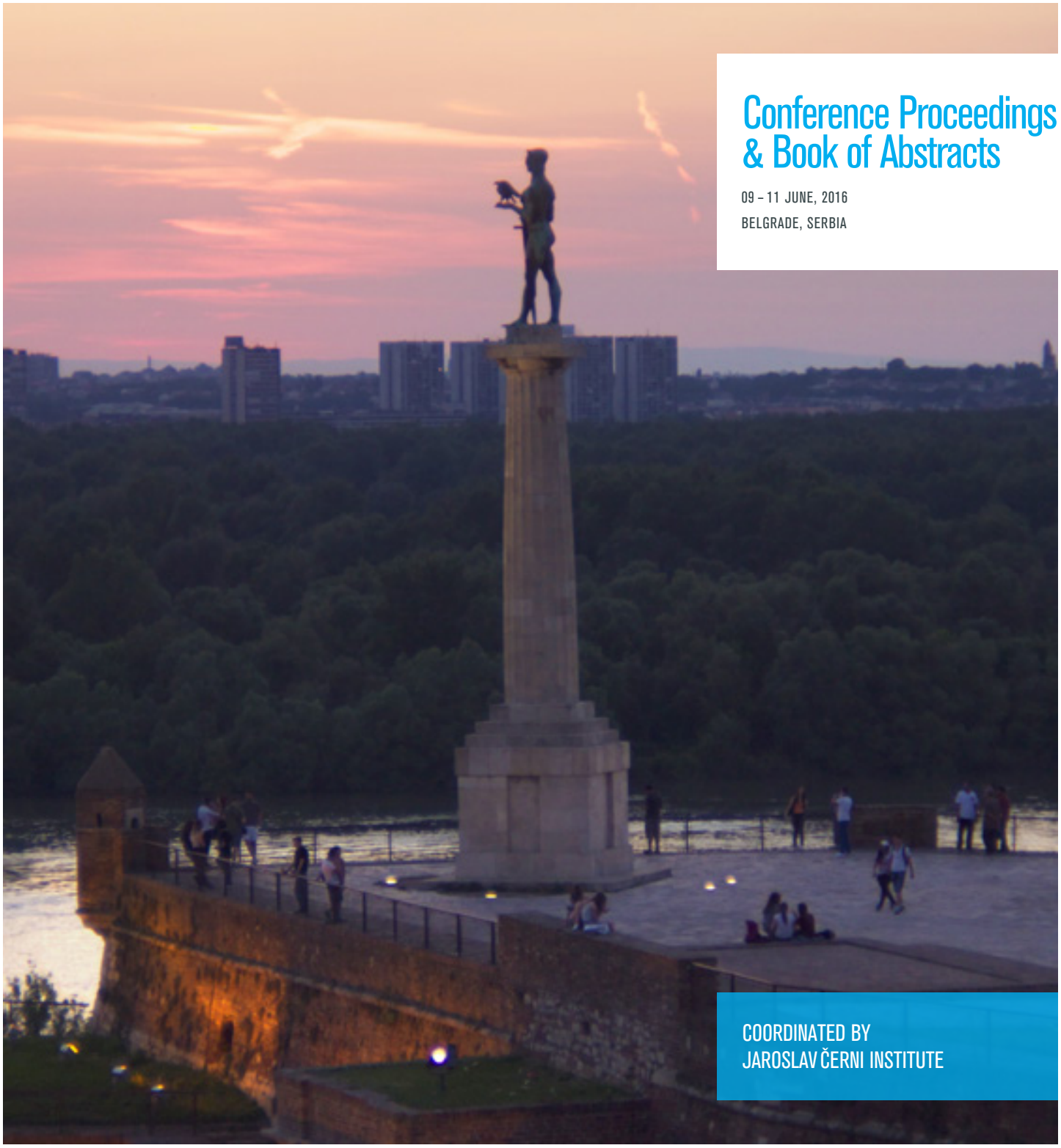
IWA SPECIALIST GROUNDWATER CONFERENCE



Conference Proceedings & Book of Abstracts

09 – 11 JUNE, 2016

BELGRADE, SERBIA

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IWA the international water association

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IWA SPECIALIST GROUNDWATER CONFERENCE

09-11 JUNE 2016, BELGRADE, SERBIA

CONFERENCE PROCEEDINGS AND BOOK OF ABSTRACTS

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INTRODUCTION

Water is the very essence of life on our planet. It constitutes 70% of our body. It is also one of the fundamental archetypes that define our existence and the state of our civilization. Sustainable management of natural resources, including surface water and groundwater, is a global necessity, which requires prudent management within watersheds and entire countries, for the benefit of each individual.

The relatively modest UN Millennium Development Goals related to progress in the areas of drinking water supply and sanitation until the year 2015 have not been achieved. We now have a new set of objectives ahead of us, as discussed at the 7th World Water Forum (Daegu, Korea, 2015), etc. The Sustainable Development Goals (SDGs), officially known as *Transforming our world: the 2030 Agenda for Sustainable Development*, were adopted at the UN Sustainable Development Summit September 25–27, 2015 in New York, USA. The goals incorporate in a balanced way all three dimensions of sustainable development (environment, economics, and society) and their interlinkages. In this context, a new goal related to water and sanitation has been proposed: *Ensure availability and sustainable management of water and sanitation for all.*

We are living in a time of strong pressures and contrasts, which threaten the continuation and development of the human society. Climate conditions, climate change, and social, economic and political pressures and disparities lead to crisis situations in social and economic spheres and in the area of sustainable use of water resources.

In ongoing circumstances, sustainable management is the promoted goal which the human society needs to attain. However, the success of achieving set objectives in the field of water is presently often relatively modest. Sustainable development of water management requires us to reach the needed level of scientific and technical knowledge, capacity, funding, and governance in general.

Groundwater is a crucial resource, as the basis of natural habitats, drinking water supply and irrigation. The goal is to attain sustainable groundwater management. The proposed topics of the Conference will virtually cover all of the scientific and technical knowledge in this field. The Conference is also expected to address very important issues and solutions relating to groundwater management.

The Conference will be the third IWA conference to be held in Belgrade (2007, 2011 and 2016), and will thus become traditional. It will also be held under the auspices of UNESCO - IHP, the Serbian Academy of Sciences and Arts, IAH, the Serbian Water Pollution Control Society, the Academy of Engineering Sciences of Serbia (AESS), IAWD, and ICPDR, and organized by the Jaroslav Černi Institute for the Development of Water Resources and WSDAC Center. We trust that this Conference, similar to the previous two, will be a significant contributor to improved groundwater management and the advancement of science in this field.

Chairman of the
Programme and
Scientific Committee

NOTES

SPECIFIC PROCESSES DRIVING THE USE AND PROTECTION OF ALLUVIAL GROUNDWATER

Prof. dr Milan A. Dimkić[1]

[1] *Jaroslav Černi Institute for the Development of Water Resources*

ABSTRACT

Groundwater provides the majority of public water supply. In Europe, 60-70% of the population relies on groundwater. In Serbia, the proportion is 70%. Groundwater also has a significant share of irrigation water supply. Given that more than half of the groundwater used for these purposes originates from alluvial environments, it is extremely important to study the processes that take place in alluvial aquifers.

The most important drivers of effective water management are:

- Economic strength of the country,
- Water abundance,
- Climate and any trend of change,
- Availability of knowledge and skills, and
- Governance.

Figure 1 is an inspiring way to understand the impact of the economic strength of the country and the abundance of water resources on the selection of the appropriate water management approach.

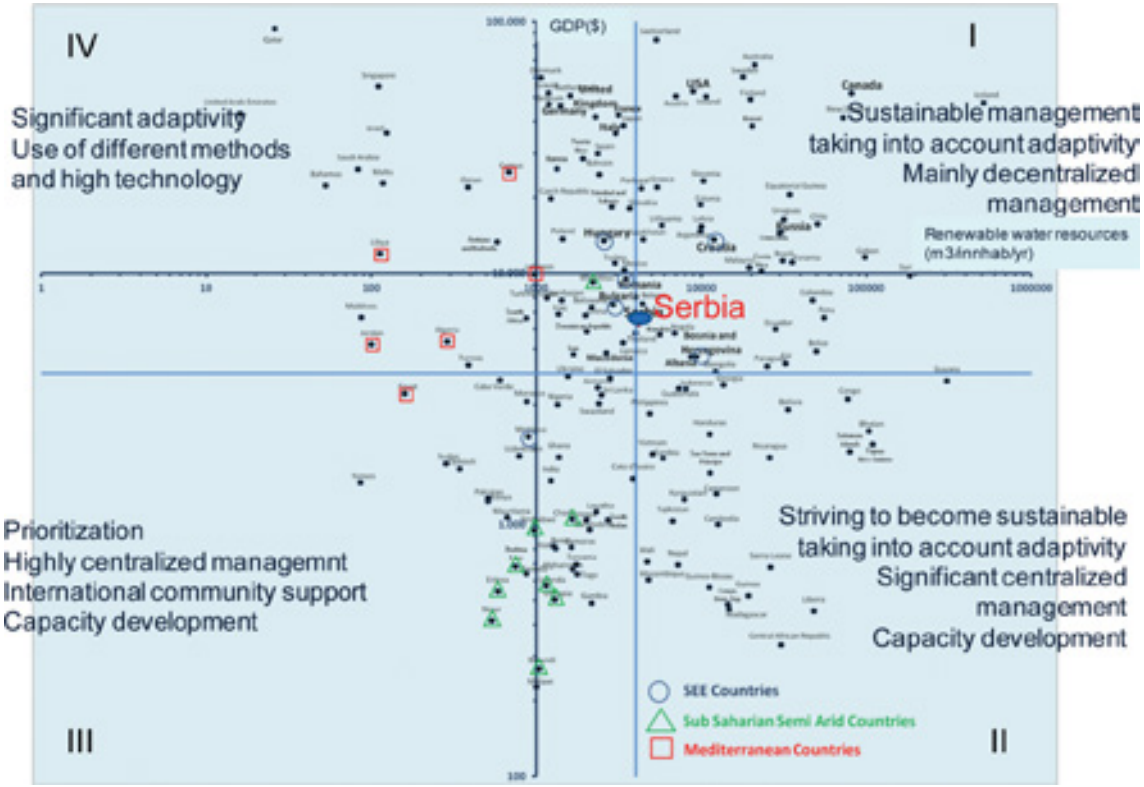


Figure 1: Economic strength and renewable water resources as indicators of the status of water management (Dimkić et al. 2011d)

These two parameters certainly affect the optimal nature of water management. The need to prioritize development is typical of developing countries and countries in transition, with moderate climates (generally part II of the diagram). In most cases, water sector development priorities include spending on the protection and use of water from alluvial aquifers.

The paper discusses the main general differences between the baseline quality of river water and oxic and anoxic groundwater.

Parameter	Surface water	Groundwater	
		Aerobic groundwater	Anaerobic groundwater
Total organic matter (COD, TOC, BOD and $KMnO_4$ demand)	Occurrence often a result of anthropogenic impact	Lower than in surface water; if present, related to dissolved solids	
Iron and manganese	Usually very low concentrations, except in eutrophic waters	Possible occurrence in low concentrations $C_{Fe} < 1$ mg/l	Occurs often in higher, even much higher concentrations than in surface water and aerobic groundwater
Dissolved oxygen	Often close to saturation point (approx. 9 mg/l)	Present in concentrations lower than saturation concentration	Virtually none $O_2 < 0{,}2$-$0{,}5$mg/l
Nitrates	Usually low concentrations (5-10 mg/l), except in polluted water	Basically occurs in low concentrations; high concentrations a result of anthropogenic impact	Usually none
Hydrogen sulfide	Usually none	Usually none	Present in stronger anaerobic conditions

Figure 2: Main differences between surface water and groundwater quality

The figure below is a simplified schematic representation of a characteristic section through the alluvion of a large river, showing largely aerobic aquifer conditions in the upper part of the river course and predominantly anoxic aquifer conditions in the lower part.

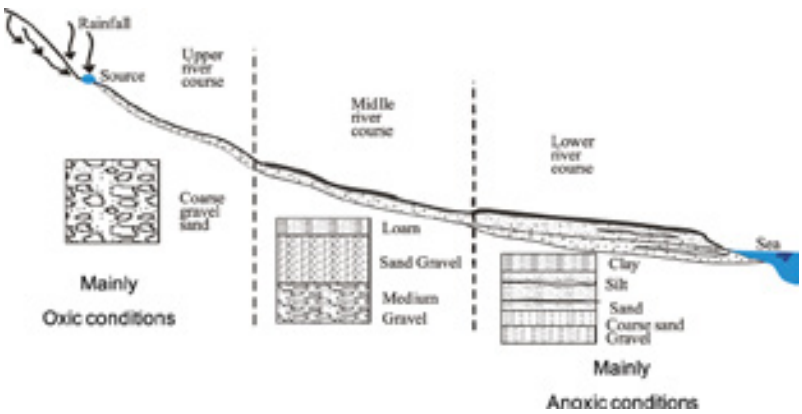


Figure 3: Change in grain-size distribution of an alluvial aquifer along a river course (Dimkić et al. 2011a)

As a rule, horizontal interbeds can be extremely important in terms of groundwater hydraulics, as well as for setting up and operating a water supply source (especially of the artificial recharge type). Figure 4 shows an artificially-recharged groundwater source, where a calcrete layer had enormously reduced the efficiency of infiltration. After this layer was removed, the capacity of the source was doubled.

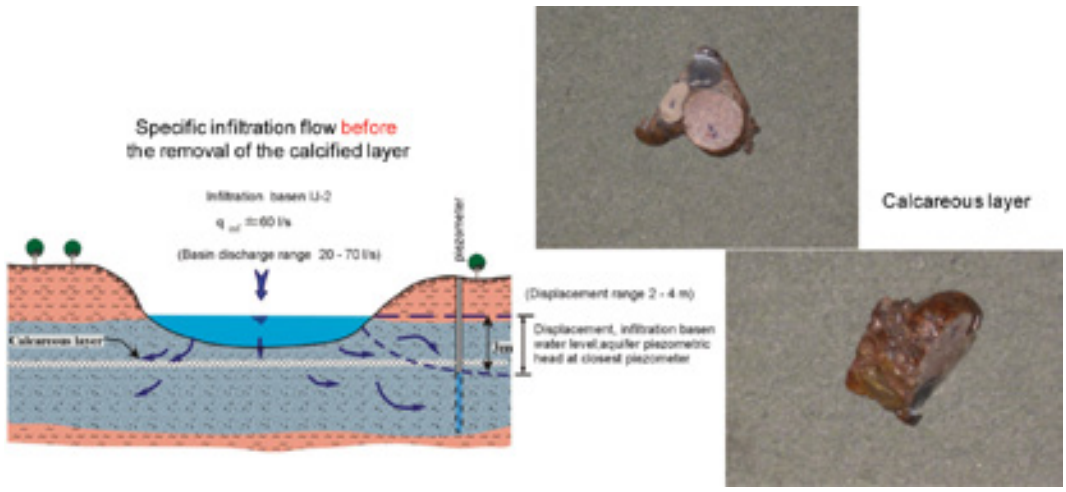


Figure 4: Schematic of infiltration before the calcareous layer was removed (Dimkić et al. 2007f)

Suboxic and anoxic aquifer conditions are result of oxidation of organic substances as well as minerals that contain bivalent iron (above all FeS_2).

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

origin $Fe^{2+} - e^- \rightarrow Fe^{3+}$

oxic state $C^{4+} - 4e^- \rightarrow C^0$

Thermodynamic prediction of the sequence of redox reactions in an underground environment (Boomer et al., 2008; Eh ranges from Millero, 1996)

Zone	Redox reaction	Redox pair	E h(mV)
Aerobic (oxic)	Aerobic degradation/ Oxygen reduction	O_2/H_2O	200 to 800
	Denitrification	NO_3^-/N_2	50 to 250 750)
Sub-oxic	Reduction of Mn (IV)	Mn^{4+}/Mn^{2+}	150 to 600
	Reduction of Fe (III)	Fe^{3+}/Fe^{2+}	-500 to 50
Anoxic	Sulfate reduction	SO_4^{2-}/H_2S	-650 to -200
	Methanogenesis	CO_2/CH_4	< -200

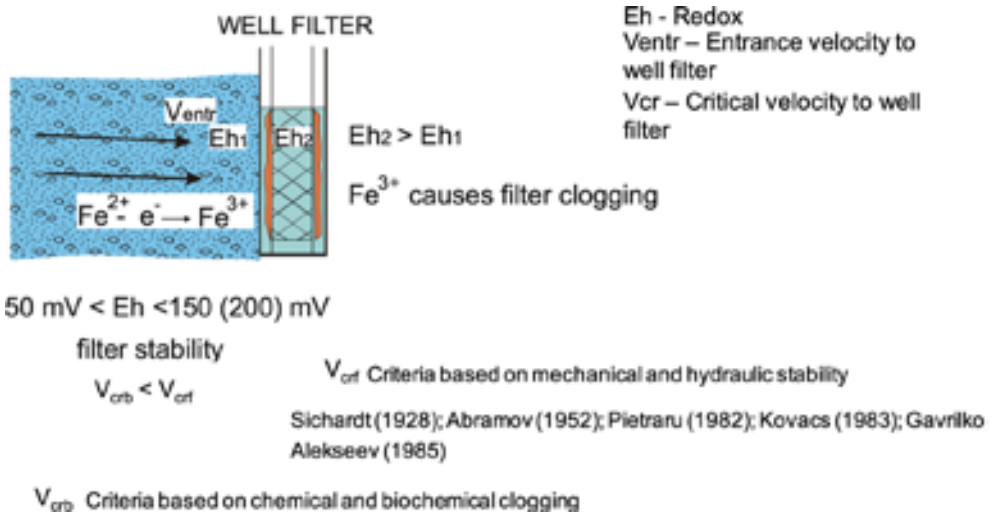
Figure 5: Sequence of oxidants depending on the oxic state /energy released during redox reactions

Incrustation of well screens with Fe3+ is an important consideration in the maintenance of alluvial groundwater sources. Under suboxic conditions, basically the biochemical process of sedimentation of

$$Fe^{2+} - e^- \longrightarrow Fe^{3+}$$

insoluble Fe^{3+} takes place on well screens, which leads to incrustation and ageing of the wells. Correlations are established between local hydraulic resistances (LHR) and the rate of change in LHR (KLHR) with physical and biochemical parameters:

$$LHR = LHR\ (Eh, Fe, v_{ent}, B, \Gamma ...)$$



A correlation is also established between these parameters and the critical entrance velocity at the well screen. The critical velocity is defined as the upper limit beyond which Fe^{3+} incrustation is much faster than the set criterion.

Figure 6: Well ageing driven by iron

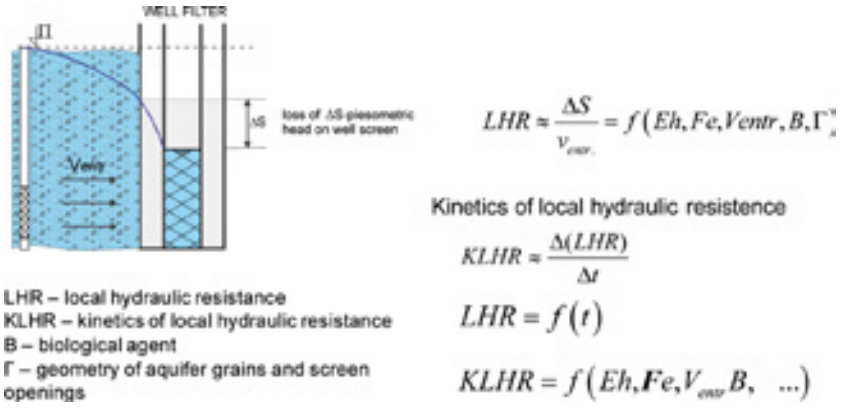


Figure 7: Well ageing driven by iron: kinetics of local hydraulic losses (KLHR) and oxic state indicators

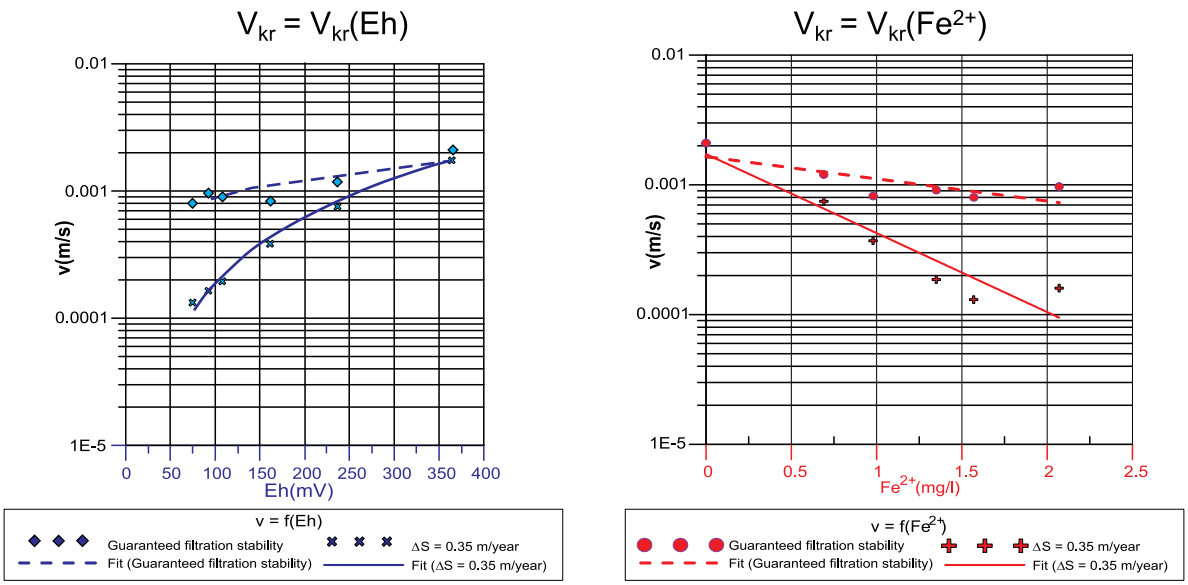


Figure 8: Well ageing driven by iron: critical velocities as a function of redox potential (Eh) and Fe^{2+} concentration in water

The correlations between the redox potential, mineral composition, grain-size distribution, chemistry and biochemistry of the aquifer, as well as the types of well encrustations, are important considerations and leave a lot of space for further research.

Proper definition of the capacity of a well in an intergranular alluvial environment and well screen entrance velocities is also very important in economic and functional terms.

The self-purification potential of an alluvial aquifer is based on a number of different processes.

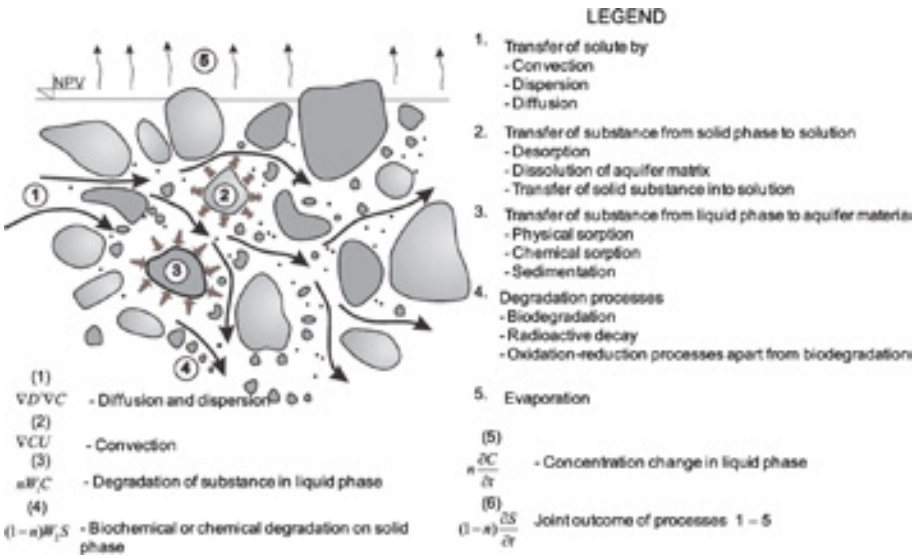


Figure 9: Schematic representation of various transfer and degradation processes (Dimkić et al 2007d)

In bank filtration, there are 3 or 4 phases in groundwater flow to the well (taking into account the oxic state of the groundwater).

Belgrade groundwater source is an example that illustrates effective purification by bank filtration.

Systematic monitoring of the water quality of large rivers – the Danube, the Sava and the Morava – as well as of corresponding bank-filtration wells was undertaken from 2009 to 2014.

Continuity equation of groundwater flow in an aquifer

$$\frac{\partial}{\partial x}\left(T\frac{\partial \Pi}{\partial x}\right)+\frac{\partial}{\partial y}\left(T\frac{\partial \Pi}{\partial x}\right)+\frac{\partial}{\partial z}\left(T\frac{\partial \Pi}{\partial z}\right)=\varepsilon\frac{\partial \Pi}{\partial t}-q$$

Continuity equation of substance travel in an aquifer

(1) (2) (3) (4) (5) (6)

$$\nabla D'\nabla C-\nabla CU-nW_1C-W_1(1-n)S=n\frac{\partial C}{\partial t}+(1-n)\frac{\partial S}{\partial t}$$

Sorption equilibrium equation

$$S=S(C) \Longrightarrow S=b*C$$

Sorption rate equation

$$\frac{\partial S}{\partial t}=f(S,C)$$

Figure 10: Groundwater flow and substance transport equations

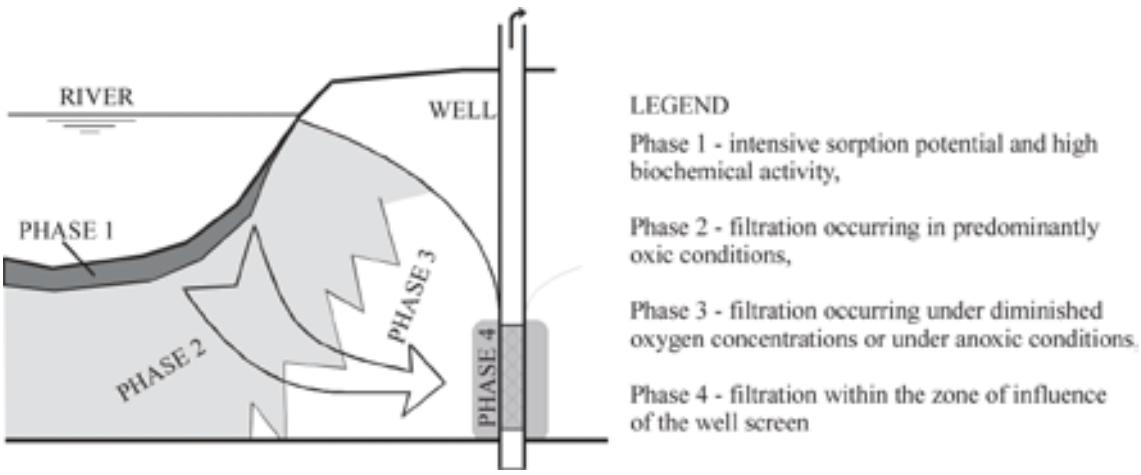


Figure 11: Phases of groundwater flow from the river to the well (bank filtration) (Dimkić et al. 2011a).

