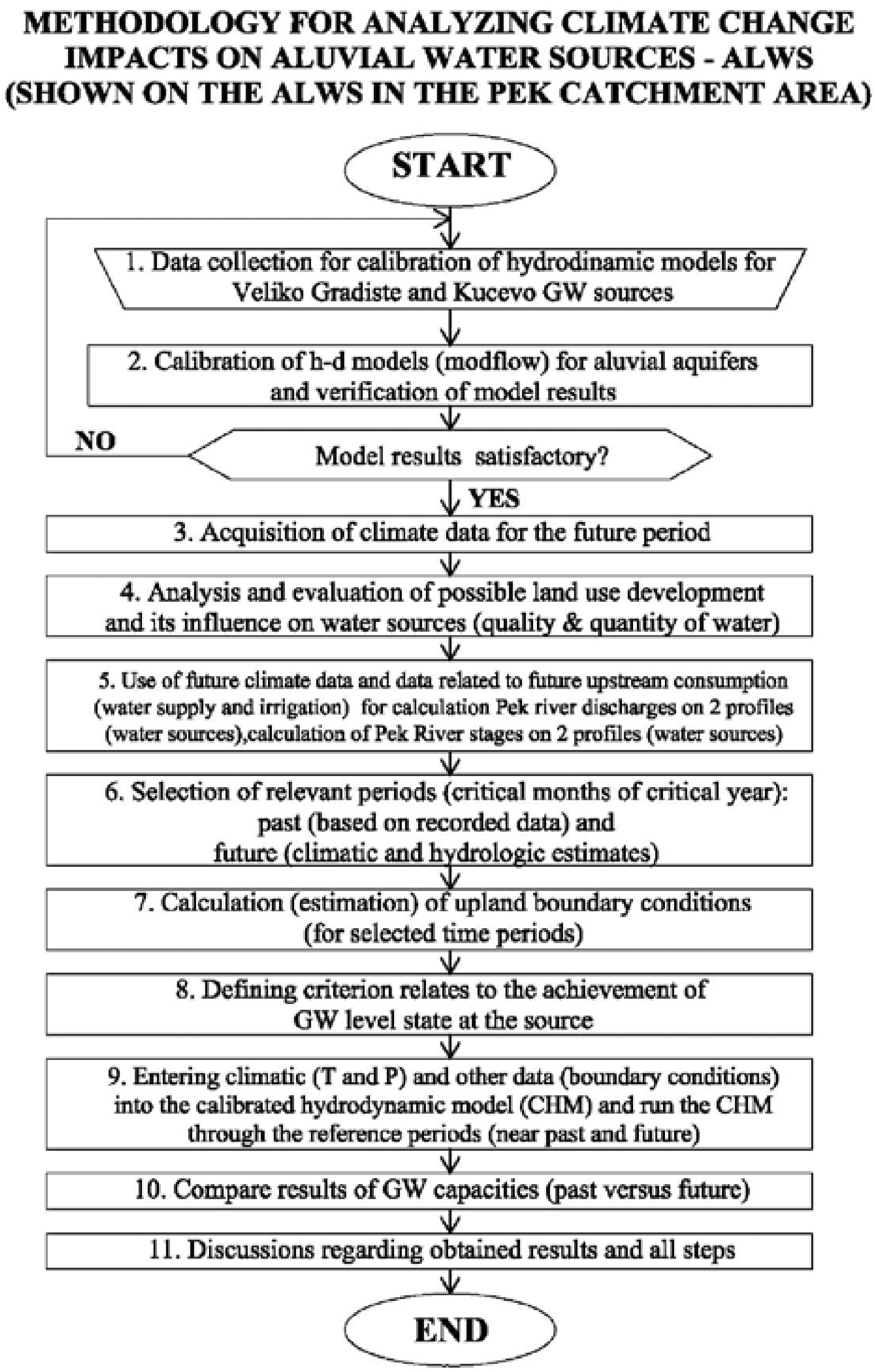


Figure 3: General methodology (GM) or needed steps.

- For the calibration period, groundwater flow from the upland was found to be about 30 l/s/km (Jelak-VG) and 18 l/s/km (Mlaka-KU). For estimated periods, groundwater flow from the upland was determined based on experience, taking into account that the downward trend of groundwater flow from the upland is about the same or slightly lower than the downward trend obtained for the Pek River, all other conditions being equal (GM, Step 7).
- Two values were assumed for the achievement of a given water level at the wells, as a criterion (GM, Step 8) which is the same for all time periods and scenarios, based on which HD model calculations were performed. The first is slightly above the aquifer floor (the average of 5 wells ≈ 68.2 m.a.s.l. at the V. Gradište ALWS, and the average of 3 wells ≈ 149.5 m.a.s.l. at the

Kučevo ALWS), corresponding to the maximum yield of the source under given conditions, while the second is about 0.5 m higher (the average ≈ 68.7 m.a.s.l. at the VG ALWS and the average ≈ 150.0 m.a.s.l. at KU ALWS), corresponding to the lower yield of each of the sources.
- The following will change in the future, relative to the present: temperature and precipitation; upstream water demand for drinking water supply and irrigation; and, as a consequence of climate change, evapotranspiration and river and upland boundary conditions.
- There are no special ecosystems; ecological criteria apply to the downstream consumer (at Kučevo) and to biodiversity of the river itself.

STRUCTURE (METHODOLOGY) OF THE CALCULATIONS

The structure of the calculations needs to be explained for:
1. HD models of the ALWSs, which were developed in Modflow,
2. Estimation of ecological water demand,
3. Calculations of the Pek River water levels at the ALWSs ,
4. Estimation of upland boundary conditions for both ALWSs,
5. Recharge and other "minor" calculations.

The most important explanations are included in the full-length paper (not this abstract).

RESULTS DERIVED FOR ALWS CAPACITIES

Tables 2 and 3 show, separately, the values derived for the entire year, and for the summer and winter periods (GM, Step 10).

Table 2 shows ALWS annual average capacities for the periods addressed (1961-1990, 2021-2050, 2071-2100). Minimum (maximum) values are given for one year (out of 30 years), in which the ALWS exhibits the lowest (highest) average annual capacity.

Table 3 shows ALWS capacities on a monthly basis during the most critical (lowest) year in the periods addressed (1961-1990, 2021-2050, 2071-2100). Minimum (maximum) values represent the month during the selected year in which the ALWS exhibits the lowest (highest) monthly average capacity. The plausible (average) value in this table is the same as the minimum value in Table 2.

Water Availability based on average annual hydrology at Jelak-VG

Table 2 - VG	**Average**			**Average for Apr. - Sept.**			**Average for Oct. - March**		
Period	Min.	Plausible	Max.	Min.	Plausible	Max.	Min.	Plausible	Max.
1961-1990 (l/s)	56	62	65	55	60	63	58	64	66
2021-2050 (l/s)	49	55	60	48	54	58	50	57	63
2071-2100 (l/s)	39	44	49	38	43	47	41	46	52
(2021-50)/(1961-90)	0.88	0.89	0.92	0.88	0.90	0.92	0.88	0.89	0.95
(2071-2100)/(61-90)	0.70	0.71	0.75	0.70	0.72	0.75	0.71	0.72	0.79

Water Availability based on average monthly hydrology (worst year of the period) at Jelak

Table 3 - VG	**Average**			**Average for Apr. - Sept.**			**Average for Oct. - March**		
Period	Min.	Plausible	Max.	Min.	Plausible	Max.	Min.	Plausible	Max.
1962 (l/s)	52	56	61	52	55	59	52	58	61
2035 (l/s)	44	49	54	44	48	53	47	50	54
2096 (l/s)	36	39	44	36	38	43	38	41	44
2035/1962	0.86	0.88	0.89	0.86	0.88	0.89	0.90	0.88	0.89
2096/1962	0.69	0.70	0.72	0.69	0.70	0.72	0.72	0.71	0.72

Water Availability based on average annual hydrology at Mlaka-KU

Table 2 - KU	**Average**			**Average of Apr. - Sept.**			**Average of Oct. - March**		
Period	Min.	Plausible	Max.	Min.	Plausible	Max.	Min.	Plausible	Max.
1961-1990 (l/s)	28	32	35	26	30	33	30	34	36
2021-2050 (l/s)	25	28	31	22	25	28	28	31	33
2071-2100 (l/s)	18	20	22	15	17	19	21	24	26
(2021-50)/(1961-90)	0.89	0.88	0.89	0.85	0.83	0.85	0.93	0.91	0.92
(2071-2100)/(61-90)	0.64	0.63	0.63	0.57	0.57	0.58	0.70	0.71	0.72

Water Availability based on average monthly hydrology (worst year of the period) at Mlaka

Table 3 - KU	**Average**			**Average of Apr. - Sept.**			**Average of Oct. - March**		
Period	Min.	Plausible	Max.	Min.	Plausible	Max.	Min.	Plausible	Max.
1961 (l/s)	24	28	33	24	26	29	25	30	33
2035 (l/s)	21	25	31	21	22	24	23	28	31
2096 (l/s)	14	18	23	14	15	16	18	21	23
2035/1961	0.89	0.89	0.94	0.89	0.85	0.83	0.91	0.93	0.94
2096/1961	0.57	0.64	0.70	0.57	0.57	0.56	0.72	0.70	0.70

When the results derived for the two ALWSs are compared, it is apparent that Mlaka (Kučevo) is more sensitive than Jelak (V. Gradište) to climate change (primarily evident from the correlation between the 2096 capacity and that of the years which are representative of the present state). The explanation of this may be sought in the lower permeability of Mlaka, as well as the proximity of the Danube River to Jelak.

DISCUSSION: RESULTS AND UNCERTAINTIES

The Climate Change and Impacts on Water Supply in SE Europe Program involves, by necessity, a large number of assumptions and calculations. Each forecast is sensitive to assumption uncertainties and calculation imperfections. They need to be examined and critically assessed. The quality of a prediction grows with increasing validation by recorded data and especially by trends. Following is a commentary on the main activities conducted under the Program.

Climate predictions

Temperature and precipitation calibrations for the Pek C.A. are deemed to be very good. Any scenario of GHG emission developments and temperature increases is, however, open for discussion. All further predictions depend on the realism of this (initial) assumption. Since only one scenario, the “middle” scenario A1B, was selected, it is safe to conclude that the climate forecast targeted the most realistic climate developments. For the Pek Test Area, the adopted climate model CNRM-RM5 predicts an increase in the average annual temperature by 3.1°C/100 years. The current temperature trend of the region which includes the Pek C.A. is about 0.4°C/100 years (the average for Serbia is slightly higher). This upward average annual trend is likely a result of the assumption inherent in the climate scenario, but the distribution of monthly trends is questionable: the highest upward trend was predicted for the months of July, August and September (in the order of 6, 5 and 4.5 °C/100 years), and is considerably higher than the predicted annual trend, while the actual trends for July and August in the Pek C.A. (and in all of Serbia as well) are only slightly higher than the annual average, and September, along with November and December, is the only month with a distinct negative temperature trend (in the order of -1.5 °C/100 years).

The precipitation situation is similar (Figure 4): For the Pek C.A., the selected model CNRM-RM5 predicts a reduction in precipitation by -9%/100 years, which matches very well the current precipitation trend in the region which includes the Pek C.A. Again the distribution of monthly trends is questionable: the highest downward trend was predicted for the months of July, August and September (in the order of -55, -45 and -25 %/100 years), which is inferior to the predicted annual trend, while the actual trends in July, August and September in the region which includes the Pek C.A. are in the order of -20, +40 and +50 %/100 years. September is at the same time the month with the highest and most constant positive precipitation trend in all of Serbia.

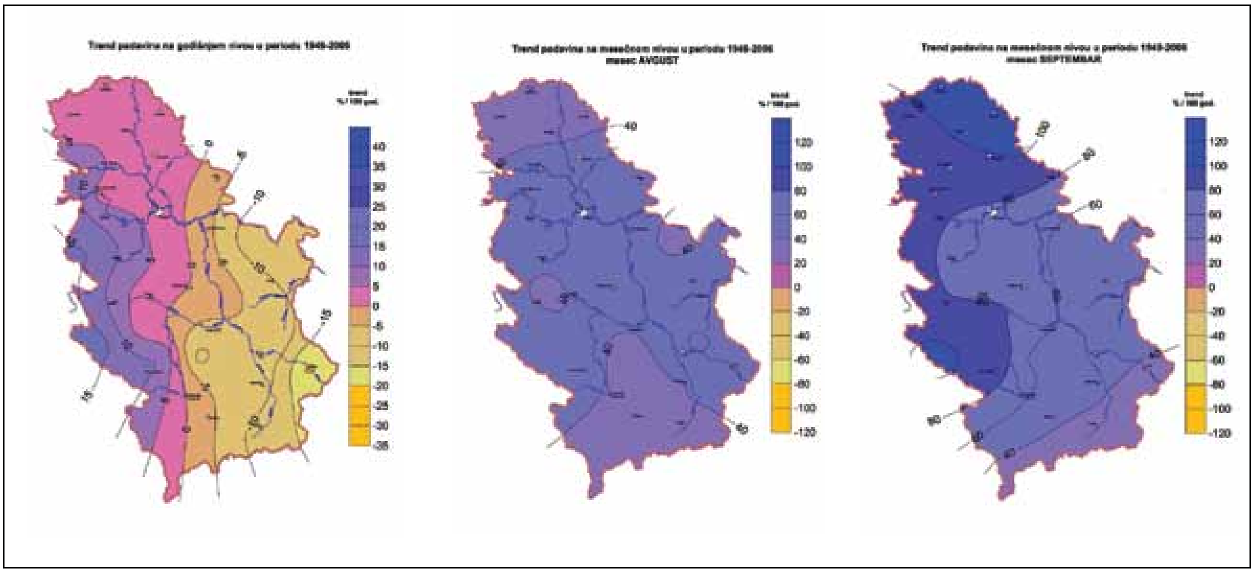


Figure 4: Approx. long-term annual and monthly for August and September precipitation trends (%/100y) in Serbia: [3],[5].

From the standpoint of critical periods for drinking water supply (July-October), the predicted climate parameters, assuming that the A1B scenario was properly selected, provide appreciably more severe (less favorable) values than those that can be deduced from analyses of the trends recorded during this part of the year.

The full-length paper contains a discussion of other predictions (land use, river hydrology, water balance, and groundwater flow, including boundary conditions), as well as general conclusions.

Although not presented in the paper, the socio-economic aspect of potential future developments (including the spending needed to ensure trouble-free drinking water supply in the future, the impact of water tariffs on water demand, and the like) was also assessed. All these analyses have provided insight into water management today and in the future.

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Notes:

Extended Abstract

KARST AQUIFER AS A "BUFFER" FOR CLIMATE VARIATIONS AND CHANGES

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INTRODUCTION

According to some estimates, around 20-25% of the world's population consumes groundwater originating from karstic aquifers. A similar situation exists in SE Europe and in Balkan countries (Stevanović, 2009). In terms of the proportion of karst waters in its water supply systems, Austria, with over 50%, is a leader. In other countries, due to the lesser extent of rich aquifers, the percentage is lower. However, the population of six capitals in the SEE region consumes water exclusively or dominantly from the karst (Vienna, Rome, Sarajevo, Tirana, Podgorica, Skopje). In Serbia, about 20% of the population also uses karst waters for drinking; this percentage increases towards eastern and western areas where carbonate rocks prevail in lithological composition. From the standpoint of water quality these are mainly waters of high natural quality that do not require expensive treatment if they are not artificially polluted.

Although important, these water resources are the least studied of water resources in Serbia (surface and underground); systematic research and monitoring is, therefore, required. Better understanding of karst and assessment of stored groundwater reserves are particularly important where the negative impact of climate changes is concerned. Some preliminary calculations which indicate abundant reserves in karst massifs (e.g. Beljanica, Kučaj, Vidlič, Pešter) have to be verified and these areas protected and preserved as an alternative source for the future water supply of Serbia.

The Earth's climate changes regularly over geological time. However, human impact is likely also to contribute progressively to global warming. In Europe, the mean annual temperature is higher by 1.4 oC than in the pre-industrial period with the warmest decade (last 10 years) in the last 150 years All existing scenarios and all utilized climate models foresee a temperature increase on the global scale: during this century the global temperature will rise by 1.8 - 4.0 oC and the warmest parts of Europe will be in the east and the south of our continent (IPCC- Intergovernmental Panel on Climate Change, 2007).

This heat-up will result in an increased evapotranspiration rate, reduced snowfall, i.e. thinner snow cover in winter, and longer rainless periods in summer/autumn. All scenarios predict more pronounced extremes in annual sum precipitations, i.e. much higher variations of annual sum of precipitations from the mean multiannual values. All this will result in more frequent floods and severe drought episodes, and this will pose a real threat primarily to water supply in urban areas.

KARST IS A “BUFFER” – DISCUSSION

The importance of karst is reflected in the ability of karst massifs to accumulate a certain water quantity and to release it subsequently through karst springs. Therefore, karst could amortize the effects of huge and intensive rainfalls, i.e. these areas could largely reduce the impact of floods. Moreover, in the case of a high degree of karstification and large extension, one could say that flood effects are generally negligible in well-developed karst. On the other hand, large static (geological) reserves that can largely help bridge the problematic rainless periods are often formed in karst. These reserves are easily recoverable in periods of high precipitation. Such an advantage has been applied in several successfully implemented regulation projects in Serbia where natural source capacities during lean periods are doubled or even quadrupled (Stevanović and Dragišić, 1997; Stevanović, 2010). And finally the advantage of underground accumulations formed in karst is that the expected (predicted) increase in temperature will not stimulate evaporation from these accumulations.

CASE STUDIES

A. Baseflow (ecological flow for dependent ecosystem) guaranteed by karst

The Mlava Spring (locally: Vrelo Mlave) is the largest in the Carpathian karst of eastern Serbia; it is still not tapped and has a large potential for regional water supply. The Mlava is one of the very few karstic springs in Serbia where springflow has been observed for a longer period of time (since 1966). Its hydrograph during an average hydrological cycle shows three maximal micro regimes followed by three minima at their ends (Ristić et al. 1997; Ristić 2007). The Mlava Spring drains northeastern parts of the Beljanica karst massif, a catchment of about 125 km^2 mostly consisting of karstic (carbonate) rocks (Milanović S., 2010).

Downstream from the spring, there are two gauging stations on the Mlava River. The Gornjak station, the upstream one (nearest to the spring), controls a catchment area of around 656 km^2. The percentage of karst terrains in this basin falls to around 35% in comparison with the spring’s surface area. Further downstream on the Mlava is the Rasanac gauging station which controls around 1063 km^2, of which only 17% belongs to the karst terrains.

In Figure 1 comparative hydrographs for the karstic Mlava Spring and for the Mlava River (gauging stations Gornjak and Rasanac) are given for the year 1984. The diagram clearly shows that during the spring months the riverflow at the Rasanac and Gornjak gauging stations is almost identical.

It should be noted that the gauging st. Rasanac controls a catchment area almost two times larger than at st. Gornjak. Moreover, during dry periods (summer-autumn) the quantities of water which are registered in all three sections are also almost equal. While the Rasanac-Gornjak-Mlava Spring catchment areas are in relation 10:5:1 the discharges in dry period are in relation 2.3 : 2.2 : 1. This shows that the base flow of the Mlava River at downstream profiles Gornjak and Rasanac almost exclusively comes from the karst aquifer and that the ecological flow strongly depends on the karst spring discharges.

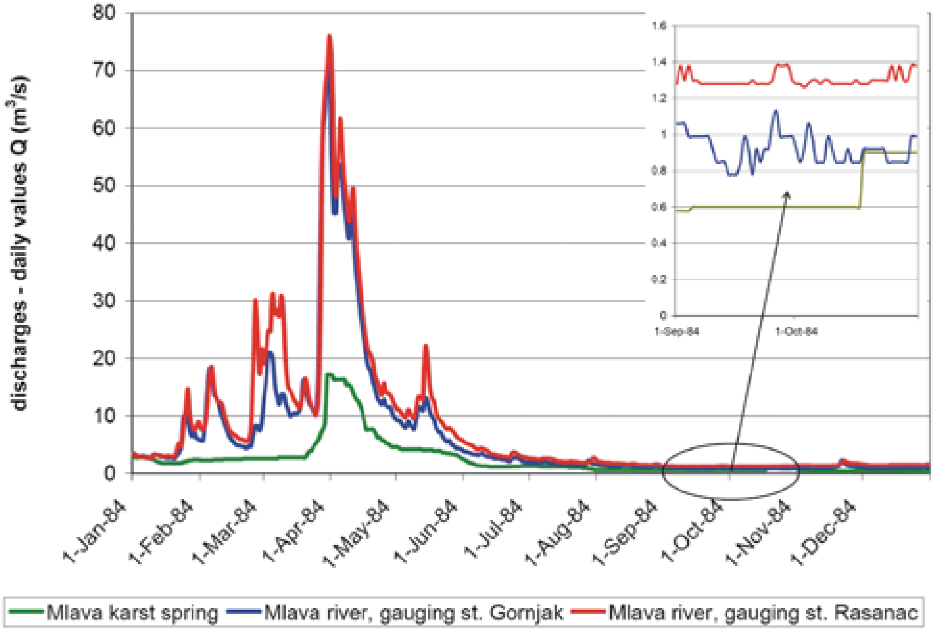

Figure 1: Mlava River discharges on three successive gauging stations for the year 1984

B. Karst aquifer richness in waters

The result of regulating or controlling the groundwater in karst aquifer should be analogous to managing the water resource of an open reservoir. For the latter, the volume of the reservoir, i.e. storage, is not difficult to calculate, but a system of fissures, channels and caverns within karst aquifer and thus water availability is very difficult to assess. Particularly problematic is the evaluation of the aquifer's deeper saturated geometry. The term storativity or storage coefficient in karst could be considered relative to the effective porosity. Knowledge of it is essential for calculating geological water reserves (Stevanović et al. 2010).

Table 1 shows the specific yield (runoff) for all three stations of the Mlava both for the entire year 1984, and for the dry season (September-October) of that year. The catchment area of the Mlava Spring is characterized by the much larger values of specific yield than the other two areas. The specific yield is two times greater than the calculated value for the downstream gauging station (Gornjak). The same situation occurs during the dry season (September-October), but the ratio increases (three times larger q for the Mlava Spring area), proving that during lean periods karstic aquifer, despite its discharge variability, is much richer in water resources than other water-bearing media, including fast discharging alluviums.

Table 1: Catchment area, percentage of karst, discharge/runoff and specific discharge for gauging stations Mlava Spring, Gornjak and Rasanac for 1984 and dry season

Year 1984	**Catchment area F (km^2)**	**% of karst**	**Q (m^3/s)**	**q (l/s/km^2)**	**Ratio 1:2:3**
1. Mlava karstic spring	125	95	2.414	19.3	1:
2. gaug. st. Gornjak	656	35	6.666	10.2	0.5:
3. gaug. st. Rasanac	1063	17	8.146	7.6	0.4
September-October 1984	**Catchment area F (km^2)**	**% of karst**	**Q (m^3/s)**	**q (l/s/km^2)**	**Ratio 1:2:3**
1. Mlava karstic spring	125	95	0.6	4.8	1:
2. gaug. st. Gornjak	656	35	0.9	1.4	0.3:
3. gaug. st. Rasanac	1063	17	1.3	1.2	0.25

Q – Average discharge of spring or riverflow during the period
q – Specific yield (runoff)

Mlava karst aquifer has potential to provide sufficient water for different kinds of consumers (water supply, industry, agricultural). However, adequate regulation measures and management (temporary over-pumping) would be necessary during expected longer dry periods.

C. Amortization of flood waves in karst

The Luznica riverflow regime was taken as an example to demonstrate the effects of amortizing flood waves in karst. The confluence of the Luznica River into the Vlasina River is in the Svodje settlement. There are two gauging stations, one controlling the Luznica riverflow (widely present karst) and the other located on the Vlasina River (mostly non-karst).

Both catchment areas are of very similar size, and they also share a similar pluviographic regime. Figure 2 shows the hydrographs of these rivers for the first half of 1994. It is clear that stronger intensity rains cause an increase in both discharges almost simultaneously, but differences in absolute discharge values are also evident. The peaks are lesser in the case of Luznica hydrographs because of more significant infiltration into the karstic rocks. Infiltrated waters were retained in aquifer for a certain period of time, sufficient to prevent flood effects. This is not the case with the Vlasina River.

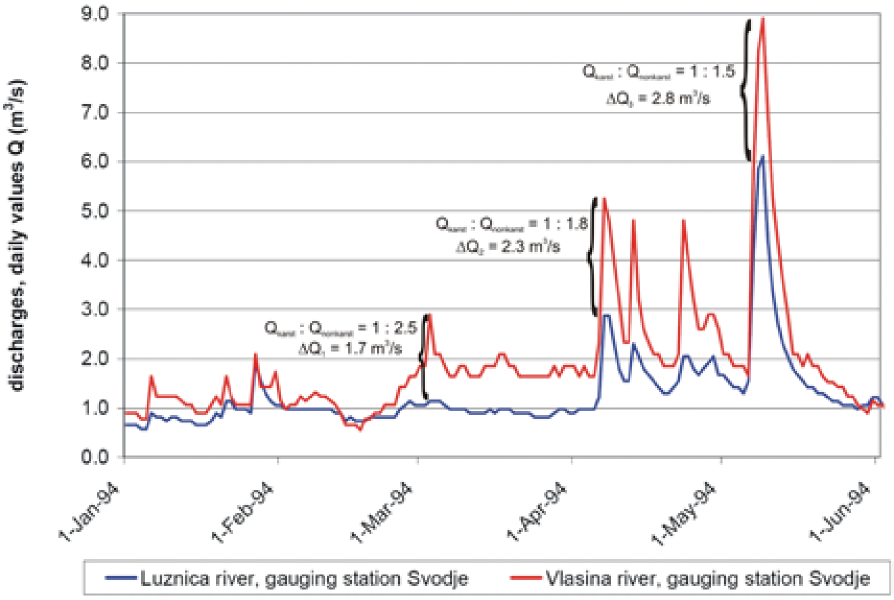

Figure 2: Hydrographs of Luznica and Vlasina Rivers for the first half of 1994.

D. Delaying of discharge in karst – residence time

Karst aquifer systems often discharge waters with some delay. Residence time can be from only a few days to several weeks or even longer, depending on actual saturation and storativity. This buffering effect sometimes enables the management of stored waters. This could be of great importance during dry periods, which are likely to be more frequent and extended in the future.

Figure 3 shows the two typical hydrographs caused by the same rainy episode. The red line shows stream flows formed at the catchment which consists mostly of low to semi permeable rocks (fissure aquifers), while the blue line represents discharge of a stream coming from a dominantly karstic area.

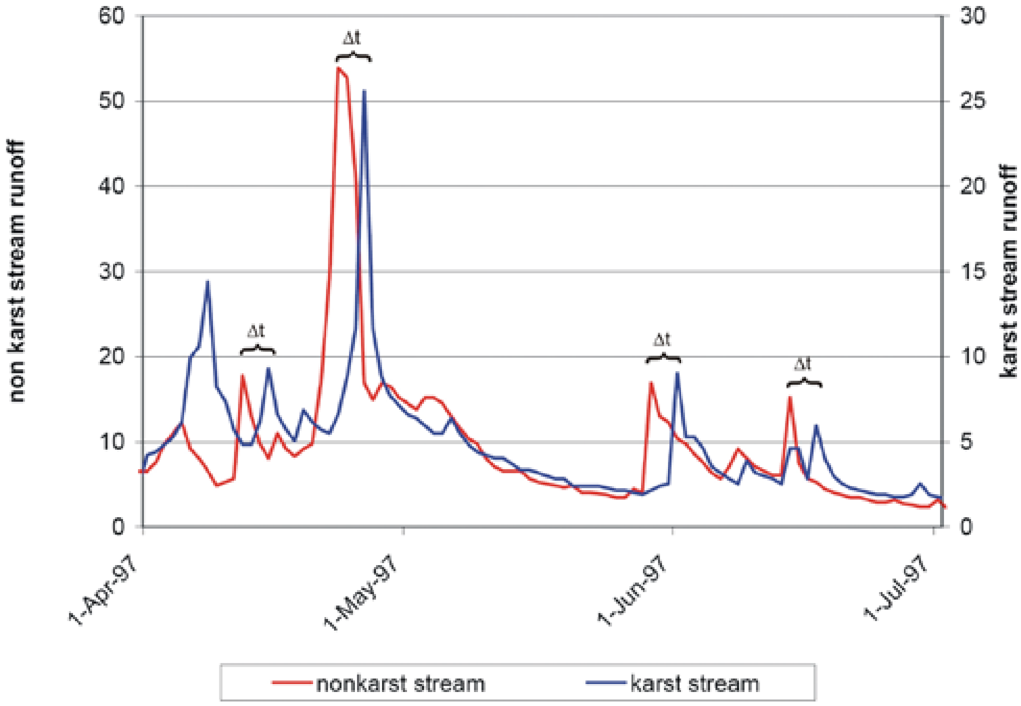

Figure 3: Typical hydrographs of non-karst and karst streams reflecting the same rainy episode

E. Limited storage of karst aquifer results with similar regime as impervious rocks

The above examples indicate the importance of karst aquifer in terms of its high porosity and storativity. In contrast, when carbonate rocks are slightly karstified groundwater reserves can be very small or limited to certain parts of the aquifer. In this case drainage behavior can be very similar to non-karst or to impervious rocks (Bonacci, 1993). The two examples presented below support such a statement:

1. An example of a rapid propagation of rainfall without water retention in karst massif is the Iška River (Globevnik and Vidmar, 2010). In the period from 17-19. 09. 2010 at the Iška the catchment area fell 539 mm (Otlica above Ajdovščina). The 3-day rains after rapid propagation through the karst formation caused a massive flood wave with a peak of 59.3 m3/s, which was recorded during the night between 19 and 20 September (see Fig. 4).

The Iška riverflow on the day before the flood event (September 17) and soon after the storm (22 September) was almost equal to 0 (Figs. 4 and 5).

2. An immediate reaction of the aquifer to intense rainfall after a longer dry period by fast increase of groundwater table usually indicates limited storage. A jump of almost 50m after only 24 hours of intensive rains is known from eastern Herzegovina (Milanović P. 2000). The typical example of fast replenishment and the appearance of a temporary spring which is draining the Shiranish formation in northern Iraq (Ali et al. 2009) is shown in Fig 6.

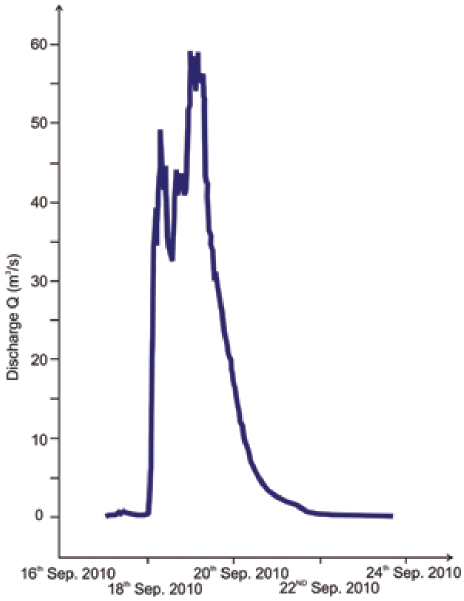

Figure 4: Hydrograph of river Iška

Figure 5: Iška riverbed

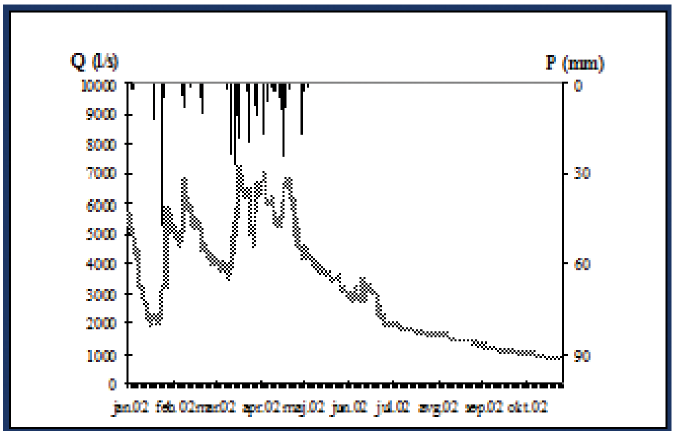

Figure 6: Hydrograph of the large Sarchinar spring (left) with longer residence time and good storage capacity (utilized for Sulaimaniya City water supply) and one temporarily activated spring (right)

CONCLUSION

The key element for successful karstic groundwater utilization for water supply or for other purposes is the storage capacity (storativity, effective porosity). In the case of well-developed karst and large storage volume the karstic aquifers usually react as a buffer and could amortize intensive rainy episodes preventing consequent flood events. Moreover, groundwater reserves could be properly regulated and utilized during subsequent longer dry seasons. However, not all aquifer are well karstified and rich in waters. For this reason, detailed hydrogeological survey and permanent discharge monitoring are a necessary base for any engineering works or intake design.

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NOTES:

THEME 4:

MANAGEMENT OF URBAN GROUNDWATER BASINS: MITIGATION OF WATER QUALITY IMPACTS FROM ANTHROPOGENIC THREATS

Full Paper

TRANSFER OF POLLUTANTS FROM AN OLD URBAN LANDFILL: PHYSICAL AND CHEMICAL CHARACTERIZATION

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Abstract: An old landfill located in the city of Nantes (west of France), was selected in order to study and understand the transfer of pollutant from the site to the underlying aquifer. The waste and interlayered anthropic materials composition, as well as leachates and groundwater quality were characterized. Among more than 100 parameters were researched: pH, electrical conductivity, Eh, dissolved oxygen, major anions and cations, trace elements (Pb, Zn, Ni, Cr, Cd, Cu, As) and organic compounds (BTEXs, PCBs, PAHs and COHVs). Data showed i) the contamination of the waste matrix with trace elements (Zn, Cu, Pb, Ni, As) and organic compounds, mainly PAHs, BTEXs and PCBs being slightly upper the limits of quantification, ii) pollution of the groundwater involving organic (PAHs) and inorganic compounds (ammonium, nickel and arsenic). The study provided input data (landfill contamination and leachates quality) and calibration data (fluctuations of groundwater quality) for simulating the reactive transport of the leachates plume to an alluvial aquifer in urban context.
Keywords: former landfill, groundwater pollution, landfill leachates, sampling, waste.

INTRODUCTION

Landfill leachates are a substantial source of groundwater pollutions. Several landfill leachate studies have shown the occurrence of a broad range of pollutants (e.g. dissolved organic carbon, cations and anions, heavy metals, xenobiotic organic compounds, etc.) which may modify the quality of groundwater and soils (e.g. Christensen et al., 1994; Christensen et al., 2001). However, many old landfills did not take into account their significant environmental impact. Understanding and identifying pollutants and mechanisms which govern the transfer of pollutants from landfill to groundwater is an important issue for enhanced risk assessment.

The purpose of this study was to identify the transfer of pollution (i.e. organic and inorganic compounds) from a closed landfill (waste, solids, and interstitial water) to underlying aquifer. The question is motivated by the occurrence of an insufficient groundwater quality in several piezometers downstream of the landfill (including suspended particles, electrical conductivity, etc.). This work involved laboratory analyses and field studies to characterize waste and anthropic materials composition, landfill leachates and groundwater quality, and the physical speciation of contaminants (dissolved vs. particulate) in order to study the reactive transfer of pollutants. This work is part of a larger project aimed at understanding and modelling the pollution plume of the landfill.

MATERIALS AND METHODS

Landfill site

The "Prairie de Mauves" landfill is located in west of France. In this landfill, six to eight metres of household and industrial waste were deposited between 1961 and 1987 (Figure 1). This old closed landfill was not equipped with clay or plastic liner to prevent the spreading of leachates to aquifers. It was constructed on alternating vases and clays associated with sandy-gravelly alluvial deposits. The landfill geometry was interpreted thanks to previous historical survey (BRGM, 1992 and ANTEA, 2005). The lithology (peat, vases, clay, sand, gravel, etc.) highlighted the strong lateral and vertical heterogeneities in the alluvial deposits. Three aquifers were identified: (1) an aquifer in the embankment (waste and anthropic materials), (2) an aquifer composed of alluvial deposits (alluvial aquifer) and (3) a bedrock aquifer (fractured micaschistous rock). The bottom of the landfill was probably under the groundwater level (Figure 1), as it was set up in a flood-risk area.

Landfill monitoring and sampling

Sampling was conducted in an area containing mainly household waste. Solid samples, excavated in early March 2010 using a shovel, were placed on plastic sheeting. Each sample was homogenized in the site and classified into five size classes (fractions > 20 mm and 5 mm, < 5 mm, > 2 mm and finally < 2 mm). The macro-waste (fraction > 20 mm) was sorted according to XP X30-408 standard (AFNOR, 2007). Only one leachate could be collected, from seepage in a layer of waste in excavation well 1.

Groundwater table was monitored using several piezometers completed by private wells (upstream and downstream of the landfill). According to FD X31-615 standard (AFNOR, 2000), boreholes were purged until the stabilization of the non-conservative parameters before groundwater sampling. Two groundwater samples were collected in January 2010: the first one in the piezometer PZ5 (downstream of the landfill) and the second one in the well 4 (upstream of the landfill). Groundwater quality is also studied by ANTEA since 2005 (once to twice a year, around 20 parameters) and every two month since January 2011 within the present study.

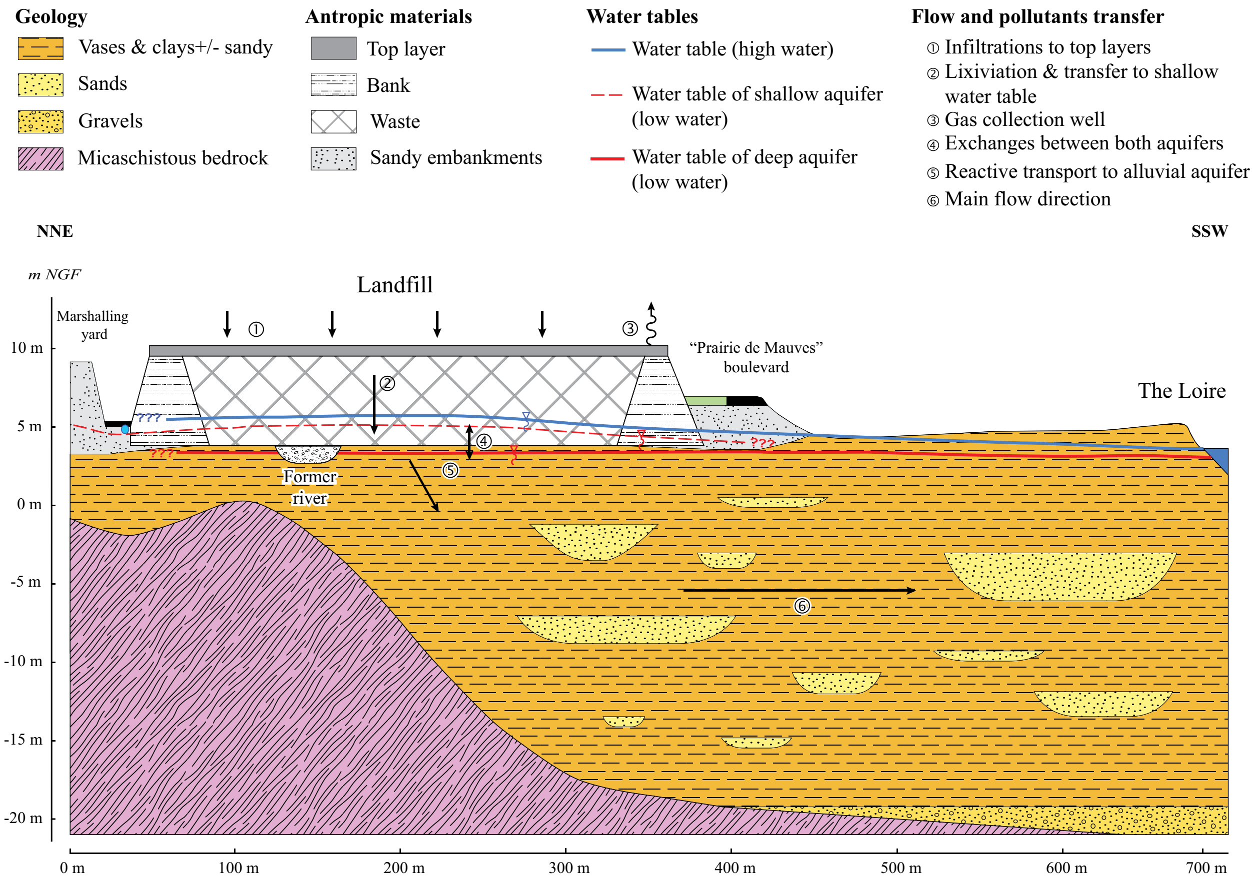


Figure 1: Conceptual model of the eastern part of the landfill.

Sample analyses

All liquid samples were analysed for anions and cations, trace elements, organic compounds, etc. Non-conservative parameters (T°, Eh, pH, electrical conductivity, dissolved oxygen) were measured on site. Series filtrations were applied on each liquid sample. Three cut-offs were performed by filtrations on an 8 and 0.45 µm pore size membrane and by ultrafiltration in 3kDa centrifuge tubes. The filters were mineralized before analyse. The five samples were analysed for anions by liquid chromatography whereas major cations and trace elements were analysed using respectively an inductively coupled plasma optical emission spectrometer (Varian ICP-OES 720-ES) and an inductively coupled plasma mass spectrometer (Varian ICP-MS 820-MS). Hydrocarbon oil index, aromatic and halogenated hydrocarbons were analysed using gas chromatography coupled to a mass-spectrometer (GC/MS (/MS)). Major elements, trace elements, pH, organic carbon and xenobiotic compounds were analysed for solid samples with methods according to AFNOR (1999).

RESULTS AND DISCUSSION

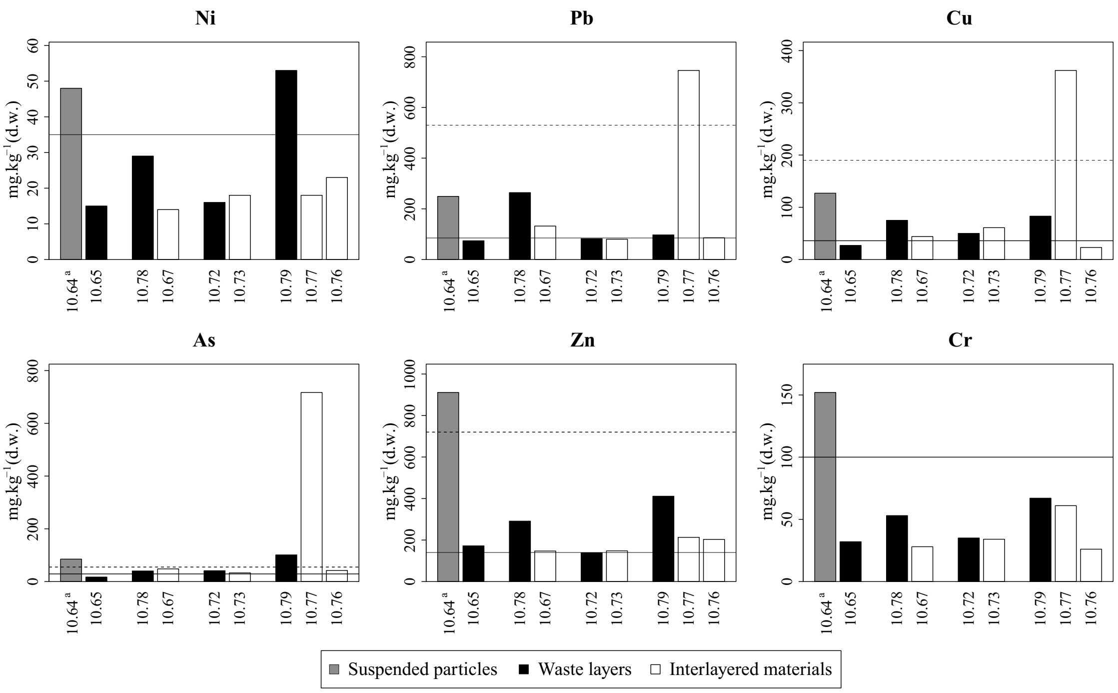
Solid and liquid analyses were compared to threshold levels defined by Dutch standard (1994) - Ministry of housing, spatial planning and environment (Spierenburg and Demanze, 1995) and French drinking water standard - System for Evaluation of groundwater Quality - Drinking water production (Agence de l'eau and MEDD, 2003). Literature data were also used for comparison.