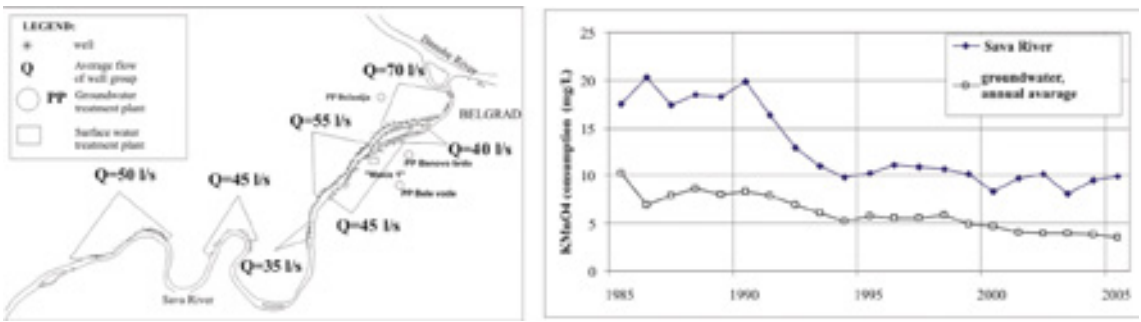


Figure 12: Belgrade groundwater source: radial wells along the Sava River and estimated monthly average concentrations of $KMnO_4$ in the Sava River and extracted groundwater (composite raw water) (JCI, 2010)

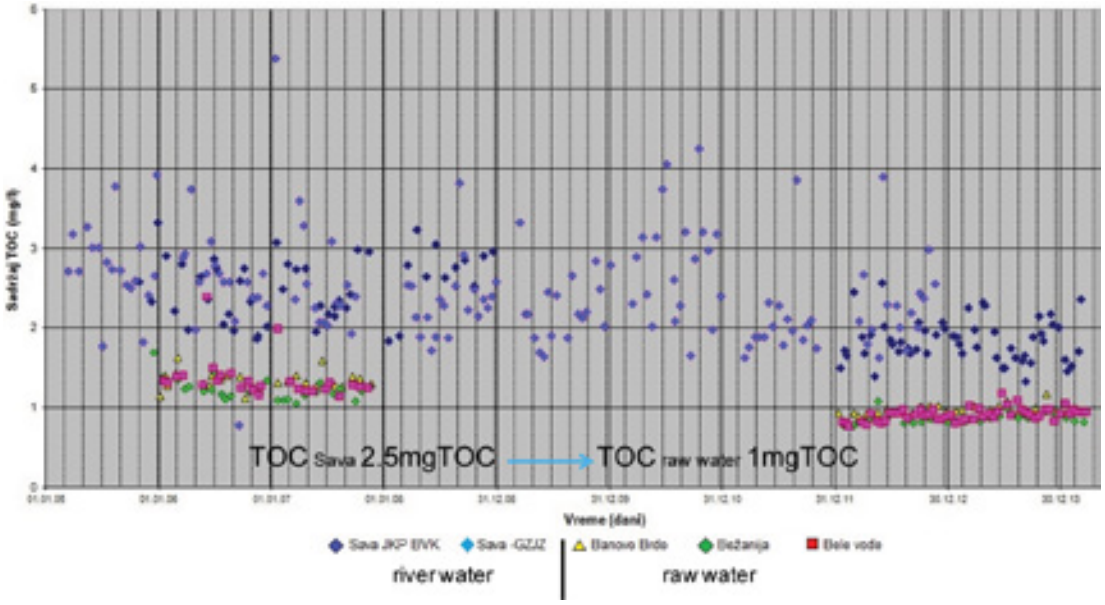


Figure 13: DOC variation in the Sava River and at Belgrade groundwater source

The analyses of surface water and groundwater samples attest to considerable purification effects of filtration through the alluvial aquifer. Belgrade groundwater source and several other large alluvial aquifers in Serbia were used here as examples. The direction of transformation of river water quality in the aquifer is towards achieving the baseline groundwater quality.

In the late 1980's the Ibar River (tributary of the Zapadna Morava, Serbia) was often heavily polluted by phenols. The groundwater source of Žičko Polje near the City of Kraljevo, which relies on the Ibar River, was especially threatened. In search of a solution, phenol tests in terms of sorption and degradation under oxic aquifer conditions (Eh ~ 350-400 mV, O_2 ~ 4-6 mg/l) were undertaken in situ.

In the first test, NaCl and phenol solutions were injected at a distance of 22 m from the test well. The test showed that the phenol did not sorb within the aquifer.

Figure 14: Analysis of surface water and groundwater quality in Serbia (2009-2014): sampling locations

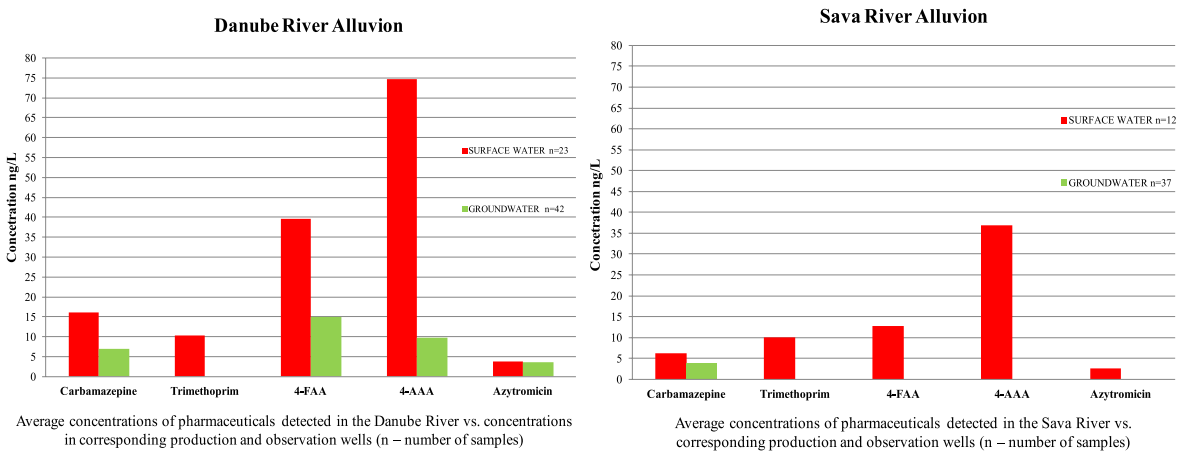


Figure 15: Overview of concentrations of pharmaceuticals in surface water and groundwater in Serbia (2009-2014)

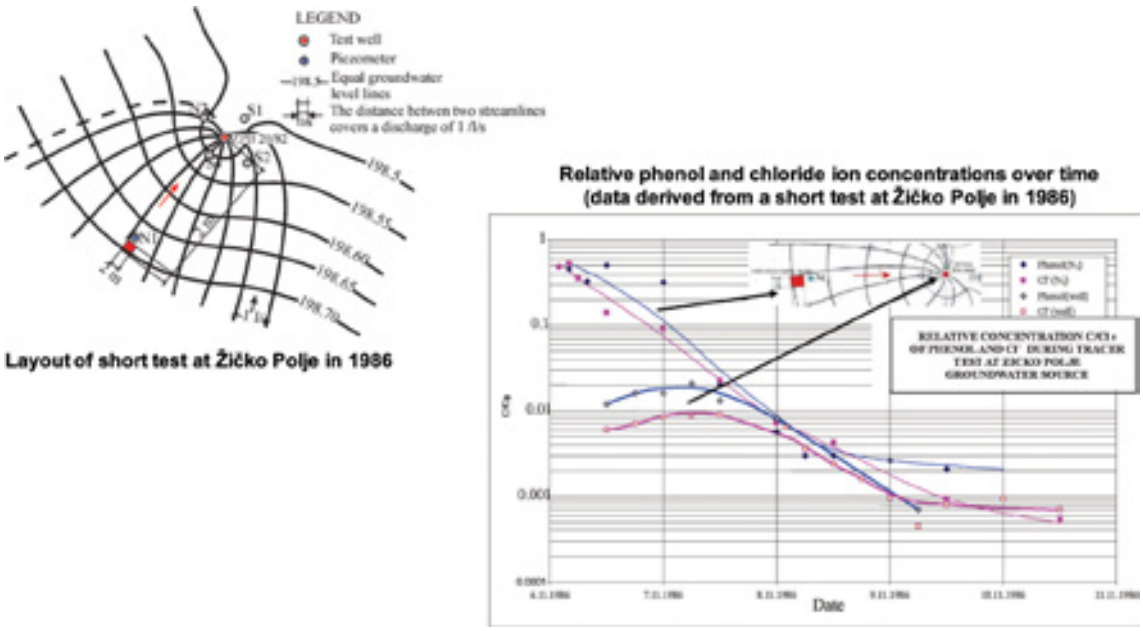


Figure 16: Phenol degradation: short test to determine phenol sorption (JCI, Belgrade, 1987)

A long test to determine phenol degradation in aerobic conditions was undertaken in the period 1991-1995. An infiltration pond and drainage well (B-3) well emplaced in the direction of groundwater flow. They constituted a closed water body into which NaCl and phenol solutions were injected. The phenol degradation half-time was found to be 3-5 days (for concentrations of about 20 µg/l). Phenol degradation products were also identified.

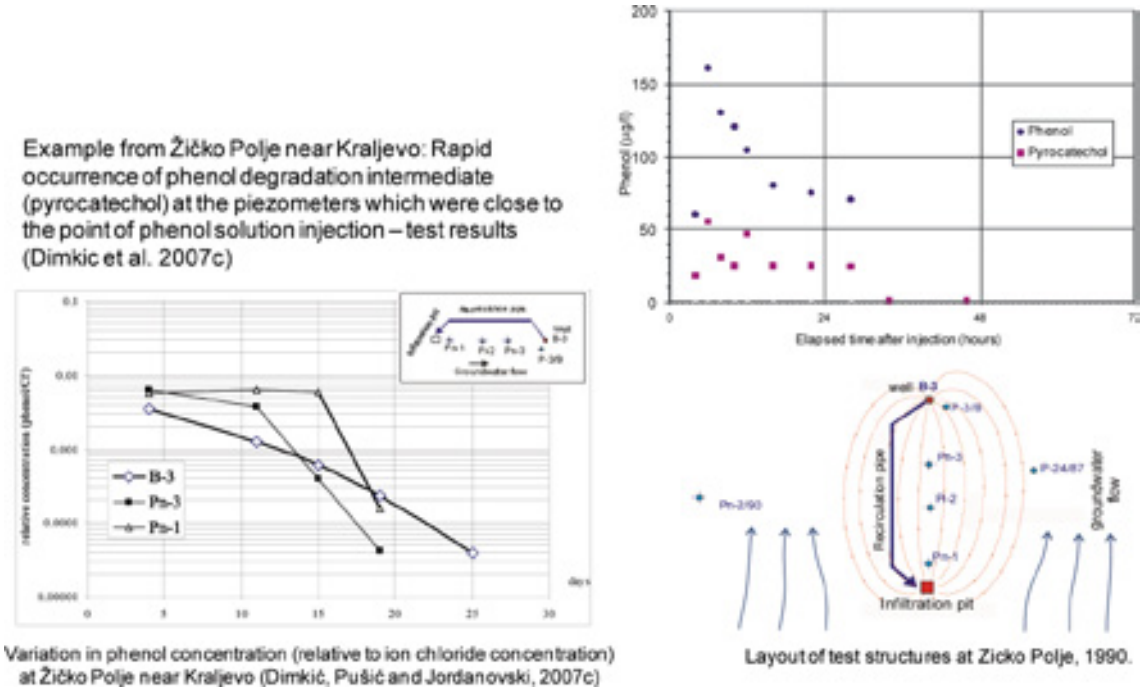


Figure 17: Long phenol and chloride transport test in aerobic conditions (Dimkić et al.2007c)

Given the importance of alluvial aquifers as valuable water resources for certain types of habitats (wetlands, forests, farmland), this is an overview and an introduction to a series of papers to be presented at the Conference. Following is a non-exhaustive list of questions pertaining to alluvial aquifers, which leaves a lot of space for present and future research:

- Further study of the correlation between well incrustation rate and intensity, on the one hand, and well screen entrance velocity, chemical composition of water, aquifer matrix grain-size distribution and mineral composition, and quality of the microbiological agent,

- Issues associated with well design, quality of extracted water, site-specific potential well discharge capacity, and well screen entrance velocity criteria (chemical and biochemical), as well as related design parameters,
- Issues associated with the present status and predicted oxic state of the aquifer,
- The impact of the aquifer's origin on its properties in terms of groundwater extraction and protection,
- The effect of glacials and interglacials on the origin of a groundwater source,
- Mineral oxygen demand,
- The effect of calcrete and other semi-permeable layers on the development of artificially-recharged groundwater sources,
- The impact of fertilizer application on groundwater and river water quality, depending on the oxic state of the aquifer, etc.

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SUSTAINABLE DEVELOPMENT OF KARST AQUIFERS IN THE MEDITERRANEAN BASIN AND ADJACENT AREAS FOR WATER SUPPLY: AN OVERVIEW

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Keywords: karst aquifer, water supply, engineering, vulnerability, sustainability

INTRODUCTION

The soluble karstic rocks occupy approximately 20% of the planet's ice-free land, of which around 10-15% is extensively karstified; however, the contribution of karstic aquifers to the world's potable water supply is higher, in magnitude of 20-25%. The Mediterranean basin and the adjacent areas are characterised by abundant but still not fully utilised karst groundwater reserves. Although some authors (Margat, 1998) estimate that carbonate outcrops cover at least 15% of the Mediterranean surface and that carbonate aquifers provide for at least 25% of the domestic water supply - not counting industrial, agricultural, and tourist consumption - our assessment is that these two figures should be increased by at least 5-10%, respectively. This has been confirmed by the on-going WOKAM project (World Karst Aquifer Map), conducted by a team of experts of the International Association of Hydrogeologists (IAH) and the German Geological Survey, and supported by many local experts as well (Goldscheider, Chen, et al. 2014).

KARST AQUIFER REGIONALISATION

This part of Europe is considered the classical karst region; not only was the term "karst" coined in this area (the German derivation of the local name "Carso"), but a new scientific discipline – karstology – was also established there at the end of the 19th century by a group of researchers led by Jovan Cvijić (1893).

The Mediterranean karst was created in the Tethys sedimentary basin and it includes three sub-groups: Littoral, Hilly-Mountains and High Alpine karst. The islands (Mallorca, Malta, Sicily, Sardinia, Corsica, Crete, etc.), shorelines and adjacent coastal areas of Northern African and Near East countries, Turkey, Greece, Albania, former Yugoslavia, Italy, France and Spain belong to the Littoral group. In the Iberian Peninsula, the major Hilly-Mountains structures with carbonate and evaporitic rocks are found in Andalucía and Murcia provinces in the South (e.g. Sierra Morena, Sierra Nevada), as well as in the Pyrenees and its foothills. In Southern France they are: Massif Central, Provencale Mts. and the Alps, which consist predominantly of carbonate rocks. The Apennines are a major Italian reservoir of karstic waters, while SE Europe has large karstic aquifers in the southern Alpine branches and mountain ranges that surround the basin: Dinarides, Pindes, Hellenides, Carpathians, Taurides massifs (Fig. 1). High Alpine karst extends over the central Alps. In the Eastern Mediterranean and in Northern Africa there are two types of structures: platform, slightly deformed karst, often covered by younger sediments (e.g. Bekaa Plain in Lebanon or Cyrenaica in Libya) and orogenic karst of the mountain ranges. Structures such as Lebanon Mountains (Jebel Liban) and Atlas Mountains in Algeria and Morocco (A. Tellien, A. Saharien, Haut, Moyen and Anti Atlas) belong to the latter group.

Bakalowicz (2015) distinguishes three major events which caused the development of specific karst drainage structures that produced the various characteristics of Mediterranean carbonate aquifers:

- the Messinian Salinity Crisis (MSC) at the end of the Miocene (5.9 to 5.3 Ma), which caused rivers to incise deep valleys in order to reach the remaining sea, 1500–2500 m below the present sea level;
- cold periods during the Quaternary that caused weathering of the epikarst, even its destruction, which led to the development of a thick sediment cover above the elevation of 1000 m; and
- post-Miocene tectonics that generated hydrothermalism and deep CO_2 flux, causing continental sediments to fill in the large basins in compressional environments.
- During MSC thick gypsum and salts were deposited in numerous small isolated hypersaline basins while along today's French coast very deep, now submerged, canyons were created as a result of intensive karstification and much deeper position of the erosional base level. One of such submarine canyons, more than 300m deep, is evidenced in Cassidaigne near Marseille (Gilli, 2001). Such deep karstification resulted in the fact that today over 90% of all the known submarine springs in the world are located in the Mediterranean basin (Fleury et al., 2007).

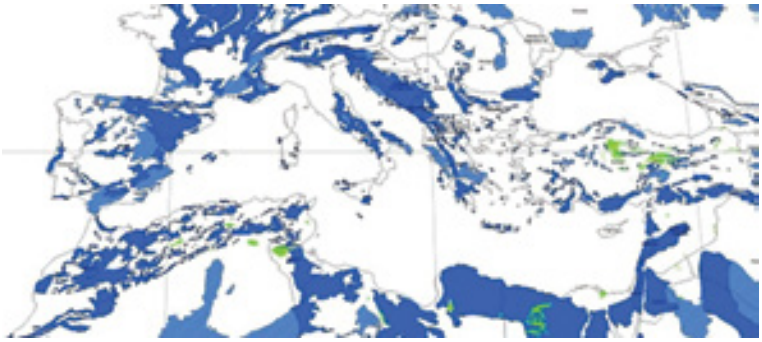

Figure 1: A part of the preliminary WOKAM map: Karst distribution in the Mediterranean basin and adjacent areas

- Mediterranean karst is very rich in various surficial and underground features. The mountain karstic relief is dissected by numerous karstic poljes and wide valleys and characterized by rough relief, steep slopes and highly folded rocks. For instance, the Dinarides contain all types of karst landforms and features (Cvijić, 1893; Herak, 1972; Stevanović 2009). As an example, the number of sinkholes (dolines) in certain Dinaric areas can reach 150/km^2; the world's largest karst polje, Livanjsko Polje, covers the area of 380 km^2; Herak (1972) confirmed that more than 12,000 caves have been explored in former Yugoslavia alone, more than 5,000 being in Croatia. At the Kameno more („Stone Sea") and the Orjen Mountain above the Bay of Kotor (Montenegro), more than 300 vertical shafts were registered within an area of only 8 km^2, with depth of 200-350 m (Milanović, 2005).
- In areas where karst is overlaid by younger sediments, the karstification may continue to occur hypogenically, depending on the faulting and fissuration and equally on the presence of thermal and CO_2 fluxes. In areas where karst is overlaid by younger sediments, In some parts of Tunisia or Algeria (Intercontinentale Calcaire), several very deep karstic structures of Upper Cretaceous or Paleogene ages, tapped by deep wells, represent the single source of water supply. Due to temperature which sometimes exceeds 50-600C, this water must be cooled before being delivered to consumers.

The climate conditions in the Mediterranean basin are quite diverse: from glacial karst at the top of the Alps to the semi-arid and arid karst in North Africa. The karstified rocks recharge predominantly from precipitation, and average infiltration rate can be very high (e.g. in certain karstic areas: 38% in Algeria, 53% in Tunisia and Israel, 69-78% in Italy; from Stevanović, 2015a). In addition to this, many perennial or temporary streams sink their waters into ponors located in karstic terrains. This is why more than 50 kilometres of riverbed of the largest European sinking stream, Trebišnjica, have been regulated in the 1970s. Prior to that, Popovo polje was almost completely dry for more than 150 days per year.

DRAINAGE AND UTILISATION OF KARST AQUIFERS

Many of the world's largest springs are draining Mediterranean karstic aquifers. The "king" among them is Fontaine du Vaucluse, in Southern France. The spring is not the world's largest if we consider its capacity – its average discharge is 20 m3/s – but it became the locus typicus for all the world's ascending springs outflowing from lake-like structures (they are now called vauclusian). Marseille and other coastal towns heavily depend on karstic springs, but the mixing of fresh and saline water represents a major problem. This is why many specific intake structures have been constructed (e.g Port Miou, Potié et al. 2005).

In Italy, there are a few hundred large springs (Fiorillo, 2009). Perhaps the most famous and largest spring on the Northern Italian coast is Timavo, which supplies water to Trieste (average discharge Q=30 m^3/s). This is a group of springs discharging at or below the sea level, and one of the first tracing experiments in the

world proved their connection with the sinking Reka River, on the Slovenian side of the border. During certain periods, the ancient Rome was supplied with 13 m^3/s of mostly karstic waters from several aqueducts, of which Aqua Marcia, constructed in the 2nd century BC and 90 km long, was one of the first (the Aniene catchment). Today, the city of Rome obtains more than half of its water from the karstic spring Peschiera (Q_{av}=18 m^3/s). Large cities in Southern Italy such as Naples and Bari are also supplied from large karstic springs such as Caposele, Serino, etc. (Fiorillo et al. 2015).

Along the Adriatic and Ionian coastal areas there are plenty of springs and their position had dictated the establishment of ancient settlements and – later on – big Roman cities (Split –Spalato, Dubrovnik – Ragusa, etc.). As such, Rižana karstic spring (Q_{av}= 4 m^3/s) is the main water source for all Slovenian coastal cities, while Riječina spring along with Zvir gallery is supplying potable water to Rijeka city and port (Q_{av}= 8 m^3/s). Jadro spring (Q= 0.5-70 m^3/s) supplies drinking water to Split, while Ombla spring (Q= 2.3 - >150 m^3/s), with >90% of its catchment in the neighbouring Bosnia and Herzegovina, represents the main water source of the city of Dubrovnik. The two latter springs are good examples of the importance of local barriers that prevent mixing of fresh karstic and sea waters (Fig.2). These local barriers, present in many locations along the coast, consist of impervious flysch sediments, and their existence increases the chances of avoiding the mixing of waters. In case of Jadro spring the barrier is high, almost 50m above the sea level, while in the case of Ombla the contact between Eocene flysch and Cretaceous karstic aquifer occurs at the altitude of only 2.3 m. Some other springs along the Bay of Kotor in Montenegro are discharging at or below the sea level as submarine springs, but their upper channels can activate an overflow during the periods of flooding. Such is the case of Sopot spring, one of the world's largest springs as regards maximal discharge (Q_{max} > 150 m^3/s), or Ljuta spring (Radulović, 2000). Before the new system was constructed (Bolje Sestre spring, Stevanović, 2015b), supplying water from the Skadar basin, the city of Kotor had used water from the Škurda spring, which issues directly at 0,0 +/- few cm. asl. As a result, and depending on the pressure in the aquifer, the local population had consumed water that was always more or less brackish. The situation is not much different in the case of Almyros, the largest spring on island Crete in Greece, which supplies Heraklion with potable water. The spring issues at the elevation of 5 m asl, but the deeper part of the aquifer is under the strong influence of salt. The spring discharge varies from 3.3 to 30 m^3/s and the problem with salinity starts with the discharge lower than about 15 m^3/s (during the minimal yields, concentration of the Cl ion reaches 6 g/l). The concrete dam constructed at the discharge point in order to increase the fresh water level only partly mitigates the problematic brackish flux (Mijatović, 2005).

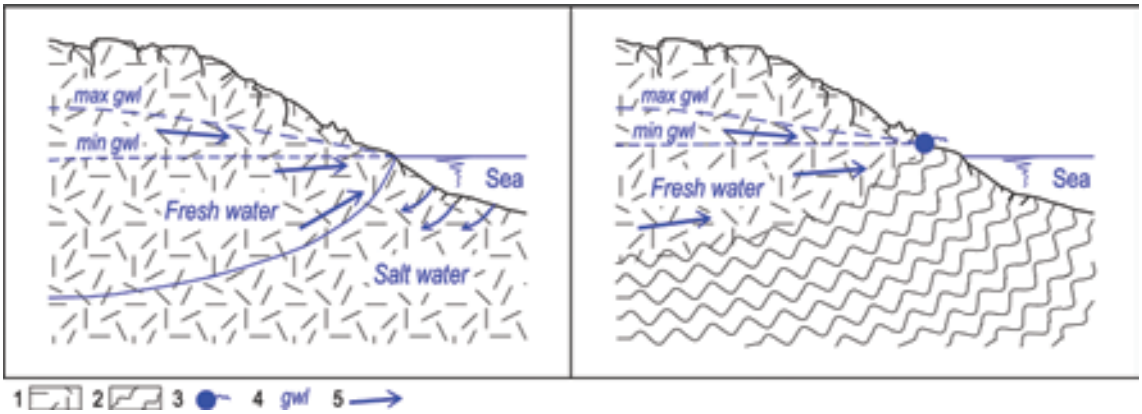

Figure 2: Left: Direct interface between fresh and salty water; Right: Flysch barrier is preventing the mixing and dictates the position of the spring which drains fresh waters from the karstic aquifer. Legend: 1. Karstic aquifer, 2. impervious flysch sediments, 3. spring, 4. groundwater level, 5. groundwater flow direction

Similarly, many coastal water intakes in Libya and Tunisia have faced saline intrusions due to forced over-pumping. In contrast, the Bistrica group of springs in Albania (including the well-known “Blue Eye” spring) has an impervious barrier at over 100 m asl. With its minimal discharge of 12 m^3/s (Eftimi, 2010), it is becoming a candidate for water export to the Puglia province in Italy through a 70 km-long overseas pipeline.

Concerning the spring discharge, of the 124 large springs in this wide region which are included in WOKAM database, 28 or 1/5 have a minimal discharge greater than 2 m^3/s which represents key evidence of water availability. The largest is the famous Dumanli spring in Turkey (38 m^3/s), nowadays impounded by the Oymapinar reservoir. As regards regional distribution, the largest number of springs regularly discharging over 2 m^3/s are in Bosnia and Herzegovina (8) and Turkey (8), followed by Montenegro (5).

In terms of proportion of karst waters in water supply systems, Montenegro, with over 75%, and Austria, with over 50%, are the leaders in the region. In some other countries (Italy, Croatia, Slovenia, Bosnia and Herzegovina, Turkey) the percentage is lower but still considerable. The population of six capitals in the wider Central and Eastern Mediterranean region consumes water exclusively or dominantly from karst (Vienna, Rome, Sarajevo, Tirana, Podgorica, Skopje). The population of neighbouring countries such as Bulgaria, Serbia and Romania also uses a considerable percentage of karstic sources for national potable water supply (ca.15-20%). However, the availability situation is not favourable everywhere, and over-extraction is present in Lebanon, Morocco and Syria. In the latter country, one of the largest springs – Ras el Ain – has completely dried out as a result of forced pumping for irrigation on the Turkish side of the border. This is just one of the many examples indicating the importance of sustainable transboundary water management. Moreover, engineers and water managers are facing many problems in their attempt to ensure water provision: due to the unstable regime of karstic springs, the main challenge for most of the waterworks is to overcome water shortage during recession periods, which coincide with summer and early autumn months when consumption is also at its highest. Several successfully completed projects based on utilisation of groundwater from considerable storage in the deeper parts of aquifers provide a new prospect for development of aquifer systems in many locations, as has been done in Lez (Montpellier, France) and Bolje Sestre (the Montenegrin coast).

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. In the event that pollutants do exist, extremely vulnerable karstic aquifers with low attenuation capacity require special protection measures which, in some cases, may result in imposing four or more protection zones with different preventive measures.

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NOTES

GROUNDWATER IN THE DANUBE RIVER BASIN: IMPORTANCE FOR DRINKING WATER SUPPLY AND POLLUTION BY HAZARDOUS SUBSTANCES

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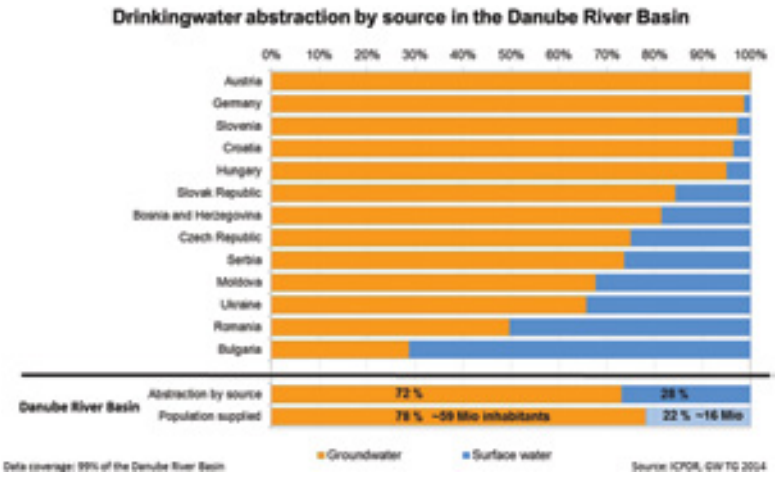
Abstract: Groundwater is the major drinking water source in most Danube countries and therefore of utmost importance requiring protection from pollution and over-use. Nearly 72% of all drinking water in the Danube River Basin is produced from groundwater, supplying at least 59 Mio of the in total 79 Mio inhabitants. The remaining 28% of the population is served from surface water. 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 varies considerably and ranges from 100% (Austria) to 30% (Bulgaria).

Keywords: Danube River Basin, ICPDR, groundwater quality, hazardous substances, pollution, water framework directive, groundwater directive.