Waste characterization

The solid samples excavated within the waste (waste and interlayered materials) have been dated to the late 1980s, and the thickness of the corresponding waste should not exceed five metres. The macro-waste generally corresponded to a set of household waste made of plastics (bottles, plastic packaging, etc.), chemicals, batteries, ferrous and aluminium containers, glass, paper and paperboard, and pharmaceutical product care. These wastes are generally associated with inert material (rubble, tiles, bricks...).

The solid samples studied correspond to the waste matrix (sample 10.65, 10.78, 10.72 and 10.79 in black in Figure 2) and to the underlying layers of waste (sample 10.67, 10.73, 10.77 and 10.76 in white). Suspended particles obtained from leachate sample decantation (sample 10.64 in gray) were also analysed. The particle size distribution of samples (< 2 mm) showed a mean D50 upper than 250 µm and a proportion of organic matter (assimilated to volatile matter) between 10 and 16 % for the waste matrix and 2 to 4 % for the others samples. It must be emphasized that 10.77 sample is silty whereas the other samples of interlayered levels are more sandy.

Excavation well 1		Excavation well 4		Excavation well 5		Excavation well 7		
10.64[a]	10.65	10.78	10.67	10.72	10.73	10.79	10.77	10.76



[a]: suspended particles in the landfill leachate ; d.w. : dry weigth

—— Polluted soil threshold level (value at which a soil is considered contaminated according to the Dutch standard (1994) / 25% clay - 10% organic matter)

----- Intervention threshold level (value at which intervention is necessary according to the Dutch standard (1994) / 25% clay - 10% organic matter)

Figure 2: Trace elements concentrations in solid samples (March 2010).

Three samples (wastes: 10.78, 10.79 and silty material 10.77) exhibited high heavy metal concentrations. 10.79 and 10.64 were characterized by high concentrations of nickel (53 and 48 $mg.kg^{-1}$ (dry weight) (d.w.)) and zinc (411 and 911 $mg.kg^{-1}$ (d.w.)). Except for 10.77 sample, arsenic concentrations are in the same range as geochemical background related to micaschistous rock (between 50 and 100 $mg.kg^{-1}$ (d.w.)). In 10.77 sample (interlayered silt) arsenic was much higher than in the other solid samples (>700 $mg.kg^{-1}$ (d.w.)). Pb and Cu concentrations of sample 10.77 were also specifically high. These findings on waste and underlying solids could be related to the pollutant sources present in the landfill such as batteries containing Pb, Ni and Zn or paint pigments composed of As, Ni and Pb. A transfer of trace elements from waste (10.79) to interlayered level (10.77) seems to occur.

Table 1: Concentrations of BTEXs and PCBs in liquid and solid samples (January and March 2010).

	LQ	Waste (10.65)	Interlayered level (10.67)	[1]	LQ	Leachate	Groundwater	[1]
Parameters	**Solids (µg.kg-1 (d.w.))**				**Liquids (µg.L-1)**			
PCB n°28	10	LQ	< LQ	Σ PCB 20/1000	0.005	0.008	< LQ	Σ PCB 0.01/0.01
PCB n°52		15	< LQ			0.01	< LQ	
PCB n°101		32	< LQ			0.021	< LQ	
PCB n°118		21	< LQ			0.01	< LQ	
PCB n°138		44	< LQ			0.02	< LQ	
PCB n°153		35	< LQ			0.016	< LQ	
PCB n°180		26	< LQ			0.008	< LQ	
Benzene	5	< LQ	< LQ	50/1000	1	< LQ	< LQ	0.2/30
Toluene		< LQ	12	50/130000		< LQ	< LQ	0.2/1000
Ethylbenzene		9	13	50/50000		< LQ	< LQ	0.2/150
Xylene		27	15	50/52000		< LQ	< LQ	0.2/70

Some of the organic compounds analyses, performed for two samples (waste matrix: 10.65 and interlayered level: 10.67, separated by 90 m distance), are presented in Table 1. Apart from Polycyclic Aromatic Hydrocarbons, only polychlorinated biphenyls and BTEXs are detected in solid samples. PAHs constituted the most important contamination in the solids (Figure 3). Indeed, several PAHs concentrations exceeded the threshold level contamination (Σ PAHs = 1000 µg.kg^{-1} according to Dutch standard). 10.67 sample showed a C10-C40 oil index more important (1286 mg.kg^{-1} (d.w.)) than 10.65 sample (435 mg.kg^{-1} (d.w.)). The texture of samples could explain these differences.

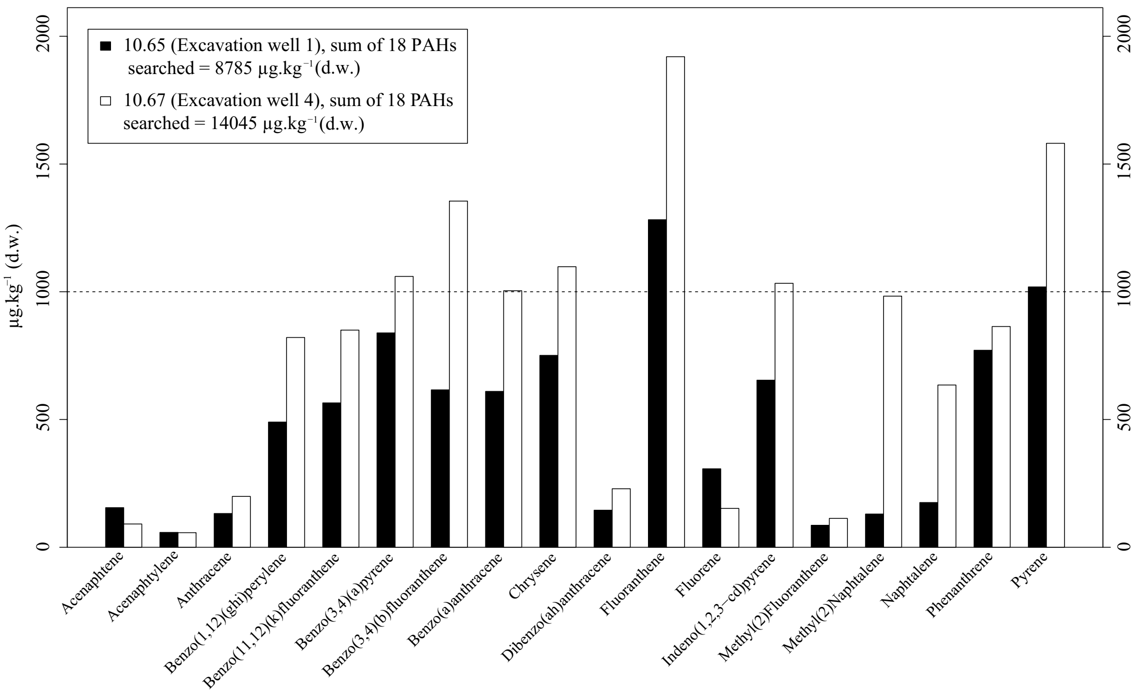


Figure 3: Polycyclic aromatic hydrocarbons concentrations analysed in two solid samples (March 2010).

Leachate and groundwater quality

The leachate sampled in 2010 is similar to the results found by ANTEA (2005), in term of chemical composition. The composition of leachates is an indicator of transformation phases of landfills. Comparing to Ehrig (1988), leachates concentrations (Ca: 399 mg.L^{-1}, Mg: 36.7 mg.L^{-1}, Fe: 6.6 mg.L^{-1}, Mn: 1.3 mg.L^{-1} and Zn: 12.7 µg.L^{-1} and high concentration of ammonium 92 mg.L^{-1} N) could be explained by a methanogenic phase transformation. The heavy metal pollution of the leachate appears limited compared to other leachates (Christensen et al., 2001). Analyses on leachate showed low concentrations of contaminants compared not only to modern landfills but also to old landfills studied in the literature (Kjeldsen and Christophersen, 2001). Moreover, literature underlined the decrease of the leachate concentrations with the age of the landfill (Kulikowska and Klimiuk, 2008).

In the groundwater, concentrations reached a few µg.L^{-1} of arsenic and nickel upstream of the landfill, but they were more important (several tens of milligrams) downstream of the landfill. Cu and Zn probably come from agricultural pollution (well 4 in kitchen garden area upstream of the site) (Figure 4). The arsenic present in the landfill leachate may come from the waste (cf. high concentrations in the waste matrix), but also from the interlayered material, some of which being possibly constituted of As-rich micaschists. The infiltration of oxygenated rainfall may destabilize the arsenic bearing minerals (mainly sulphurs) and liberate some arsenic. The arsenic present in the groundwater downstream may also possibly come partly from the bedrock aquifer, if somehow it was connected to the other aquifers at the bottom of the landfill (to be verified).

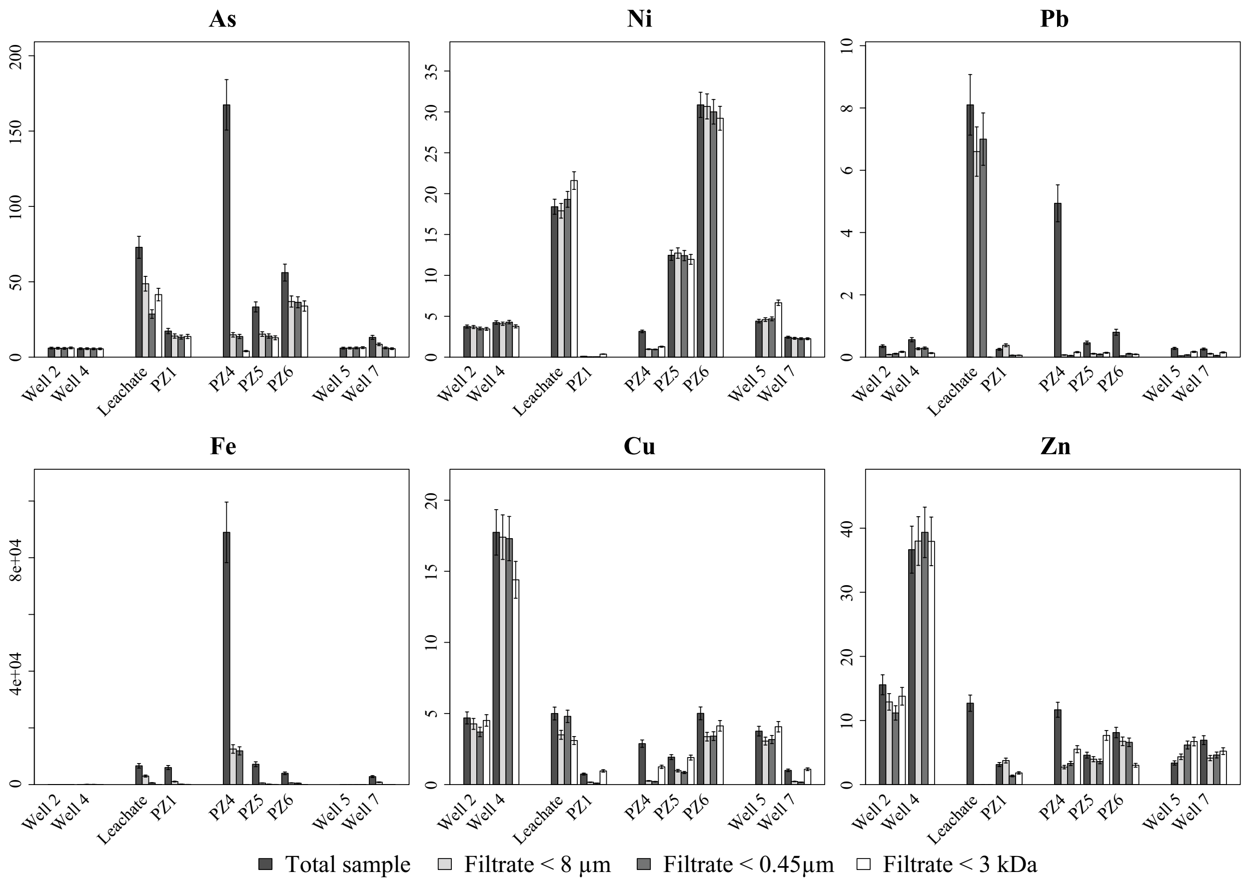


Figure 4: Trace element concentrations in groundwater from upstream (Well 2 and 4) and within the landfill (leachate and PZ1), to near downstream (PZ4, PZ5 and PZ6) and faraway downstream of the landfill (Well 5 and 7) in March 2010 for leachate and March 2011 for groundwater (µg.L^{-1}).

The range of values observed in groundwater (anions, cations and trace elements) of the landfill of "Prairie de Mauves" (1993-2011) (Figure 4 and 5) was in the same order as that of Thornton et al. (2000) and Rapti-Caputo and Vaccaro (2006). The influence of the landfill on groundwater quality was shown. Thus, as seen in Figure 5, all samples showed high ammonium concentrations. These values exceeded the threshold level (4 mg.kg^{-1}) at which a groundwater is considered as not suitable for drinking water production (Agence de l'eau and MEDD, 2003).

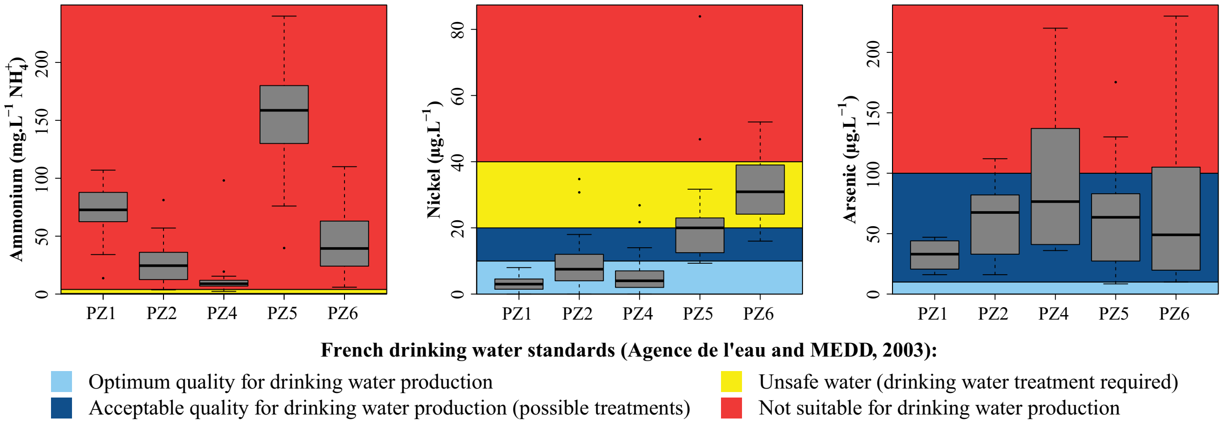


Figure 5: Groundwater quality for ammonium, nickel and arsenic between 1993 and 2011.

The filtrations of samples were aimed at describing the distribution of metals and metalloids between particulate, colloidal and dissolved fractions (Figure 4). Ni is only present in dissolved fraction whereas Zn, Cu, As and Cr were present in particulate and dissolved fractions. Cd, Pb and Fe exhibit a high or a total particulate behaviour. Concentration of As may be linked to the concentration of Fe (Figure 4). The affinity of As for iron precipitates is indeed well known (e.g. Le Guern et al., 2003). The iron colloids may thus play a role in the transfer of As in the alluvial aquifer.

Almost all PAHs detected in groundwater were also measured with highest concentrations in the waste leachate: naphtalene (0.893 µg.L^{-1}), fluorene (0.293 µg.L^{-1}), acenaphtene (0.267 µg.L^{-1}), phenanthrene (0.212 µg.L^{-1}) and fluoranthene (0.206 µg.L^{-1}). However, the sum of four PAHs (benzo (b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene) corresponded to good quality standards, as defined by French drinking water production standard. As seen in Table 1, no PCBs and no BTEXs were detected in groundwater. Nevertheless, PCB n°101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB n°153 (2,2',4,4',5,5'-Hexachlorobiphenyl) were detected in the landfill leachate (93 ng.L^{-1} for eight PCBs) and matrix of waste (183 µg.kg^{-1} (d.w.)). Degradation and/or adsorption processes could explain these results.

CONCLUSIONS

To conclude, significant concentrations of arsenic and nickel, as well as concentrations of some PAHs and PCBs have been detected in solids and leachate in the landfill of "Prairie de Mauves". A limited contamination of nickel (31 µg.L-1 in January 2010 for PZ5) and arsenic, a high concentration of ammonium and the occurrence of the most soluble PAHs (naphthalene, acenaphthene, fluorene, etc.) and PCBs were also observed in the groundwater and highlighted the hydraulic communications between the landfill and underlying aquifers. Further investigations are needed to better define the natural attenuation processes (role of clay formations, iron, redox processes and microbiological activity in the retention of pollutants) and understand groundwater quality fluctuations. For instance, additional piezometers would allow to follow the water table and the quality of the superficial groundwater in the landfill (embankment), whereas core drilling would give indications of pollutants vertical transfer.

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Extended Abstract

EVALUATION OF THE ORIGIN OF NITRATE INFLUENCING OF WATER SOURCE KLJUČ, SERBIA

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Keywords: BARTs testers, groundwater, nitrate, stable isotopes

INTRODUCTION

It is believed that the natural background concentrations of nitrates in groundwater, resulting from infiltration of precipitation and mineralization of organic substances of plant and animal origin is generally far below 10 mg NO_3^-/l [1]. Concentrations above this value usually reflect the impact of human activity on water quality. As a by-product of agriculture (inorganic fertiliser and animal manure), human waste disposal (septic and sewage effluents), industry, and emissions from combustion engines (airborne nitrogen compounds) nitrates present one of the most common contaminants in groundwater world-wide.

Conventional nitrate analysis only provides quantitative concentration data and does not discriminate between sources. The combined determination of the isotopic ratios of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotopes of dissolved nitrate provides a tool for distinguishing among four major nitrate sources: (1) nitrate derived from nitrification in soils, (2) nitrate from manure and sewage, (3) nitrate-containing synthetic fertilizers, and (4) atmospheric nitrate deposition. A dual isotope approach can be used to: (1) evaluate the source of nitrate in groundwater, (2) evaluate the processes of nitrate attenuation in groundwater, and as a special case evaluate the nitrate behavior in riparian zones (i.e. due to groundwater-surface water interface) [2].

The purpose of this study was to demonstrate how analysis of the stable isotopic composition of nitrate can be used to better define their dominant source and influence on groundwater quality.

MATERIALS AND METHODS

Study area

The Morava River Basin (37,966 km^2) encompasses almost the whole southern and central parts of Serbia. The Velika Morava River (VMR) is formed by the merging of the West Morava and South Morava rivers near the town of Stalać. From this point to its confluence with the Danube, the VMR flows through the vast Morava Valley which extends over 1000 km^2 . The main aquifer is formed in alluvial (sandy-gravel) sediments. Total thickness of the quarternary sediments ranges typically between 15 and 25 m with high permeability (hydraulic conductivity in the order of 10^{-3} m/s) [3]. Silty-clayey roof layers are continually deposited over water-bearing horizons with variable thicknesses (average 3 m).This area represents important resources for municipal drinking water supplies. The city of Pozarevac (about 43,000 inhabitants) extracts drinking water from the aquifer at a rate of roughly 240 l/s from the so-called Kljuc groundwater source [4]. The water source is recharged from the direction of the VMR and from the direction of the hinterland which holds human settlements without access to a sewer system. The whole surrounding is agricultural area.

The nitrate concentration in groundwater source Ključ has continuously upwards trends from 2000 to 2006 year. The average annual nitrate concentrations in groundwater during the period 2003-2006 increased from 35.8 to 51.9 mg NO_3^-/l reaching up 100 mg NO_3^-/l at some particular spots at hinterland. However, in the area closer to the Velika Morava River, the nitrate concentrations were lower (5-20 mg NO_3^-/l) due to lower concentrations in river water (less than 10 mg NO_3^-/l).

In the order to protect groundwater, the infiltration-protective system was put in operation in September 2006. The system consists of 9 abstraction wells adjacent to the VMR, pipeline for delivering abstracted water to infiltration basins, and 5 infiltration ponds built at the water source location. The formation of hydraulic barrier enabled the usage of the entire existing water supply infrastructure. The solution with the wells near the Morava was designed as a temporary solution previous to the construction of river water intake and pretreatment of water for infiltration.

Sampling and analysis

A sampling campaign was carried out during period of low flow condition (September 2007). Groundwater samples were collected for chemical and isotopic analyses from 13 observation wells (samples N2-N14) completed in the aquifer, and operating wells (N1-domestic well in Lucica settlement, N15- water from the wells close to the Velika Morava River, N16-water from all wells at groundwater source Kljuc) as well as surface water from the Velika Morava River (N17) (Fig 1). In situ measurements of temperature (T), pH, electrical conductivity (EC), dissolved oxygen (O_2), and redox potential (Eh) were carried out using a digital multiparameterprobe MPS-D system (SEBA, Hydrometrie GmbH). Samples for stable isotope of hydrogen, oxygen and nitrogen were stored following standard procedures [5]. Laser absorption spectroscopy (LGR DLT-100, at Jaroslav Cerni Institute for Development of Water Resources, Serbia) was applied for isotope analyses of ^{2}H and ^{18}O in water [6]. Isotope measurements of δ^{15}N and δ^{18}O in NO_3^- were conducted at the Department of Geosciene, University of Calgary, Canada using methods already described [7]. All stable isotope results are reported in the usual delta (δ) notation in per mil (‰) relative to the V-SMOW (Vienna Standard Mean Oceanic Water) standard (δ^2H, δ^{18}O, δ^{18}O-NO_3^-), or AIR (^{15}N). The precision of measurements was usually better than ±1‰ for δ^2H and ±0.2‰ for δ^{18}O. In NO_3^- analyses, AIR is standard for (δ^{15}N) with an analytical precision of ±0.3% and ±0.5% for δ^{15}N-NO_3^-.

The actual microbiological quality of groundwater was determined using Biological Activity Reaction Tests (BART, Droycone Bioconcepts Inc. Canada) to determine the level of activity of denitrifying bacteria (DN-BART™) and nitrifying bacteria (N-BART™) based on bacterial biochemical activity in a selective culture medium by the time lag (TL). The longer the TL (the number of days from the start of the test to when a reaction is observed) before the observation of activity, the less aggressive the bacteria are in that particular sample.

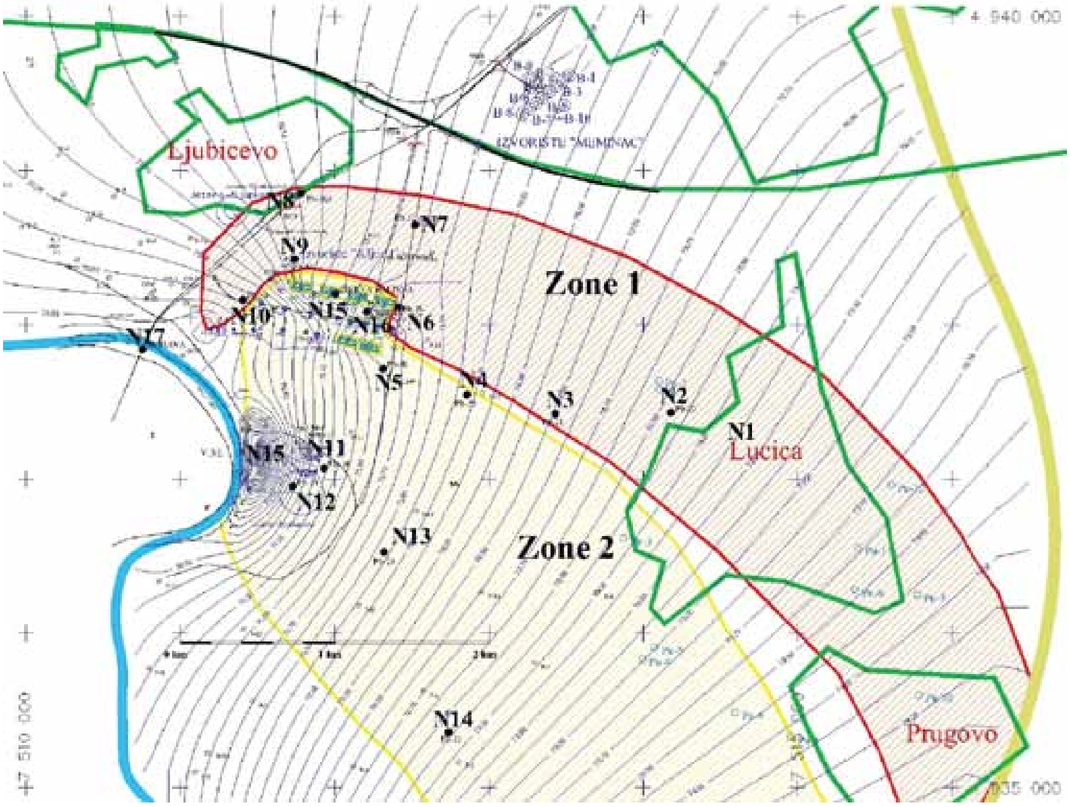

Figure 1. Location map of the water source Kljuc (Pozarevac, Srbia) and the layout of the water sampling from observation wells (N2 to N14), wells (N1, N15, N16), and river water (Velika Morava River, N17) with the identification of Zone 1 and Zone 2. Numbers on contour lines are altitude in meter a.s.l.

Groundwater regime of alluvial aquifer was analyzed. Licensed software for mathematical simulation of groundwater flow was used in the hydrodynamic calculations. The Groundwater Vistas interface, Version 4, developed by the US Company Environmental Simulations, Inc., was used to enter and interpret calculation results. The calculations were aided be MODFLOW 2000 software. Transient simulation has been done. Contours lines and path lines were analyzed.

RESULTS AND DISCUSSION

The groundwater pH was close to neutral (6.8–7.3) at shallow depths (5.7–9.5 m bgl) with relatively high redox potential (337 to 368mV). There was a strong positive correlation between nitrate concentration and EC (r=0.84, n=14). In the Zone 1, the average electrical conductivity was 1356 µS/cm accompanied with nitrate concentration of 173.7 mg NO_3/l, while in the Zone 2 the corresponding values were 997µS/cm and 38.2 mg NO_3/l, respectively (Table 1).

Table 1. The range of measured hydrogeochemical parameters of groundwater samples in two zones.

Zone	Value	T [°C]	pH	EC [µS/cm]	Eh [mV]	O_2	NO_3^- [mg/l]
Zone1	Average	13.1	7.0	1356	363	7.4	173.7
	Minimum	13.0	6.8	1165	339	5.2	62.5
	Maximum	14.3	7.3	1785	371	8.3	245.9
Zone 2	Average	13.1	6.9	997	360	7.1	38.2
	Minimum	12.6	6.9	917	346	6.9	3.4
	Maximum	13.3	7.0	1127	369	7.2	78.9

The $\delta^{15}N$ nitrate values ($\delta^{15}N\text{-}NO_3^-$) ranged from +5.3‰ to +16.9 and $\delta^{18}O$ values of nitrate ($\delta_{18}O\text{-}NO_3^-$) varied between -2.3‰ and +5.0‰ (Fig. 2). The highest values for $\delta^{15}N$ (+16.9‰) and $\delta_{18}O$ (+5.0‰) were observed in the Velika Morava river water. Analyzed chemical fertilizer samples, which are typical for those used in the study area (N-18 urea $CO(NH_2)_2$, N-19 KAN 27%, and N-20 NPK) and usually derived from atmospheric nitrogen, had $\delta^{15}N\text{-}NO_3^-$ values between -0.8 to 1.0 ‰.

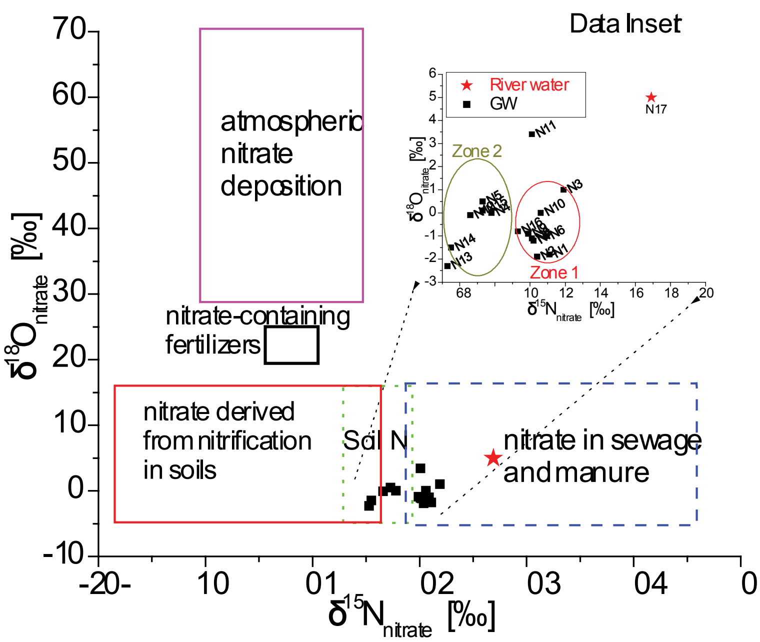

Figure 2. Schematic diagram of the isotopic composition of typical nitrate sources including data for groundwater and the Velika Morava River in the vicinity of the Kljuc groundwater source.

The results of the present study revealed an absence of nitrate originating from mineral fertilizers. The reason may be little use of mineral fertilizers, which is assessed as the most probable, or the proper use of fertilizers according to the needs of the plants and soils.

The application of the dual isotope method of measuring both the $\delta^{15}N$ and $\delta^{18}O$ values of dissolved NO_3^- in this study identified two major contamination sources with values characteristic for [8]: nitrate derived from soil organic nitrogen (+5.3 to +7.8 ‰ for $\delta^{15}N$, Zone2, Fig. 1) under nitrate concentrations (33.6 and 78.8 mg NO_3^-/l) and nitrate derived from animal wastes or human sewage, e.g. via septic systems (+9.9 to +11.9 ‰ for $\delta^{15}N$, Zone 1, Fig. 1) resulting in elevated nitrate concentrations (31.2 -245.8 mg NO_3^-/l). The mean $\delta^{15}N$ value for the latter of +10.6 ±0.6 ‰ (n=8) is consistent within the range expected for animal waste-impacted groundwater. Denitrification in the study area is unlikely because dissolved oxygen concentrations ranged from 5 to 8 mg/l [9]. According to the groundwater modeling results, Zone 1 mainly covers the part of the aquifer under the settlements Lucica and Prugovo, while Zone 2 represents the part of the aquifer next to the mentioned human settlements.

The $\delta^{18}O\text{-}NO_3^-$ values in groundwater obtained from the study area showed a narrow range from -2.3 to +3.4‰ (Fig. 2). These low $\delta^{18}O\text{-}NO_3^-$ values confirm that denitrification is not occurring in the study area. NH_4^+ and NO_3^- from chemical fertilizers are rapidly immobilized as organic nitrogen in agricultural soils. NO_3^- produced during subsequent soil nitrification is reported to contain two-thirds of the oxygen from soil water and one-third of the oxygen from atmospheric oxygen (~ +23.5‰) [10]. If the oxygen from these sources is incorporated without isotope fractionation, using the $\delta^{18}O$ values of groundwater in the study area that range from -10.1 to -9.3‰ and $\delta^{18}O_{O2}$= +23.5‰ for molecular oxygen, the expected $\delta^{18}O\text{-}NO_3^-$ values in the groundwater typical for nitrate derived from nitrification would be around +1.1 to +1.8‰. This is close to the observed $\delta^{18}O\text{-}NO_3^-$ values in the groundwater of the study area.

The groundwater samples in the Zone 1 showed lower $\delta^{18}O\text{-}NO_3^-$ (-1.9 to +1.0‰, mean -0.8‰, n=8) values than those from the Zone 2 (-2.3 to +3.4‰, mean 0.0‰, n=6). $\delta^{18}O\text{-}NO_0^-$ values of water cannot explain the difference in $\delta^{18}O\text{-}NO_3^-$ values between two zones because the difference of mean $\delta^{18}O$ of local groundwater is about 0.2‰. It is possible that the lower $\delta^{18}O\text{-}NO_3^-$ values in the Zone 1 indicate more intensive nitrification than in the Zone 2. In the case of the sample N11, measured values for isotope content ($\delta^{18}O\text{-}NO_3^-$ = +10.1 ‰, $\delta^{15}N\text{-}NO_3^-$ =+3.4 ‰) indicate the presence of denitrification phenomena that can be attributed to the local hydrogeological conditions. The BART tests showed low microbial activity in most of the measured samples.

This is in conjunction with special distribution of those locations. The Zone 2 is under the anthropogenic impact of upstream human activities, while a strong influence of local sources is dominant in the Zone 1. The nitrates that reach groundwater are the result of natural biological processes associated with the decomposition of organic debris (plant residues and organic matter), known as nitrogen mineralization [11]. Since ammonia is the first stable product, this biological conversion is called ammonification. As a positive charge, ammonium can be adsorbed and fixated (stuck) on to the negatively charged soil particles, or be taken up by plants. Under aerobic soil conditions, ammonium–nitrogen undergoes nitrification, and formed nitrates (after step to nitrites) could leach very effectively by water as it percolates downward through the soil.

Nitrate concentration for river water at the profile Ljubicevski most for a long time record (1989-2008) were between 0.4 and 33.2 mg NO_3^-/l [12]. High content both oxygen and nitrogen isotopes in nitrate pointed out that a microbial transformation (denitrification) has occurred along the path from the source of pollution to the river. The elevated $\delta^{15}N_{NO3}$ value in the Velika Mora River is in agreement with recoded values for surface water from point sources during low flow periods [13] indicating the dominant origin of nitrate contamination present due to waste water influence.

CONCLUSIONS

The dual isotope approach measuring both the $\delta^{15}N$ and $\delta^{18}O$ in dissolved nitrates has been applied for evaluation of the origin of nitrate influencing of water source Kljuc. Higher nitrate concentrations were associated with higher $\delta^{15}N$, and vice versa. The low $\delta^{18}O$ values in relative narrow range indicate that groundwater nitrate is derived from nitrification of organic soil nitrogen and manure and that denitrification is negligible due to the aerobic conditions in the aquifer. This study identified two major contamination sources with values characteristic for nitrate derived from soil organic nitrogen and nitrate derived from animal wastes or human sewage that is tightly coupled with spatial recognition of sampling sites. In spite of agricultural activities in the area under investigation a little influence of mineral fertilizers occurs. A very good agreement of hydrodynamic and isotope data was found.

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Extended Abstract

CHEMICAL REACTIONS IN THE AQUATIC PHASE OF A HETEROGENEOUS LANDFILL SYSTEM

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Keywords: Aqueous chemical species, contamination, chemical equations

INTRODUCTION

Groundwater is quantitatively the most significant freshwater resource on Earth. The landfill body is a typical heterogeneous, multi-component complex system with chemical reactions occurring on the surface of the phase boundary. Hydrophilic substances (inorganic, organic and ionic), as the products of various chemical reactions in aquatic media, can migrate and penetrate on the vertical scale to groundwater aquifers. Products of chemical reactions from unsanitary landfills can contaminate the aquifer, as well as accidental events, as was the case during the 1999 bombing of the Novi Sad Oil Refinery. Different chemical species remain exposed for a long time to various physical, chemical and biochemical processes (oxidation/reduction, neutralization, hydrolysis, enzymatic reactions, sorption/desorption, diffusion, dispersion and others), which take place in groundwater, the aquifer skeleton of interfaces between different phases. But the emphasized self-purification potential of an aquifer through complex processes leads to the changing of water quality in the aquifer, usually in the positive direction.

The phenomena of the contamination process are transporting to the landfill by diffusion and dispersion. Diffusion and dispersion are two mechanisms by which leachate is diluted by the aquifer. Because the leachate has a chemical concentration that is different from the background water, it tries to equilibrate with the ambient water quality through diffusion. Diffusion is essentially a physicochemical phenomenon, but on the other hand, dispersion is more often a mechanical phenomenon. Dispersion can occur in a longitudinal or transverse direction. Longitudinal dispersion occurs in the direction of the flow and is caused by different macroscopic velocities, as some parts of the invading fluid move through wider and less tortuous pores. Transverse dispersion occurs normal to the direction of the flow and results from repeated splitting and deflection of the flow by solid particles in the aquifer. Transverse dispersion is effective only at the edges of the contamination source. It was found experimentally that diffusion was important when the Reynolds number is less than 10^{-3}.

CHEMISTRY OF THE AQUEOUS MEDIA (AQ) IN THE LANDFILL BODY AND DISCUSSIONS

Table 1: List of chemical components in water samples using water leach test

Component	
Inorganic (cationic, anionic, redox couple)	**Organic**
Aluminum Al^{3+}(aq)	Phenol
Arsenic As^{3+}(aq)	Phentachlor phenol
Antimony Sb^{3+}(aq)	Chlordane
Arsenic As^{2+}(aq)	DDT & DDA & DDE
Barium Ba^{2+}(aq)	Aldrin
Beryllium (Be)	Dieldrin
Boron (B)	Benz(a)anthracene
Cadmium Cd^{2+}(aq)	Benzo(a)pyrene
Chloride Cl^{-}(aq)	Benzo(b)fluoranthene
Chromium, tot. Cr^{3+}/ Cr^{6+} (aq)	Benzo(ghi)perylene
Copper Cu^{2+}(aq)	Benzo(k)fluoranthene
Total cyanide CN^{-}(aq)	Chrysene
Fluoride F^{-}(aq)	Dibenz(ah)anthracene
Iron Fe^{2+}/ Fe^{3+} (aq)	Fluoranthene
Lead Pb^{2+}/ Pb^{4+}((aq)	Fluorene
Manganese Mn^{2+}/ Mn^{4+}	Indeno(123-cd)pyrene
Mercury Hg_2^{2+}(aq)/Hg^{2+}(aq)	1-Methyl naphthalene
Molybdenum Mo^{3+}(aq)	2-Methyl naphthalene
Nickel Ni^{2+}(aq)	Naphthalene
Nitrite & Nitrate, NO_2^-/NO_3^- (aq)	Phenanthrene
(NO_2+NO_3-N)	Pyrene
Selenium (Se)	
Silver Ag^{1+} (aq)	
Sulfate/sulfide	
SO_4^{2-}/S^{2-} (aq)	
Thallium Tl^{3+}	
Zinc Zn^{2+}	

The reduced and oxidized species in the half reaction form a redox couple Ox/Red.

Bulk chemical reactions can take place in the aqueous media within the landfill body with different hydrophilic or hydrophobic products. Chemical analyses of water leach testing confirm various organic, inorganic and ionic species. According to chemical analyses, there is a list of chemical components which could be detected in the water layer as inorganic species (anionic & cationic chemical species) and organic compounds (Table 1).

CHEMICAL REACTION FUNDAMENTALS

Biochemical Reactions

The following chemical equations are used to represent the major biochemical reactions that take place in the model of the water layer.

Plant photosynthesis and respiration in the presence of the ammonium cation as the substrate:

$$106CO_2(aq)+16NH_4^+(aq)+HPO_4^{2-}(aq)+108H_2O(aq)\underset{R}{\overset{P}{\rightleftarrows}}C_{106}H_{263}Q_{110}N_{16}P_1(aq)+107O_2(aq)+14H^+(aq) \quad (1)$$

In typical reversible processes, P is photosynthesis and R is respiration

Nitrate as substrate:

$$106CO_2(aq)+16NO_3^-(aq)+HPO_4^{2-}(aq)+122H_2O(aq)+18H^+(aq)\underset{R}{\overset{P}{\rightleftarrows}}C_{106}H_{263}Q_{110}N_{16}P_1(aq)+138O_2(aq) \quad (2)$$

Nitrification:

$$NH_4^+(aq)+2O_2(g)\rightarrow NO_3^-(aq)+2H^+(aq)+H_2O(aq) \quad (3)$$

Denitrification:

$$5CH_2O(aq)+4NO_3^-(aq)+4H^+(aq)\rightarrow 5CO_2(q)+2N_2(aq)+7H_2O(aq) \quad (4)$$

COMMENTS AND DISCUSSIONS

The presented chemical equations are in stoichiometric and charge net system. It will be commented: phosphorous, nitrate, nitrate/nitrogen, dissolved organic nitrogen, ammonia nitrogen and carbon dioxide as the main components in the above chemical equations.

Dissolved organic phosphorus increases due to dissolution of detritus. It is lost via hydrolysis. Nitrate nitrogen increases due to nitrification of ammonia. It is lost via denitrification and plant photosynthesis. Inorganic phosphorus increases due to dissolved organic phosphorus hydrolysis and plant respiration. It is lost via plant photosynthesis. Dissolved oxygen increases due to plant photosynthesis. It is lost via rapid oxidation, nitrification and plant respiration. Depending on whether the water is undersaturated or oversaturated, it is gained or lost via reaeration,

Dissolved organic nitrogen increases due to detritus dissolution. It is lost via hydrolysis. Ammonia nitrogen increases due to dissolved organic nitrogen hydrolysis and plant respiration.

It is lost via nitrification and plant photosynthesis. In water, the total ammonia consists of two forms: ammonium ion, $NH_4^+(aq)$, and unionized ammonia, NH_3. At normal pH (6 to 8), most of the total ammonia will be in the ionic form. However, at high pH unionized ammonia dominates.

Carbon dioxide saturation is in relation with Henry's Law.

$$\left[\mathbf{CO_2}\right]_S=\mathbf{K_H P_{CO_2}} \quad (5)$$

where K_H = Henry's constant [$mole^{-1}$]
and p_{CO2} = partial pressure of carbon dioxide in the atmosphere [bar].

$$\mathbf{CO_2(g) \rightleftharpoons CO_2(aq)} \qquad (6)$$

The carbonate species in solution are in a dynamic equilibrium with the CO_2 gas in the atmosphere above the solution. Very often the hypothetical species $H_2CO_3^*$ are used to represent CO_2 (aq) plus H_2CO_3(aq).

Chemical processes that occur in the aqueous phase include the following groups of dynamic equilibrium processes:

- oxidation/reduction,
- ionization/molarization,
- hydrolysis/hydrolytic condensation,
- precipitation/dissolution,
- neutralization/hydrolysis,
- sorption/desorption,
- complexation/decomplexation (forming of metal complexes), and other processes.

CONCLUSIONS

Hydrophilic chemical species – cations, anions and polar molecules, as well as hydrophobic chemical compounds, are found in an aqueous state (A^-(aq), B^-(aq), AB(aq) and CD(aq) lypophilic). The main physical parameters that determine the type of chemical reaction are aerobic and anaerobic conditions, especially in the case of oxidation-reduction processes. Chemical products which are generated in the aqueous layer of a landfill body heterogeneous system can contaminate the aquifer by diffusion, dispersion and sorption processes. The coordination number of the central atom with the ligands of the water molecule are two, four, six and eight.

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Full Paper

THE IMPACT OF SAND OPEN PIT "JAKOVAČKA KUMŠA" ON GROUNDWATER IN A PART OF BELGRADE SOURCE

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Abstract: The need for quality underground drinking water is always current. On the other hand, industrial development, which is unavoidable in modern societies, as time passes, is beginning to threaten the sources of groundwater. It is sometimes impossible to find a compromise between these two important factors of human development and sometimes it is possible, with specific measures that reduce the effect of possible impact on the quality and quantity of groundwater to an acceptable one. The role of detailed hydrogeological research and hydrogeologists in solving problems of preventive protection of groundwater sources is of great importance. One such problem was successfully resolved on a part of Belgrade water source in the zone of Jakovo (Municipality of Surčin) where the sand open pit "Jakovačka Kumša" is located.
Keywords: preventive protection, groundwater, water supply, water source of Belgrade

INTRODUCTION

Public enterprise "Surčin" from Surčin, in order to provide their own high-quality raw material of sand, which would be used for construction and reconstruction of roads, wastewater network and other civil engineering objects in the municipality, launched activities to determine the possibility of finding this material on the location "Jakovačka Kumša".