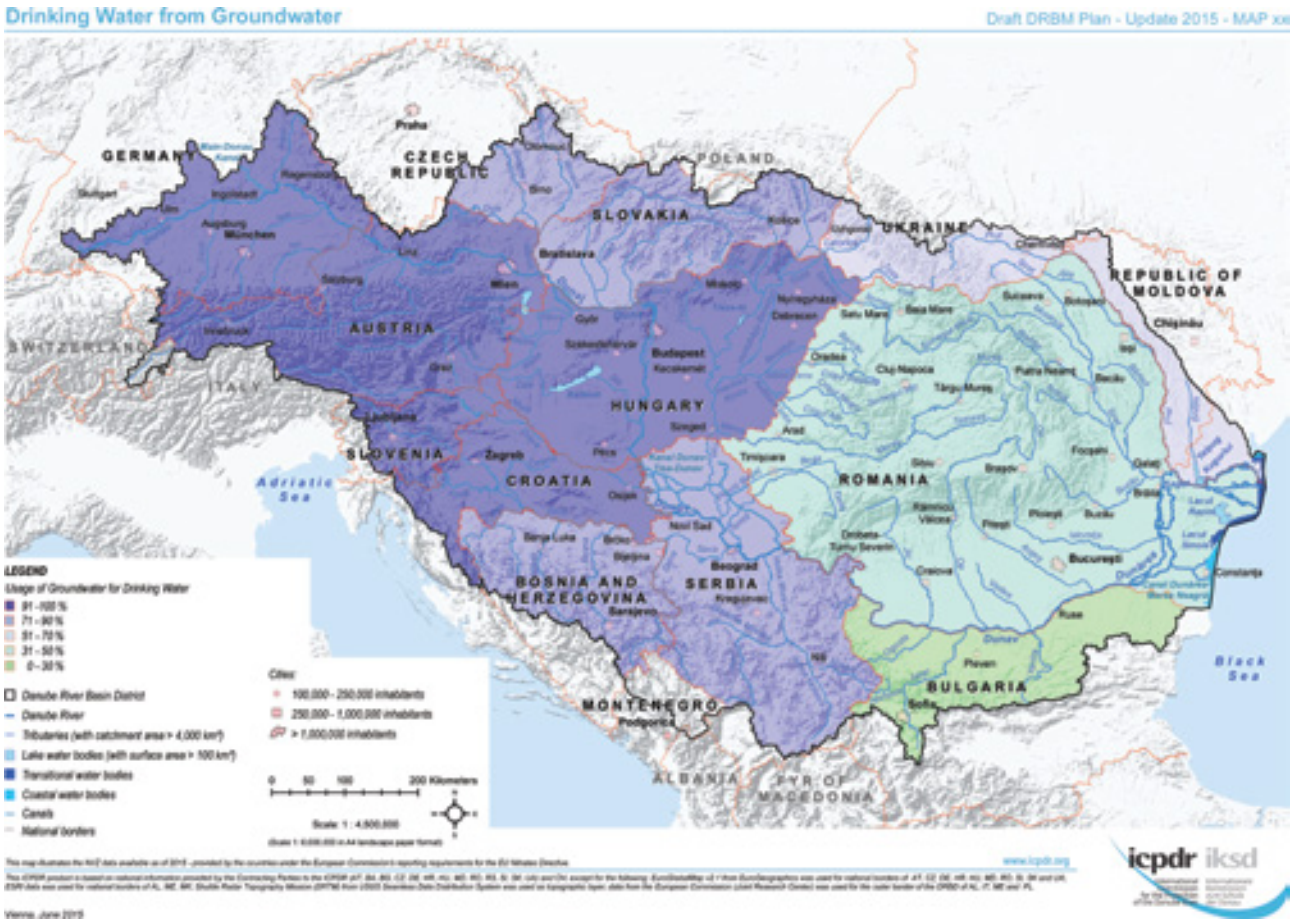


Apart from the aspect of groundwater as a source for drinking water, it is also an important source for agricultural production, industry and thermal uses. Furthermore, it plays an essential role in the hydrological cycle, being critical for the maintenance of wetlands and feeding river flows. It acts as an important buffer during dry periods and it provides base flow to many surface water systems.

The connection between surface water and groundwater is frequently utilised in the form of abstracting bank filtered water for drinking water purpose, making use of the natural purification and filtration properties of the underground along the pathway from the river to the abstraction well. An inventory of the approximately 40 most important and largest bank filtration abstractions along the Danube River demonstrated that about four Mio inhabitants are actually served and an additional five Mio people could be served (considering the permitted annual abstractions). Hence, in this context it is not only the quality of groundwater which is crucial but also the quality of the surface water potentially affecting the health of the human population living in the Danube Basin.

The Water Framework Directive (WFD, 2000/60/EC) is the central legislative tool for comprehensive management and protection of fresh surface and groundwater, coastal and transitional waters in the European Union, considering protection and safeguard of legitimate uses of water and the protection of ecosystems which are associated or dependent to this water. It follows a river basin approach and requests for a system understanding where the level of detail/understanding is depending on the significance of the pressures and

of the importance of the water body (risk based approach) to focus efforts in a targeted and cost efficient way. The WFD requires the setting and achievement of environmental objectives and the establishment and cyclic update of River Basin Management Plans including their programmes of measures to achieving the objectives by a set deadline.



Within the Danube River Basin District all countries co-operating under the Danube River Protection Convention (also the non EU Member States) decided to make all efforts to implement the WFD throughout the whole basin and to prepare a common River Basin Management Plan (RBM Plan). The International Commission on the Protection of the Danube River (ICPDR) serves inter alia as the platform for the elaboration of such plans, focusing efforts and activities on aspects of basin wide importance. Therein, groundwater aspects are covered by the Groundwater Task Group which was established in the process of WFD implementation.

The River Basin Management Plans (RBMP), which had to be established in 2009 for the first time, provide an excellent overview of the chemical and quantitative status of groundwater and the factors threatening their status within the European Union. By the end of 2015 the second RBMP for the Danube River Basin District was published by the ICPDR. Regarding groundwater, the pressures on the bilaterally agreed eleven groundwater bodies of basin wide importance (which are formed by 59 individual national groundwater bodies) had not changed since 2009. Nitrates from diffuse sources are still key factors posing significant pressures on groundwater chemical status and over-abstraction is the key pressure affecting good quantitative status.

Beside nitrate as the dominating factor of threatening good chemical status of Europe's groundwater also various hazardous substances are causing significant groundwater pollution. Again, the RBMPs provide an excellent source of information for identifying most relevant hazardous substances. An analysis of all substances reported to WISE (Water Information System Europe) causing failure of achieving good chemical groundwater status within the Danube River Basin was performed on the basis of the first cycle RBMPs (2009–2015).

From the 722 groundwater bodies in the Danube River Basin District 153 (21%) groundwater bodies were failing good chemical status and 54 (7%) groundwater bodies due to hazardous substances. In total 32 different hazardous substances (six naturally occurring and 26 synthetic) in 6 Member States are causing poor groundwater chemical status of at least one groundwater body in the Danube River Basin. Further indication of hazardous substances being considered relevant are those posing a risk of failing good chemical status. For those substances groundwater threshold values and appropriate measures have to be established. A respective

analysis identified another 51 substances/indicators (pesticide substances, metabolites, hydrocarbons or other synthetic substances) where groundwater threshold values have been established and which are posing a risk of failing good groundwater chemical status.

A further strong indication of the relevance of hazardous substances gives national legislation which implements Article 6 of the Groundwater Directives, identifying all those nationally relevant substances or groups which have to be prevented from entering groundwater.

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NOTES

RAPID AND SLOW RECHARGE TO THE DEEP KARST AQUIFERS OF THE GRAND CANYON REGION

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Abstract: The Colorado Plateau of the southwestern United States is comprised of multiple stacked sedimentary rock aquifers, some of which have depths to water exceeding 1,000 m below land surface. Recharge to these deep, regional aquifers supplies springs discharging in the Grand Canyon and adjoining areas. One spring is the main water supply for Grand Canyon National Park, which received over 5 million annual visitors. Previous regional studies only determined recharge with annual or decadal water balance estimates and approximations from numerical modeling techniques. Recent studies are designed to observe and measure the temporal and spatial variability of fast and slow recharge in this arid to semi-arid region. Winter precipitation is typically distributed into frontal storms dominated by snow, while convective thunderstorms prevail in summer monsoon rains with dryer periods occurring in spring and fall seasons. Precipitation increases with elevation in the region. Recharge is episodic and focused through enhanced permeability faults, fractures, and dissolution enhanced features. A precipitation derived chloride mass balance study defined the seasonality of slow recharge by precipitation and the magnitude of recharge dependent on vegetation cover type. This study demonstrated the importance of upland forest vegetation management in influencing the timing and magnitude of recharge. A qualitative tracer study coupled with detailed measurements of temperature at springs emanating from the deep regional aquifers is helping to determine the locations and travel times of fast recharge focused in sink holes. These measurements indicated travel times of a few days from spring snow melt entering sinkholes on the surface of the Kaibab Plateau to discharge at springs over 1,000 m deep and 1,000's of meter lateral flow. Together, these studies show that previous estimates of uniform spatially distributed, mean annual estimates of recharge in this region do not adequately reflect observation and direct measurement of recharge. These improvements in fast and slow recharge measurements are laying the foundation for construction of models with better spatial and temporal resolution of recharge and improved management of limited groundwater resources.

Keywords: Recharge, Grand Canyon, Karst, Dye Tracing, Chloride Mass Balance

INTRODUCTION

Although nearly 25 % of the Earth's surface is karst, studies on the recharge and travel processes of karst aquifers with steep hydrologic gradients are limited. Deep karst aquifers are important for providing baseflow to local and regional streams and providing downstream water supplies. Limited studies indicate that karst aquifers are unique in having both fast flow from recharge events, on the order of days to 10s of days (Spangler 2001, Lauber and Goldsheider 2014), and slower flow from areal recharge on the order of seasons to years. While the connection between watershed land cover and the magnitude and timing of surface water flows has long been recognized (Bosch and Hewlett 1982, Robles et al. 2014), recent studies have highlighted the importance of ecosystem health in the contributing area of an aquifer for reliable groundwater resources (Wyatt et al. 2014). In many parts of the world, land use and land cover change from factors such as agriculture, forest management, climate change, and fire suppression have altered ecosystem health with potential impacts on groundwater supplies. Discharge from karst aquifers has been shown to be more sensitive to perturbations in water quality due to the combination of fast- and slow-flow contributions (Vesper et al. 2001).

Grand Canyon National Park (GRCA) is a large karstic system in northern Arizona, USA. Second to the Everglades National Park in Florida, it contains the largest karst surface in the US National Park system, with over a million hectares classified as karst or possible evaporate karst (Weary and Doctor, 2014). The area is a snowmelt dominated karst system, meaning the majority (over 60%) of snow precipitation occurs during late fall through early spring, and enters the groundwater system during late spring and summer. Runoff and precipitation infiltrates the Kaibab Plateau through faults, fractures, and sinkholes (or "parks"). Sinkholes are formed via open vertical joints, or by the chemical dissolution of Kaibab evaporites (Hill and Polyak, 2010). The density of the sinkholes on the Kaibab Plateau are between three and five sinkholes for each squared kilometer. Once the groundwater enters the subsurface, however, the hydraulics of the karst aquifer are poorly understood. Groundwater flow is able to cross faults and even move opposite to dip, making aquifer properties and groundwater flow patterns difficult to establish.

As groundwater moves downward through the strata of the Kaibab Plateau, it travels through shallow perched aquifers such as the Coconino Aquifer (C-aquifer), which consists of the Coconino Sandstone Formation, and finally to the Redwall-Muav Aquifer (R-aquifer). The R-aquifer consists of both Redwall Limestone and Muav Limestone, the main karst horizons in the Grand Canyon stratigraphy (Hill and Polyak, 2010). Most groundwater discharges from springs in the R-aquifer, perched above the Bright Angel Shale, which acts as an aquitard. Water is discharged in the form of springs, often from hydrologically active unconfined caves. One such example is Roaring Springs, located at the meeting of two faults in the canyon wall in the Muav Limestone (Hill and Polyak, 2010).

The Kaibab Plateau is a classic representation of a snowmelt-dominated karst aquifer system. Snowmelt runoff and precipitation infiltrates the Kaibab Plateau rapidly via sinkholes, faults, and fractures and slowly through diffuse infiltration. Once in the subsurface, it travels hundreds of meters vertically before moving laterally through the karst system in the North Rim's R-aquifer (Brown 2011). We describe recent studies to measure fast and slow recharge to the deep regional aquifer of the Grand Canyon region.

METHODS

Fast recharge was measured with dye tracer studies and slow recharge was measured with a chloride mass balance technique. The artificial dye component of this study began with the introduction of two dyes into two different sinkholes within the boundary of GRCA in April 2015. However, the dye insertion occurred after peak snowmelt, and never discharged from the aquifer in 2015. Two additional dyes were introduced into two separate sinkholes on the Kaibab Plateau in the U.S. Forest Service land in February 2016. The two 2016 dyes are different than the 2015 dyes, so all four dyes can be differentiated from each other when they emerge in springs. The dye introduction sites were chosen based on their inclusion within bounding faults of the Roaring Springs contribution area. Dye insertion at sinkholes was preferred, because these sites carry the dye directly into active conduits. Because this is a snowmelt dominated system, the dye was introduced in late February of 2016.

To qualitatively monitor the connectivity of the two sinkholes with springs, charcoal packets have been placed at 23 springs, representing possible discharge locations since early in 2015. Charcoal packets were installed not only at likely sites of discharge, but also at less likely or possible sources, to increase objectivity and limit preconceptions of the aquifer system. These packets are replaced monthly or quarterly, depending on backcountry access. Once collected, the charcoal packets are sent to Karst Works Inc. in San Antonio, Texas, for further analysis.

Chloride mass balance (CMB) is a common approach to measure recharge in arid and semiarid regions (Guan et al. 2010). Natural atmospheric-sourced input of chloride in precipitation, as well as dry deposition, is concentrated in the soil water by evapotranspiration, which does not remove chloride. By measuring chloride concentration in precipitation, runoff, and soil water over a depth profile, the rate of areally distributed, deep drainage below the root zone can be determined. Precipitation was sampled using upright tubes containing plastic sample bags with bags constricted to minimize evaporation. Ceramic cup lysimeters were used to sample water from the soil profile by vacuum pressure. Precipitation and soil water samples were collected monthly. Surface discharge was calculated during ephemeral flow, and samples of runoff were collected for chloride analysis.

RESULTS

Measurements of stage and temperature data for Roaring Springs show pronounced snowmelt discharge peaks and related temperature declines. An unusual, strong and wet summer monsoon season in 2013 brought fast recharge conditions to Roaring Springs (Schindel 2015). Temperature responses from recharge pulses

in sinkholes on the Kaibab Plateau were observed in Roaring Springs in less than three days. 2014 was a dry year with a much lower spring discharge. 2015 was also a dry year with a relatively small spring discharge peak. El Niño winter of 2015-2016 ended up bringing below average winter snow, further delaying the arrival of the dyes introduced in 2015 and 2016 at the sinkholes.

Recharge measured with the CMB varied from 27.1 mm yr-1 in ephemeral channels to 7.1 mm yr-1 in unthinned forest (Aldridge 2015). Ample data were collected to attain successful recharge measurements in one gradually sloping catchment. In a steeper gradient catchment, lack of precipitation data at high elevations caused precipitation to surface water runoff imbalance and thus incomplete recharge measurement. Successful recharge measurements using the CMB are within the range of model estimates of Wyatt et al (2015), but provide temporally and spatially robust information about seasonal recharge patterns with respect to land feature type.

DISCUSSION

Aldridge (2015) successfully demonstrated the CMB technique by conducting a pilot study for northern Arizona ponderosa pine forests. Measurements were taken for one year in a small, experimental forest restoration plot and a nearby control forest. Precipitation during the study period was anomalous with strong summer monsoon precipitation (23% above average). Winter snowpack was 40% below average, but heavy spring rains brought winter precipitation totals to near average. Measured recharge rates were higher in a mechanically thinned forest than an unthinned forest, particularly during the wet monsoon season.

Measurements of temperature and pressure response at springs discharging from the R-Aquifer of the Kaibab Plateau indicate a very rapid response from recharge (Schindel 2015). A qualitative dye tracer study is in progress to determine which sinkholes on the Kaibab Plateau connect to which springs in the Grand Canyon. Unfortunately, a series of below average snowfall winters since the dyes have been introduced have not allowed the dyes to be observed, yet.

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PRESSURES ON WATER SECURITY IN ETHIOPIA

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Ethiopia is pushing for economic growth. The intended growth is water and land centered and is intended to come through push for infrastructure development in irrigation, hydropower, urbanization and industry. At the same time poverty reduction strategies are being implemented parallel to the drive for growth. Among other the infrastructure development include expansion of sugarcane irrigation farms to hundred thousands of ha, expansion of hydropower from the current 2000 MW to over 20000, expansion of irrigation schemes to reach 2 million ha, and reaching universal provision of urban water supply and reaching 98 % in rural water supply.

The impacts of infrastructure development based push for growth on the water security for poverty reduction is already felt. Regardless of the positive gains in terms of GDP and income poverty reduction, some negative consequences exist and are feared to create problems to the poverty reduction as a whole. Examples are a) urban water production cost is rising as a result of pollution from growing irrigation expansion and thereby affecting water affordability for urban poor; b) water scarcity as a result of irrigation development is leading to water depletion downstream thereby affecting water availability for pastoralists who bear currently the damage from El Nino related droughts; c) urban centers are facing water shortages as a result of upstream diversion and obliged to invest on costly water alternative sources; d) erosion of customary land and water management practices and thereby degradation of landscape leading to poverty trap. More than any time in history of water resources development in Ethiopia the interdependency of water security-poverty-infrastructure investment has become strong. This calls for an appropriate approach to deal with balancing investment, institution and water resources knowledge. The purpose of this paper is to provide an overview of the current state of water management practices in Ethiopia in relation to poverty, infrastructure and water security with specific examples from hot spot areas where problems are emerging.

NOTES

THE INTERNATIONAL ASSOCIATION OF HYDROGEOLOGISTS – MISSION AND OUTLINE OF SOME RECENT ACTIVITIES IN THE WESTERN AND CENTRAL EUROPEAN REGION

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Keywords: IAH, national chapter, groundwater, aquifer, Europe

GENERAL OVERVIEW OF IAH AT THE BEGINNING OF 2016

The International Association of Hydrogeologists (IAH) was established in 1956 with the aim of fostering the understanding, protection and management of groundwater resources world-wide. It is a scientific and educational charitable organisation with more than 4100 members from all over the world. IAH collaborates with international organizations like UNESCO, FAO, World Bank, IAEA, WMO, with other water-related NGOs, and is a member of the World Water Council and UN-Water.

The commitment of IAH in raising awareness of groundwater issues and in the governance of conjunctive use of surface and groundwater is made with the help of its global membership. IAH has a Council which comprises the president, past president, secretary-general, vice president for finance and membership, vice president for programme and science coordination and 8 regional vice presidents (North America, Latin America and the Caribbean, Western and Central Europe, Eastern Europe and Central Asia, Asia, Australasia and the Pacific, Sub-Saharan Africa, North Africa and the Middle East).

Membership passed the 4000 threshold in 2012 showing a very small fluctuation around that number since then. Due to renewals in Australia and a slight increase in the student members, 2015 has been a good year, with overall membership again above 4000. The distribution of membership within the regions for the last 8 years is shown in table 1.

Region	2008	2009	2010	2011	2012	2013	2014	2015
Sub-Saharan Africa	200	247	231	233	267	265	281	277
North Africa & Middle East	90	74	99	97	101	94	109	117
Asia	288	214	191	191	229	259	300	316
Australasia & the Pacific	493	599	582	656	799	697	589	708
Eastern Europe & Central Asia	355	145	125	122	124	141	136	140
North America	669	672	654	632	659	574	602	583
Latin America & the Caribbean	194	177	177	197	179	182	197	229
Western & Central Europe	1496	1796	1726	1656	1716	1685	1747	1733
Total	3786	3894	3785	3784	4074	3897	3961	4103

Table 1. IAH Membership by Region between 2008-2015

A further increase in membership is expected which will hopefully be stimulated by the reduced membership fees for students, the very active Early Career Network, and the wide scale of activities of the different commissions and networks of IAH.

Currently the following commissions and networks are operating:

- Commission on Groundwater and Climate Change
- Commission on Groundwater and Energy
- Commission on Groundwater Outreach
- Commission on Karst Hydrogeology
- Commission on Managing Aquifer Recharge
- Commission on Mineral and Thermal Waters
- Commission on Regional Groundwater Flow
- Commission on Transboundary Aquifers
- Burdon Groundwater Network for International Development
- Early Career Hydogeologists' Network
- Network for Coastal Aquifer Dynamics and Coastal Zone Management (CAD-CZM)
- Network on Fractured Rock Hydrogeology
- Network on Groundwater and Ecosystems
- Urban Groundwater Network

In 2009 IAH reviewed its mission, making an assessment of the place of IAH among water science professional associations and on how IAH was perceived by non-member hydrogeologists and the wider water resources community. A Forward Look – Forward Actions 2010 – 2020 initiative was launched in 2010 regarding the future of IAH with an action plan comprising five main elements.

- Education & Academic Development
- Internal Development of IAH
- Inform & Influence Global Policy
- Enhance Alliances with External Agencies
- Enhance the Development of Science

IAH released three Strategic Overview Papers in 2015 which are available for download from its website (https://iah.org/news/iah-strategic-overview-series; https://iah.org/wp-content/uploads/2015/12/IAH-Resilient-Cities-Groundwater-Dec-2015.pdf). These deal with Food Security and Groundwater, Energy Generation and Groundwater, and Resilient Cities and Groundwater.

SOME RECENT ACTIVITIES IN THE WESTERN AND CENTRAL EUROPEAN REGION

IAH encourages the formation of National Chapters by its individual members as well as a regional collaboration between chapters. Western and Central Europe has 22 National Chapters and more than 1700 members, making it the largest region. Many of these European chapters are very active, organizing national and international conferences, workshops, contributing to education and also reaching out to different stakeholders, which is a result of their long tradition of involvement, rather than just their large membership.

The largest IAH event of 2015 was the organization of the IAH Congress by the Italian National Chapter, with 832 participants, including 155 students. This congress, in line with its theme "Back to the Future", combined previous experiences with the technical and scientific tools and needs of the 21st century. A selection of meetings from 2015 includes:

- The meeting of the IAH Karst Commission in Birmingham, UK in June 2015.
- The conference on Hard Rock aquifers: up to date concept and practical applications, organized by the French IAH National Chapter in La roche sur Yon in June 2015 with an excursion to Basse Normandie in October 2015.
- The Polish National Chapter of IAH and the University of Silesia hosted a conference on "Groundwater vulnerability: from scientific concept to practical application" at Ustron in the Carpathian Mountains in June 2015.
- A joint all-day meeting of the British IAH National Chapter and the Hydrogeological Group of the Geological Society on the topic of sustainable groundwater under multi-functional pressures, including both the 2015 Darcy and 2015 Ineson Lectures, in London in October 2015.
- A symposium on the value of groundwater organized by the IAH Netherlands Chapter in cooperation with the Netherlands Hydrological Society (NHV) and VVM, KWR Water, Deltares and IHP Belgium in Nieuwegein in September 2015.

Although groundwater played and plays an important role in the Central part of Europe which has a long tradition of producing excellent hydrogeologists, the establishment of these National Chapters and then their active participation in the “international groundwater community” started and developed slowly.

Following the aims of IAH in stimulating and supporting regional activities, the Hungarian National Chapter has initiated a series of conferences, starting with the organization of the first Central European Groundwater Conference in 2013 in Mórahalom. As the Central European region is rich in (transboundary) thermal groundwater, and there is a growing need for their exploitation, the topic of the conference was on geothermal applications and issues related to groundwater flow and resources. In total more than 80 participants from 9 countries representing 6 National Chapters attended the conference. The conference also reaffirmed that cooperation between national chapters can result in a more efficient sharing of information and knowledge.

Several national chapters showed their willingness in organizing the second Central European Groundwater (CEG) Conference. The representatives of 6 Central European IAH National Chapters met at the international conference 'Karst Without Boundaries' organised in the framework of the DIKTAS project in Trebinje in June 2014, where they summarised their activities over the previous year and discussed the organization of the second CEG Conference. A proposal by the Romanian National Chapter to host the second CEG Conference in Romania was supported by all national representatives.

The second CEG Conference was held in Constanta in the Black Sea region of Romania in October 2015, with the title ‘Groundwater risk assessments in urban areas’. The meeting attracted 65 participants from 10 countries and resulted in new ideas for cooperation between the Chapters.

The Croatian National Chapter of IAH, together with the Croatian Geological Survey will organize the 44th IAH Congress which will be held in Dubrovnik in September 2017 on the topic of Groundwater Heritage and Sustainability. The 3rd CEG conference will also be held as part of this congress.

2016 is the 60th anniversary of IAH, and beside the different worldwide activities and celebrations, the 43rd IAH Congress will be held in Montpellier between 25-29 September 2016. A meeting of the representatives of the European National Chapters is also planned for Montpellier in order to become better aware of each other’s activities, to promote cooperation and to plan a joint meeting. The Congress is being organized by the French and the German National Chapters, who played a determining role in the formative years of IAH and the event will present an opportunity to look at the future evolution of IAH, taking into account the lessons learnt from our 60 years of experience.

Clearly there is a trend of increasing involvement in Western and Central Europe in hydrogeology and related topics, mirroring an awareness at National (governmental) level that groundwater is an inseparable part of our society, and governance and management, particularly in the international sphere, will become a dominant factor in regional politics. It is rewarding to see that the involvement of young hydrogeologists also continues to increase, following the trend of societal and political awareness. IAH must continue to coordinate, motivate, and support these activities, enabling the other regions to increase their level of involvement. The 60th anniversary of IAH shall mark the start of the next sixty years of growth and development in hydrogeological sciences.

NOTES

THE ROLE OF GROUNDWATER IN THE ECOSYSTEMS: IMPLICATIONS OF DIFFERENT MANAGEMENT SCENARIOS ON SUSTAINABILITY

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Abstract: Ecosystems are part of the landscape; many of them are integrated into the water cycle and are able to provide services that contribute to human well-being. Water management in general, and groundwater management in particular, lead to modifications of groundwater flow networks causing significant changes in the quality and quantity of groundwater that many ecosystems receive. In this context, wetlands are perhaps the most threatened type of ecosystem, particularly in the countries of the Mediterranean region. Groundwater management should not only ensure but demonstrate the sustainability of the use of groundwater resources. In this sense, ecosystems's resilience is an aspect little known from the point of view of the abiotic processes which take place in the ecosystem's functioning, but that could be of great assistance in the groundwater resources sustainability. This paper presents two different management scenarios. The first scenario presents the Tablas de Daimiel, representative of a wetland considered (at one time) to be in an irreversibly transformed state, which has since recovered due to a combination of favorable climatic and anthropogenic conditions. The second scenario considers the Clot de Galvany, representative of an altered coastal wetland, also transformed and with poor prospects for recovery given its socio-economic framework. The results of the analysis demonstrate a series of conclusions about the effectiveness of management practices in each case. It is important to distinguish between a management approach aimed at restoring ecosystems and one aimed at transforming ecosystems. In both cases, it should be recalled that the ecosystems can continue to provide services to human beings. Are those transformations absolutely necessary for the well-being of present and future generations? If what is sought is to obtain a pond for ducks, the transformation is viable but it is prudent to consider not only current needs for action, but also the consequences of this actions in the short, medium and long terms, and finally its end result, which may be irreversible.

Keywords: ecosystem services, groundwater dependent ecosystems (GDE), wetlands, Spain, water management, sustainability, resilience.

INTRODUCTION

All ecosystems need water but some of them require groundwater to survive (SKM, 2012). Groundwater dependent ecosystems (GDE) are defined as natural ecosystems that require access to groundwater to meet all or some of their water requirements on a permanent or intermittent basis, so as to maintain their communities of plants and animals, ecosystem processes and ecosystem services (SKM, 2012). They cover a wide range of ecosystems: GDEs that rely on the subsurface presence of groundwater (vegetation), which are mainly terrestrial ecosystems (forest, peats, etc); GDEs that rely on the surface expression of groundwater (rivers, wetlands, springs); and Subterranean GDEs (caves and aquifers) (SKM, 2012).

Groundwater management, mainly groundwater extraction, causes changes in groundwater flows, and negative impacts (Foster et al., 2006; De la Hera et al., 2016) in different parts of the landscape. These changes mean a reduction in groundwater quantity and quality that the wetlands receive.

Groundwater management may lead to significant damage or changes to ecosystems. Is this necessary or could it be avoid? From the ethical point of view, it is important not to mix two connected and relevant issues: a) the ethical obligation of providing drinking water to the poor (the right to water or social ethics); and b) the ethical obligation of avoiding ecological disasters in aquatic ecosystems (saving the planet or environmental ethics) (Llamas and Martínez-Cortina, 2009). This paper focuses mainly on the resilience capacity of aquifers to climatic or anthropic perturbations in the framework of GDE management.

PREVIOUS CONSIDERATIONS

Sustainability is a complex concept which may imply at least nine dimensions when we consider groundwater resources sustainability (Llamas et al., 2007): hydrological, ecological, legal, institutional, affecting also intergenerational and intragenerational issues, involving stakeholders and social and political issues.

The ecosystems are formed by some biotic (mainly flora and fauna) and some abiotic (water, soil, climate) components. They are both equally important as they together constitute the ecosystem.