In the area near the location where the exploitation of sand is planned, there are several tapping objects used for Belgrade water supply – four Ranney wells and nine tubular wells.

The location which is planned for exploitation of sand, is in the inner zone of sanitary protection (zone II), in a part of the existing water source in Belgrade. Also, due to the need for additional quantities of water, Belgrade waterworks have already initiated activities to develop technical documentation for the opening of a new infiltration type water source in the location "Zidine" which is close by.

For this reason, the problem of preventative protection of groundwater in this part of Belgrade source in the mentioned zone must be given proper and adequate attention.

GOAL

The aim of the research was to determine the possible impact of the sand open pit "Jakovačka Kumša" – Jakovo on a part of the existing groundwater source. It was necessary to determine the possible increase in vulnerability of groundwater due to the removal of the overlying layer of captured aquifer and to define the conditions of exploitation, in order to maintain the quality and quantity of groundwater. It was also necessary to simulate a possible scenario in which the accidental pollution comes to the aquifer, in order to determine the reaction time.

GENERAL CHARACTERISTICS OF RESEARCH AREA AND APPLIED METHODS

Research area is located 30 km southwest of Belgrade (Fig. 1). It covers about 16 ha, while the wider research area covers an area of about 320 ha.

Figure: 1: The geographical position of the research area

Based on the data obtained from boreholes, from a geological aspect the presence of deposits of Pleistocene and Holocene age was detected. Within this zone it is possible to single out deposits of marsh and alluvial origin. They consist of sands and alevrits (b), gravel, sand and clayey sands (a) and sands and alevrite sands (ap).

Based on the geological structure of the terrain, the represented lithostratigraphic units and their structure type of porosity, as well as hydrodynamic conditions, within the research area it is possible to single out: intergranular high hydraulic conductivity aquifer formed in the sandy-gravel sediments, intergranular lower conductivity aquifer formed in the yellow and fine grained sands and alevrite sands, and areas of little or no significant groundwater (Fig. 2, Tab.1).

Table 1: Model layers with appropriate lithological members of the hydrodynamic model

Model layers	Lithological layers	Elevation of layers (m.a.s.l.)
First less permeable layer	Complex of alevrite and yellow sandy overlying sediments with interlayers of clay	68,22 - 57,30
Second water bearing layer	Gray sands	62,70 - 54,74
Third water bearing layer	Water bearing sandy gravels	58,55 - 37,24
Layer of little or no significant groundwater	Clayey sediments	37,24-

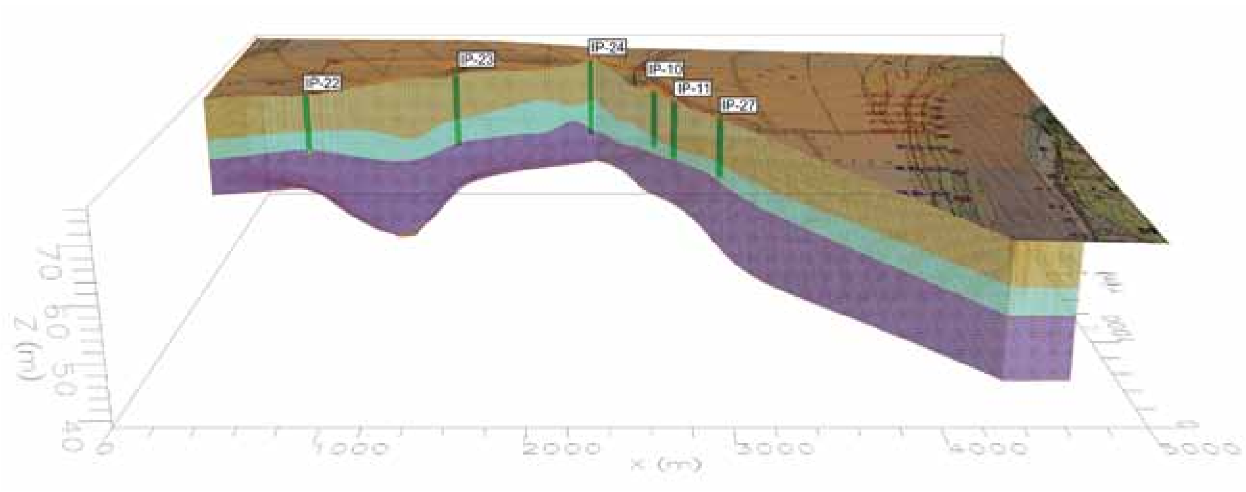

Figure 2: 3D Hydrogeological cross-section of the terrain

For the purposes of sand mine research 54 boreholes and one well were made (Milićević R. et all, 2009). Field surveys for hydrogeological purposes consisted of making 27 exploration boreholes (piezometers) which were used for defining geometric and seepage characteristics of the aquifer in the wider research area which was affected by the hydrodynamic model of groundwater flow. The position of exploratory boreholes is shown in Fig. 3 and 4. Samples of rock material were taken during the drilling from boreholes IP-5, IP-13, IP-15, IP-17, IP-9, IP-22 and IP-25 (3-4 per borehole) for the purpose of completing a grain-size analysis. On the basis of the grain-size analysis hydraulic conductivity of sands and gravels was calculated.

With the aim of determining the zero state of groundwater regime (water tables, quality and quantity of abstracted water) at objects of Belgrade waterworks and sand mine, monitoring of groundwater regime (quantity of abstracted water, water tables) was carried out in the period 12.02-10.05.2010. Dynamic of the monitoring was adapted to provide valid data for development of a hydrodynamic model of groundwater flow. In Fig. 3 and 4, the isolines of the maximum and minimum water tables are displayed.

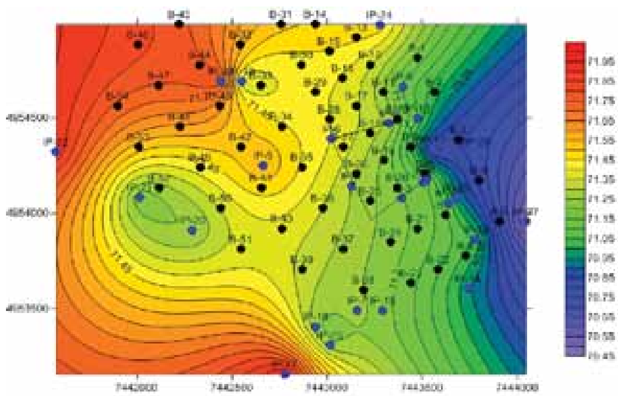

Figure 3: Isolines of the maximum water tables
Legend: black-boreholes, blue-piezometers, rectangle-research area

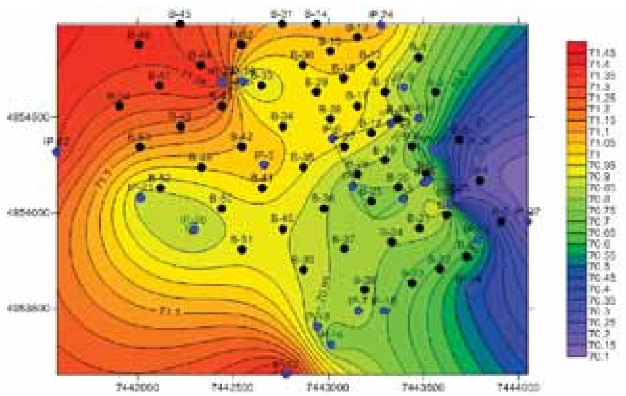

Figure 4: Isolines of the minimum water tables
Legend: black-boreholes, blue-piezometers, rectangle-research area

The laboratory part of the research included performing 27 grain-size analyses of samples of the rock material, to determine the lithological profile in the research area.

In order to determine the seepage characteristics of the aquifer, a pumping test was done on the well IB-1, while the water tables were also monitored at the piezometers IP-1, IP-2 and IP-3, which are located nearby.

Along with the quantitative observation, monitoring was carried out for qualitative groundwater regime, too. Three chemical analyses were carried out (objects IP-23, IB-1 and IP-27). Specifically, the locations of sampling objects were chosen so that they cover three profiles. The first profile was the input to the direction of groundwater flow (above the current mine) with the object-piezometer IP-23. The second was located directly below the landfill of the municipal waste (well IB-1) which is within the current mine, while the third - output profile was covered by piezometer IP-27.

Performing experiments

For the purpose of determining the physical and chemical characteristics of rock mass and possible pollutants, it was necessary to carry out a series of laboratory experiments. Samples were collected from fine-grained yellow and alevrite sands. Research methods were divided into two parts. The first part referred to the "undisturbed" samples, which relatively credibly reflect terrain conditions, and the other to the determination of characteristics of disturbed samples. With an adequate sampler (steel cylinder with a plastic cartridge) 10 "undisturbed" samples were taken from the mine. Also about 20 kg of material were taken as a disturbed sample from the same location.

In the experiments the seepage characteristics of the material were determined first. Since calculated data for various parameters already existed, these experiments were expected to confirm obtained values. Experiments were performed so that they simulated terrain conditions ("in situ").

Based on the analyses results of groundwater quality from monitoring objects, parameters with value above MAC were selected and they were used in the experiments performed under laboratory conditions. Only the review related to petroleum (D2) is given here because the possibility of its leaking during the breakdown of machines and trucks exists. Adsorption properties of sediments were determined and the time of penetration of petroleum through the individual samples was registered. Based on these values, it is possible to calculate the time of petroleum penetration to the groundwater, with the aim of determining the time of intervention.

The samples were treated in static and dynamic conditions. Static conditions were applied on disturbed samples. 16.3 kg of material were taken and filled with petroleum (D2) to complete saturation. After that, a complete decanting of the sample was done. Based on the difference in weight before and after the experiment, quantity of petroleum adsorbed by the sample material was calculated. Experiment consisted of 5 samples of material and calculated values were in range from 14.5 to 18.9 weight% depending on the sample density (Matić I. et all, 2011). In other words, 1 m3 of material weighing 1.5 tons (volume density of the sample is 1.5 kg/dm3) has the ability to adsorb from 145 to 189 l of petroleum (D2).

In dynamic conditions samples were firstly subjected to long-term water infiltration and hydraulic conductivity was determined again. After that, pure petroleum was filtrated under conditions with hydraulic gradients slightly higher than natural.

The obtained values of hydraulic conductivity were around 2.5 x10-6 m / s and they roughly correspond to the previously obtained laboratory values.

Time of petroleum (D2) penetration through the "undisturbed" cylindrically shaped sample (length 42 cm, diameter 9.2 cm) had an average value of 17-22 hours or about 38-50 hours for 1 m of overlying aquifer.

Understanding of the hydrogeological environment in the area of mine exploitation and in this case petroleum as the only likely potential pollutant of groundwater, is imperative to the timely undertaking of preventive measures to protect the water source.

Hydrodynamic analysis

For the purpose of performing an analysis of the impact of alevrite sands exploitation on groundwater quality, a complex hydrodynamic analysis of the groundwater regime in the wider area of Jakovačka Kumša was conducted.

The concept of development of hydrodynamic model of the wider area is based on three-dimensional simulation of groundwater flow. The development of the model was started from the basic interpretation of input data, schematization of the porous medium, flow field and flow conditions so that the model could be formed and calibrated. Natural factors were the most important ones for the selection of the model's concept, such as type and geological characteristics of represented units, distribution of water bearing and impermeable layers, seepage characteristics of the porous medium, conditions, mechanism and regime of groundwater flow, as well as the desired goal within a task. In selecting the basic design features, a multilayer model was made, with the possibility of an automatic change of flow field, depending on flow conditions.

Calculations were conducted on the licensed Visual MODFLOW 2009.1, which is among the top world programs of its kind.

Basic matrix dimensions that covered the studied area were 5000 m x 3000 m, which encompasses the area of 15 km^2. Lateral discretization of the flow field in the wider research area was executed with a basic cell size of 50 m x 50 m, while the cell size in the zone of Jakovačka Kumša was 25 m x 25 m.

For the analysis of travel time of potential pollutants from the open pit to the source wells, a simulation of "ideal" particle movement (conservative, nonresponsive) or tracer was carried out. Particles were placed on the contour of the mine and one was placed in the center of the mine in the first layer of model.

Hydro dynamical model showed that it takes 35-39 months for the "ideal" particle to come from the open pit to the source wells for the capacity of 88.9 l/s. It was also concluded that all particles gravitate towards the well RB-65 as a result of the highest drawdown of the water table in this object, due to its location in the middle of the series and its highest capacity. For a capacity of 240 l/s, the situation is similar, except that the retention time of particles on their way from the open pit to the wells is 18-23 months. Fig. 5 and 6 show the analysis of "ideal" particle travel from the open pit to the source wells.

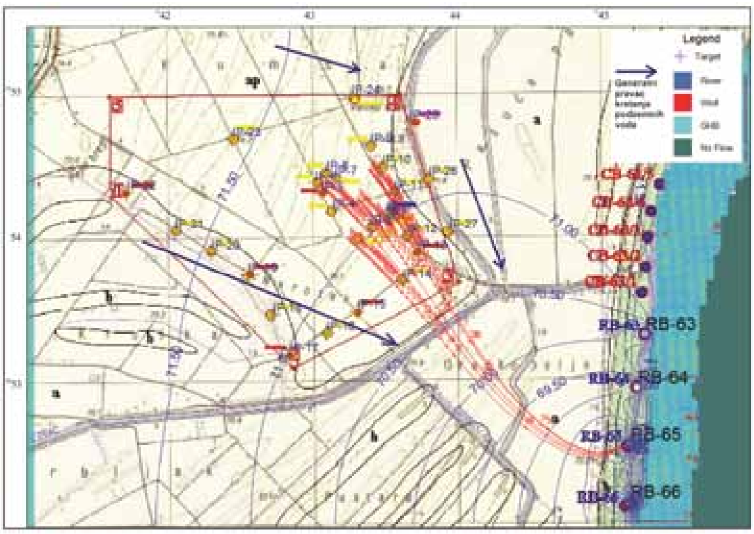

Figure 5: Map of piezometric levels with travel time of "ideal" particle to the wells of Belgrade water source (in months) for its capacity of 88.9 l/s

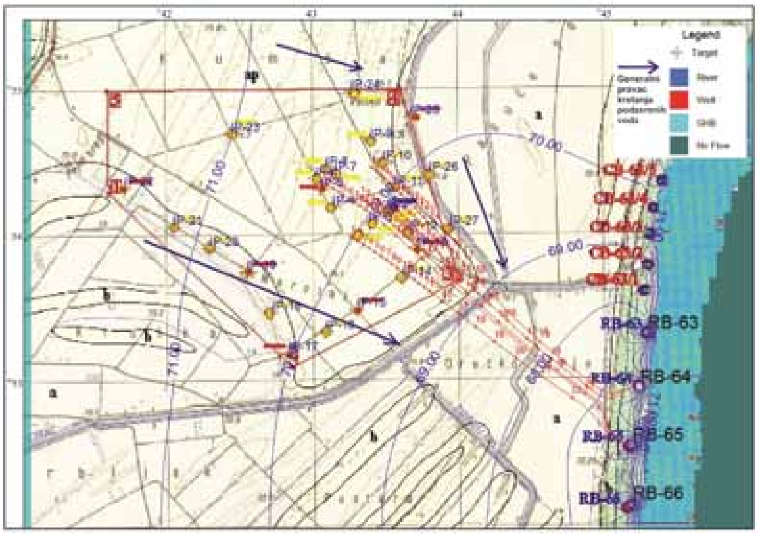

Figure 6: Map of piezometric levels with travel time of "ideal" particle to the wells of Belgrade water source (in months) for its capacity of 240 l/s

RESULTS

Based on all previous and new researches, measures were determined that should be implemented for preventive groundwater protection.

It was determined that it is necessary to keep the protective layer of yellow and alevrite sands 3 meters thick. This buffer zone will be sufficient to prevent possible leakage of potential pollutants (especially D2), which was proven by laboratory experiments. Extremely high adsorbing capability of alevrite sands and relatively low penetration speed of petroleum through this environment leave enough time for possible intervention.

Hydro dynamical analysis showed that the travel time of the "ideal" tracer is in the order of 18-39 months depending on the capacity of the objects of Belgrade's water source, and that the travel time of particles of possible pollutants will be much slower depending on their adsorption as an additional benefit in terms of taking protection measures.

It is suggested to repair and reclaim the local "wild" municipal waste landfill located within the area of research.

In order to monitor the impact of the mine on the quantitative and qualitative characteristics of groundwater during and after the operation, it is necessary to schedule an adequate program of monitoring. The "zero" state of groundwater quality has been determined and selected parameters reflect the real situation in relation to existing and potential polluters. The measurements of water tables were conducted too. In the future, the monitoring of water tables at the monitoring objects at all sites should be done on a monthly basis, and as for the observation of qualitative features, they should be monitored at three profiles as before. In the case of possible accidents and the cases of increased concentrations of some pollutants, it is necessary to expand the network of monitoring objects. Monitoring of surface water channels, as the recipients, should be provided, too.

At the end of sand exploitation it is necessary to conduct reclamation of the open pit. At this location the exploitation of sand is going to last for many years, according to the opening stages of certain parts of the mine. A phased reclamation should be conducted as well.

CONCLUSIONS

Hydrogeological studies of the assessment of impact of the designed sand open pit “Jakovačka Kumša”- Jakovo on groundwater, a part of Belgrade source, have clearly defined the conditions and measures to be observed by the future user of the specified research area in order to eliminate the possibility of its contamination.

Special measures to be implemented in the open pit zone are determined in such a way that it is necessary to keep the protective layer of alevrite and yellow sands, perform reclamation of the existing “wild” landfill, perform continuous monitoring of water tables (once a month at all sites), carry out continuous monitoring of groundwater quality in the three profiles on the already determined parameters and perform reclamation of the open pit after the ending of exploitation.

Research results have allowed prescription of measures on one hand, for the permanent protection of one part of Belgrade groundwater source, on the other for an undisturbed exploitation of sand in the mine “Jakovačka Kumsa” in Jakovo. This presents the basis for the dual-purpose use of the study area and its sustainable development.

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Notes:

Extended Abstract

EVALUATION OF ANTHROPOGENIC INFLUENCES ON GROUNDWATER SUPPLIES TO THE CITY OF NOVI SAD (SERBIA)

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Keywords: groundwater, water source, contamination, Novi Sad, Danube

INTRODUCTION

The City of Novi Sad is supplied exclusively by water sources in the Danube alluvial layer. The Danube River mediates the flow to water supply facilities and the regions of river bank in the immediate vicinity of the city are relatively rich in gravely sand layers. These layers lie at a depth of 20-30 m and have good contact with the Danube, which enables very good feeding from the river. Water is pumped from three sources: “Štrand”, “Petrovaradinska ada” and “Ratno ostrvo”. Complete protection of the water sources is difficult, due to the influence of residential and industrial facilities and activities nearby.

The “Štrand” source: the location of this source is very unfavourable for security and protection (in direct contact with a residential area, bathing, rowing and boating clubs, restaurants, etc.).

The “Petrovaradinska ada” source: the environs have a high degree of risk from potential contamination. Behind the source are the Petrovaradin settlement, “Pobeda”, a former factory, and an area of weekend cottages without basic sanitation (inadequate septic tanks, absorbing wells, etc.). Additionally, the “Dunavac” marina is immediately next to well BHD-5, while well BHD-6 is next to a boat anchorage and the “Šaran” restaurant.

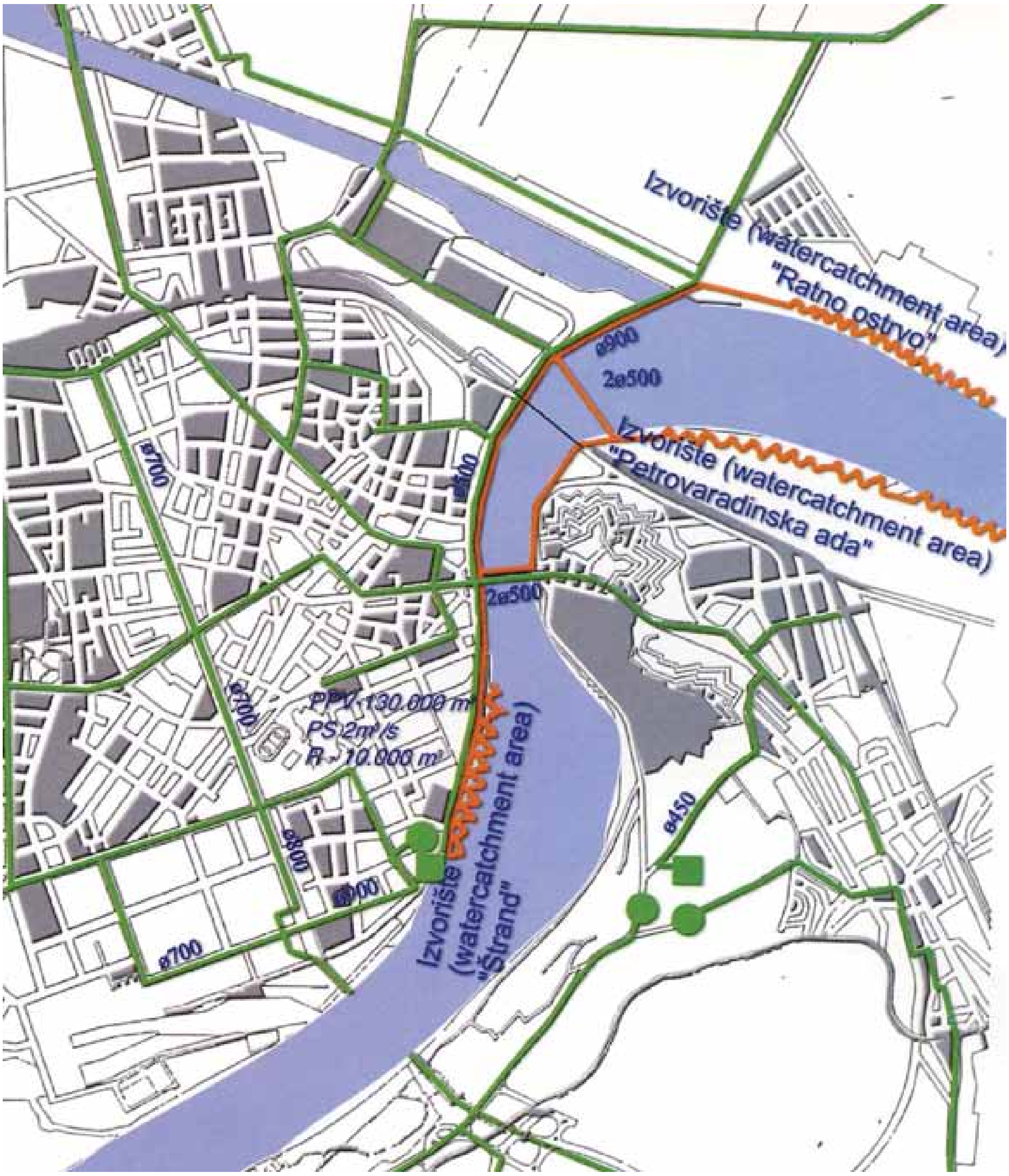


Figure 1: Location of the Novi Sad sources

The “Ratno ostrvo” source: an oil refinery, a thermal power-plant and the Village of Šangaj are all next to this source, and upstream along the Danube are the confluence of the DTD Canal and a discharge point for municipal sewage effluents.