A perturbation affecting an ecosystem may cause a set of responses, but they could be reduced to two main responses: (1) to keep functioning without modifying its structure and functioning (resilience capacity); this means to adapt to the dominant circumstances; (2) to transform its structure and functioning to the new situation. Resilience is seen in this paper as a process more than as a result. It refers not just to a state but to a set of dynamic conditions intrinsic to the system. Managers may begin thinking about the resilience of ecosystems, and of aquifers in particular, as an additional tool to preserve groundwater sustainability. In this paper resilience is defined as a process affecting a dynamic system, not as a result. As a physical property it needs to be defined as a vector of one thing applied to another: in this case, aquifer resilience to groundwater management is considered.

SOME EXAMPLES RELATED TO GROUNDWATER DEPENDENT ECOSYSTEMS MANAGEMENT IN SPAIN

The following examples represent two different scenarios of management, one inland wetland and one coastal wetland. Both of them correspond to Spanish protected wetlands related to groundwater bodies declared at risk according to the requirements of the WFD.

2.1 Tablas de Daimiel (Ciudad Real, Guadiana river basin). It is located in the Upper Guadiana Basin, and provides an example of conflict caused by the over-exploitation of water resources in a semi-arid region. Since the 1970s, uncontrolled abstraction of groundwater for crop irrigation has lowered the water table in places by up to 50 m, causing the main rivers channels to run dry and wetlands to become desiccated. The Tablas de Daimiel National Park is the most high profile victim of this desiccation process. The abstraction has also supported a booming agricultural economy with all the associated social benefits. After years of conflicts between farmers, local government, regulators and conservationists, to find a solution the Ministry of the Environment developed a Special Plan for the Upper Guadiana. This Plan, today inoperable, devised a water consumption scenario compatible with a mid-term water table recovery (by the year 2027) and identified water management tools to deal with the Upper Guadiana groundwater crisis, such as wells of artificial recharge along the Guadiana River upstream of Tablas de Daimiel. Today, Tablas de Daimiel, against some of the predictions which established the irreversible situation of this wetland from the outcomes of groundwater flow models, has recovered almost completely its flooded, unperturbed state. This has been due to the groundwater level rise produced as consequence of intensive rainfall that occurred in 2005-2014 and the application of other planned measures considered in the Special Plan. Nevertheless, the maintenance of the good wetland state and reestablished wetland-aquifer relationship have still to be studied in the near future. A key aspect should be recognized: the importance of abiotic processes in the ecosystem survival.

The system response to wet years shows that the aquifer is able to absorb significant quantity of water from precipitation. The system response to dry years shows two patterns of level decline in the central and eastern part of the aquifer: a gradual decline till January-1989 followed by a steep decline. In the analyzed temporal scale (1980-2013) there are significant fluctuations between dry and humid periods which affect also the aquifer. This fact shows that the aquifer does not have a significant resilience capacity, however, when artificial recharge through the Guadiana river channel is operative, the aquifer resilience improves. Despite that the aquifer has improved considerably, it has not yet achieved a good ecological status and the problems persist related to water governance issues, social conflicts, limited social participation and unlikely economic growth.

This case study demonstrates how improved aquifer resilience contributes to the good ecological status of Tablas de Daimiel National Park, in conjunction with sustainable groundwater use (De la Hera et al., 2014).

2.2 Clot de Galvany (Elche, South of Alicante, Júcar river basin). It is a protected area recognized as Site of Community Interest (SCI) included in the Nature 2000 network. It is extremely altered due to drainage activities carried out inside the wetland, dividing its surface into five water bodies. The area is surrounded by important industrial and touristic activities. The main sources of water were two springs, one of which disappeared in 2005 due to groundwater depletion. The second spring is active, but does not have sufficient flows to support the current protected area. The wetland was related to the groundwater body of the Bajo Vinalopó, declared at risk from the qualitative and quantitative point of view. The local council of Elche has decided to pump treated water from the Los Arenales del Sol industrial water treatment station, to some of the water bodies of the wetland. This maintains the inundation level artificially. Nevertheless, the main problem seems to be the desalination station of Alicante located 5 km north of the wetland along the coast line, which seems to be capturing groundwater flows from a radius of 5 km (Fornés et al., 2013).

This example illustrates how the change of management induced by several circumstances can significantly alter the state of a wetland. In this case, the recovery of groundwater levels in the aquifer and the good groundwater quality status are difficult goals, considering that it is a coastal aquifer providing groundwater to important industrial and tourist activities.

CONCLUSIONS AND FINAL REMARKS

These two examples allow us to draw the following conclusions:

1. It is extremely difficult to provide a “general guide to groundwater sustainability”. Emphasis on one or another of the different dimensions of this concept is likely to depend on economic, social, cultural and political constraints.
2. Groundwater management requires a higher degree of user involvement than is required by surface water management.
3. User participation requires a degree of awareness about hydrogeological principles.
4. Appropriate groundwater management requires a significant degree of trust among stakeholders.
5. 5. Decisions on groundwater management regarding particular protected areas should consider the changes and damages that the decision may cause to the ecosystems involved and take into account the capacity of these systems to recover. Data and studies should be developed in this research line, which is well advanced in the ecological field but not yet in the domain of hydrogeology.
6. Some management strategies referring to wetlands do not lead to the restoration of a wetland (i.e. recovery of its unperturbed status) but rather to its transformation to a new system able to provide different ecosystem services. Decisions taken about these changes are important and should be regulated, or at least, involve some ethical considerations in view of to future generations. When making decisions, it is important to undertake an analysis that compares the unperturbed wetland state with the new wetland state. Even in cases with no previous data, this analysis could be performed with indirect information.
7. The two examples presented show that aquifer resilience is a key property of the ecosystem which may provide enough capacity to the wetland ecosystem to counteract perturbations.

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GROUNDWATER LEVEL CHANGES DUE TO EXTREME WEATHER - AN EVALUATION TOOL FOR SUSTAINABLE WATER MANAGEMENT

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Abstract: In the past decade, multiple extreme and exceptional droughts have significantly impacted many economic sectors in different US regions, e.g. California, Texas, and Oklahoma (Folger et al., 2013). The 2011-2014 drought in Texas affected almost 90% of the state areas (NDMC, 2013), and caused economic losses to the agricultural sector of $7.6 billion in 2011 alone (Fannin, 2012; Guerrero, 2012), while almost $17 billion in the entire Texas economy (Ziolkowska, 2015). Similarly, in Oklahoma 95% were in exceptional drought causing $1.6 billion loss in agricultural sector alone (Drought Monitor, 2015; Stotts, 2011).

Drought has been impacting both surface water and groundwater resources, although implications on groundwater aquifers have been more critical and affecting all economic sectors, and a large group of population. In addition, many regions in the US have been experiencing increasing population numbers, which has magnified water scarcity problems. Thus, extreme weather events, in combination with socio-economic developments, have emphasized the need to evaluate the actual groundwater availability. This can be useful for improving water management strategies and long-term planning for emergency situations.

Despite an abundant numbers of studies emphasizing importance of groundwater and sustainable water management strategies (Sesmero, 2014; Condon et al., 2015; Foster et al., 2015), research on groundwater resources and their geospatial availability is still missing, mainly due to limited data and hydrological measurements (Lia and Rodell, 2015).

This study aims at contributing to filling this gap. We developed a model to analyze fluctuations of groundwater levels over time and in different geographical locations in two case study states: Oklahoma and Texas. The selection of the case study examples was determined by data availability and the geographical location of the states. Both states are exposed to extreme weather events (droughts and floods) both during summer and winter seasons. In addition, Oklahoma has the highest quality weather network in the world (Mesonet) (Brock et al., 1995) with 120 stations across all 77 countries in Oklahoma, monitoring weather related variables around the year around. Texas, on the other hand, has a comprehensive database with regular groundwater measurements.

The model was developed for the time span of 12 years (2003-2014), with 3-year sections: 2003-2006, 2007-2010, and 2011-2014, which allowed us for a temporal analysis of the trends in groundwater levels and drought.

The model is a multi-dimensional interactive evaluation framework that consists of three integrated evaluation components:

1. 4D geospatial visualization model of groundwater well levels in Oklahoma in Texas
   This model component represents groundwater level changes over time in a 4D perspective, visualizing latitude on the x-axis, longitude on the y-axis, time on the z-axis, and the extent of groundwater scarcity as color-shaded spheres.
   The model is based on USGS water data base on 20,162 wells in Oklahoma and from Texas Water Development Board on ~140,000 monitored water wells in Texas. Due to data disparities, we determined a selection criterion for each well, and thus specified 7,211 water wells in Texas and 390 water wells in Oklahoma. We further normalized the data in order to provide a data-based benchmark and comparison basis for all groundwater data entries.

We used C++ language to develop and generate KML data files that allow model users to interact with the results both in Google Earth and Google Maps. The model shows three categories of regional trends and variations in well water depletion over the analyzed time span: increasing, decreasing, and inconclusive trends (no change in water levels) in different regions of Oklahoma and Texas. The trends indicate regions of current water scarcity and potential limited water availability in the future.
Due to its interactive feature, the model allows both for a close and a broader perspective of groundwater level changes in all counties in Oklahoma and Texas over the analyzed time span 2003-2014. The model can be used as a valuable tool for decision-making purposes to instantly recognize groundwater scarcity and evaluate potential socio-economic implications.

2. Gradient Palmer Drought Index Model measuring water supply and demand, while also incorporating temperature and precipitation
This model component was used as a direct indicator of change based on a commonly known and widely recognized drought methodology.
The Palmer Drought Index was used to correlate drought with decreasing water well levels in Oklahoma and Texas. Data from the Drought Monitor was evaluated for each week in the entire analyzed time period 2003-2014. A total of 206,544 samples for all counties in Texas and Oklahoma were used for the analysis. The samples represent drought indexes [D0 D1 D2 D3 D4] reflecting the percent of the county in each of the drought conditions, respectively. The indicator is a model component itself, while it also serves as validation of the geospatial groundwater level visualization framework.
3. Soil moisture change index
The third model component is based on data from the Oklahoma Mesonet on changes in soil moisture levels over time. It allows us to detect hydrological changes in and interactions between the soil water levels and groundwater levels. The overlapping results of this indicator and the Palmer Drought Index and their timely correlations constitute a sound proof of critical fluctuations in groundwater resources in Oklahoma and Texas.

Based on the model results, we estimated the extent of water shortage as a result of drought in 2003-2014, and further the lingering uncertainty of water availability and potential socio-economic implications of groundwater shortages in the future.

The results show that there is a correlation between the model input variables and anomalies of interest for weather prediction. The results can be used to enhance and improve indicator methodology related to drought measurements. This research also accentuates socio-economic implications of water shortage for different economic sectors in terms of the production output, water prices, social welfare, and economic growth.

The framework allows for a comprehensive analysis of the past and current water availability (and water scarcity) at the state, regional and local level. It can be used as a decision-making support tool to recognize and analyze patterns in water level changes over time, assess regional water changes in the future, and analyze potential impacts of those changes.

Keywords: Groundwater management, drought, visualization, geospatial model

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GROUNDWATER MANAGEMENT IN IRAQI KURDISTAN REGION; SULAIMANYAH GOVERNORATE AS A CASE STUDY

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Abstract: Groundwater resources play a vital role in maintaining Kurdistan's agriculture sector and environmental sustainability, and in some places is the sole source for drinking purposes.

There is a shortage of perennial surface water in the Lower Zagros foothills in the Kurdistan in compare to the mid and south of Iraq, with the exception of a few major rivers, including the Great, Small Zab, and Serwan Rivers which all originating from Iranian and partly from Turkish territory and facing discharge decline due to management actions upstream. Therefore, groundwater management and preventing groundwater resources quantitatively and qualitatively is the demand of the day.

Focus in this study is put on the main water resources in Sharazoor-Piramagroon Basin which is one of the most important basins in Sulaimanyah Governorate from the point view of the availability of groundwater and fertility of the land.

During an average year, Sharazoor-Piramagroon groundwater basins and sub basins contribute approximately 15 percent of the Sulaimanyah's total water supply. During dry years, groundwater contributes up to 35 percent annual supply. Many rural areas depend on groundwater for 100 percent of their water supply needs. Groundwater extraction more than natural and managed recharge has caused considerable water table decline in many parts of Sulaimanyah.

The relatively thick aquifers of alluvial intergranular aquifers could be considered the most promising area for drilling successful and productive wells, particularly in the eastern and central parts of the basin. Karstic and karstic fissured aquifers draining some relatively large springs comprise the main water supply sources for some urban part of the basin and source for irrigation for some other parts.

The long-term rainfall data divided into two periods, one from 1980-1990 and the other from 2000-2015, and it concluded that there is a dramatic decline in rainfall from 740 mm to 633 mm annual rainfall.

The main problems regarding the sustainability of the groundwater resources are shown. The current demand for water and that for the next 25 years are determined. Because it has the highest population compared to the other parts, the western part of the basin was found to be under stress. The current exploitation in Sulaimani area is more than the safe yield while in the other parts of the basin it is still below the safe yield. Solutions to get larger amounts of water from the karstic aquifers than those yielded by the springs during the dry season are proposed. Convenient sites for artificial recharge and construction of subsurface dams are also proposed.

For better sustainable groundwater management some recommendations are proposed for the decision-makers to introduce in new legislation and regulations to acquire better control of the surface and groundwater resources.

Keywords: Groundwater, management, karstic aquifers, Transboundary River, drought

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LONG-TERM EXPERIENCE IN MANAGING A TRANSBOUNDARY DEEP GROUNDWATER BODY

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Abstract: The thermal groundwater of the Malmkarst (Upper Jurassic) in the "Lower Bavarian and Upper Austrian Molasse Basin" is of transboundary importance. To avoid an overexploitation and to guarantee a sustainable use of the thermal water detailed research work has been done. It had become necessary because of the increasing economic importance of thermal –water use in the affected area on both sides of the German-Austrian border. Especially the thermal-water uses for spa and for hydro geothermal purposes are of immediate importance. From 1995 to 1998 a model for the thermal-water aquifer was developed in a German –Austrian cooperation. First a hydrogeological model was developed to describe the hydrogeological, geothermal and water management facts. Based on these facts a conceptual model has been adapted and processed by a mathematical 2D- hydraulic groundwater model. In order to deal with these questions a 3D- hydraulic-thermal combined groundwater model was developed from 2005 to 2007. The main aim of this research work was to gain knowledge and a better understanding of the thermal- hydraulic system and the given relations between the major processes, and furthermore to elaborate common management strategies. In order to be able to manage the thermal water resources in a sustainable way and according to the best available state of technology an expert group was asked to elaborate joint protection and utilization strategies and to lay down the results in guidelines.

INTRODUCTION

The thermal groundwater of the Malmkarst (Upper Jurassic) in the "Lower Bavarian and Upper Austrian Molasse Basin" extends from Regensburg in the north to Linz in the south. Its eastern border follows the river Danube on a long distance. With a total area of 5.900 km² the length is 150 km and the width is 55 km. The top of the Malm reaches a depth of about 2000m below sea level. The thickness of the karstic Malm is about 300 m. The temperature rises up to 120° Celsius. Due to the most hydro-geological conditions, the pressure conditions of the thermal water resources over wide area are artesian.

The thermal water is used for spa purposes and to gain hydro geothermal energy. The thermal water use in the German Bad Füssing, Bad Birnbach, Bad Griesbach and Simbach and in the Austrian Altheim, Geinberg, Braunau and St. Martin got an increasing economic importance.

In the year 1987 between Germany and the EG on the one side and the Republic of Austria on the other side an international Treaty about the water management cooperation in the catchment area of the Danube was established. A permanent commission was set up, called the „Ständige Gewässerkommission nach dem Regensburger Vertrag".

In the 70s and 80s of last century there was a significant decrease of the pressure conditions in the used thermal water wells on the German side. This moved the permanent commission to instruct an expert group with members from Austria and from Germany. From case to case some external advisers also were consulted.

The expert group has to supervise the elaboration of investigations and studies about the thermal ground water aquifer of the Malm and to make proposals on how to manage the groundwater resources. Today the expert group has to lead and accompany the management of the thermal groundwater in the transboundary area. This also includes the accomplishment from further research.

INVESTIGATION AND STUDIES

To avoid an over-exploitation and to guarantee a sustainable use of the thermal water detailed research work has been carried out. It has become necessary because of the increasing economic importance of thermal water use in the affected area on both sides of the German-Austrian border. Especially the thermal-water uses for spa and for hydro geothermal purposes are of immediate importance.

Model for Balancing the Thermal Water Resource

As a first step the basis for the quantitative management for the relevant area of the thermal water resources should be created. This requires that conceptions should be developed over the groundwater flow conditions and the groundwater balance. Thus the management of the thermal water aquifer should be put on a technically reliable basis. Therefore a Model for balancing the thermal water resource was elaborated.

Hydrogeological Model

The purpose of the hydrogeological model was to describe, to abstract and to schematise the existing knowledge about geological, structural, hydrogeological, hydro chemical, isotopic, geothermal and water management facts. Based on these facts it could be adapted and processed by a mathematical groundwater model.

Based on existing data the sedimentological character within the Malm was worked out, structural and isopach maps of the Malm were developed, the thickness of the water bearing aquifer, the pressure head of the thermal aquifer taking in account a defined virtual model water, the different perm abilities of fault zones and tectonic blocks, the distribution of temperature and the hydro chemical and isotopical groundwater situation in the investigated area were elaborated and described.

The complete flow of thermal water within the Lower Bavarian and Upper Austrian Molasse-Basin was balanced to 620 l/s. About 130 l/s (25 %) are already being utilized for different purposes. About 490 l/s are discharged to the Danube River. With regard to the existing intensive use of thermal water in Lower Bavaria and Upper Austria it must be pointed out that a considerable amount (330 to 340 L/s) of the thermal water is recharged in the aquifer eastward and therefore downstream of the main users. This high part of balance is only available for users east of Haag in Upper Austria, whereas the users west of Haag (at present 55 %) don't have an advantage of this recharge. The present safe yield of about 70 l/s in this area is low compared with the upstream recharge of about 280 l/s to 290 l/s. Thus the development in the central region with 25 % is very high.

The hydrogeological model is based on the most actual scientific knowledge. It allows regional, reliable and consistent description of the study area and the thermal ground water. This hydrogeological model is a reliable basis for the mathematical groundwater model.

Mathematical Groundwater Model

The mathematical modelling of the groundwater flow for an extremely heterogeneous karstic aquifer caused by fractures and karst-tubes was done by a two-dimensional steady flow mathematical groundwater model with a numerical solution. For the mathematical modelling a 2D-Version of that software was used. The mathematical program combines a continuous approach with a discontinuous model and is able to simulate the influence of fractured zones and of karstic tubes on the permeability and thus on the groundwater flow system.

The most important advantage of this program can be seen in the fact, that it is able to respect regionally differing transmissivities, groundwater recharge areas and discharge areas as well as areas of boundary inflow. In addition all the tectonic structures being mapped can be introduced to the numerical model.

The various calculations show that temporarily changing production rates and the influence of geohydraulic tests and re-injection tests on neighbouring thermal water utilizations can only be calculated by a non-steady flow groundwater model. For this reason a non-steady flow model was used in order to simulate the thermal water withdrawals taking into consideration the temporal decrease of pressure of the highly confined deep thermal water. The results of the calculations with the non-steady flow model show a sufficient correspondence between the calculated and the measured values. Also the connection of the drawdown and the uplift curves of the locally differing storage coefficient could be well simulated.

This mathematical (hydraulic) model is the relevant instrument for authorities on both sides of the border in the transboundary area for evaluating the required water extractions, the potential yield and the implications on other existing wells on a reliable basis.

International Workshop Munich 2002

The increasing number of sites which re-inject geothermically used water creates a large number of questions which cannot be answered by using only a hydraulic model.

Within the framework of an international workshop held in Munich in 2002 those questions which would have to be clarified from the point of view of water management were formulated in order to ensure a sustainable geothermal use of thermal water:

- Is there a relation between the reduction of the temperature in the deep thermal aquifer and the existing pressure condition?
- Is there a relation between temperature and the relevant hydraulic parameters as permeability and storage coefficient?
- How can the quality of those parameters be influenced, if the temperature in the deep aquifer is decreasing?
- Is there a relation between the extraction of thermal water and the quantity of water (yield) which can be collected from the deep groundwater body?

Other questions concern the way in which the temperature of the re-injected water, the location of and the distance between the boreholes for extraction and re-injection and the operational mode can influence the thermal conditions such as the temporal and spatial distribution of temperature in the deep thermal groundwater body.

Hydraulic-Thermal Combined Ground-Water Model

In order to deal with these questions a 3D- hydraulic-thermal combined groundwater model was developed in German – Austrian cooperation from 2005 to 2007. The project was co-financed by the EU within the framework of the INTERREG IIIA program. The detailed studies were carried out by a German-Austrian-Swiss consortium of engineers.

On the basis of the results of the model from 1998 a hydraulic-thermal combined groundwater model was developed in the Bavarian-Upper Austrian border region. This model is based on the regional geological and hydro-geological situation in the “Lower Bavarian and Upper Austrian Molasse Basin”.

The main aim of this research work was to gain knowledge and a better understanding of the thermal-hydraulic system and the given relations between the major processes, and furthermore to elaborate common management strategies.

The comparison of the results of the calculations carried out with the available measuring data from existing wells or boreholes has shown that the hydraulic as well as the thermal conditions in the model area can be simulated.

MANAGING A DEEP GROUNDWATER BODY

The results of the studies carried out show clearly that a further use of the thermal water resources will be possible only if the thermal water is used economically and the existing hydrostatic conditions will in general be preserved.

To achieve this objective, strategies have been developed for managing the thermal water resources of the Malmkarst. These contain an amazing regular information exchange, the elaboration of guidelines, a concerted application of the mathematical model and a representative monitoring on both sides.

Exchange of information

Both countries start on the assumption that an efficient management of the thermal groundwater resources will only be possible if both sides have the same information standard at any given time. Thus, regulations have been worked out to clear the way, respectively the form of the exchange of information and data in the future.

Currently, the exchange of information in the expert group is mainly about thermal water. The experts will meet each other three or four times a year. Here, the German and Austrian side report on current developments and upcoming planned project approvals.

Similarly, a regular exchange of data collected from both sides is carried out. Each side will present the yearly withdrawal data for the individual wells to the other side, so that the other side has always the same information.

An aspect of the Expert Group meeting is to exchange experiences according to the information contained in the guidelines regulations, especially those in connection with the authorization and the way facilities for the use of thermal water resources is operated. The coordinated regulation is running well, but there is room for improvement and the basis for a continuation of the guidelines could be created.

The expert group will prepare further necessary investigations and accompany their assignment professionally.

The information to a wider audience on the main results of investigations undertaken and the related discussions are also to contribute to the development of management strategies.

Guidelines

In order to be able to manage the thermal water resources in both countries in a sustainable way and according to the best available state of technology the expert group was asked to elaborate joint protection and utilization strategies and to lay down the results in guidelines.

The guidelines have been enacted since 2002. The experiences gained during its application over a period of about 10 years have prompted the expert group to revise the document. The practical knowledge and the change in the state of the art facilities for the use of deep thermal groundwater have incorporated to revise the document. Completion of this work is expected to be at the end of 2011. It is the intention that the „Ständige Gewässerkommission nach dem Regensburger Vertrag“ shall adopt the revised guidelines over the next year, and recommend this for both sides to use.

The guidelines contain not only water management principles but also instructions for the preparation of projects and operators of facilities for the use of thermal water resources. In addition, regulations concern the further exchange of information and the future application of the mathematical Model agreed as part of management.

Management Principles

Basis for the management of the thermal water resources was a common understanding of the objectives to be achieved and the resulting derived principles for further action. They include among others the following aspects:

- comprehensive protection of the groundwater resources in quantitative and qualitative respects
- far-reaching preservation of the natural hydrostatic pressure conditions
- groundwater extraction only according to the natural groundwater recharge
- priority of the use for spa purposes over the geothermal use in the form of geothermal use
- secondary utilization of the water used for spa purposes (heat recovery)
- obligatory re-injection of the geothermally used water

Dimensioning of Plants for the Thermal Water Use

The basis for a joint management of the thermal water resources is the determination of the water demand for the individual utilizations according to standard criteria. The decisive dimensioning units have been determined separately for spa purposes and geothermal plants. The determined values are obligatory for both sides (Austria and Germany) and will be used in order to protect the thermal water resources in a sustainable way.

The pre-existing facilities in the state of the art represent a particular challenge. The experience of recent years has shown that a reduction of withdrawal quantities were especially possible when major changes were carried out simultaneously in the plant.

Required Application Forms

Application forms must include the information related to hydraulic engineering and water management necessary for the evaluation of a project, the provisions on protective measures and the safeguarding of a sustainable use of water resources.

A catalogue of documents to be submitted to the authorities has been established in order to ensure for both countries a standard procedure and the compliance with the best available state of technology. The catalogue comprises the following issues:

- construction of thermal water wells
- execution and documentation of field experiments regarding water management
- operation of thermal water plants as well as data collection and documentation
- requirements to model calculation
- closing of thermal water wells

Catalogue of requirements

In order to ensure that uniform principles are applied to the construction and the operation of the plants and, in particular, to the data collection, a standard catalogue of aspects to be followed has been compiled.

This compilation is used by both sides in connection with the authorization of facilities for the use of thermal water resources.

Groundwater Model

As mentioned before the mathematical model is a relevant instrument for authorities on both sides of the border of the thermal groundwater body to evaluate the required water extractions, the potential yield and the implications on other existing wells.

Especially with respect to required groundwater extraction in this area, prognoses are possible for thermal groundwater management as well as detailed statements about existing thermal water use.

The 2D mathematical model allows for the accounting and recording of groundwater flow conditions in the thermal water aquifer of the Malm. This model represents a concerted effort between the German and Austrian compartment basis and also forms an essential basis for water law approval process on both sides. The principles on the applications of the mathematical groundwater model were also laid down in the guidelines.

It has been determined in detail how to proceed in the application, maintenance and further development of the model and how the documentation of the calculations should have to take place. Therefore a procedure of the application of the model as well as the obligatory exchange of information was elaborated.

New data and insights have been received since the development and publication of this mathematical model in the balance area. Thus, there is a new technical basis. The expert group therefore stated that it would be necessary to determine whether a mathematical model is still suitable.

Appropriate preparations for the implementation of this deficit analysis were made by the expert group in the years 2010 and 2011. The aim of the project is to review the existing mathematical model in terms of its suitability for further use in the Water Act approval process.

Taking into account the existing data, the project is designed for the future use of the mathematical model and to make decisions.

Monitoring

The protection and the management of a groundwater body are not possible without relevant data. Therefore, programmes for a comprehensive quantitative and qualitative monitoring system for the deep groundwater body were established.

In general, the design of a network is strongly dependent on the geological and hydrological situation. Therefore it is important to have a thorough understanding of the groundwater flow system, and of groundwater recharge and discharge areas in particular.

For transboundary groundwater bodies it is recommended that the monitoring programmes on both sides of the border should be combined and harmonised.

The access to information about deep groundwater bodies is extremely difficult. This is first and foremost due to the fact that the establishment of measuring sites is technically very complicated and very expensive. It has therefore not been possible for the water management administrations of both countries to set up and maintain a separate comprehensive measuring and monitoring network for the deep groundwater body in the Lower Bavarian – Upper Austrian molasses basin.

Because of these facts, existing boreholes, where the thermal water for geothermal or spa purposes is extracted, were used as measuring and/or sampling sites. Measurements and sampling are carried out during operation by the private operators of the plants according to the requirements laid down by the authorising bodies of both sides.

At all sites data are measured or sampled by private companies which follow the obligations of the local administration.

SUMMERY AND CONCLUSIONS

In 1998 detailed thermal water balancing was carried out for the deep thermal groundwater aquifer in the Lower Bavarian and Upper Austrian Molasse-Basin. In the course of this balancing an exploitation of the available thermal water resources by thermal water abstractions of about 25 % was stated.

In the meantime the extent of utilisation has been considerably reduced due to successfully implemented management measures - among other things the obligation of reinjection of thermally used thermal water only.

In order to be able to manage and protect the thermal water resources in a sustainable way and according to the best available state of technology guidelines have been elaborated. Thos guidelines will be the basis of the German-Austrian cooperation in this field. Data registration should be coordinated as well as data exchange should be guaranteed.

The groundwater model, which was developed in German-Austrian cooperation, is a reliable instrument for the German and the Austrian authorities to evaluate the demanded water extractions. It enables the water administrations

- to balance the groundwater occurrence in the Lower Bavarian and Upper Austrian Molasse-Basin,
- to quantify the groundwater recharge with sufficient precision
- to quantify possible influences on existing neighbouring wells.

New data will be available by changing water extraction- and reinjection-configurations and by additional thermal water extractions and reinjections. Based on these data a new calibration of the mathematical model can be carried out from time to time. Thus the exactness and reliability of prognoses can be improved and therefore stated more precisely.

The good results of the groundwater model and the results of the expert group have finally shown that the common efforts on both sides - the German and the Austrian one - were worthwhile.

But there must not be only common interest of the authorities to evaluate the groundwater occurrence in this area correctly. Especially the thermal-water users in the spas and health resorts as well as the users of hydro geothermal energy should have a special interest to know more about their thermal water resource. They must learn to utilize thermal water economically and carefully. This is necessary to reach a sustainable use for the following generations and for the existence of the health resorts.

Apart from the quantitative and qualitative results of the groundwater model the most important result should be the knowledge that the German and Austrian authorities as well as the thermal-water users on both sides of the river Inn are in the same boat that means they have to take care of the same valuable deep thermal-water resource. For a sustainable use of this resource it is necessary to have a close and trusting cooperation of all people involved in this subject.

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GROUNDWATER QUALITY OF THE MAIN DRINKING WATER WELLS TAPPING THE MOUNTAIN AQUIFER OF THE WEST BANK, PALESTINE

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Abstract: This paper describes the physical and chemical quality of water samples taken from domestic water wells representing diffrent domestic well fields in the West Bank of Palestine. Emphasis was given on assessing the potential pollution of groundwater with human surface activities like sewage disposal, solid waste dump sites, etc. The results revealed that the concentration of the ions and parameters affecting the aesthetic and heath related quality such as Cl, Na, TDS, NO_3, minor and trace constituents are within the limits recommended by the WHO and Palestinian Standards. Signs of pollution were observed even in some deep wells tapping the Lower Ceneomanian confined aquifer. It is now clear that the main source of groundwater pollution is wastewater, so it is strongly recommended to prevent the wastewater from reaching the aquifer systems.

Keywords: groundwater quality, pollution, wastewater

INTRODUCTION

The water is an important issue in the arid and semi arid areas including Palestine. Beside the water resources being scarce, available water resources are subjected to deterioration in quality. The limited rain fall results in a limited groundwater recharge. The recharge water infiltrates into the aquifers and appears in some places as springs providing fresh water needed for different purposes. The springs are not available in all parts of the West Bank, so groundwater wells are drilled to abstract groundwater to supply the inhabitants with the needed water for domestic and irrigation purposes. This study will deal with the chemical characteristics of the water of the wells in the West Bank used for domestic purposes only. In the last few decades most of the water realted studies in the West Bank concentrated on the hydrology and hydrogeology with less attention to water chemistry and water quality, although the West Bank Water Department collected and analyzing a number of water samples from selected wells and springs in the West Bank. The Palestinian Water Authority pays great attention to the water quality (PWA, 2004). Despite of the invested effort, several key water quality parameters were never examined. For instance there is no information about possible arsenic presence, and some other (heavy) metals in the drinking water wells. Considering the fact that wastewater of 94% of West Bank population is disposed untreated in nature, anthropogenic influence is not yet clearly elucidated. There are numerous potential groundwater pollution sources throughout the West Bank, and these fall into the following broad categories Wastewater, Solid waste, Industrial and hazardous waste and Agriculture (UNEP, 2003). The overall objective of this research was to study quality of groundwater used as drinking water in the West Bank Palestine, with emphasis on minor and trace constituents, and geochemical nature of aquifers, and to identify possible groundwater contamination with from human activities.

MATERIAL AND METHODS

The study area covers the West Bank of Palestine, specifically with the focus on small drinking water wells. From hydrogeological point of view, the West Bank is divided into three main aquifer basins, namely, the Eastern Aquifer Basin, the Western Aquifer Basin, and the Northeastern Aquifer Basin.

The sampled wells are mainly used for domestic purposes. They were chosen carefully to represent different well fields as well as different aquifers and basins. These wells were selected from the three groundwater basins and they mainly represent the Upper and Lower aquifers. The reason is that most of the domestic wells are tapping these 2 aquifers. The wells that are tapping the shallow aquifers (Eocene - Alluvium) had been excluded because they are not used for domestic purposes. Water samples from 29 drinking water wells were collected and analyzed in situ and in the lab according to standard procedures. Wells included in the study have various depths ranging from less than 150m (e.g. Habla Well) to more than 800 m (Al 'Ezariya No. 3 well). Analyses of anions and cations were carried out at the Birzeit University Testing Laboratories, Birzeit, Palestine.

RESULTS

The chemical analysis of the water samples reflects clearly the nature of the carbonate aquifers tapped by the water supply wells. The EC and the TDS of the water is relatively low with values not exceeding 620 µS/cm and 450 mg/L, respectively. In most of the samples Ca and Mg are the most important cations, while the HCO_3 is the most important anion. Most of our samples are characterized by low [K] and low [SO_4]. The correlation coefficients between the different measured parameters and ions for all samples show that no correlation is significant between the different parameters except:

- *Na and Cl: significant direct correlation with correlation coefficient of 0.994*
- *Na and TDS: significant direct correlation with correlation coefficient of 0.91*
- *Na and EC: significant direct correlation with correlation coefficient of 0.846*
- *Cl and EC: significant direct correlation with correlation coefficient of 0.837*
- *Cl and TDS: significant direct correlation with correlation coefficient of 0.919*

Much less significant direct correlation can be observed between:

- *NO_3 and EC: Correlation coefficient of 0.502*
- *NO_3 and TSD: Correlation coefficient of 0.46*
- *NO_3 and Na: Correlation coefficient of 0.531*
- *NO_3 and Cl: Correlation coefficient of 0.523*
- *Ca and Mg: Correlation coefficient of 0.572*

The above results clearly show that the TDS of the water of the domestic wells is a function of both [Cl] and [Na]. No significant correlation can be observed between the concentrations of other major aquifer components namely Ca, Mg, HCO_3 and TDS. There is only a moderate correlation between NO_3 and EC, TDS, Na and Cl. This indicates that the [NO_3] may partially have the same origin as Na and Cl. To explain the elevated concentration of Na and Cl in most of the domestic wells in the West Bank, another source of these ions must be present that causes the contamination of the water of the wells. This source must be rich in Na and Cl ion. Because the wells are abstracting water far away from the coastal area, the sea water contamination is not likely. Other possible source of Na and Cl ions could be the municipal wastewater, which may seep into the aquifer systems with associated contamination.

The concentration of the trace constituents including the heavy metals in all the analyzed samples (Table 1) are far below the maximal acceptable concentrations based on WHO drinking water guidelines. Arsenic (A)s was not detected in any of the analyzed samples.

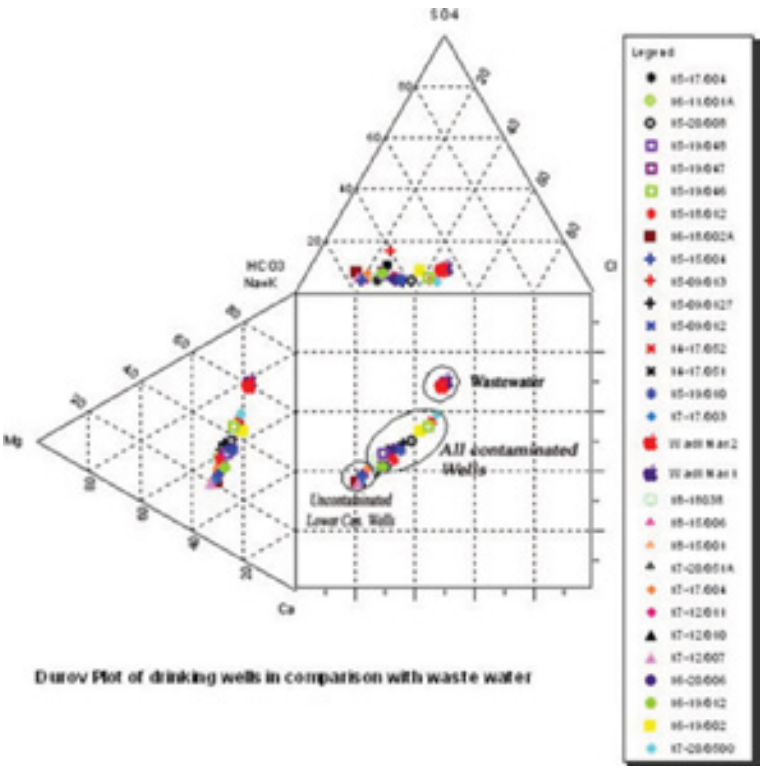

Figure 1: Durov diagram showing the relation between the water of the drinking wells and wastewater (Legend stands for well ID)

Well Code	pH	EC	Water Type	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3	TDS
16-11/008	7.25	403	Ca-Mg-HCO_3	54	20	21	0	254	37	32	6	297
15-09/013	7.27	440	Ca-Mg-Na-HCO_3-Cl	48	21	36	8	238	55	48	4	339
15-17/004	6.86	553	Ca-Mg-Na-HCO_3-Cl	58	23	35	0	258	53	12	26	336
15-19/048	7.2	451	Ca-Mg-Na-HCO_3-Cl	51	20	35	19	246	55	18	22	343
16-18/003A	7.42	426	Ca-Mg-HCO_3	51	19	21	6	258	33	19	22	300
18-15/006	7.15	402	Ca-Mg-Na-HCO_3-Cl	48	18	25	3	230	38	8	23	278
16-12/004	7.32	380	Ca-Mg-HCO_3-Cl	51	19	23	0	241	38	12	19	283
17-17/003	7.87	405	Ca-Mg-HCO_3	47	18	23	2	228	34.2	11	19	268
17-12/007	7.09	385	Ca-Mg-HCO_3	49	20	22	0	273.9	38	14	3	265
17-17/004	7.25	408	Ca-Mg-Na-HCO_3	48	20	31	0	236	38.2	17	25	297
15-15/004	7.58	292	Ca-Mg-HCO_3	52	20	23	11	244	38	10	30	306

* All concentrations are in mg/L

Table 1. Physical parameters and concentration of major ions in the water of the domestic wells tapping the Lower Cenomanian aquifer

All groundwater found in water supply wells of the mountain aquifer included in this study, is a mixture of two water sources: the alkaline groundwater with prevailing bicarbonate (Ca-Mg.HCO_3 type), which is considered to be the uncontaminated recharge water type with the Na-Cl rich member; the wastewater, which plots on Piper diagram in the area of alkaline water with prevailing chloride (Figure 1). Because the contaminated wells still have relatively low TDS and their water type does not become Na-Cl type, the portion of wastewater mixing with the recharge water is considered to be small. In other words wastewater seeps into the aquifers in small amount to contaminate the groundwater causing the increase in Na, Cl and TDS concentrations of the groundwater from the wells. In other words the portion of wastewater is low compared to the recharged precipitation water.

CONCLUSIONS

- The concentrations of the ions and parameters affecting the aesthetic and heath quality such as Cl, Na, TDS, NO_3, minor and trace constituents are within the limits recommended by the WHO drinking water quality guidelines. Arsenic was not detected in any of the tested wells.
- Signs of pollution are observed even in some deep wells tapping the Lower Ceneomanian confined aquifer.
- The source of this pollution is very likely uncontrolled disposal of wastewater.

ACKNOWLDGMENT

This study was carried out as a part of the HYDRAS project of which Birzeit University/ Palestine, Blas Pascal University/ Argentina and UNESCO-IHE/ the Netherlands are partners. The project was financially supported by the UNESCO-IHE Partnership Research Fund (UPaRF) that is partly funded by the Dutch Ministry of Foreign Affairs (DGIS). Technical support provided by Dr. Qasem Abdel Jaber is appreciated.

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NOTES

DISPUTE SETTLEMENT IN INTERNATIONAL LAW AND SHARED/DIVIDED WATER RESOURCES

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Keywords: dispute settlement, international law, international treaties, shared water resources, shared natural resources, environment, Southeast Europe.

There are several examples that suggest that the management of shared water resources (being the borderline or transection of two or more states) is an extremely sensitive issue. Some estimates indicate that this issue will become even more pressing as the utilization of water resources on the territory of one state may jeopardize the vital interests of the other or more of them. What is more, there is a prevailing stance in the literature on water resources that the state of the water resources, manner of managing water resources and various other circumstances are to become, to even greater extent, a cause of disputes between the states. The conflict potential grows as water needs increase and relations between states complicate due to various other reasons. Hence, the question of dispute settlement may become extremely important for relations between the states and international security. Examples from the current practice of the states' conduct and certain indicators from the relations between the states in some regions clearly confirm this. In an analysis of ways of settling disputes, it should be borne in mind that this issue is strongly linked to the several other questions. One of the key issues is that of liability/responsibility, but when it comes to water resources also the question of how to define the notion of water resources and other concepts (integrated management, surface water, groundwater, etc.), the question of regulating the state borders on the rivers, historical circumstances and development of the ways of using water resources, waste management, biodiversity protection, climate change impact, international treaties enforcement, etc. may also become the subject of the preliminary discussions. When it comes to liability, aside from classical rules of the states' liability for the violation of the norms of international law, in the field of environment and water resources, liability rules for damages caused by the activities not prohibited by international law could be of the particular significance.

Rules on dispute settlement between the states were established under various international agreements, including international agreements in the field of water resources management. Although the obligation to respect international treaties is considered to be one of the fundamental principles of the legal order, disputes concerning the interpretation and application of international treaties may occur due to several circumstances. Among these circumstances may be unclear provisions of the contracts, gaps in the contracts, changed circumstances, etc. Changes in the level of technological development may affect the new (subsequent) consideration of the interests of the relevant states and the manner of interpretation of certain obligations and rights stipulated by the international agreement.

As a general framework, modern international law provides with several ways of resolving disputes by peaceful means: 1) diplomatic (negotiations, good services or mediation, conciliation, inquiry commissions) and 2) judicial (arbitration, the International Court of Justice, etc.). Some awards of the arbitral bodies and of the International Court of Justice in some previous cases represent an inexhaustible example of variations in the interpretation of certain rules of international treaty law pertaining to water resources management. Recent international agreements which have for their object the regulation of the particular issues in the field of shared natural resources or international agreements in the field of water resources and the environment, in a similar way regulate these issues. Most frequently, Member States undertake to settle their disputes concerning the interpretation or application of an international agreement through negotiation processes, but if they fail, two general ways of resolving disputes are offered. These are the arbitration or submission of the dispute to the International Court of Justice (United Nations Framework Convention on Climate Change, Art. 14; the Convention on Biological Diversity, Art. 27; the United Nations Convention to Combat Desertification in those countries

experiencing serious drought and/or desertification, particularly in Africa, Art. 28; the Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal, Art. 20, etc.) At the same time, Member States of the contract at the time of its ratification, acceptance, approval, accession or at some time later are often provided with the possibility to opt for one of these two ways of judicial settlement of disputes. Generally speaking, such a practice also exists in the international multilateral treaties of direct relevance to the region of Southeast Europe. Convention on the Law of the Non-navigational Uses of International Watercourses also provides for the possibility for countries to opt for one of the two ways of disputes settlement. It is similar situation also in the cases of the Convention on the Protection and Use of Transboundary Watercourses and International Lakes ("Off. Gazette FRY–International Treaties", no. 1/2010), the Convention on Cooperation for the Protection and Sustainable Use of the Danube River ("Off. Gazette FRY–International Treaties", no. 2/2003), the Framework Agreement on the Sava River Basin ("Off. Gazette SCG", no. 12/2004). However, there are some differences. The Convention on Cooperation for the Protection and Sustainable Use of the Danube River in its Article 24 provides for the obligation of Member States to find a solution to the disputes through negotiations or through some other form of dispute settlement acceptable to the Contracting Parties to the dispute. The possibility that the assistance is rendered by the International Commission for the Protection of the Danube River is also available. However, if the parties to the dispute are unable to resolve the dispute within 12 months after the International Commission has been notified about the dispute by the parties, the dispute shall be solved in one of the quiet ways: through the International Court of Justice, or the arbitration in accordance with Annex V to this Convention. Arbitration is preferred if the state parties to the dispute have not accepted the same means of dispute settlement, or in the event that a Member State has not opted for one of the available means of dispute settlement. However, in the case of the Helsinki Convention on the Protection and Use of Transboundary Watercourses and International Lakes preference is given to resolving the dispute before the International Court of Justice (Art. 22 of the Convention). Framework Agreement on the Sava River Basin firstly enumerates all the "classic" methods of dispute settlement (negotiation, "good services, mediation or conciliation from a third party"), and then leaves the possibility of resolving the dispute through arbitration or the International Court of Justice. This agreement provides for the opportunity to introduce the possibility that any Party concerned "may request that an independent fact-finding expert committee be established" if, within six months from submitting a request, the concerned parties are unable to resolve the dispute through negotiation, good services, mediation or conciliation (Art. 22 -24).

The main objective of this paper is the assessment of the specificities in regulating the ways of dispute settlement concerning interpretation and application of international agreements in the field of water resources, of importance to the region of Southeast Europe.

MODEL-BASED ANALYSIS OF HYDRAULIC LOSSES AT DRAINAGE WELLS ALONG THE DANUBE RIVER

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Abstract: The main role of the riparian land drainage system is to protect lower agricultural areas from elevated groundwater levels, in order to avoid damage and flooding of agricultural crops. Drainage system is made from an open-channel network, in combination with free-flowing wells and a pumping station. Free-flowing wells were carried out on drainage channel sections, where, due to the large thickness of the overlying layer, channels' bottoms did not make any contact with the aquifer. Development of the mathematical groundwater flow model, aims to examine the need for wells recovery using hydraulic calculations.The aim of this paper is to show how wells could be represented with a different type of border conditions, by using this particular software. The conceptual approach to the drainage wells simulation in given conditions, can serve as an example for problem solving in other locations.

Keywords: drainage systems, free-flowing wells, mathematical model.

INTRODUCTION

The construction and exploitation of the Đerdap 1 (Iron Gates) hydroelectric power plant dam has impacted large areas and farms along the Danube riparian land and its main tributaries due to elevated stages in the accumulation, as well as higher groundwater levels in the area to the point of reaching backwater. This has necessitated the construction of drainage systems, to protect riparian lands and communities from the adverse effects of the backwater. All systems have been designed to meet the certain criteria, by maintaining specific groundwater levels under all hydrologic conditions.

The main role of each drainage system is to protect low-lying farmland from elevated groundwater levels and thus prevent damage from flooding of crops (Jaroslav Černi Institute, 2007). The levees in this sector, which protect farmland, the village of Knicanin and the lowest parts of the village of Centa from surface water, have been built along the Karasac, Danube, Tisa and Begej rivers (Fig. 1).

Today, the Knicanin-Centa drainage system comprises a network of channels in combination with free-flowing wells and a pump station (Centa PS). Channel II was built parallel to a line of levees; it is about 4 m long and 2-3 m wide at the bottom. The free-flowing wells were built along certain sections of Channel II, where the thickness of the aquifer roof prevents the bottom of the channel from coming into contact with the aquifer. There is a total of 66 free-flowing wells, 15-30 m deep, which have been in service for more than 30 years (Radanovic, Nikolic, 2012), (Fig. 1).

The role of the wells is to lower the piezometric pressure in an aquifer and thus prevent caving of slopes and rising of the bottom of the channel. The free-flowing wells deliver groundwater to the channel and the pumping station evacuates it from the area (Radanovic, Nikolic, 2012).

Long-term testing of the wells has revealed increasing hydraulic resistances in the near-well region, which have reduced the specific discharges of the wells. It is well known that well efficiency (discharge) declines over time due to well ageing, until the wells are ultimately decommissioned. Well ageing is caused by clogging of the well screen and near-well region. This results in increasing piezometric head in the flood-protected area, which might lead to considerable damage (Dimkic et al., 2011). It was therefore necessary to rehabilitate the wells, or replace those that did not have a drainage function, and thus ensure protection according to design criteria.

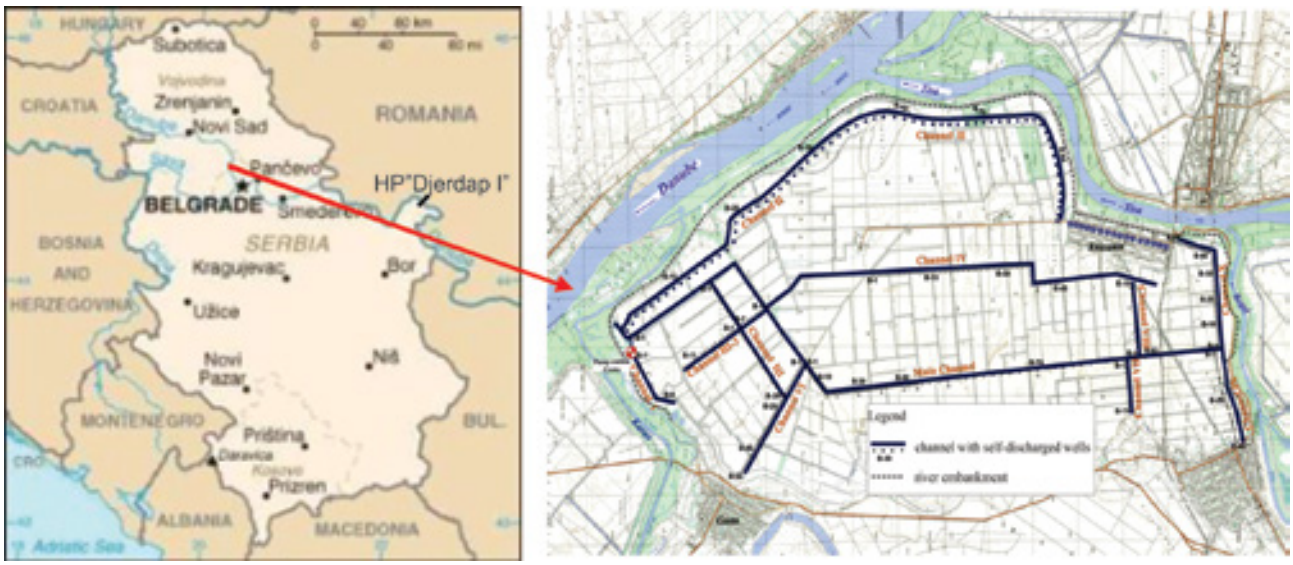

Figure 1: Map and layout of Knicanin-Centa drainage system

A schematized series of free-flowing wells along Channel II and groundwater drainage from the aquifer into the open channel are shown in Fig. 2. Free-flowing wells are not equipped with a pump; instead, the water flows on account of natural pressure and is discharged via a horizontal pipe.

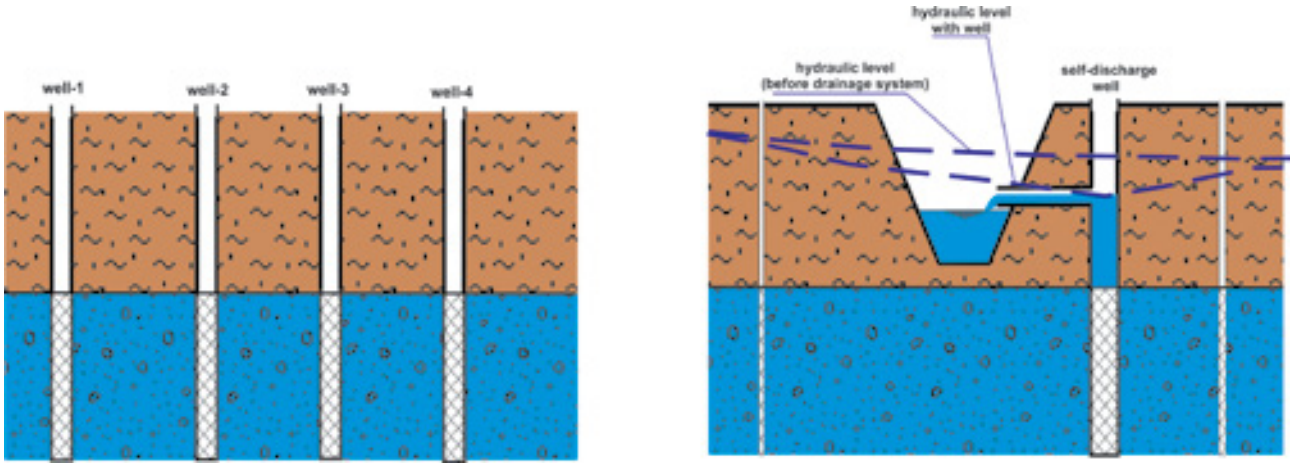

Figure 2: Schematized system comprised of a series of free-flowing wells and a drainage channel.

METHODS

Groundwater Vistas (Version 6.74) – integrated 3D software for mathematical modeling of groundwater flow – was used to analyze the groundwater regime in the study area. (Chiang, Kinzelbach, 1998)

The purpose of developing a mathematical model of groundwater flow was to simulate the conditions prevailing in the area of Channel II of the Knicanin-Centa drainage system, with a series of free-flowing drainage wells operating under present conditions, and then conduct hydraulic analyses to examine the need for rehabilitation (Zivanovic, 2015).

The mathematical model was developed on the basis of available data, the results of field investigations, and systematic monitoring of groundwater level. The flow field was schematized as a dual-layer porous medium, whose characteristics were heterogeneous in both plan view and cross-section.

The aquifer geometry was specified in the model by means of the elevations of the aquifer roof and floor, based on previous investigations. The main aquifer is situated below a semi-permeable overlying layer; it is comprised of sand and gravel sediments. The impermeable underlying layer is made up of Pliocene clay.

In the hydrodynamic model, the Danube and the Tisa were specified as river-type boundaries. They are in direct hydraulic contact with the aquifer and are the main drivers of the local groundwater regime.

The drainage channels were represented in the model by drain-type cells. The channel water level was specified on the basis of continuous water level monitoring at the delivery channel to Centa PS, and the hydraulic conductivity of the bottom of the channel was specified depending on whether the bottom was in the overlying strata or the water-bearing layer. This was verified by calibration of the mathematical model.

The free-flowing drainage wells along Channel II were represented in the model by drain-type cells as well, upon adjustment of certain parameters. The specified inputs were the water level in the cell and the hydraulic conductivity, and the output was discharge. In the calibration process, hydraulic conductivity was specified depending on the drainage function of a particular well. The function of this boundary condition was as follows: When the hydraulic water level in the cell was higher than the elevation of the water inside the drain, the water flowed to the drain. The flow to the drain was zero when the hydraulic water level was equal to or lower than the water level in the middle of the drain. Flow from the drain was always zero, regardless of the hydraulic water level in the aquifer (Chiang, Kinzelbach, 1998, Rumbaugh, 1996). The operation of the free-flowing wells was simulated with the elevation of the center line of the free-flowing well pipe corresponding to the water level in the middle of the drain (or well). The standard procedure is to specify the well as a boundary condition of the well type, as well as the discharge (or flux), and the result is the piezometric head in the "cell". This water level was at a distance of 0.208 Δx from the center of the cell, where Δx is the cell width (Fig. 3). As such, the water level at the said distance did not correspond to the real water level in the well because additional losses in the near-well region were disregarded (Vukovic, Soro, 1984). In practice, this raises the question whether "realistic" results are obtained since *Groundwater Vistas* does not recognize a well as a real structure, only as the specified discharge (flux).

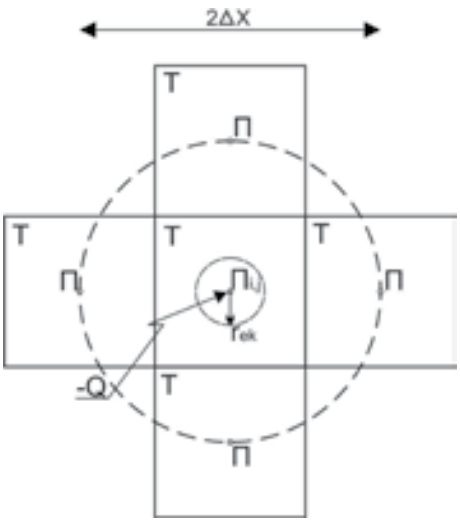

Figure 3: Discretized cell with simulated well in the center of cell i,j.

r_{ek} – equivalent radius of influence of imaginary well;

Δx – cell width;

$r_{ek} = 0.208\ \Delta x$

Πij – piezometric head in discretized cell

The additional loss in the near-well region, or the piezometric head when the transition is made from the imaginary to the real well, was derived from an expression of the form (Vukovic, Soro, 1984):

$$\Delta S = \frac{Q}{2\pi T} \ln \frac{r_{ek}}{r_0} + B * Q^2$$

where:

ΔS – analytical additional loss [m]

Q – well discharge [m^3/s]

T – transmissivity of the water-bearing layer [m^2/s]

B – coefficient of quadratic loss [$m^{-5}s^2$]

r_0 – well radius [m]

The piezometric head of the real well was obtained by deducting the analytical additional loss from the piezometric head in the discretized cell.

Consequently, to get an accurate result, it was necessary to either analytically calculate the water level in the cell with additional losses or alter the discretization (increase cell density) such that it corresponded to the real cell size.

RESULTS AND DISCUSSION

The flow domen was discretized in plan view by a grid of squares, with divisions consistent with the orientation of model boundaries. The cell size was 50 x 50 m. The model was made up of 340 rows and 250 columns, or a total of 170,000 cells, of which 28,745 were active. The surface area represented by the mathematical model was 213 km^2.