This paper presents the results of an investigation into the chemical and microbiological quality of the groundwater from the “Štrand”, “Petrovaradinska ada” and “Ratno ostrvo” sources, carried out during 2010. The aim of this investigation was to obtain information on the possible movement of pollution and to evaluate the threatened wells and wider area sources.

During this investigation, water quality was monitored from: water intake wells, shallow and deep piezometers in the immediate vicinity of the wells, the wider area of the sources and from nearby contamination sources, i.e. in the directions of possible contamination penetration. Samples were analyzed for the content of specific organic substances: total hydrocarbons and mineral oils, volatile organic compounds (VOCs), and qualitative GC/MS characterization, in addition to the microbiological characterisation in which the following bacteria numbers were determined: organotrophs, facultative oligotrophs coliforms, faecal coliforms, aerobic mesophiles, lipolytic and hydrocarbon-oxidizing bacteria.

At the “Štrand” and “Petrovaradinska ada” groundwater sources, high concentrations of vinyl chloride, an extremely carcinogenic compound, were found:

- “Štrand” (2010 mean): Š-9 - 313 μg/l, Š-27 - 199 μg/l, Š-26 - 58 μg/l, Š-17 - 33 μg/l, Š-7 - 21 μg/l, Š-8 - 17 μg/l. Vinyl chloride was also found in the water pumping wells, with levels as high as 21 μg/l (MAC = 0.5 μg/l) found in RB-4.
- “Petrovaradinska ada”: certain piezometers in the area between the industrial zone and the wells (PA-14 in April 2010 had as much as 214 μg/l, PA-15 up to 42 μg/l, PA-3/07 up to 56 μg/l, PPA-4/07 up to 47 μg/l), in the wells (Bhd-1 up to 7.3 μg/l, Bhd-6 up to 12 μg/l, Bhd-7 up to 57 μg/l, Bhd-8 up to 2.1 μg/l), and the composite raw water concentration for the source was 12 μg/l (April 2010).

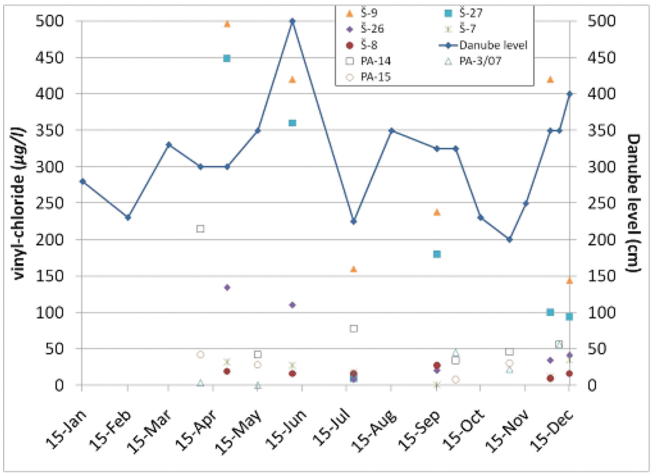
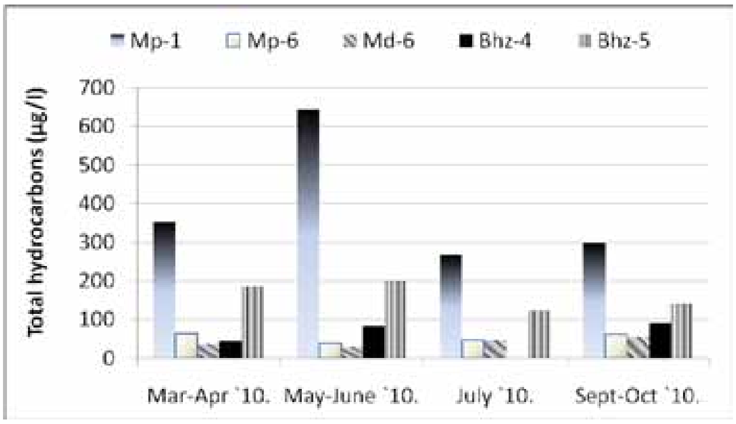


Figure 2: Vinyl chloride concentrations in the underground voids of the Štrand and Petrovaradinska ada sources and the level of the Danube at Novi Sad during 2010

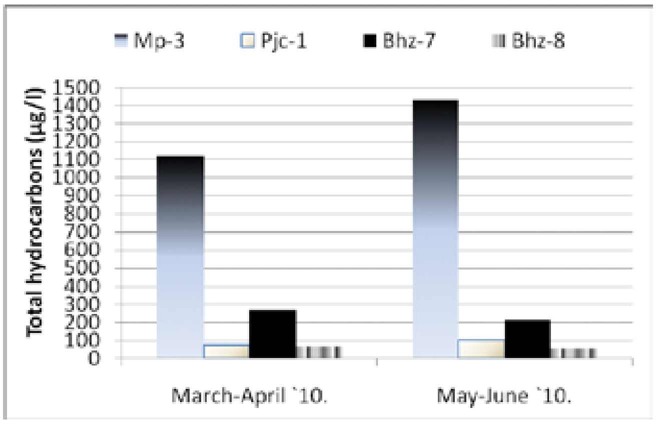
Significantly lower concentrations of vinyl chloride than usual were detected during July 2010 at piezometers Š-26 (7.6 μg/l), Š-27 (9.5 μg/l) and Š-9 (160 μg/l), suggesting that the very high level of the Danube in June had a diluting effect on the piezometers near the river bank (figure 2).

In the composite raw water from wells in the “Petrovaradinska ada”, the content of mineral oil exceeds the limit values allowed in drinking water up to 2 times during the 2010: 11-21 μg/l (mean 16 μg/l).

Examination of the boundary zone of the Oil Refinery and “Ratno ostrvo” shows that there are higher concentrations of hydrocarbons in the border zone between the refinery and the source than in the sources located behind the refinery, and the direction of possible oil pollution penetration to the source was detected (direction of observation “Mp-1 - Mp-6/Md-6 - Bhz-4/Bhz-5” and “Mp-3 – Pjc-1 – Bhz-7/Bhz-8”). High hydrocarbon concentrations were detected in wells Bhz-5, -6 and -7 (Figure 3). The “second line” of piezometers at the refinery (i.e. piezometers Mp-1 and Mp-3) is very polluted, which shows that the area of the refinery is still polluted and exerts a constant pressure on the source. At piezometer Mp-3, high concentrations of benzene (April – 23 μg/l, June – 7.5 μg/l) and xylene (April – 308 μg/l, June – 109 μg/l) were found. In the composite raw water from the “Ratno ostrvo” wells, the content of mineral oil exceeded the maximum value allowed in drinking water up to 2 times during 2010: 7-21 μg/l (mean 13 μg/l).



a) direction of observation "Mp-1 - Mp-6/Md-6 - Bhz-4/Bhz-5"



b) direction of observation "Mp-3 – Pjc-1 – Bhz-7/Bhz-8"

Figure 3: Total hydrocarbons content in the groundwater at the border zone between the "Ratno ostrvo" source and the oil refinery

A large number of organic compounds (30-50) were detected by the qualitative GC/MS characterization of the groundwater, mostly long chain aliphatic hydrocarbons, aldehydes, ketones and alcohols, which together with the organic acids and esters of organic acids may represent hydrocarbon oxidation products (benzaldehyde was also detected). Many of the compounds identified in the groundwater sources were also found in the water from the Danube next to the sources, which shows that the presence of xenobiotics in the Danube River significantly impairs the water quality at the sources, and that the infiltration through the sand-gravel layer along the bank does not prevent the penetration of these compounds into the sources. Significant finds amongst the compounds present in both the Danube and the water sources include phthalates, which are widely used as plasticizers in industrial oils and lubricants, antifoam agents, cosmetics and insecticides, and which are important in ecotoxicology due to their classification as endocrine disruptors. Thus, di(2-ethylhexyl)phthalate is on the list of priority pollutants of the EU Water Framework Directive (Directive 2008/105/EC), and dibutylphthalate is on the list of "other substances" in Slovakia and Finland (Londesborough, 2003). The phthalates frequently detected in the samples were dimethyl- and diethyl-phthalate. Furthermore, certain PAHs were detected: anthracene, pyrene, methyl-phenanthrene; alkyl-substituted benzenes typically present in pollution from transportation fuel oils (propyl-benzene, 1,3,5-trimethylbenzene, 1-ethyl-2-methyl-benzene, 1,3-diethyl-benzene); glycol ethers used as paint solvents (2-phenoxyethanol, 2-(2-butoxyethoxy)-ethanol); menthol, caffeine, vanillin (food, perfume and cleaning products), benzophenone (sun creams and lotions), 2-ethyl-1-hexanol (cosmetics), palmitoleic acid (methyl ester (Z)-9-octadecene acid - cosmetics and hygiene products); benzothiazole and 2-(methylthio)benzothiazole (on the Slovakian "other substances" list - used in the rubber industry as accelerators), 1-hexadecanol (hygiene product ingredient, especially shampoos), p-cresol (wood protection), p-tert-butylphenol (hardener in paints and varnishes), 2,4-di-tert-butyl-phenol (lubricant, stabilizer in oil and chemistry industries), and others.

Microbiological contamination was repeatedly detected in some water intake wells at the "Štrand", and the contaminated samples in most cases contained sulphite reducing clostridia and faecal streptococci. The most common causes of microbiological contamination are the coliform and faecal coliform bacteria, and a significantly high number of potentially pathogenic aerobic mesophilic bacteria counts were also detected. Organotrophs are extremely numerous in the R2A medium, and this is a true indication of the number of bacteria in these water areas.

During these investigations of the groundwater sources of Novi Sad, specific organic compounds (including the highly carcinogenic vinyl chloride) were detected, as were faecal coliform bacteria at the "Štrand" source, which indicates a significant anthropogenic impact on the water quality. It is necessary to implement certain measures to protect the water sources from further adverse impacts, in order to ensure an uninterrupted water supply to the population:

- "Štrand": sewer system rehabilitation around the source.
- "Petrovaradinska ada": ban or suspend further construction in the vicinity of the source protection zone,
- "Ratno ostrvo": phytoremediation of the border zone between the source and the oil refinery by planting poplar trees.
- Improvement of current drinking water preparation technology - upgrade WTP "Štrand" to introduce ozone and activated carbon to the existing line of technological processes.

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Notes:

Extended Abstract

ORGANIC XENOBIOTICS IN THE FIRST LAYER OF GROUNDWATER NEAR PIG FARMS

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Keywords: xenobiotics, groundwater, piezometers, pig farm

INTRODUCTION

As a source of nutrients and organic materials, animal manure from pig farms is often used in agriculture for the improvement of soil properties. Irrigation of soil with liquid manure also represents a natural pattern of its decomposition and a correct aspect for reducing the use of an inorganic fertilizer.

As stated in the Hyderabad Declaration on Wastewater Use in Agriculture: “without proper management, wastewater use poses serious risks to human health and the environment” (Muñoz et al., 2009). Presence of hazardous material in waste water is possible, considering the variety of components used in animal production as animal feed additives, pharmaceutical products for disease treatment and prevention, pesticides, mineral oils, disinfectants and cleansers. The most probable contaminants in waste water are nutrient matter, organic load in water, and organic and inorganic xenobiotics. Metabolites created by metabolism are of great importance, as are different products of xenobiotics degradation in nature formed under the influence of microorganisms or just chemical processes. By discharging waste water into surface water, irrigation, then leaking into soil, contaminants reach both groundwater and drinking water.

Groundwater bodies are protected by a soil layer, which provides the inertia in quality changes and slower penetration of contaminants as well. These are the reasons for the sensitivity of groundwater bodies to pollution; once contaminated, effects could be irreversible or at least with hard and expensive remediation.

Due to the growing concern regarding the safety of drinking water and the quality of natural water, research carried out on groundwater from piezometers near pig farms is of great importance. Regulatory monitoring usually includes only well known parameters which are specific for animal farms (COD, BOD, settled material, suspended material, total nitrogen, total phosphorus, heavy metals), but there is an increasing need for the investigation of other contaminants, e.g. organic xenobiotics.

This work presents the results of research on groundwater quality from a network of surveillance facilities near livestock farms. Samples were analysed for parameters characteristic of animal production, but a larger number of organic compounds were detected by a qualitative GC/MS method.

Qualitative analysis actually presents a chemical status indication of the examined part of groundwater. Qualitative GC/MS analysis shows the presence of different types of organic pollutants in the first layer of groundwater (n-alkanes, phenols, substituted benzene and benzene derivatives, alcohols, aldehydes, ketones, ethers, phthalates, organic acids and their salts, polycyclic aromatic hydrocarbons, organic nitrogen compounds, organic phosphorus compounds, steroids, heterocyclic compounds).

Disinfectants and cleansers in animal production must have a wide range of activities. At best, during one operation they must disinfect, deodorize and purify the premises and the area. Good disinfectants and cleansers are those that kill germs and fungi, and are the means against tuberculosis and viruses.

In many agents intended for disinfection on farms, in households and in hospitals, active ingredients are present in different percentages and they are all based on phenol compounds.

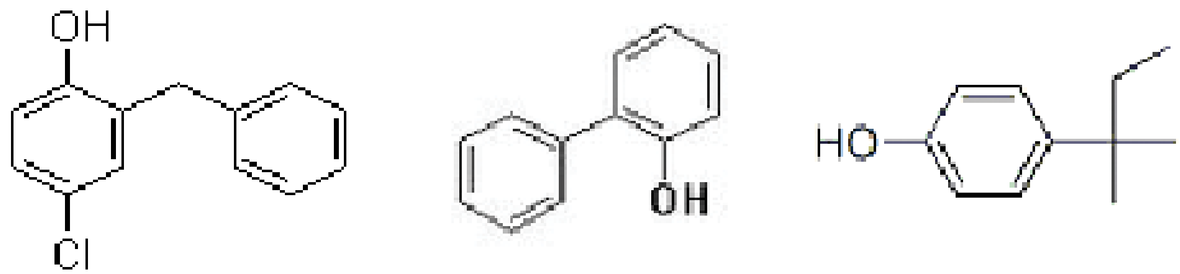

Figure 1: Chemical structure of three active ingredients: o-benzyl-p-chlorophenol, o-phenylphenol, p-tertiary amylphenol

Disinfectants used on examined farms are based on o-phenylphenol (OPP), o-benzyl-p-chlorophenol (OBCP) and p-tertiary amylphenol (PTAP). Active compounds in the disinfectant are present in the following amounts expressed as a percentage by weight: ortho-phenylphenol 14.00% w/w, ortho-benzyl-para-chlorophenol 10.50% w/w and para-tertiary amylphenol 3.00% w/w.

The chemical structures of these three active ingredients are shown in Figure 1.

A small number of studies describe the ecotoxicity of biocidal agents with the above-mentioned three active ingredients. Although they predicted that the ecological levels of these components will be reduced quickly because of bacteriological degradation, results from this research clearly demonstrate that the ecologically relevant alga, primary consumers, and fish species are all adversely affected by low concentrations of these chemicals (EC/LC_{50s} 0.6-4.2 mg/l). A deleterious effect on even one of these aquatic organisms could have significant knock-on implications for other organisms in the aquatic food chain (Davoren and Fogarty, 2005). They have not found any information regarding the ecotoxicity of p-tertiary amylphenol.

Although a disinfectant's components are biodegradable, by daily use and emission into the environment they became persistent, because constant emission prevents the elimination of pollutants from the environment by biodegradation.

In Directive 1999/45/EC (classification, packaging, and labelling of dangerous preparations), OPP is classified as "R50, very toxic to aquatic organisms", OBCP is classified as "R50/53, very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment", and PTAP as “R51/R53, toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment” (Davoren and Fogarty, 2005).

In waste water from animal farms, xenobiotics pass through various transformations which take place under certain conditions faster or slower, producing new products. One part of the disinfectant’s active components and arisen metabolites partly accumulates into the solid manure or sludge, or they attain to arable land. They can also leak into groundwater and surface water, especially if the active parts of biocidal agents are soluble in water. Due to inadequate degradation of active components, the growth of a microbiological population resistant to the disinfectant’s active components is possible. This process has a negative impact on microbiological degradation of other components in waste water (veterinary antibiotics, pesticides).

Diverse alkylphenols have been detected by GC/MS scanning of groundwater samples from piezometers near pig farms (3-methyl-phenol, 4-methyl-phenol, 2,4-bis(1,1-dimethylethyl)phenol, m-tert-butylphenol, p-tert-butylphenol, 2-methyl-5-(1-methylethyl)phenol, 2,4-dimethyl-phenol, 4,4’-bis(1-methylidene)phenol) as well as a large number of substituted benzenes and benzene derivates (tert-butylbenzene, 1-methylethyl-benzene, 1-methyl-3-propylbenzene, 1-methyl-2-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1-ethyl-2-methylbenzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, propylbenzene, 2,4-diisocyanato-1-methylbenzene, 4-methylbenzene sulfonamide, butylhydroxytoluene, 1-ethyl-2,4-dimethylbenzene, 1-ethyl-3,5-dimethylbenzene, 4-ethyl-1,3-benzenediol, dibenzofuran, hydroxybiphenyl).

It is assumed that most alkylphenols and some representatives of substituted benzene in groundwater originate from the degradation of a disinfectant’s phenol components. Alkylated benzenes in groundwater can originate from fuel oil which is used on farms for heating. Their degradation in the environment depends on microbiological activity, enzyme reactions, and the transformation of active components through hydroxylation or oxidative decarboxylation.

Dibenzofuran in water from piezometers may trace to insecticides as well as PVC production. Interaction between alkylphenol components and the endocrine system is known as to occur during which such substances increase, inhibit or imitate hormone activity. Among 118 substances classified in the EU as hormonally active compounds, o-phenylphenol takes a priority place.

O-phenylphenol is widely used on farms as a protection for citrus fruits and vegetables, for its efficiency on mould, fungi and ferment. During research of the content of canned beer, Coelhan et al. (2009) proved the presence of o-phenylphenol’s biocide in concentrations higher than 33.5 μg/l. They also detected its presence in 49 out of 55 analysed samples of soft drinks from various producers; therefore cola enriched with lemon contains 16.9 μg/l and ice tea 10.3 μg/l of o-phenylphenol.

Khodja et al. (2001) also consider as a very important issue the presence of o-phenylphenol in the environment. They did not detect the products of photodegradation in the absence of oxygen, but they found some products in an aerobic environment, such as phenylhydroquinone (PHQ), phenylbenzoquinone (PBQ) and 2-hydroxydibenzofuran, as the result of further phenylbenzoquinone degradation. In the presence of nitrate ion further o-phenylphenol’s degradation products are dihydroxybiphenyls and hydroxynitrobiphenyls.

Rayne et al. (2009) carried out research to understand photochemical degradation of phenol compounds. The transformation of p-chlorophenol in an aqueous solution (it is easiest to explain photochemical degradation of chlorophenol derivates on p-chlorophenol) mostly depends on substance concentration, presence of oxygen and pH values. The main products of photodegradation in the presence of oxygen are: 1,4-benzoquinone, 1,4-hydroquinone, 2-hydroxy-1,4-hydroquinone and polyhydroxybiphenyl, e.g. 4,4’-dihydroxybiphenyl, 5-chloro-2,4’-dihydroxybiphenyl and 2,4’,5-trihydroxybiphenyl. In the absence of oxygen, there is no creation of 1,4-benzoquinone and 2-hydroxy-1,4-hydroquinone, and if there is any, it occurs in small quantities. With increasing pH values the production of 1,4-hydroquinone and 1,4-benzoquinone reduces, while the generation of 2-hydroxy-1,4-hydroquinone increases.

The presence of a large number of xenobiotics in groundwater from piezometers located near investigated animal farms indicates the necessity of future research in order to comprehend the transport mechanisms of these substances. Of course, the source of some xenobiotics in groundwater is not animal production exclusively, which gives rise to an even greater concern, for it was already contaminated upstream from animal farms as the source of pollution.

Samples of the first layer of groundwater near pig farms were analysed for the content of volatile organic compounds, some of which are listed as priority and priority hazardous substances in surface water. Analyses show satisfactory results, because the concentrations of most volatile organic compounds are under MDL values (1,2-dichlorobenzene, 1,4-dichlorobenzene, bromoform, o-xylene, m-xylene, p-xylene, ethylbenzene, chlorobenzene, tetrachloroethylene, toluene, DBHM (dibromochloro-methane), trichloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, chloroform).

Benzene concentration in groundwater was between 0.05 and 0.25 μg/l in 50% of the samples, while the DBHM substance was detected in only 10% of groundwater samples under the practical determination limit value, and chloroform in only 3 samples of water from piezometers under the PQL values.

Annex to the X Directive 2000/60/EC (Water Framework Directive, WFD) contains a list of priority substances that pose a significant risk to the aquatic environment or a risk through the aquatic environment. Certain priority substances from this list were detected in the samples of the first layer of groundwater from several piezometers. Besides already mentioned benzene and trichloromethane, by GC/MS qualitative analyses the following priority substances were detected as well: naphthalene, anthracene present in almost 50% of water samples, fluoranthene, then benzo(a)pyrene and indeno(1,2,3-cd)pyrene which are present in several samples of water from piezometers. Bis(2-ethylhexyl)phthalate as one of the most critical substances from WFD's list was present in almost all examined groundwater samples. Besides bis(2-ethylhexyl)phthalate, the presence of the following phthalate derivates was confirmed in most of the water samples: dinonyl phthalate, dibutyl phthalate, diethyl phthalate, dimethyl phthalate, benzyl butyl phthalate, phthalic anhydride and phthalic acid.

Phthalates are mostly used in the PVC industry, in insecticide and resin production as a plasticizer, based on which we can conclude that the source of organic xenobiotics in groundwater was most probably not animal production.

Phthalates are one of 20 substances which are currently investigated worldwide, considering the suspicion of their hormonal activity. Besides phthalates, this group includes alkylphenols, bisphenol A, hormones and benzophenones (benzophenone was also confirmed in several samples of groundwater from piezometers). Polycyclic aromatic hydrocarbons are classified as organic components with hormonal activity. Certain organic substances which belong to the PAH group (besides those already mentioned) were detected in samples of water from the piezometers, such as pyrene, chrysene, 4-methyl-9H-fluorene, 11H-benzo(b)fluorene, 3,4-dihydro-1(2H)naphthalenone, indane, 2-methylantracene.

Figure 2 shows the frequency of detection of organic xenobiotics in the piezometers, from the first layer of groundwater near pig farms.

Due to changes in environmental conditions such as temperature, moisture, light, presence of other organic and inorganic matter, contaminants can often be partially degraded, completely degraded or remain unchanged.

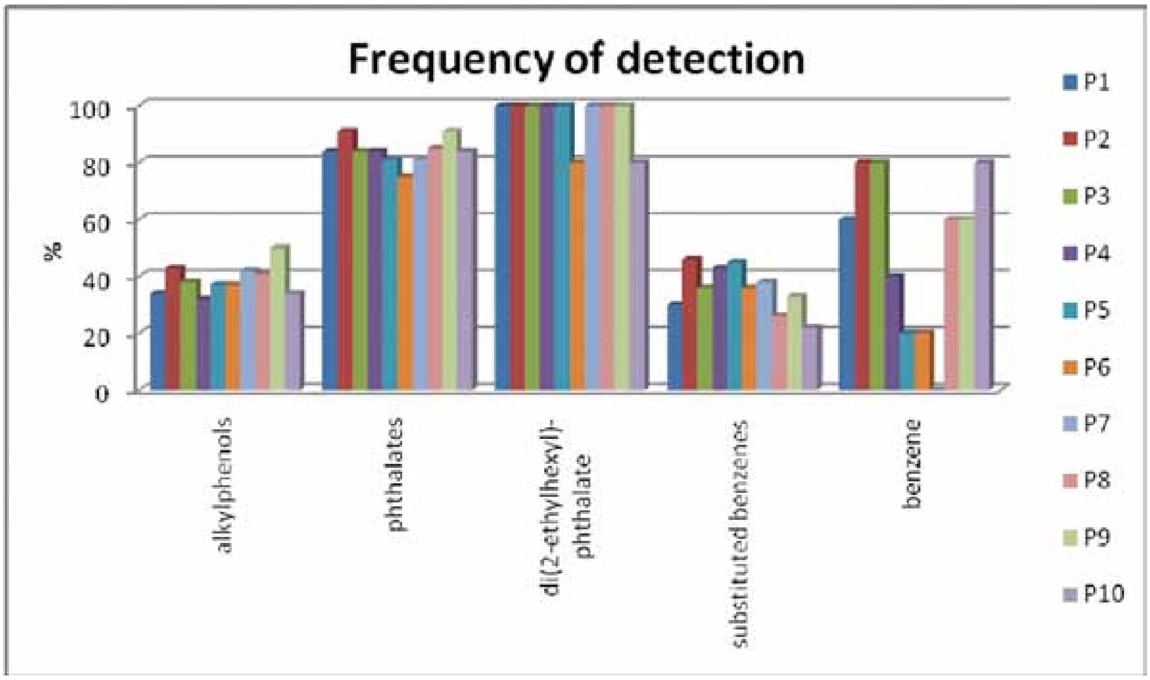

Figure 2: Frequency of detection of organic xenobiotics in piezometers

By reasons of diverse transformation of components in the environment, the presence of other organic matter was confirmed in water samples from examined piezometers, such as: n-alkanes, branched alkanes, alcohols, ethers, aldehydes, ketones, organic acid and its salts, esters, steroids, various alkaloids, heterocyclic compounds, organophosphorus and organonitrogen compounds.

Vanillin was detected in almost every sample of water from the piezometers, and it may originate from animal feed and some pharmaceutical preparations. Acetophenone and its derivates could also be found in some pharmaceutical preparations, as well as benzaldehydes and its derivates.

Although the concentrations of most organic xenobiotics in groundwater are very low, the mere detection of these components in analysis leaves a great concern to the scientific world, since there is no recommendation for most of these components.

Considering the fact that health safety of drinking water depends on groundwater quality, groundwater degradation entails the risk of excessive intake of various substances into the living organism.

Based on such studies, the question can be raised whether daily use of bottled drinking water is just the new generation's trend or a necessary evil?

References

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Khodja A.A., Sehili T., Pilichowski J.-F., Boule P. (2001). Photocatalytic degradation of 2-phenylphenol on TiO2 and ZnO in aqueous suspensions. Journal of Photochemistry and Photobiology A: Chemistry, 141, 231-239.

Muñoz I., Gómez-Ramos M.J., Agüera A., García-Reyes J.F., Molina-Díaz A., Fernández-Alba A.R. (2009). Chemical evaluation of contaminants in wastewater effluents and the environmental risk of reusing effluents in agriculture. Trends in Analytical Chemistry, 28(6), 676-694.

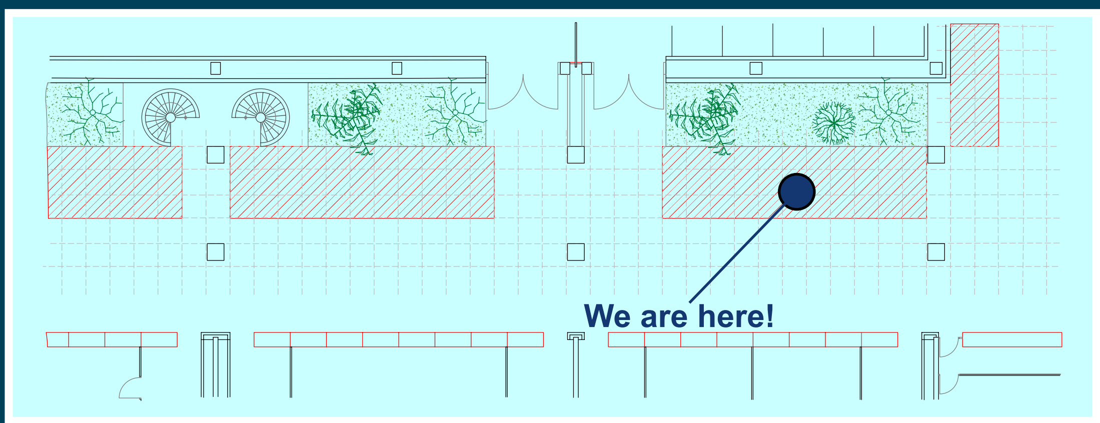
Rayne S., Forest K., Friesen K.J. (2009). Mechanistic aspects regarding the direct aqueous environmental photochemistry of phenol and its simple halogenated derivates. A review. Environmental International, 35, 425-437.

NOTES:

SPONSOR SECTION

ХЕ ЂЕРДАП

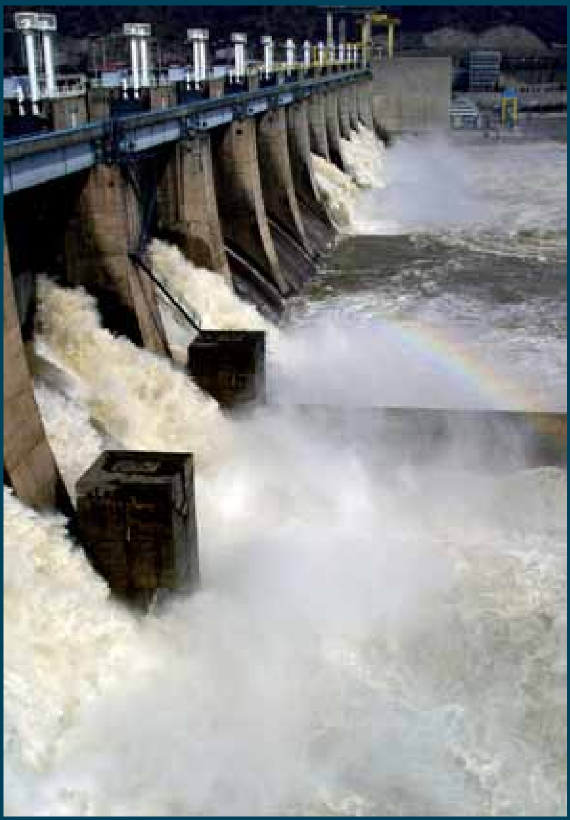
HPPs Djerdap Ltd., Kladovo, Serbia



We are the largest producer of hydroelectric power in Southeast Europe.

We have assumed a leading strategic role in Serbia's energy sector.

We produce high-quality hydroelectric power at seven hydroelectric power plants.



COMPANY PROFILE

Full registered name: Privredno društvo "Hidroelektrane Djerdap", d.o.o. Kladovo (Hydroelectric Power Plants Djerdap Limited Liability Company, Kladovo, Serbia).
Short name: HE Djerdap d.o.o. Kladovo (HPPs Djerdap Ltd.).

Establishment: HPPs Djerdap Ltd. changed its previous legal status under a government decision on the incorporation of public enterprises engaged in the production of hydroelectric power, which came into force on 1 January 2006.

Ownership Structure: Wholly-owned by the Republic of Serbia.
Certificate of Incorporation: 102734/2005 issued by the Serbian Business Registers Agency.

Registered Address: Trg Kralja Petra 1, 19320 Kladovo, Serbia
Corporate ID Number: 07715226
Tax ID Number: 100695213

Core business activity: Production of hydroelectric power (Code 40101)
Other business activities: River and lake transportation services/operation of navigation locks (Code 63222)

CERTIFICATES AND LICENSES

HPPs Djerdap Ltd. was the first producer of hydroelectric power to be licensed in Serbia.
The Council of Serbia's Energy Agency granted a hydroelectric power license to HPPs Djerdap Ltd. at its 19th meeting held on 6 July 2006.
All our hydroelectric facilities, at four different locations: Kladovo, Negotin, Pirot and Surdulica, have been licensed.
Our license was issued for a period of 10 years and attests to the fact that HPPs Djerdap Ltd. meets all legal requirements pertaining to technical integrity, fire and explosion protection, environmental protection, professional staffing, and availability of resources needed to engage in the production of hydroelectric power.
HPPs Djerdap Ltd. has implemented an Integrated Management System (IMS), certified by the Swiss certification body SGS from Zurich and comprised of three management components:

- QUALITY MANAGEMENT per ISO 9001:2008 (re-certified on 8 February 2011);
- ENVIRONMENTAL MANAGEMENT per ISO 14001:2004 (re-certified on 10 March 2011); and
- OCCUPATIONAL HEALTH AND SAFETY MANAGEMENT per OHSAS 18001:2007 (re-certified on 8 February 2011).

ЛИЦЕНЦА

SGS

Javno preduzeće
"Elektroprivreda Srbije"
Privredno društvo
"Hidroelektrane Đerdap" d.o.o.

ISO 9001:2008

SGS

Javno preduzeće
"Elektroprivreda Srbije"
Privredno društvo
"Hidroelektrane Đerdap" d.o.o.

OHSAS 18001:2007

SGS

Javno preduzeće
"Elektroprivreda Srbije"
Privredno društvo
"Hidroelektrane Đerdap" d.o.o.

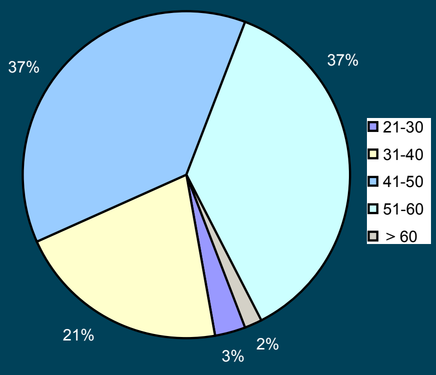
ISO 14001:2004

ORGANIZATION AND HUMAN RESOURCES

To ensure technical, technological and economic unity of our electric power system, as well as efficient and judicious performance of the company, the internal organization of HPPs Djerdap Ltd. is based on the following principles:

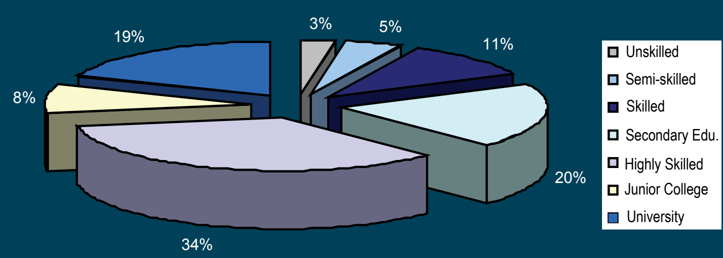
- Function-based divisions;
- Cohesive and coordinated electric power industry services;
- Integration of similar and interrelated activities under appropriate organizational units;
- Hierarchical organization of work processes;
- Efficient management;
- Optimum utilization of human resources.

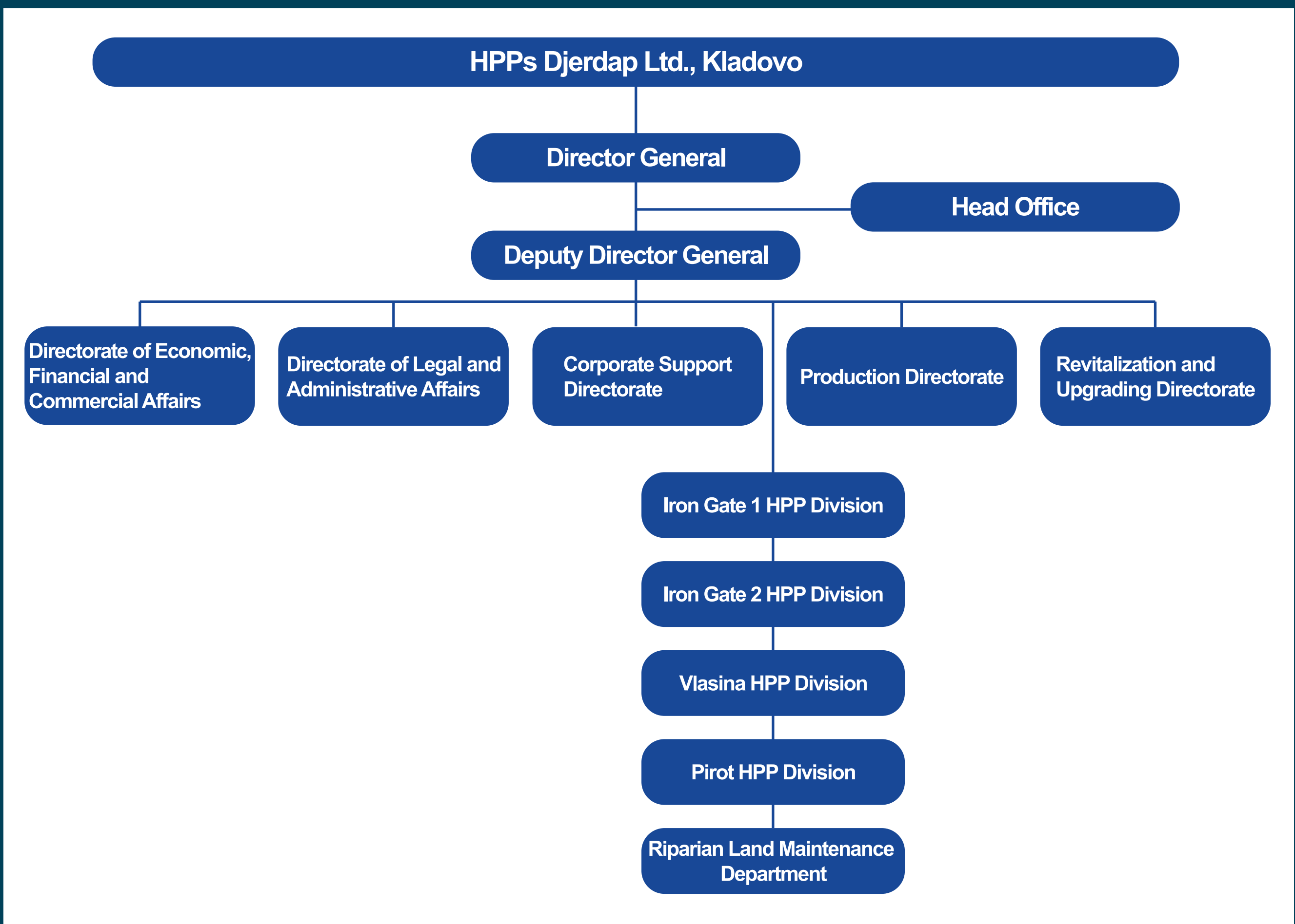
Human Resources Structure by Age

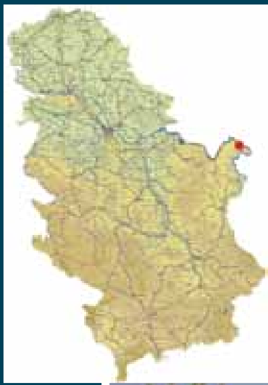


At the beginning of 2011, HPPs Djerdap Ltd. had 1010 employees. Previously, this number was 30% higher. Our restructuring and retrenchment have not affected performance. Instead, HPPs Djerdap Ltd. improved its efficiency.

Structure of Human Resources







IRON GATE 1 HPP

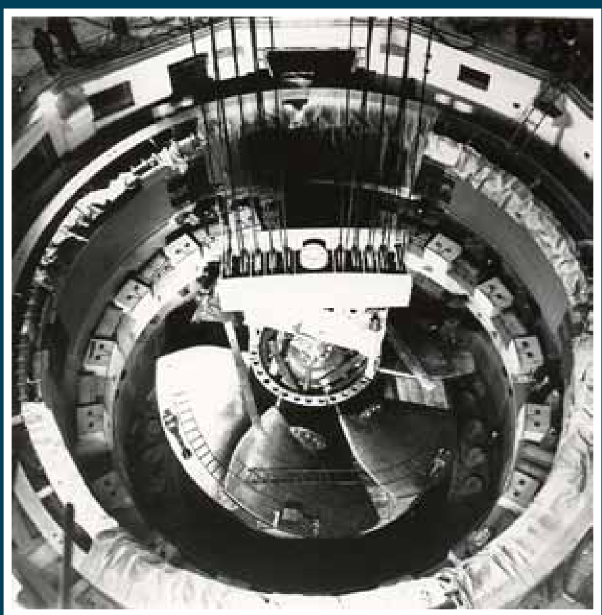
Construction of the Iron Gate 1 Hydropower and Navigation System on the Danube River was more than a challenge for Yugoslav and Romanian engineers. In principle, each party undertook construction within its territory, while fully synchronizing its activities with the other party and strictly adhering to the agreed timeframe.

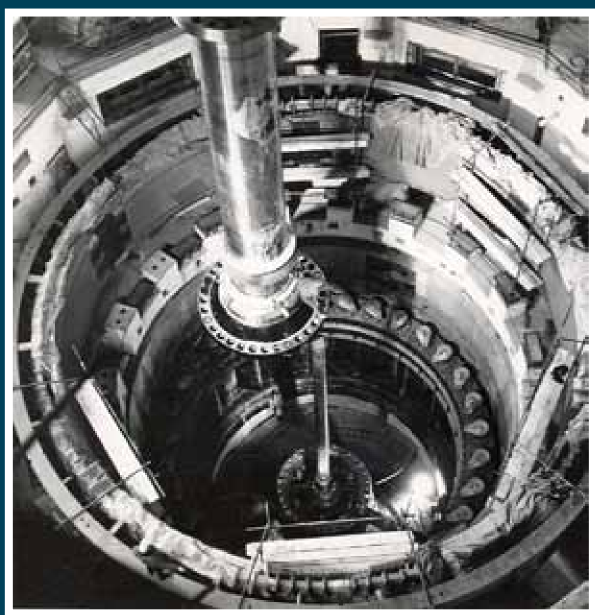
Construction formally began on 7 September 1964 and the first power generating units were simultaneously placed online in both the former Yugoslavia and Romania on 6 August 1970.

The Romanian lock became operational on 3 August 1969 and the Yugoslav lock in October 1970. Final impoundment of the Danube took place on 13 August 1969.

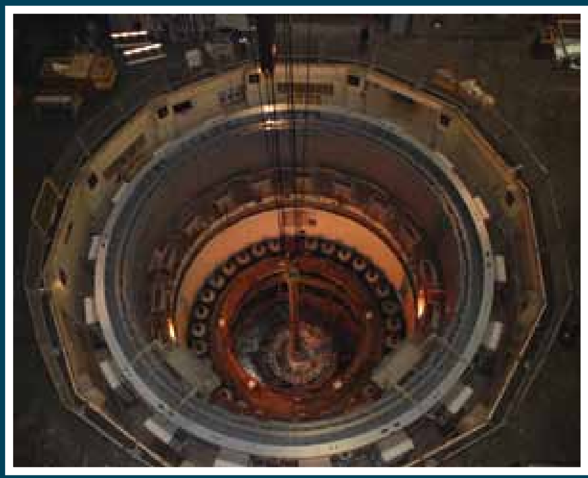
During construction of the dam, 13.4 million cubic meters of gravel and river sediment and 7.2 million cubic meters of rock were excavated, 3.2 million cubic meters of concrete and 167,000 tons of reinforcement and steel structures incorporated, and 69,000 tons of equipment installed.