The hydrodynamic model of groundwater flow was simulated under stationary conditions (May 2012). In the calibration process, it was necessary to match analytical groundwater levels to those recorded by existing piezometers and adjust the resulting water balance to the flow rate at the pump station, given that the pump station received all waters from the study area.

The results of the hydraulic analysis with the calibrated and verified model indicated which wells were not functioning (the resulting discharge was zero and the ultimate water balance of the system was consistent with real data). The mathematical model calculations were assessed and the best solution selected for the operation of the drainage channel in the design range of operating water levels at the pump station, which called for replacement of 17 free-flowing wells along the most threatened sections of the drainage channel, to neutralize large differences between the piezometric head in the area of Channel II and the water level in the channel. Replacement of the 17 wells resulted in a new water balance and flow pattern as achieved by the rehabilitated system.

CONCLUSION

The aim of this research was to show that the above-described software can be used to represent a well by a different type of boundary condition (i.e. “drain” instead of “well”). The advantage of such a model is that for an accurate result it is not necessary to increase the discretization density, to correspond to the real size of the cell which contains the well. When the drain-type boundary condition was used, the model had much fewer active cells and the calculations took much less time, given that the speed directly depends on the grid density and number of active cells.

This conceptual approach to the simulation of drainage wells under the given conditions can be used as an example when similar problems are addressed at other locations.

ACKNOWLEDGEMENT

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TACKLING CHALLENGES OF SOCIAL AND CLIMATE CHANGE BY A NEW SUSTAINABILITY CONTROLLING APPROACH FOR GROUNDWATER MANAGEMENT

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Abstract: The circumstances and requirements of groundwater management for urban water suppliers are under constant strain and exposed to unsteady frame conditions associated with climate change, shifting social and economic patterns and regulatory circumstances. At the moment no suitable management instrument exists that enables the identification and the assessment of sustainability risks systematically and deducing measures for risk prevention and reduction. This paper introduces a new sustainability controlling approach, which addresses urban water service providers and decision-makers. It focuses on a methodological framework for multidimensional risk identification and system analysis as a result of the collaborative research project NaCoSi. It is based on an interdisciplinary and transdisciplinary approach. Various sustainability risks can be identified and controlled to achieve a sustainable groundwater management. The methodological framework identifies and systemizes complex and dynamic cause-effect relationships in water systems using a causal chain approach. Sustainability risks are made accessible to different methods for subsequent risk assessment. The sustainability controlling was successfully tested and improved by an iterative process of case studies in cooperation with 12 practice partners from the German water sector.

Keywords: ground water management, sustainability controlling, risk management, causal chain concept, cause effect relationships,

INTRODUCTION

Global groundwater resources are facing increasing pressures, resulting from regional consequences of climate change and/or shifting demographic and economic patterns (Taylor et al, 2013). Failure of climate change mitigation and water crises are ranked as most significant long-term risks (World Economic Forum, 2016). Challenging factors for sustainable water management are for example fast growing water demands in urban and suburban areas, changing the required quantity of groundwater, while other factors like severe chemical contamination are affecting the quality of groundwater bodies (McDonald 2011, McDonald et al., 2011, 2014, Vörösmarty et al., 2000). Therefore, these causes are influencing not only the conditions but also the requirements for groundwater management and are related to different time periods and effects. In order to systemize, monitor and evaluate all these complex and interrelated cause- effect- relationships, an adaptable management concept is needed. Decision-makers have to manage indispensable groundwater resources in a sustainable manner and observe potential risks for various uses.

For this purpose the collaborative inter- and transdisciplinary research project “Sustainability Controlling for Urban Water Systems” (NaCoSi), which is funded by the German Federal Ministry of Research and Education, developed a risk based sustainability controlling approach, which can be used to identify and efficiently tackle future risks at an early stage. This management approach allows water service providers and decision-makers to identify and evaluate sustainability risks in the long term, comprising amongst others groundwater related risks. A method for risk identification has been developed, which allows the diverse risk factors and risk pathways to be systematically gathered, in order to make them accessible for a subsequent analysis.

Groundwater resources are a key component of the NaCoSi approach and part of the adaptable risk database. This paper outlines the approach and methods, from which the NaCoSi sustainability controlling is assembled.

METHODS

The sustainability controlling approach is based on common process-oriented management systems. It is designed as a continuous improvement process and consists of different interacting steps which in turn include several methods, Fig. 1.

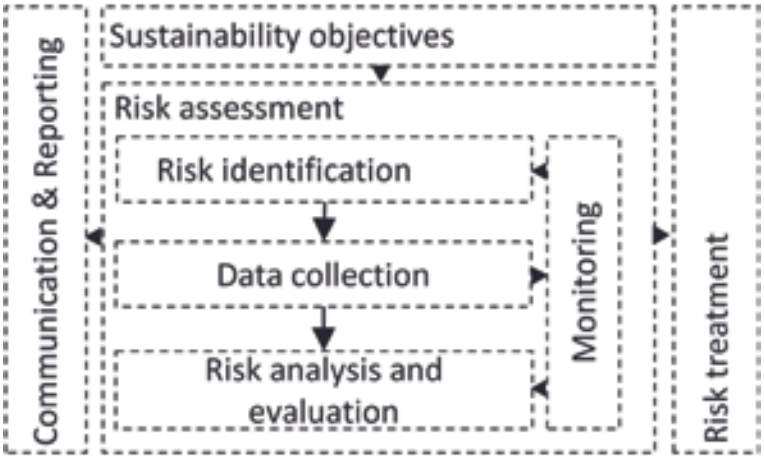

Figure 1: NaCoSi sustainability controlling approach

In particular, elements of risk management are used (ISO 30010:2009). The link with existing management systems allows a streamlined implementation or expansion of existing management systems towards an integrated management system. In order to understand and encounter complex and dynamic causes in water systems, cause-based risks were identified and systemized by using the causal chain concept. In water systems, a single cause can have various effects and subsequently can affect various sustainability objectives. On the other hand, a single sustainability objective might be affected by several causes. The aim of the causal chain concept is to minimize the complexity of multidimensional, interrelated sustainability risks in order to create a consistent database. On this basis, different methods for risk assessment, monitoring and trend analysis were developed and tested (Geyler et al., 2015).

The starting point is a system of sustainability objectives. These were developed in cooperation with partners from technical, economic and socio-ecological research facilities and practice partners from the German water sector e.g. water service providers. The objectives serve for the operationalization of sustainability in the water sector and ensure a general understanding of all features concerning sustainability (Eller et al, 2014). The systematization of the sustainability objectives was orientated at the five-pillar model of the DVGW (German Technical and Scientific Association for Gas and Water) and the DWA (German Association for Water, Wastewater and Waste) (DVGW W 1100, 2008). A long term perspective together with the intergenerational justice was included for the understanding of sustainability for water management. The target group of the developed sustainability objectives are at the moment water service providers. Because of the broad target group of the goals and the comprehensive understanding of sustainability, the goal systems gives an ideal basis for further specification and adaption. The developed sustainability objectives have an open and adaptable structure and it is easy to add respectively change different goals in order to adjust them to other requirements of different stakeholder, like water authorities or groundwater departments of water companies.

In the first step –the risk identification-, a systemized risk database with over 300 cause effect chains was created by literature and expert knowledge, regarding groundwater as a decisive component of the database. The complex networks of cause-effect relationships are disassembled into unbranched linear causal chains, which are managed and systemized as records in a risk database. In figure 2 the systematization and examples of the causal chain concept are shown. The risk source triggers the cause of a sustainability risk and thus is causally prior to the risk's cause. It provides additional information about the origin and character of the risk and thereby helps to specify the cause category. As a cause may be gradually traced back infinitely, the cause of a sustainability risk is defined as the last event of a sequence of causal events that directly draws an impact on the water system. The consequence, which is defined as an observable effect of a related cause, is associated to a certain system, subsystem and process in the water supply system. The sustainability hazard specifies why and how exactly the corresponding sustainability objective is affected. It is characterized by an indicator, which has a yellow and red threshold. The yellow threshold describes a noticeable indicator value, while the red threshold describes a critical state. The indicators make the sustainability hazard measureable and serve for a monitoring tool. As the last element of each causal chain the affected sustainability objective, as described above, is addressed. Finally, the endangered sustainability objective is assigned. The causal chains are management in a risk database, which is open-ended and can be expanded with future risks.

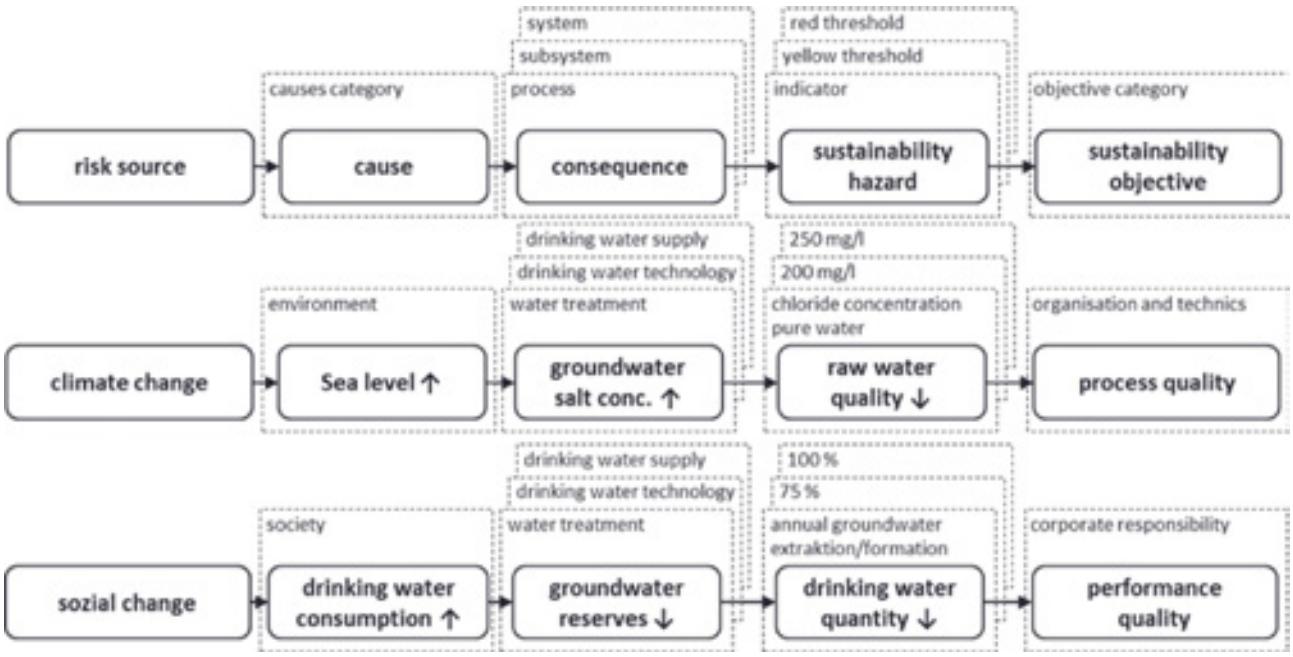

Figure 2: Systematization and examples of the causal chain concept

Figure 2 shows two examples of the causal chain. In the first example the sea level is rising (cause), because of the climate change (risk source). The cause category is environment. A rise of the sea level may lead to an increasing salt concentration in the groundwater (for example sea water intrusion into coastal aquifer), which affects the system drinking water supply, the subsystem drinking water technology and the process water treatment. The sustainability hazard results from decreasing raw water quality, which can be indicated by a chloride concentration of drinking water (indicator). It has a threshold of 200 mg/l (yellow) and 250 mg/l (red) and is assigned to the sustainability objective process quality. The thresholds, which describe the deviation of the sustainability objective, are derived by the German drinking water ordinance. The sustainability objective process quality is assigned to the objective category organization and technics. The second example follows the same structure regarding social change. The presented structure helps to manage the database in terms of reducing the complexity, extracting specific information and identifying vulnerabilities.

In the second step -the data collection-, user specific data are recorded. Every causal chain describes a potential risk, which is characterized by the extent of loss and the probability of occurrence. These are conditioned by of the selected period, the specific cause and the level of the threshold. With the help of this information, a detailed questionnaire regarding indicators, the extent of loss and the probability of occurrence for every causal chain are derived. The structure the causal chains open the possibilities to filter the database for certain processes or subjects and keep the effort for the data collection as low as possible.

In the third step –the risk analysis and evaluation (Figure 3), the identified risks are visually ranked by risk matrices, which are commonly used as a risk screening tool (ISO 30010:2009). Risk Profiles depict the risk situation at a glance as the risks are summarized for each sustainability category and plotted as radar charts. Indicators are aligned to boundary values (monitoring) and with the help of indicator

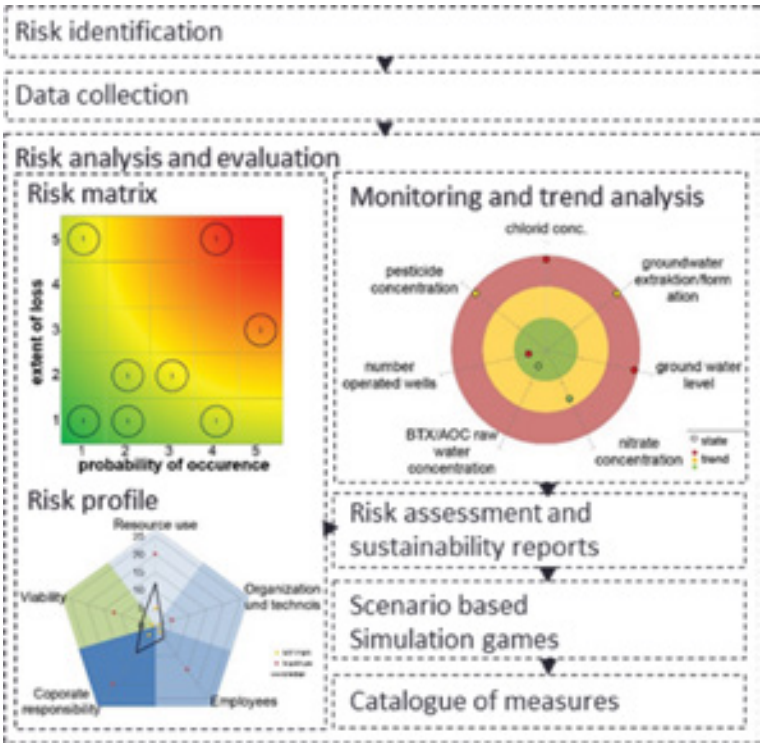

Figure 3: NaCoSi tools

time series, a trend analysis is conducted. The results from both tools were used to examine the conformity in order to validate the risk level of every causal chain and to subsequently evaluate them. The results of the risk assessment are summarized in sustainability reports as successful risk assessment is dependent on effective communication and consultation with stakeholders. Based on the reports, future worst case scenarios are developed. Workshops regarding different risk scenarios are organized. In these workshops simulation games with different stakeholder characters are conducted and simulated by the participants. As a result of these workshops, strategies are developed to avoid or exit the different future worst case scenarios. As an important outcome of the workshops a catalogue of measures for short and long term risks are developed.

RESULTS AND DISCUSSION

One of the main results is the created approach for sustainability controlling. It was tested by twelve practice partner within two different runs. In the first run the developed approach, the required completeness of the causal chains and the fulfillment of the different demands could be tested. After the first run the interface of the different developed steps and instruments has been harmonized. The data collection has been divided into a basis and a company specific data collection to reduce the effort for the participating companies. Within the second run the optimized version of the approach for sustainability controlling was tested and validated. The applied and sophisticated approach for sustainability controlling can be focused on groundwater risk management. With the extension of new groundwater causal chains the data collection can be adapted. It could be shown, that groundwater related issues, which are not presented by the database now, can be easily added. Especially future risks regarding long time processes, like social and climate changes can be managed by the database and the developed tools for risk assessment can smoothly process the new data. This paper shows that the causal chain concept is an effective approach to systematically record groundwater related risks, describe them with indicators and assign them to sustainability objectives. Because of synergy effects from existing management approaches, users have an easy and adaptable access to the NaCoSi methods. The objective to support the participating companies on their way to a long-term sustainable performance was achieved.

CONCLUSION

The successful application by twelve water service providers of the NaCoSi sustainability controlling has shown that the developed causal chain concept can be an effective approach for the identification of groundwater related risks. The NaCoSi sustainability controlling generates a conceptual method in which different steps and processes are defined, delimited and described. Sustainability objectives for water management have been evolved. A risk assessment has been developed, which consist of risk identification, data collection, risk analysis and evaluation and monitoring. The risk assessment is already used for groundwater related risk and an adaption is not required.

The causal chain concept for risk identification is the basis for the NaCoSi sustainability controlling approach and the focus of this paper. It allows the systematical identification of sustainability risks by the help of the causal chain concept. The causal chains are collected in a risk database, which include among others groundwater related risks and can be easily expanded by specific groundwater threats. By means of different systematization options of the risk database vulnerable processes, potent risks and especially endangered sustainability objectives can be spotted. It could be shown that the adjustable structure provides a versatile basis for risk analysis and has the potential for a risk based ground water management with a focus on sustainability.

The objective to support users on their way to a long-term sustainable performance and to minimize the complexity of multidimensional, interrelated sustainability risks has been achieved. Because of synergy effects from existing management approaches, water management has an easy and adaptable access to the NaCoSi sustainability controlling approach.

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NOTES

VULNERABILITY OF GROUNDWATER TO POLLUTION USING VLDA MODEL IN HALABJA SAIDSADIQ BASIN, IRAQ

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Abstract: Groundwater considered being the most vital source of water in several regions in the world. Specifically in the Halabja-Saidsadiq Basin, groundwater plays an important role as one of the essential source of water supplies. Therefore, it needs to be taken care of. In this study, VLDA method applied to model a map of groundwater vulnerability to contamination. The VLDA model classified the area into four categories with different coverage area: low (2%), moderate (44%), high (53%) and very high (1%). After constructing every vulnerability maps, it required to be confirm in order to estimate the validity of the theoretical sympathetic of current hydrogeological conditions. In this study, nitrate concentration analysis was selected as a contamination indicator to validate the result. The nitrate concentration between two different seasons (dry and wet) was analyzed from (30) water wells, considerable variations in nitrate concentration from dry to wet seasons had been noted. Consequently, it point toward that groundwater in the HSB are capable to receive the contaminant due to suitability of overlies strata in terms of geological and hydrogeological conditions. Based on this confirmation, the result exemplify that the degree and distribution of vulnerability classes acquired using VLDA model are more sensible.

Keywords: Vulnerability, VLDA, Nitrate concentration, Halabja Saidsadiq Basin (HSB).

INTRODUCTION

Groundwater considers being an important water sources in various region. Halabja and Saidsadiq Basin(HSB) that is located in the northeastern part of Iraq (figure 1), is one real example as a source for drinking, industrial and agricultural activities. This area in the past was destructed by army attacks by chemical weapons. After 2003, the area is experiencing considerable economic development and enhanced security. In view of these changes, there is an increase in the numbers of people heading to live in this basin and its surrounding regions. This is imposing a growing demand for water which has placed substantial pressures on groundwater resources. While, the studies of the groundwater resources and its potential pollution in the area has not been taken into account yet in the area.

Groundwater vulnerability is a measure of how easy or how hard it is for pollution at the land surface to reach a productive aquifer. The vulnerability studies can provide valuable information for stakeholder working on preventing further deterioration of the environment (Mendoza & Barmen, 2006). To simplify the identification of the groundwater state and to resist the pollutants in the reservoirs, several methods were recommended such as DRASTIC, VLDA, COP, GOD, SINTACS, etc. These different methods are offered under the form of numerical excerpt systems based on the negotiation of the different factors affecting the hydrogeological system (Attoui and Bousnoubra 2012). Therefore, the objective of this study is to model the groundwater vulnerability map using VLDA method as the first attempt to protect the groundwater from contamination.

Study Area

Geographically, Halabja Saidsadiq Basin is located in the northeastern part of Iraq between the latitude 35” 00 00" and 35" 36’ 00" N and the longitude 45” 36’ 00" and 46” 12’ 00" E (figure 1). Ali (2007) divided this basin into two sub-basins including Halabja- Khurmal and Said Sadiq sub-basins. The whole area of both sub-basins is about 1278 square kilometers with population of about 190,727 in the early 2015. About 57% of the studied area is an arable area due to its suitability for agriculture (Statistical Dtectorate,2014). Consequently, the use of fertilizers and pesticides are common practices, so it affects the groundwater quality (Huang et al, 2012).

Geology and Hydrogeological Setting

Geologically, the studied area is located within Western Zagros Fold-Thrust Belt. Structurally, located within the High Folded zone, Imbricate and Thrust Zones (Jassim and Goff, 2006). The age of the exposed rocks in the area is from Jurassic to the recent. In addition, the area is characterized by at least four different hydrogeological aquifers due to presence of different geological units. The characteristic features of the aquifers and all exposed rocks in the basin are tabulated in the table (1).

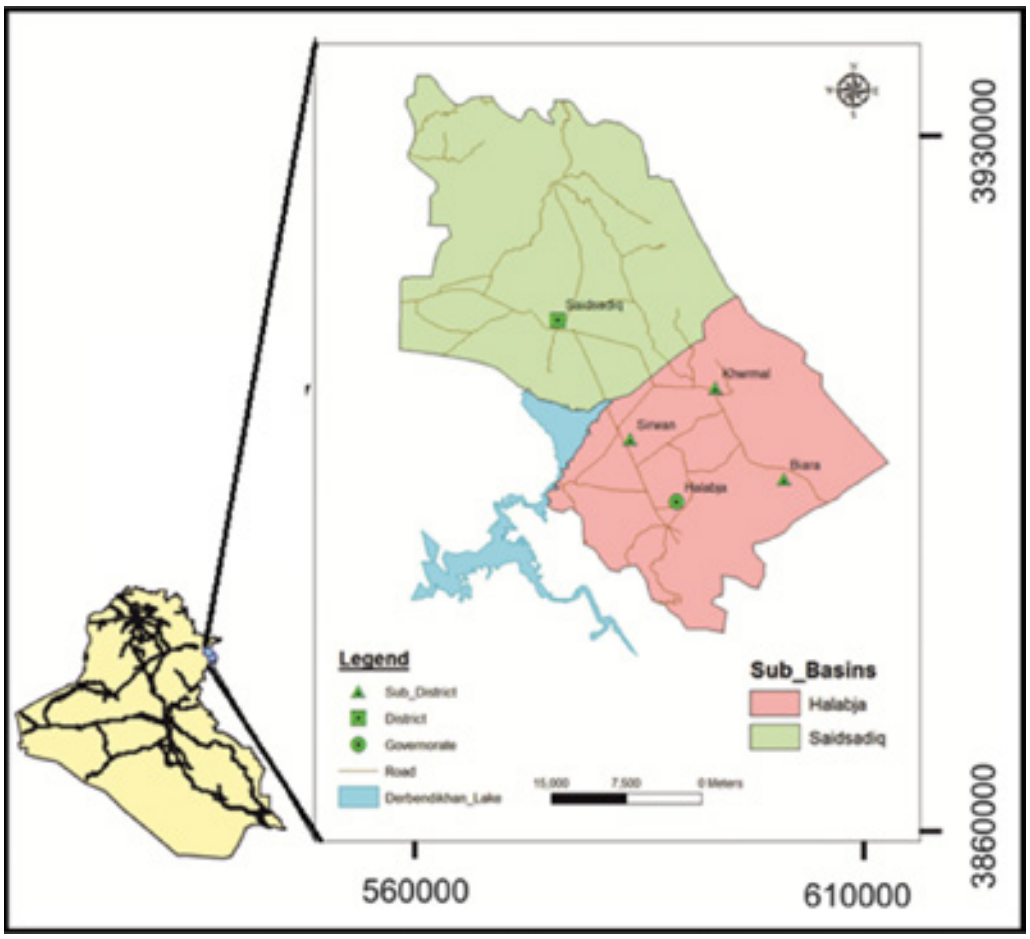

Figure 1: Location map of study basin.

Aquifer type	Geological formation	Thickness (m)	References
Intergranular Aquifer	Quaternary deposits	more than 300	Abdullah 2015 a
Fissured Aquifer	Balambo Kometan	250	Ali,2007
Fissured-Karstic Aquifer	Avroman Jurassic formation	200 From 80 to 200	Jassim and Goff,2006
Non-Aquifer (Aquitard)	Qulqula Shiranish Tanjero	more than 500 225 2000	Jassim and Goff,2006

Table 1. Type of aquifers in the study basin.

The data used for groundwater vulnerability mapping using VLDA method were collected from the field and officially from archives of all related offices. Features were used to create the shape files with GIS (Arc Map 10) software. On the basis of the DRASTIC model for assessing groundwater vulnerability and in accordance with certain principle, VLDA model is proposed by (Zhou et al, 2012). VLDA principally reflects lithology of vadose zone (V), pattern of land use (L), groundwater depth (D), and aquifer characteristics (A). In addition, consistent weight can be assigned to each of the four indexes depending on its impact on groundwater vulnerability.

The vulnerability comprehensive assessment index (DI) is the sum of the above-mentioned weighted four indexes, as computed conferring to the following formula:

$$DI = \sum_{j=1}^{4} (\mathrm{WijRij}) \qquad (7) \quad \text{(Zhou et al, 2012)}$$

Where DI is the comprehensive assessment index of the ith sub-system of the groundwater vulnerability system in the HSB. W_{ij} is the weight of the jth comprehensive assessment index of the ith sub-system, and $\sum_{j=1}^{4} \mathrm{Wij} = 1$, R_{ij} is the value of the jth assessment index of the ith subsystem; 4 is the quantity of indexes.

The slighter the DI signifier to the lower vulnerability of the groundwater system and the better the stability will be. For evaluating the groundwater vulnerability, different weights were proposed by different researchers. As a result, on the basis of the arithmetic averages from previously applied normalized weights, the weight value for VLDA proposed to be 0.286, 0.251, 0.191 and 0.271 respectively. While, for this study, the new corresponding weights in HSB were proposed using sensitivity analysis method (Abdullah 2015 b). According to the result of sensitivity analysis, the proposed weights used for VLDA model measured as 8.2, 4.8, 5.2 and 4.8, and after normalization, the weight is 0.357, 0.209, 0.226 and 0.209, respectively, (table 2).

Calculation of indexes	Lithology of vadose zone (V)	Pattern of land use (L)	Groundwater depth (D)	Aquifer characteristics (A)
Weights-Sensitivity analysis	0.357	0.209	0.226	0.209
Weights-previously proposed	0.286	0.251	0.191	0.271

Table 2. Weights of indexes in VLDA model

RESULT AND CONCLUSIONS

The vulnerability outcome (figure 2), reveals that a total of four ranges of vulnerability indexes had been noted ranging from low to very high with vulnerability indexes (2.133-4, >4-6, >6-8 and > 8). The area of low vulnerability with vulnerability index (2.133-4) occupy an area of (26 Km^2) or (2%) of the whole area and located in the south west of the basin. While very high vulnerability class covered the central part of the basin with index value of (>8) and an area of (1%) or (13) Km^2. This area is characterized by high water table level and presence of several springs with fractured limestone, it means such area where (V, D and A) have the highest value. The High vulnerability class occupied the most of mountains area that surrounding the basin and the central part of HSB. This vulnerability zone covered an area of (677) Km^2 or (53%). Finally, medium vulnerability zone cover an area of (562) Km^2 or (44%) of all studied area and positioned southeast and northwest of the basin. The last two vulnerability classes (high and moderate) that occupied most of the studied basin refer to the exhaustive human activities, good water yield property of the aquifers and fissured limestone and coarse-grain aquifers as vadose zone type.