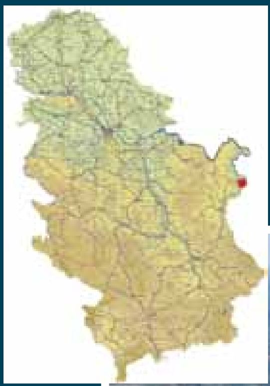
INSTALLATION OF EQUIPMENT DURING CONSTRUCTION:





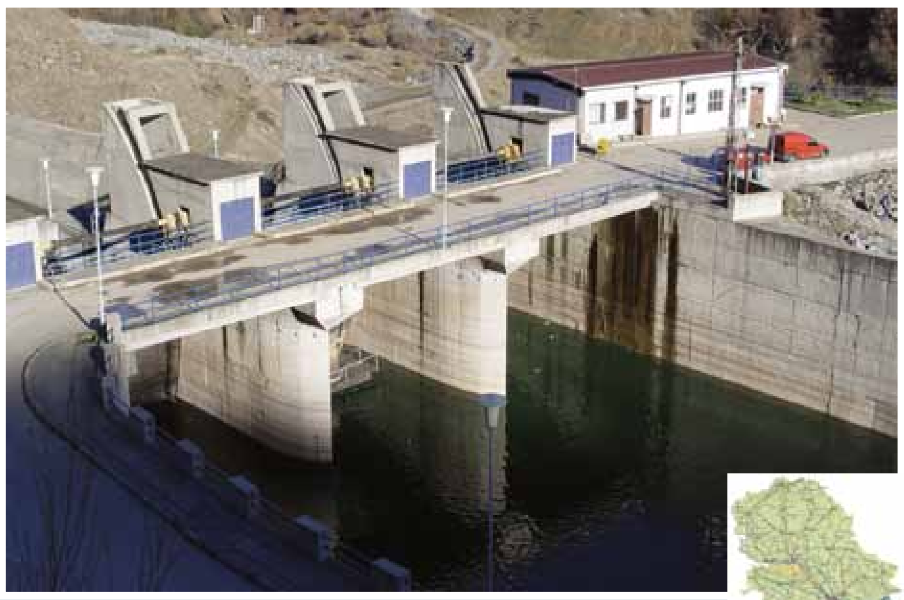
REVITALIZATION OF UNIT 6 IN 2010/2011:

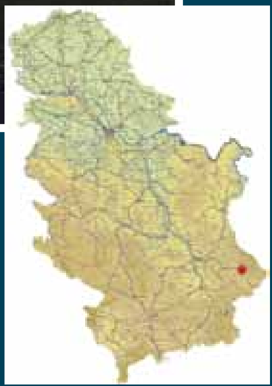




IRON GATE 2 HPP

PIROT HPP

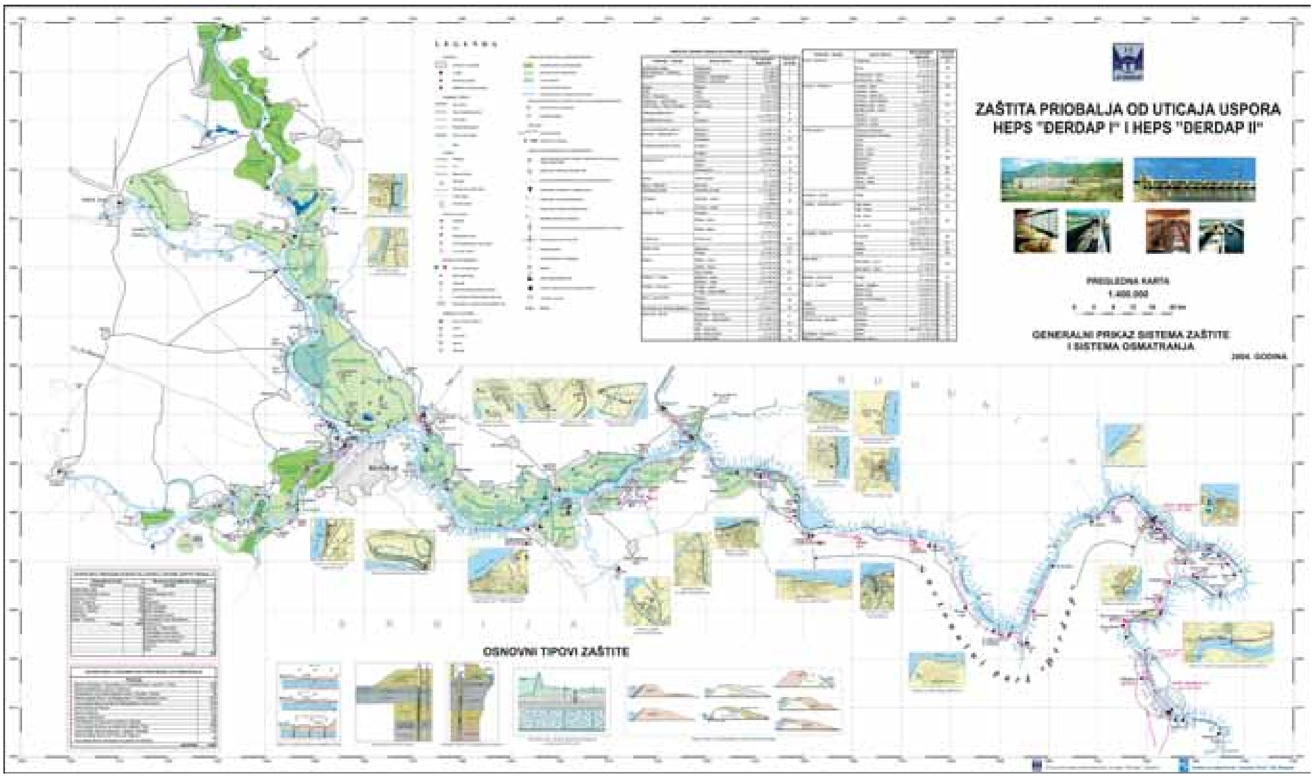




VLASINA HPPs

IWA SPECIALIST GROUNDWATER CONFERENCE

RIPARIAN ZONE PROTECTION



08-10 September 2011, Belgrade, Serbia

LOCATIONS

ХЕ ЂЕРДАП

HPPs Djerdap Ltd. Headquarters
Trg Kralja Petra 1, 19320 Kladovo, Serbia
Director General
Directorate of Economic, Financial and Commercial Affairs
Directorate of Legal and Administrative Affairs
Corporate Support Directorate

Iron Gate 1 HPP
Trg Kralja Petra 1, 19320 Kladovo, Serbia
Iron Gate 1 HPP Division

Iron Gate 2 HPP
Kraljevića Marka 2, 19300 Negotin, Serbia
Iron Gate 2 HPP Division

Vlasina HPPs Head Office
Kej Rade Cvetković 15, 17530 Surdulica, Serbia
Vlasina HPPs Division

Pirot HPP
Berilovački Put, 18300 Pirot, Serbia
Pirot HPP Division

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Pop Stojanova 2a, 11000 Belgrade, Serbia
Production Directorate
Revitalization and Upgrading Directorate

Požarevac Office
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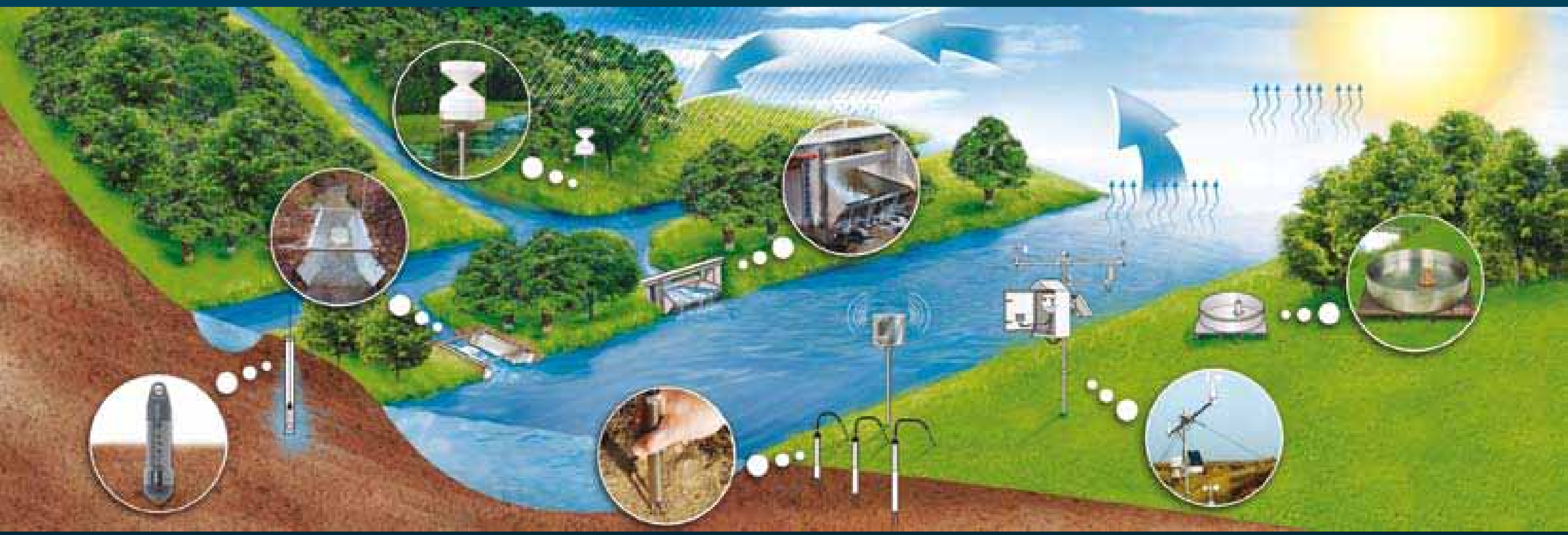
headoffice@jcerni.co.rs;

http://www.jcerni.org



Eijkelkamp Agrisearch Equipment BV is an international organisation that supplies all types of equipment in the area of environmental and agricultural research. The range of products that Eijkelkamp has to offer can best be described as equipment used for researching soil, water, earth monitoring and sludge & slurry. And this all is for the benefit of agricultural, hydrologic and environment-related studies. Eijkelkamp also has a modern Education and Training Centre that offers a range of courses, training sessions and workshops.

Product ranges includes equipment for:

SOIL
- Soil drilling and sampling
- Soil- and sediment samplers
- In-situ soil physical research
- Soil physical research in the laboratory
- General field equipment

WATER
- Hydrological research
- (Ground-)water sampling
- (Ground-)water analysis

SLUDGE & SLURRY
- Samplers for (layered) liquids
- Check-kit Chemviro
- Automatic sludge & slurry sampling

EARTH MONITORING
- Meteorological instruments
- Dataloggers, sensors and measuring stations
- e-SENSE®
- Plant physiological research
- Solar radiation measurements

e-SENSE®: **measuring and monitoring that crosses boundaries**

Measuring and control devices increasingly need to be used at a (greater) distance. Adjusting settings, reading data followed by taking appropriate action, if necessary, from a location of your own choice are possibilities that are now very much part of the standard package of requirements. With the use of e-SENSE, taking measurements of data via intelligent sensors such as the e+ sensors from Eijkelkamp Agrisearch Equipment or the Diver® from Van Essen Instruments has become more than just measuring. Intelligent sensors measure data in the field and store these internally. The e-SENSE field modem makes it possible to then transmit your data or alarms to a data base which is located either on your own computer (e-SENSE direct) or at a central database.

Available sensors:
- The e+ SOIL MCT®-sensor/logger measures soil moisture, conductivity and temperature. Available in various lengths for measurements from the surface to a depth of 1 m.
- Two e+ RAIN® sensors / loggers are available: one with a synthetic and one with a metal rain gauge. The e+ RAIN sensors measure the intensity of the rainfall over certain periods but also record the total quantities (integration function).
- The e+WATER L® (level)-sensor is an intelligent and accurate sensor for measuring and recording the level and the temperature of the surface water. The level measurements are automatically (internally) compensated for variations in the air pressure and for variations in the density that is the result of temperature fluctuations. The sensor is freeze proof and can be used without problems in all seasons. The e+ WATER L is available in various lengths (for water level fluctuations of maximum 2 metres).
- The e+ OVERFLOW® sensor is an intelligent and accurate sensor for measuring and registering sewer overflows (how often and for how long do overflows occur). The level measurements are automatically compensated internally for air pressure variations and density variations of water due to temperature.
- All members of the Diver family can be used as e+ sensors in the e-SENSE system. The Diver is the smallest device in the world for automatically measuring and recording groundwater levels and groundwater temperatures. The CTD-Diver also measures conductivity of the water.

THANK YOU FOR BEING ACTIVE FOR THE RIVERS

THE CITIZENS OF THE REPUBLIC OF SERBIA SYMBOLICALLY CELEBRATED THE DANUBE DAY THIS YEAR AS WELL AND THEREBY GAVE THEIR CONTRIBUTION TO PRESERVING ONE OF THE GREATEST EUROPEAN RIVERS. THE CELEBRATION TOOK PLACE IN BELGRADE, ZEMUNSKI QUAY ON JULY 2.

THE TRADITIONAL DANUBE DAY CELEBRATION IS AN INTERNATIONAL EVENT WHICH TAKES PLACE IN 14 EUROPEAN COUNTRIES WITH THE AIM TO RAISE AWARENESS ON IMPORTANCE OF PRESERVING THE DANUBE RIVER AND PROTECTING ENDANGERED SPECIES (BOTH PLANTS AND ANIMALS) THAT INHABIT IT. WHITE LILY, PYGMY CORMORANT, BELUGA, RED OAK, BLACK STORK AND OTTER ARE ONLY SOME OF THE SPECIES THAT ARE SLOWLY DWINDLING AWAY FROM THE DANUBE AND ITS BANKS. SINCE HUMAN FACTOR CONTRIBUTED THE MOST TO DISTORTION OF FLORA AND FAUNA, THE IDEA OF DANUBE DAY WAS DESIGNED TO INSPIRE CITIZENS TO PARTICIPATE IN PROTECTION OF THE DANUBE MORE ACTIVELY, THE RIVER WHICH CONNECTS 18 EUROPEAN COUNTRIES AND THEIR CITIZENS. THE INITIATORS OF THE DANUBE DAY IN SERBIA ARE MINISTRY OF AGRICULTURE, FORESTRY AND WATER MANAGEMENT AND THE COCA-COLA SYSTEM. THE EVENT TOOK PLACE IN 2004 FOR THE FIRST TIME AND IT WAS ESTABLISHED BY AN INTERNATIONAL COMMISSION FOR THE PROTECTION OF THE DANUBE RIVER (ICPDR).

icpdr iksd
International Commission for the Protection of the Danube River
Internationale Kommission zum Schutz der Donau

Република Србија
Министарство пољопривреде,
трговине, шумарства и водопривреде
Републичка дирекција за воде

Coca-Cola

Razvojnu karakteristiku poduzeća čine stalna proširivanja proizvodnih pogona i njihova modernizacija, rast kvalitete proizvoda i širenje proizvodnog programa, sve veće sudelovanje u poslovima međunarodne saradnje i sve veći udeo inostranog tržišta u ukupnoj prodaji.

MISIJA I VIZIJA

Naša vizija je postati svetski konkurentna i prepoznatljiva kompanija za proizvodnju armatura i fazonskih komada i nodularnog lijeva. Misija nam je voditi se načelima poslovne i društvene odgovornosti te održivog razvoja koristeći se pritom svojim znanjima, iskustvima i novim tehnologijama kako bismo u proizvodni proces, uz tradiciju, utkali inovativnost i time postali prepoznatljivi na tržištu nudeći kvalitetan proizvod našim kupcima.

STRUČNI KADROVI

Prateći zahteve domaćeg i inostranog tržišta, poduzeće se kod uvođenja novih proizvodnih postupaka, modernizovanja opreme i pogona, promena u proizvodnom programu i poboljšanju kvaliteta proizvoda, oslanja na vlastite stručne kadrove koji rade u konstrukcionim i projektnim biroima, razvojnim odelenjima i istraživanju.

Odelenje istraživanja i razvoja danas čini šest diplomiranih inženjera mašinstva, koji za projektovanje koriste programe, kao što su Solid edge i Microstation. Kontinuirani razvojdanašnjeg proizvodnog programa dokazuje i razvoj preko 3.000 standardnih proizvoda kao i preko 30.000 njihovih modifikacija.

SEDAMDESET POSTO PROIZVODA ZA IZVOZ

U poslovnoj saradnji s velikim proizvođačima armature u Evropi, danas poduzeće plasira na inostrano tržište 70 odsto svojih proizvoda. Armatura se izvozi na tržišta svih kontinenata, a ugrađena je u vodovodne i kanalizacijske sisteme nekih svetskih metropola. S godišnjom proizvodnjom od 9000 tona odljevaka i 7500 tona armatura i fazona "MIV" se ubraja među najveće proizvođače ovakve opreme u Evropi.

KVALITET I SIGURNOST

Celovitost tehnološkog procesa: izrada modela, ljevaonica nodularnog lijeva i obojenih metala, mašinska obrada, gradnja čeličnih konstrukcija, montaža, ispitivanje i površinska zaštita, omogućuje kontrolu proizvodnog procesa u svim njegovim fazama. Taljenje sirovine vrši se u ekološki prihvatljivoj srednje−frekventnoj peći kapaciteta 5 tona na sat.

Potvrda kontrole proizvodnog procesa prema normi ISO 9001:2008, dobijena je od LRQA 22. maja 2007. Time je osigurana visoka pouzdanost našeg proizvodnog programa i sigurnost naših proizvoda u eksploataciji. Kvalitet naših proizvoda verifikuju klasifikacijska društva: Lloyd's register, Bureau Veritas, Det norske Veritas, Hrvatski registar.

ZAŠTITA OKOLINE

Ušavši u nov milenijum, postali smo svesni problematike onečišćenja okoliša na globalnom nivou. Tema očuvanja životne sredine nije bila toliko aktuelna kao što je danas. U rapidno brzom napretku tehnologija svesni smo činjenice da su zanemarena najveća bogatstva Sveta, zanemarivala se lepota prirode i njena bogatstva flore i faune. Od strane Lloyd's Register certificirani smo prema normi za sustave upravljanja okolišem ISO 14001:2004. 2010. godine

INVESTICIJE I ULAGANJE

Ukupne investicije tokom 2007., 2008. i 2009. godine:

- Ekologija i modernizacija (1,6 milijuna evra)
- Modernizacija (3,7 milijuna evra)
- Rekonstrukcija i gradnja (1,7 milijun evra)

Srpsko društvo za zaštitu voda

Serbian Water Pollution Control Society (SWPCS) is non-profit independent organisation of experts in water sector established in 1966. Main objective of the Society is to create and foster the network of leading water professionals through the provision of services and products to members, including conferences, publications and support for member groups. In addition, to represent the views of members in national and international forums aimed at advancing best practice in sustainable water management.

Activities of Society include organization of scientific and technical Conferences and Workshops, providing information services for society's members, as well as cooperation and exchange of information with other similar national or international associations. SWPCS is a country representative and governing member of the International Water Association (IWA) and the European Water Association (EWA).

Contact Details:

Address: Serbian Water Pollution Control Society (SDZV), Kneza Miloša 9/I, room 105, 11000 Belgrade, Serbia

Fax: +381 (0) 11 3241 656; E-mail: office@sdzv.org.rs

www.sdzv.org.rs

The International Association of Water Supply Companies in the Danube River Catchement Area

The International Association of Water Supply Companies in the Danube River Catchement Area (IAWD) is concerned with improving and safeguarding the water quality of the Danube and its tributaries. IAWD encourages all measures and attempts directed at avoiding and eliminating all contamination of, and hazards to, the raw water quality in order to ensure reliable drinking water supply.

To achieve these goals, all efforts are undertaken to unite the water companies of all countries in the Danube catchment area in IAWD to encourage concentration on the following objectives:

- Developing a uniform, internationally agreed monitoring and investigation programme to safeguard water quality as well as evaluating and publishing the results thus obtained
- Making the results of this work available to national and international institutions
- Public relations
- Maintaining a regular and continuous exchange of experience between members
- Co-operating closely with other organisations pursuing similar objectives

www.iawd.at

The International Commission for the Protection of the Danube River

The International Commission for the Protection of the Danube River (ICPDR) works to ensure the sustainable and equitable use of waters and freshwater resources in the Danube River Basin. The work of the ICPDR is based on the Danube River Protection Convention, the major legal instrument for cooperation and transboundary water management in the Danube River Basin. Since its creation in 1998 the ICPDR has promoted policy agreements and the setting of joint priorities and strategies for improving the state of the Danube and its tributaries.

The goals of the ICPDR

- Safeguarding the Danube's Water resources for future generation
- Naturally balanced waters free from excess nutrients
- No more risk from toxic chemicals
- Healthy and sustainable river systems
- Damage-free floods

www.icpdr.org

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Supporting Organizations

International Water Association

Jaroslav Černi Institute for the Development of Water Resources

□overnment of the Republic of Serbia
□inistry of Agriculture, □rade, □orestry and Water □anagement □ Directorate for Water
□inistry of Education and Science

Serbian Academy of Sciences and Arts

United Nations Educational, Scientific and Cultural Organization

Iron □ate □ydroelectric Power Plants □□C

International Commission for Protection of the Danube River (ICPDR)

International Association of Water Supply Companies in the Danube River Catchment Area (IAWD)

Belgrade Water Supply and Sewerage Company

Srpsko društvo za zaštitu voda
Serbian Water Pollution Control Society

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http://www.jcerni.org/activities/conferences/iwa_specialist_groundwater_conference_2011