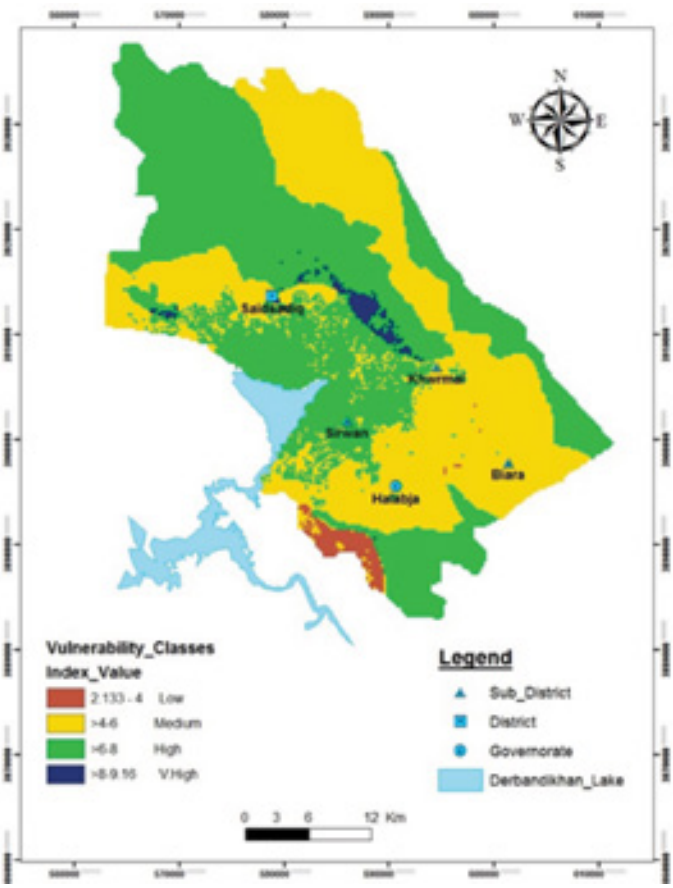

Figure 2: VLDA Vulnerability Index Map of HSB

VALIDATION OF THE RESULT

Each vulnerability maps should be confirming after constructing in order to estimate the validity of the theoretical sympathetic of current hydrogeological conditions (Bruy`ere et al,2001and Perrin et al, 2004). In order to validate both applied models at HSB, nitrate concentration analysis has been selected. In the particular studied case, the nitrate concentration differences between two following seasons (dry and wet) were analyzed from (30) water wells. The selected wells for nitrate concentration measurement located nearly in all vulnerability zones at each models. The average of nitrate concentration in dry season were (>10) mg/l for both classes respectively. Whereas, for the wet season the concentration were considerably risen up (>30) mg/l for each class. Therefore, these considerable variations in nitrate concentration from dry to wet seasons, figure (3), verify the sensibility of the degree and distribution of vulnerability levels acquired using the VLDA model.

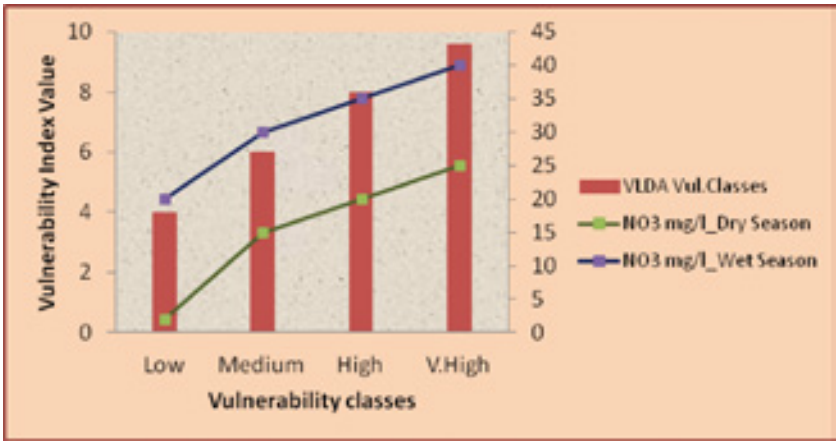

Figure 3: Comparison of Both model with nitrate concentration.

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GROUNDWATER MANAGEMENT IN THE METROPOLITAN ZONE OF GUADALAJARA: THE CASE AQUIFER RECHARGE ZONE CALLED "EL BAJIO DEL ARENAL"

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Abstract: This paper consists in presenting a specific groundwater problematic in the metropolitan zone of Guadalajara (MZG), which is the second largest city in Mexico. The water supply of this urban concentration is 30 % dependent on groundwater; the rest comes from surface sources. During the last years the urbanization was been expanded with out order covering almost the surface of the watershed. This situation has produced a contradictory situation. In one side, the urbanization avoids the infiltration rate that reduces the groundwater availability, and in the other hand, it is produces floods every year. This situation is more serious because the urbanization is still covering the aquifers recharge zone specially "El Bajío del Arenal" that is located in the western part of Guadalajara. This area is part of La Primavera Forest, which is being threatened by developers. Already this area has been affected by the construction of Soccer Stadium and Pan-American dorms built for the games celebrated in 2011. Nevertheless, the local government is still promoting the urbanization of the rest of the zone. This situation has provoked a complex debate between voices in favour the urbanization and voices against. This paper shows the arguments from both sides during an intensive debate that endures more than one a half year through more than 20 technical and political meetings. From this experience arose the lack of official technical groundwater information and opened the need to study more about its situation. Besides, arose some questions as such as: how much water do we have in order to supply the next generations? What would happen if Guadalajara still pumping groundwater with out measurements? How much time do we have to solve this problematic? This paper analyzes the groundwater management in the zone, describes the debate, presents the agreements after the controversy and establishes a technical and political proposals in order to detain the damage and restore the aquifers.

INTRODUCTION

The groundwater management is an important issue in the world, more than a half o population in the world depends on this vital resource. The NASA and UN have stated that in 2050 maybe there will not be more groundwater for the human beings. This situation needs to be studied carefully in every region of the planet. MZG is one of the biggest urban concentrations in Latin America. This represents a huge environmental problem in the Mexican republic that should be assessed carefully because the scarcity is growing up alarmingly. In the other hand, in Guadalajara is flooded every reason producing high economic and human losses. For this reason it is necessary to realize a serious study about the groundwater situation in Guadalajara that shows the groundwater situation in terms of quantity and quality in order to meet the present and future thirst. Nowadays, the urban growth is pressing the natural resources with out concern about is state, producing serious environ damages that could be difficult to restore in the next years. El Bajío del Arenal is one of the recharge zones affected by the urbanization recently and it suffering the urban from developers who want to finish this disordered growth. This situation opened a debate between urban developers and environmentalists. This paper shows the result of this controversial process.

BACKGROUND

Water supply for Guadalajara comes from Chapala Lake (60%), Atemajac and Toluquilla aquifers (30%) and Calderon Dam (10%). As it can see, the dependence from groundwater is relevant because after Chapala source, the aquifers offer the third part of water supply. The scarcity of water is big problem for the city that it has

been addressed properly because the water policy has been based only on the construction of dams that have destroyed entire communities and natural resources and ecosystems, without solving the problem. Contradictorily the recharge zones have been covered by concrete reducing the infiltration rate and increasing the floods every rainy season. In 2006 the National Commission of Water stated the aquifers are overexploited and the recharge is quite minimal. Also, there was a controversy between the government and academic sector referring the urban planning. The first actor wants to plan urban development over recharge zones because there is a still need for housing, and the second actor is struggling against this, because is affecting the availability of groundwater. Besides, the government is planning to invest more than 44 million dollars for increasing the discharge capacity that will convey the rainwater into the drainage. In midst of this situation, the theme of groundwater management is gaining relevance. One of the main points is that there is no available technical information of groundwater status so the urban planning needs to take into account it, if it is to secure the long-term sustainability of water resources.

ZONE OF STUDY

The MZG Is located in western Mexico over three watersheds: Blanco River, Atemajac and El Ahogado at the time, under of them are located the Atemajac and Toluquilla aquifers. The zone of study covers the following municipalities: Zapopan, Guadalajara, Tonalá, Tlaquepaque and El Salto. The Atemajac aquifer that is mainly under Zapopan and Guadalajara municipalities is overexploited. Also the Toluquilla aquifer, which is mainly under part of Zapopan and Tlaquepaque, part of Tonalá, and Tlajomulco de Zuñiga municipalities is overexploited.

PROBLEMATIC

Lack of water in Guadalajara is an important issue in the public agenda. During the last years the urbanization was been expanded with out order covering almost the surface of the watershed. This situation has produced a contradictory situation. In one side, the urbanization avoids the infiltration rate that reduces the groundwater availability, and in the other hand, it is produces floods every year. This situation is more serious because the urbanization is still covering the aquifers recharge zone specially “El Bajío del Arenal” that is located in the western part of Guadalajara. Figure 1 shows the groundwater flow from the recharge zone called El Bajío, towards the discharge zone through Huentitán Ravine.

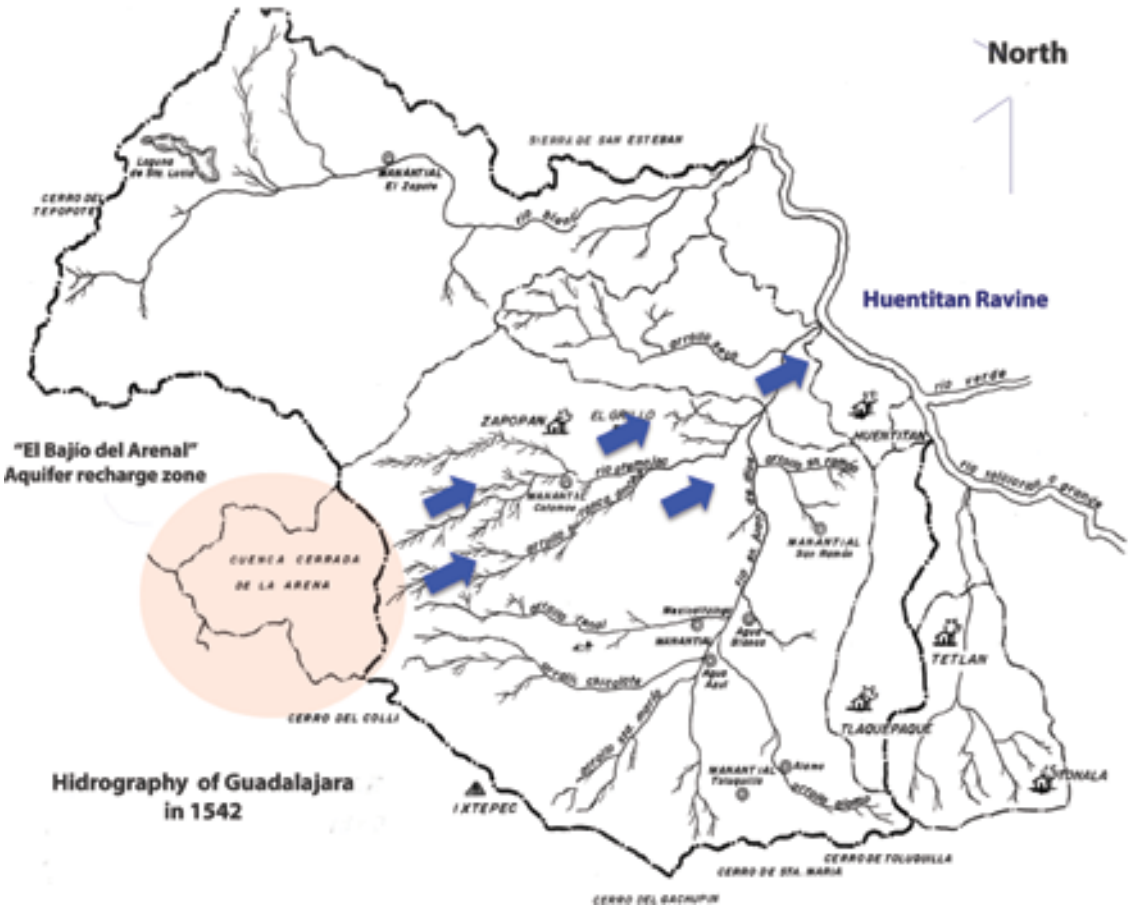

Figure 1: Groundwater flow from recharge (El Bajio) to discharge zone (Huentitan Ravine)

This area is part of La Primavera Forest, which is being threatened by urban developers. Already this area has been affected by the construction of Soccer Stadium and Pan-American dorms built for the games celebrated in 2011 (Figure 2). Nevertheless, the local government is still promoting the urbanization of the rest of the zone. This situation has provoked a complex debate between voices in favour the urbanization and voices against. Both sides have their own arguments showed in an intensive debate that endures more than one a half year through 20 technical and political meetings. From this experience arose the lack of official technical groundwater information and opened the need to study carefully the case. Besides, arose some questions as such as: how much water do we have in order to supply the next generations? What would happen if Guadalajara still pumping groundwater with out measurements? How much time do we have to solve this problematic? This is an example of bad groundwater management in the zone.

Figure 2: Stadium built in the recharge zone “El Bajío”

Intensive debate

The city government of Zapopan in 2013 invited experts in order to debate about the feasibility to urbanize the zone. The experts group stated, if the recharge zone was covered by concrete, it might affect the water supply from more than one million habitants of the western part of Guadalajara without considering the future generations, inclusive, they propose to destroy all the buildings in the area. The second group, the so-called the developers, insisted in urbanize in sustainable way the recharge zone, proposing an alternative technologies that can protect the zone.

After lengthy disputes, both groups came together to two basic agreements. First of all, it necessary to realize a serious technical assessment for the zone in order to define the state of damage and determine if the constructions are need to be destroyed or there will be necessary to implement restoration strategies. Secondly, it would be necessary to design a new land-use plan that can protect the zone as well as to develop the land in a sustainable way. The municipal president realized these agreements to public opinion but in contradiction, he authorized the installation of new human settlements. Now, the parliament of settlers of Guadalajara has pursued a court action against the current land-use plan, which prohibit any new construction. So, this problem is still in legal controversy under the threat of eminent urbanization that might affect the recharge zone irretrievably.

NOTES

INTEGRATING GROUNDWATER MANAGEMENT AND FLOOD CONTROL IN CHENNAI, INDIA: A STUDY OF LAW AND POLICY

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Keywords: groundwater, flood, land use, Chennai, laws

INTRODUCTION

'Groundwater recharge' gains prominence during summer and 'flood control' fascinates discussions during monsoons. It is speculative and distorts the major premises involved in the subject. A holistic approach to flood management shall include the physical and social aspects of groundwater recharge systems. This paper focalises on the interface between groundwater management and flood control in Chennai. It argues and presents that policy, law and governance mechanisms shall inter alia undertake a review of existing land use, and removal of encroachments in water bodies and waterways. The paper draws its ideas from the floods during December, 2015 and the draughts of previous years. The author putforths suggestion as to policy and legal measures for the sustainable and optimal use of water sources.

METHODS

This paper analyses the legal and policy documents pertaining to groundwater and flood management with the support of field observations. The author made field visits to tanks and waterways in and around Chennai to observe the flood situation during December, 2015. The author has also conducted unstructured interviews with government officials, volunteers, activists and scholars of various disciplines about the flood situation and reasons for this unprecedented damage. Many observations regarding groundwater management were collected from the participants of workshops conducted by the author during previous years.

DISCUSSION AND RESULTS

Chennai is the capital city of the Indian state of Tamil Nadu. It is one of the biggest industrial and commercial centres in India. It is the fourth-largest city and fourth-most populous metropolitan area in India with a population of 7 million. It is one of the first settlements for British in India. Therefore, the city has the longest and continuous civic management system which has regulated water supply, groundwater recharge, maintenance of reservoirs, and sewerage management (P. Sakthivel 2012).

The average annual rainfall of Chennai is about 1400 mm spread over 70 rainy days. Arani, Koratallai, Cooum and Adyar are the four important rivers draining in and around Chennai. The water demand

for the present population is approximately estimated to be 1000 million litres per day (MLD). About 930 MLD of water is supplied from various sources including five surface reservoirs namely Sriperumbadur, Chembarambakkam, Poondi, Redhills, Cholavaram and by extracting groundwater from the well fields (Panjetty, Minjur Tamarapakkam, Kannigaiper, and Poondi) located north of Chennai. The approximate contribution towards city water supply from the surface reservoirs, well fields, desalination plant, Veeranam tank and Krishna River is 51%, 1%, 17%, 19% and 11% respectively (Parimalarenganayaki 2014). The available data shows only the supply of government and its agencies. The extraction of groundwater by individual houses, apartment complexes and commercial establishments are not estimated by the government agencies. As such, most of the available literature on the sources of water supply restricts with the government data. However, one study estimates that around 60% of the water used by Chennai comes from sources other than the official supplier of water to Chennai (i.e., Metro water) (Roumeau, et al. 2015). It could be well argued that groundwater extracted from the plot of Chennai residents constitutes a minimum of 60% of water used by Chennai. In the given circumstances, groundwater sustainability is an important component of water supply to Chennai city.

On December 1, 2015, some parts of Chennai received more than 500mm of rain, at least 250 people have died, several hundreds have been critically injured, and thousands lost their homes by the flooding that ensued (PTI 2015). Chennai city and the surrounding districts have an extended network of tanks, reservoirs to store the water and replenish the groundwater. These water bodies (more than 5000 lakes) were built consistently for more than 1500 years to cater the irrigation requirements. Presently, irrigation requirements have diminished due to real estate boom in these districts. An unfortunate consequence of this unplanned development is the loss of waterways due to encroachments and negligent maintenance. A few water bodies that are part of the urban water supply system such as Chembarambakkam Lake are maintained properly. Even these water bodies do not maintain their drainage system to the optimal level to manage the flood. There were many allegations that the unplanned opening of Chembarambakkam Lake lead to floods that ensued after the December 1, 2015 rains.

The author accompanied with a group of social activists and engineers visited the chain of lakes in and around Chennai during January, 2016. A senior citizen, an advocate, a resident of Chembarambakkam village, and an environmental activist, Mr. Natarajan opined, “Chembarambakkam receives water from many water bodies such as Somangalam Lake and Pillaipakkam Lake. It is part of the larger Palar river-lakes network. As the governments cared a lot for the safety and maintenance of Chembarambakkam Lake, it forgot the maintenance of waterways and water bodies that are part of the larger network.” To narrate it differently, a large number of water bodies were neglected for a significant number of years. This prolonged negligence has diminished the storage capacity of lakes. The amount of flood damage could have been reduced if Chennai lakes and waterways were maintained properly. Summarily, Chennai water bodies lost their original purpose, and their contemporary relevance is not realised.

How should Chennai utilise the potential of these huge number of water bodies? Firstly, information pertaining to these water bodies are minimal and community knowledge has ceased to exist on these water bodies due to lack of irrigation. Hence, water bodies should be surveyed properly to upkeep its boundaries and avoid encroachments. Secondly, earnest efforts should be taken to include them as a part of water supply to Chennai city. Thirdly, these lakes should be utilised as groundwater recharge systems (S.Janakarajan 2013). A legal mechanism is in place for the past 10 years through the Tamil Nadu Protection of Tanks and Eviction of Encroachment Act, 2007. Regrettably, this law has not been significantly used to its full potential to survey and protect the water bodies from encroachment and pollution. This law also brings mechanisms to protect waterways. Alternatively, a 100 year old enactment is also in force to deal with eviction of encroachment in every public place including water ways (The Tamil Nadu Land Encroachment Act, 1905). Another colonial enactment, the Tamil Nadu River Conservancy Act, 1884 has found a purpose by an order of National Green Tribunal to appoint a conservator for the Cooum River in Chennai (TNN 2015).

The Tamil Nadu Irrigation Tanks (Improvement) Act, 1949 for the conservation tanks provides powers to District collectors to determine the need to repair and improvement of tanks (Section 5). The revenue officials and the district administration are given wider powers under two enactments against encroachment. The 1905 enactment permits the District collector or any authorised person to take efforts to remove encroachment in general and water body encroachment in particular (Section 6). Similarly, the 2007 law to protect the water bodies against encroachment has accorded similar powers to revenue administration. The power to survey or initiate survey to protect the tank boundaries are performed by surveyors on the instance of a request from revenue or Public Works Department (Sections 5 and 6). The enactments meant for protecting the interest of stakeholders in a water body, do not provide any legal right to farmers or other stake holders to initiate proceeding in the court of law. There is no executive mandate or procedure to prioritize the survey or choice of evicting the encroachments.

The courts usually have upheld the validity of executive action to remove the encroachment. In a significant decision relating to encroachment of water bodies, the court has held, "...it is for the respondents to decide about the granting of alternate sites to the petitioners considering the long time they have been in possession, but that cannot be the reason for the petitioners to continue to be in possession of Oorani lands" (Oorani is a kind of lake) (High Court of Madras 2008) . In a similar case, the court has ordered to protect the water body while constructing roadways. The court has given a clear order to align the highway by constructing over brides after providing Hydraulic and Hydrologic analysis, so as to prevent any obstruction to the inflow and outflow of the tanks. Similarly the court has ordered to protect the supply channels from any obstruction or encroachment (High Court of Madras 2011).

The regulations relating to groundwater and flood are predominantly expressed in various local laws (Government of Tamil Nadu 2011). The Tamil Nadu laws are the first of its kind to provide compulsory rainwater harvesting structure in every establishment and household. It is pertinent that these laws come into effect and operate only during difficult water situations and enforced vigorously for a particular period of time, and not as culture and industrial practice. The Tamil Nadu Groundwater (Development & Management) Act, 2003 was enacted, but was not notified, and was finally repealed by the State in September 2013, but some of its provisions have been converted to Government Orders. The Act was intended to deal with most of the issues relevant to groundwater protection and recharge. The Act envisaged the establishment of an authority to be constituted, a mechanism for groundwater licensing and for registration of wells. The Act had considerable scope for groundwater protection, but the enforcement of this law was expected to be detrimental to some stakeholders (Brunner, et al. 2014). On the other hand, there is no effective flood control management scheme and policy. This is despite few studies conducted by the central government on the effects of flood. The flood control laws are restricted to disaster management and laws of certain north-eastern states.

In this context, the need for integrating groundwater management and flood management arise. The recent inundation in many unexpected places is due to mismanagement of various water sources (DHAN Foundation 2009), water ways and adjacent lands (P. Sakthivel 2015). The State might have prevented or significantly reduced inundation if tanks had been maintained to optimal levels, tank encroachments removed (at least to the extent of protecting water levels), sluices maintained to release excess water through additional outlets and above all, the drainage restored to its breadth. The new roads laid at a greater height, created new low-lying areas and devastated many lives. The orders of High Court are seldom enforced with full vigour to protect water bodies. Thus,

these water bodies should have retained more water and augmented groundwater sources for summer; also the damages due to floods might have been minimised. The laws relating to groundwater recharge require a sincere adoption: If it is so, aquifer recharge mechanisms should have retained some flood water.

CONCLUSION

Urban planners seem to have forgotten the pertinent truth that lakes were built on or along waterways. They are structures for water storage and prevention of floods. However, available laws and regulations do not provide the required clarity for the proper governance and protection of groundwater. Further, the national agencies such as Central Ground Water Board and Disaster Management authorities may not really influence decision making, as the projects are approved by state agencies. Urban Rain Water Harvesting is already mandatory, but it can be made more effective by continuous enforcement (monitoring) and maintenance to minimise the floods.

Therefore, three suggestions are given to secure better water governance for Chennai,

1. Developing water monitoring systems, data updates, experimenting on different methods of water harvesting based on soil conditions and mapping of groundwater sources.
2. Adopting improved standards prescribed in the Union model laws, coordination amongst government departments to implement water related laws and make scientifically relevant and technically feasible rules.
3. Improving drainage systems with best available technologies, and regulate land use by strictly enforcing laws against encroachment.

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NEGATIVE IMPACT OF BACKWATER LEVELS OF DANUBE RIVER AND ITS TRIBUTARIES TO THE GROUNDWATER REGIME IN MELIORATED RIVERSIDE AREAS

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Abstract: This paper describes updated calculation methodology of Danube backwater impact, occurred as a consequence of "Đerdap I" hydropower plant operation, onto the meliorated riverside areas. This methodology is based on hydrodynamic analysis of groundwater regime (size, duration, level and inflow changes) and quantification of melioration areas impairment which is caused by "Đerdap I" hydropower plant operation. By comparing the groundwater regime elements, obtained by variant hydrodynamic calculation in mathematical models for natural – not backed up and actual – backed up water level regime, and also designed backwater regime, the first step was to define boundary, size and duration of Danube backwater impact within this boundary, i.e. impact onto the piesometric levels within the analyzed meliorated areas. Then, additional inflow (size and duration) coming from water flows into previously defined impact zone was quantified and energy consumption necessary for operation and pumping of additional water quantities was determined. In the end, participation (in percentage) of hydropower plant in costs related to establishing and operation of the existing and designed area protection systems. This paper presents the calculation results for three distinctive meliorated areas affected by the Danube backwater (the Nera river-DTD channel, Ivanovo-Pančevo and Elemir-Aradac). The presented methodology, besides defining and quantifying the impact of "Đerdap I" hydropower plant, may be applied for system selection and optimization of riverside melioration area protection, and for presentation of adequate response to a very sensitive issue concerning objective share estimation of relevant participants in protection cost of all melioration areas under the influence of the hydropower plant backwater.

Keywords: HPP "Djerdap 1"; backwater influence; groundwater regime; hydrodynamic analysis; melioration area; drainage system; additional energy engagement

INTRODUCTION

After construction and commissioning of the "Đerdap I" hydropower plant in 1972, water level of Danube river and its tributaries (the Sava and the Tisa rivers) backed up, which caused increase of groundwater level and additional (extended) impairment of melioration areas in riverside areas of these rivers (Figure 1).

When considering operation of „Đerdap I" hydropower plant, since commissioning until present, three operating regimes, i.e. exploitation regimes may be selected: regime "68/63" (1972-1977), regime "69.5/63" (1977-1985), regime "69.5 and higher", i.e. "up to level 70.30 mnm" (1985 – until present). For lower backwater levels, in the period until 1985, negative impact of Danube backwater level propagated exclusively in the riverside area, downstream from Belgrade. When „Đerdap I" hydropower plant operation transferred to the higher backwater levels, since 1985, this negative impact included the significant part of Danube riverside, with propagation upstream to Novi Sad, and significant part of coastal area of its largest and most important tributaries – the Sava and Tisa rivers (Fig 1). Presently, the actual backwater regime is "69.5 and higher" regime, i.e. "up to level 70.30 mnm" and melioration areas in the Danube riverside are under the negative impact of „Đerdap I" hydropower plant – from the hydropower plant (km 943+000) to Novi Sad (km1255+100), then melioration

Figure 1: Melioration areas under the Danube backwater negative impact for the present operating regime of the HPP "Đerdap I" ("69.6 and higher, up to the 70.30 masl")

areas in the Sava riverside – from the confluence into the Danube to Šabac (km 105+100), and also melioration areas in the Tisa riverside – from the confluence into Danube to Novi Bečej (km 60+850).

Prior to construction of hydropower plant and backwater formation (1972), melioration areas in riverside areas of the Danube and its tributaries were mostly impaired by high groundwater levels only under extremely unfavorable hydrological conditions – long-term high water levels. In the beginning, these melioration areas were mostly protected only by dewatering system for agricultural areas, and later by established protection system for external and internal waters (protective embankments along the water flows, open, shallow channel network inside the territory with pumping stations, and other). By transferring to the higher Danube backwater regimes, the existing system mostly proved as insufficient, i.e. inefficient system. The new systems were established and the old ones were subsequently refurbished and upgraded to fulfill the newly set and more strict criteria for protection of these melioration areas.

APPLIED METHODOLOGY

The presented calculation methodology for Danube backwater impact is based on hydrodynamic analysis of groundwater regime and quantification of area impairment caused by Đerdap I hydro power plant operation. Hydrodynamic analysis included preparation of mathematical models of groundwater flows (plane and cross-section) in unsteady filtration conditions, for the period from 1985 until 2011, for natural – not backed up and observed – backed up, and also designed – Danube backwater levels. The applied methodology is based on numerical – engineering solution for partial differential equation system which define flow in two-layer porous media. The engineering solution of unsteady flow differential equations consists of approximation of unsteady state of the flow process with a series of steady motions with finite time interval Δt. Theoretical bases are well known to the engineering public and thus here shall not be presented in detail.

Input data for conducting mathematical modeling are: monitored water levels of Danube and its tributaries, simulated in conditions prior to hydropower plant construction and commissioning, and calculated designed water levels of Danube and its tributaries; water levels (monitored and designed) in pumping stations of drainage system, monitored groundwater levels in the existing piesometric network at the observed area; elements of vertical balance (effective infiltration and evapo-transpiration) etc., and other results of previous and newly purpose made investigations. Spreading and discretization of mathematical models are defined based on natural and adopted hydrodynamic boundaries of mathematical models. Data on spreading and hydrogeological properties of basic and surface low-permeable layer are obtained by data interpretation gained from structural and piesometric boreholes and wells and from results of other purpose-designed investigations (aquifer geometry (terrain level, layer boundaries and thickness, etc.), hydraulic conductivity, porosity, specific

yield, etc.). Depending on available data for certain area, time discretization (calculation step) accounts for 7 days or 30 days for the period from 1985 to 2011.

Calculations were conducted on formed mathematic 2D and 3D models for the following boundary conditions:

- For natural Danube water levels, for conditions that would have been created if there had not been "Đerdap I hydropower plant backwater and formation of protective system;
- For natural Danube water levels, for conditions that would have been created if there had not been "Đerdap I" hydropower plant backwater with drainage system operation simulation in designed and monitored regime,
- For monitored Danube water levels and water levels designed for backwater regime "up to level 70.30 mnm at the Nera river confluence", without drainage system operation,
- For designed Danube water levels in backwater regime "up to level 70.30 mnm at the Nera river confluence" and drainage system operation as per design,
- For monitored Danube water levels in backwater regime "up to level 70.30 at the Nera confluence" and monitored operation of drainage system.

According to performed hydrodynamic calculations, calibration and verification of mathematical models, valid results are obtained in the form of groundwater level fluctuation and duration, groundwater flow fluctuation and duration through water-bearing layer by sections of calculation profiles, for the named conditions, and in the form of groundwater inflow into drainage channels and pumping stations.

By comparing obtained results (fluctuation and duration of level and flow) of groundwater regime for named boundary conditions (natural and monitored Danube levels), an impact boundary of "Đerdap I" hydropower plant onto analyzed meliorated areas was set within such defined boundary. This boundary of "Đerdap I" hydropower plant backwater impact was defined as part of the area where achieved and natural groundwater levels (and flows) equalize, in the named Danube water level conditions and for the same (identical) conditions of area regulation (with or without protection system). Further, a zone is analyzed within melioration areas where groundwater level are observed to be higher than designed, in order to define the efficiency of the existing drainage systems for different durations (10% and 50% duration).

Also, the amount (percentage) of impact was determined for "Đerdap I" hydropower plant backwater onto the analyzed meliorated areas. "Đerdap I" hydropower plant operation and backwater formation caused increase of groundwater inflow into the observed meliorated areas. This inflow increase, within the previously defined backwater impact zone boundary, expressed in percentage in relation to the natural status, is also defined by calculations in mathematical model, for the characteristic levels of area regulation and different boundary conditions of Danube and Tisa river water level. Share coefficient of increased inflow (for monitored and designed conditions in reservoir) is equal to:

$$K_Q^{monitored} = \frac{Q_{monitored\_river} - Q_{natural\_river}^{monitored\_system\_operation}}{Q_{observedriver}} \quad (1)$$

$$K_Q^{designed} = \frac{Q_{designed\_river} - Q_{natural\_river}^{designed\_system\_operation}}{Q_{natural\ \ river}} \quad (2)$$

In the presence of "Đerdap I" hydropower plant backwater, due to increase water inflow from the river into the water-bearing medium and increased suction lift during pumping, in relation to natural regime, pumping stations operate more intensively at the observed meliorattion areas. The calculation results of groundwater inflow in the named conditions were firstly used for power calculation, and then energy necessary for water evacuation from the area during different river water level regimes and operation of the existing systems. Simplified equation (Vuković and Soro) for power necessary for pumping of waters inflowing to the pumping stations:

$$E = 15\ x\ Q\ x\ (\Delta H + \xi)\ x\ t \quad (3)$$

where is: Q - flow or quantity of pumped water (m^3/s), ΔH - difference between water level in Danube and water level in channel in pumping station (m), ξ - hydraulic loss, t - time (s)

Energy is calculated as a product of calculated necessary power and total number of hours in calculation interval. In the end, participation (in percentage) of "Đerdap I" hydropower plant in total used energy for water evacuation from the area during different river water level regimes and operation of existing systems was defined. Share coefficient of increased energy consumption (for monitored and designed conditions in reservoir) is equal to:

$$K_E^{observed} = \frac{E_{monitored\_river} - E_{natural\_river}^{monitored\_system\_operation}}{E_{omonitored\quad river}} \tag{4}$$

$$K_E^{designed} = \frac{E_{designed\_river} - E_{natural\_river}^{designed\_system\_operation}}{E_{designed\_river}} \tag{5}$$

RESULTS AND DISCUSSION

Restricted by the paper itself, the following areas have been selected as representative examples for considering the presented upgraded calculation methodology for Danube backwater impact onto the riverside meliorated areas from the stated aspects: Nera river – DTD channel, on Danube river (No. 19, Fig. 1), as area closest to the Đerdap I hydropower plant; Ivanovo – Pančevo, on Danube river (No. 21, Fig. 1), as area in the middle of Đerdap I hydropower plant backwater impact; Elemir –Aradac, on Tisa river (No. 25, Fig. 1), as area at the longest distance from "Đerdap I" hydropower plant.

Results of the conducted groundwater flow mathematical modeling are presented in Table 1 for piesometric levels of characteristic duration of 10% and 50% along the calculation profiles for the period from 1985 until 2011.

River regime			Melioration area		
			Nera – Kanal DTD	Ivanovo – Pancevo	Elemir – Aradac
Reservoir backwater	Backwater regime	Water level duration	Elevation (mnm)	Elevation (mnm)	Elevation (mnm)
Non-retarded	Natural	10%	68.2 -68.5	70.0 -70.4	73.2 -74.0
		50%	66.8 -68.0	68.8 -69.0	72.2
Retarded	Monitored	10%	68.5 -70.0	68.8 -70.2	73.4 -74.2
		50%	68.0 -69.8	68.2 -69.5	72.4 -72.7
	Designed	10%	66.5 -70.0	68.8 -70.2	73.4 -74.2
		50%	66.5 -69.8	68.2 -69.5	72.4 -72.7

Table 1. Piesometric level values in riparian parts of chosen melioration areas (between river dikes and the first drainage line), for different regimes of the Danube and its tributaries, for calculation period 1985-2011.

By analyzing the monitored and calculated groundwater regime with Danube water level changes within the investigated melioration areas, the areas with characteristic conditions for groundwater regime formation may be observed: riverside area, internal (protected) part of the areas and area along the hinterland. In riverside parts of melioration areas, surface water level changes have dominant impact onto the groundwater level change, and then effects of the area protection drainage system operation. In the internal (protected) are of melioration area, the most significant impact on groundwater levels have effects of drainage system operation and vertical balance parameters. The operation of drainage system within Danube backwater level conditions not only eliminates harmful effect of backwater, but provides favorable groundwater regime in the most part of the area and decreases their impairment, which further reflects on damage decrease and provision of better conditions for agricultural production (Pajić and Urošević, 2012). In part of melioration areas along the hinterland, dominant impact is taken over by groundwater inflow from the direction of hypsometrical higher terrains.

According to the calculation result analysis of groundwater regime (groundwater level fluctuation and their flow through water-bearing layer), position of backwater impact boundary was defined for different conditions in Đerdap reservoir. Backwater impact boundary can be defined for not backed and backed water regime in the river and for the same conditions of area protection. Figure 2 presents an example of defining backwater impact boundary in the area profile Nera river – DTD channel.

In melioration area Nera river – DTD channel, backwater impact boundary spreads in parallel to DTD channel, at the distance of 0.8 to 1.5 km and in parallel to Danube river, at distance of 1.5 to 1.8 km to Nera river, at melioration area Ivanovo – Pančevo spreads in parallel to the Danube river, at distance of 3.0 to 4.0 km from the river, and in melioration area Elemir – Aradac, it is parallel to Tisa river, at distance of 1.5 to 2.5 km from the river.

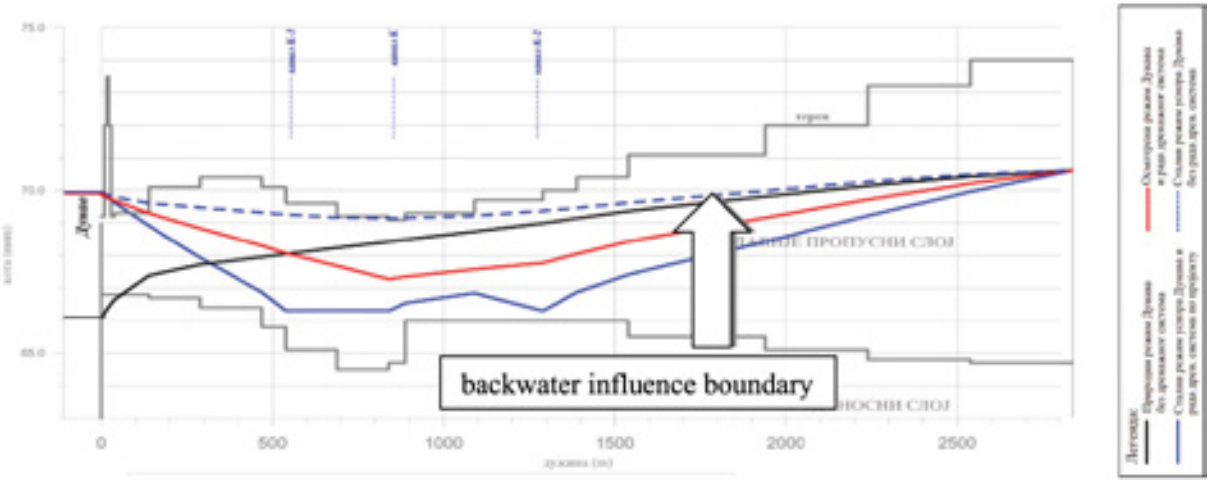

Figure 2: 50 % duration groundwater level lines, for different reservoir, area protection and backwater influence boundary conditions, calculated for the Nera-kanal DTD area profile.

Analysis of calculation results in mathematical model shows that groundwater inflow into pumping stations increases in backwaters, for monitored and designed regime, in relation to natural regime, which is a consequence of increased Danube water levels and their prolonged duration. By comparing the results of groundwater inflow for named conditions in Danube river and area protection system operation effects, values of participation of increased calculation inflows due to backwater are calculated as total inflow to pumping stations in the selected melioration areas. Table 2 shows the participation coefficient of increased calculation inflows due to backwater in total inflow into pumping stations of the selected meliorated areas (as per formulas 1 and 2), for the period from 1985 to 2011. It may be concluded that in downstream melioration areas, which are closer to "Đerdap I" hydropower plant, where river backwaters are more significant, share coefficient of increased calculated inflows due to backwater is higher within the total inflow into pumping stations; and vice versa.

According to the mathematical model results, energy necessary for groundwater evacuation from selected melioration areas is calculated, for Danube natural and backed up water levels and monitored and designed operation regime of drainage protection systems (Table 3). Calculation result analysis in mathematical model shows that in backed up conditions, for monitored and designed regime, due to increased groundwater inflow into pumping stations, in relation to natural regime, electricity consumption increases to order to pump the groundwater into the recipient. Table 3 shows participation coefficient of increased energy consumption due to backwater in total consumption for evacuation of collected groundwater in pumping stations in the meliorated areas (as per formulas 4 and 5), in calculation period from 1985 until 2011. In downstream melioration areas, due to larger Danube backing up, the share coefficient of increased calculation energy consumption in total energy consumption in pumping stations is higher, and vice versa.

Analysis of all calculation results of groundwater flow simulation at selected melioration areas in the named conditions quantifies impact of "Đerdap I" hydropower plant backwaters onto the groundwater regime formation. "Đerdap I" hydropower plant backwater impact within the defined spreading boundary is defined according to evaluation coefficient of backwater impact. The evaluation coefficient of "Đerdap I" hydropower plant backwater onto the groundwater regime formation in meliorated areas is proportional to average monthly participation (share) of energy consumption in total energy consumption for groundwater evacuation in the

Melioration area (pumping station)	River regime	Drainage system regime	Groundwater inflow (m^3/s)	Share of increased in total inflow, due to the backwater effect (-)	
				(1)	(2)
Nera – Kanal DTD (Karaš 1)	natural	designed	0.52	0.74	0.91
		monitored	0.08		
	designed	designed	2.03		
	monitored	monitored	0.94		
Ivanovo – Pancevo (Marijino polje) (Ist drainage line /basin)	natural	designed	0.16 (0.26)	0.47 (0.22)	0.48 (0.37)
		monitored	0.12 (0.18)		
	designed	designed	0.30 (0.41)		
	monitored	monitored	0.23 (0.20)		
Elemir – Aradac (Elemir – Aradac (4-5)) (1st drainage line /basin)	natural	designed	0.11 (0.18)	0.21 (0.15)	0.19 (0.13)
		monitored	0.11 (0.17)		
	designed	designed	0.14 (0.20)		
	monitored	monitored	0.14 (0.20)		

Table 2. Average monthly groundwater inflow and the share coefficient of increased calculated inflow in total groundwater inflow for the chosen melioration area pumping stations.

monitored backwater and area protection conditions.

CONCLUSION

This paper presents updated methodology calculation of (negative) backwater impact, on the example of three melioration areas on the Danube and the Tisa riverside, which is based on hydrodynamic analysis of groundwater regime and quantification of observed melioration areas impairment. By comparing groundwater regime, obtained by variant hydrodynamic calculations in mathematical models for natural, not backed up, and actual (monitored and designed) backwater regime, boundary and impact size are defined for Danube backwater within this boundary, introducing additional groundwater quantities and additional energy necessary for pumping additional groundwater quantities, formed as a consequence of the before mentioned backwaters.

Melioration area (pumping station)	River regime	Drainage system regime	Energy consumption E(MWh)	Share of increased in total energy consumption (-)	
				(4)	(5)
Nera – Kanal DTD (Karaš 1)	natural	designed	13.9	0.87	0.94
		observed	3.0		
	designed	designed	105.7		
	observed	observed	48.5		
Ivanovo – Pancevo (Marijino polje) (Ist drainage line /basin)	natural	designed	7.8 (11.2)	0.49 (0.49)	0.50 (0.51)
		observed	5.5 (7.6)		
	designed	designed	15.2 (21.6)		
	observed	observed	11.0 (15.6)		
Elemir – Aradac (Elemir – Aradac (4-5)) (1st drainage line /basin)	natural	designed	(2.5) 5.1	0.22 (0.19)	0.22 (0.17)
		observed	(2,5) 5.1		
	designed	designed	(3.2) 6.3		
	observed	observed	(3.2) 6.3		

Table 3. Average mouthy energy consumption and the share coefficient of increased calculated inflow in total groundwater inflow for the chosen melioration area pumping stations.

The presented methodology, beside the fact that it defines and quantifies the “Đerdap I” hydropower plant backwater impact, may serve as valid response to very sensitive question of objective share estimation of relevant participants in cost of protection of all meliorated areas under the backwater impact of the named hydropower plant, according to the share (in percentage) defined by presented methodology of backwater impact evaluation. Apart from that, the presented methodology is practical and universal as it can be applied for all other melioration areas in the riverside of the Danube and its tributaries, and with (possible) smaller adjustments to the actual conditions, to all other examples where similar natural and/or artificial conditions are present essential for backwater formation in water flow.

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A TREE-BASED STATISTICAL CLASSIFICATION ALGORITHM (CHAID) FOR IDENTIFYING VARIABLES RESPONSIBLE FOR THE OCCURRENCE OF FAECAL INDICATOR BACTERIA DURING WATERWORKS OPERATIONS

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Keywords: groundwater quality, drinking water, total coliforms, classification tree, CHAID

INTRODUCTION

Microbial contamination of groundwater used for drinking water can affect public health and is of major concern to local water authorities and water suppliers. To guarantee microbial safety a multi-barrier approach as being proposed by the WHO (2011) focuses on the reduction of pathogen entry into water resources and raw water. The identification of potential hazards and hazardous events is therefore considered as a basic requirement for developing effective mitigation measures to secure water quality and reduce the purification treatment required.

A useful first step towards identifying possible contamination sources is to analyse any existing data that might be available. Since water suppliers are often subject to strict regulation (EC, 1998; USEPA, 1996), during both approval and operational processes, they are likely to possess large sets of investigative and operational monitoring data on hydro-meteorological, chemical, and microbial parameters.

Stochastic data models such as principal component analysis, or discriminant analysis, are powerful tools to investigate large data sets. However, they rely on assumptions about the data distribution, linearity, independence, etc., that are not always valid in environmental data. In contrast, algorithmic models use only the input variables to explore relationships without making any assumptions about the distribution of the data (Breimann, 2001). We propose a non-parametric data mining technique for exploring the presence of total coliforms (TC) in a groundwater abstraction well and its relationship to readily available, continuous time series of hydrometric monitoring parameters (seven year records of precipitation, river water levels, and groundwater heads). The main aim of this study was to identify monitoring parameters associated with the occurrence of TC in a drinking water production well by a classification tree model based on the Chi-Squared Automatic Interaction Detection (CHAID) algorithm (Kass, 1980).

MATERIAL AND METHODS

Site description

The area investigated lies within a mesoscale alpine headwater catchment with a glaciofluvial aquifer comprised mainly of coarse carbonate gravel. The catchment is drained by two rivers, one of which (R1) is believed to infiltrate into the aquifer. Groundwater is abstracted with a horizontal drainage well and used directly for drinking water supply, generally without any further treatment or disinfection (mean well discharge: 1.5 $m^3 s^{-1}$).

Due to water abstraction the groundwater level has fallen several meters since extraction began, resulting in a hydraulic disconnection of between the aquifer and the adjacent river (effluent conditions). Depth to the groundwater table (which extends beneath the river) is approximately 5 to 6 m in the wellhead area, and the aquifer is recharged by river water infiltration under all flow conditions. Four piezometers (A-D) are located on a profile along the main groundwater flow direction between the production well and river R1.

Data Set

A seven year record (01 January 2006 - 31 January 2013) of microbial, hydrologic, and hydraulic data provided by the local waterworks served as a data base for this research. Data points were only used if microbial data was also available, resulting in a total sample size covering 1746 days. Total coliforms (TC) were only reported in a binary code signifying either presence (1) or absence (0). Daily totals for precipitation (P) and daily means for water level of the river (WL), groundwater head (GWH), and discharge from the production well (QWPW) were used. In addition to these daily values, sums and means were also calculated for periods of up to five days. In order to take into account the dynamic behaviour of the system, differences were calculated for the river level, groundwater level, and well discharge over periods of between one and five days. Moreover, a time lag up to five days was applied to all variables in order to analyse how earlier events may have influenced the occurrence of TC. In total, 400 variables were generated for inclusion in the CHAID analysis.

Classification tree – CHAID algorithm

The relationships between hydro-meteorological and hydraulic variables (explanatory), and the occurrence of TC (response variable) were assessed using a tree-based model, the Chi-squared Automatic Interaction Detector (CHAID) developed by Kass (1980). All calculations were run using SPSS 19 software (IBM, 2010). The results were evaluated using cross-validation; the significance level for splitting nodes and merging categories was set to a p-value of 0.01.

RESULTS AND DISCUSSION

Temporal variability of monitoring variables

Flow conditions are subject to seasonal variations but can also vary from year to year (Figure 1). A seasonal pattern can be observed for 2010, between a dry winter period from mid-November to mid-May and a wetter summer period (Figure 1a). Large rainfall events during the summer months resulted in higher water levels in the river, and groundwater levels also responded to these high flows, exhibiting a damped version of the river hydrograph signal that indicated connectivity between the river and the aquifer system. The well discharge is closely related to the groundwater level and consequently yielded higher discharge rates during the summer season. Positive TC results were mainly clustered around precipitation and high flow events, but also occurred sporadically in between, and after, such events (upper row of Figure 1a).

In contrast, the year 2012 was characterized by average and low flow conditions; rainfall events were of lower intensity and river water levels lower throughout the year than in 2010. Groundwater levels during 2012 remained nearly constant and production well discharge was below average. TC occurred less frequently than in 2010 but with individual incidents recorded throughout the year (Figure 1b).

Classification tree for hydrometric variables and TC in the production well

Cumulative precipitation over two days (P s_2 t-0) was found to be the most significant variable. At the first tree level this variable was split into three subgroups (Fig. 2), with the highest probability (13.7%) of TC being found in the subset when rainfall exceeded 22 mm in 48 hours. The outbreak of waterborne diseases is known to often be triggered by extreme weather events involving heavy rainfall and flooding (Cann et al., 2013). During extreme rainfall events microorganisms can be mobilized from non-point sources such as agricultural surfaces (Collins et al., 2005), consequently increasing the availability of bacterial loads in a catchment by some orders of magnitude compared to dry conditions (Dechesne and Soyeux, 2007; Kistemann et al. 2002). This node represented a terminal node, while the remaining two subsets were divided further:

The splits were realised by variables derived from groundwater heads, based either on groundwater levels from piezometer D (left branch), or fluctuations in the near-by piezometers A and B (centre branch). Elevated TC probabilities were found for groundwater heads from piezometer D in excess of 634.45 m a.s.l. (GWH D m1 t-0). During moderate rainfall fluctuating groundwater levels in piezometers A and B, which were located in the

immediate vicinity of the production well, became important explanatory variables. Both variables were most significant with time lags of two days and five days (GWH B d3 t-2, GWH A d2 t-5); changes may have been caused by infiltration of surface water from the river, or by rapid groundwater recharge from the unsaturated zone. Rising groundwater heads may also mobilize mircoorganisms from the interphase between the phreatic and the vadose zones (Unc et al., 2013).

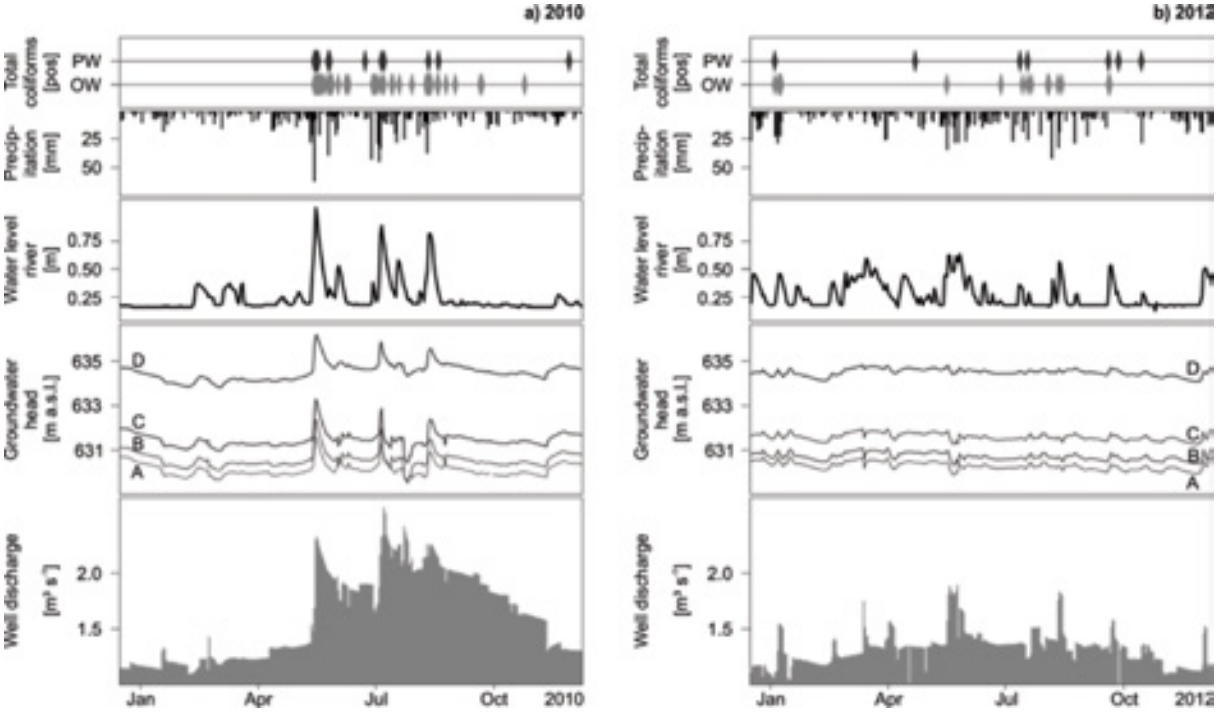

Figure 1: Overview of monitoring variables for selected years: 2010 (high flow conditions) and 2012 (average/low flow conditions)

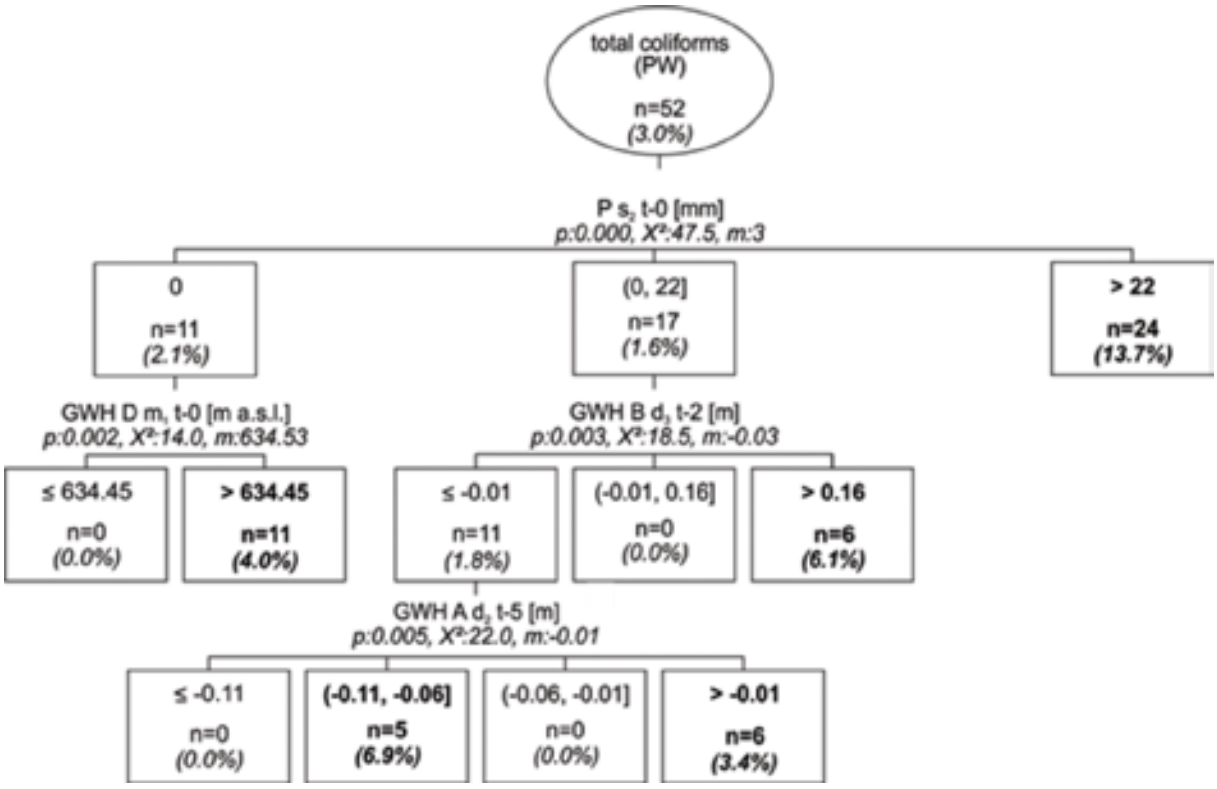

Figure 2: Classification tree of hydrometric variables for the production well, with p-value, significance (X^2), and median (m). Each box (node) represents a subclass of an explanatory variable, with the variable value on top and the number of TC positives (n) in the centre; values in brackets denote percentages within the subset. Nodes are marked in bold font where the initial probability exceeds 3.0%.

CONCLUSIONS

The CHAID algorithm was able to identify hydrometric parameters that were significantly related to the occurrence of TC in a drinking water production facility. Exploring statistical relationships between hydrometric variables and microbial indicators provided valuable indications of the likely sources of the pathogens. The significant variables could be used as proxy indicators for critical conditions, which would be of particular interest as they can be predicted using independent models (from, for example, precipitation, or a river's stage). Moreover, the proposed algorithm proved to be a useful tool with which to reduce a large data set to a much smaller number of significant variables. This is particularly valuable as enlarging the readily available monitoring dataset by creating generic variables was clearly shown to improve significance levels. A major advantage of the tree-like structure is the intuitive interpretation of the results. Complex relationships can be displayed in a clear and comprehensible way, providing easily understandable information to researchers and water managers.

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BASIS FOR DETERMINING CRITICAL SCREEN ENTRANCE VELOCITIES WHERE WELLS HAVE A PROPENSITY FOR IRON INCRUSTATION

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Ageing of water wells due to screen clogging is a problem known for ages. The economic and technical significance of the phenomenon is enormous. Mechanical clogging due to excessive screen entrance velocities has been studied and the related criteria identified by Abramov (1952), Cistin (1965), Gavrilko and Alekseev (1985), Johnson (1975), Kovacs and Ujfaludi (1983), Sichardt (1928) and others.

Biochemical clogging occurs as a result of various processes in suboxic and anoxic groundwater conditions. Many researchers, such as Dubina (1978), Gavrilko and Alekseev (1985), Houben (2003), Hoben and Treskatis (2007), and Vuković and Pušić (1992), Dimkić and Pušić (2008), Dimkić et al. (2011 a,b), Dimkić and Pušić 2014, have studied iron incrustation of well screens, due to bivalent iron converting into trivalent iron.

$$Fe^{2+} - e^{-} \longrightarrow Fe^{3+}$$

During the period from 2004 to 2015, the research projects of Jaroslav Černi Institute (JCI) included a systematic study of the correlation between KLHR (Kinetics of Local Hydraulic Resistance Growth) and physical and biochemical parameters (JCI 2010 a,b, 2011). In anoxic conditions (Eh>50 mV in the study areas), the main drivers of iron incrustation of well screens, in addition to flow velocities at the screens (v), are the redox potential (Eh) and iron (Fe) concentration in water.

In general terms:

$$KLHR = KLHR\ (v, Fe, Eh, B, \Gamma, ...)$$

where: v – entrance velocity, Fe – iron concentration in well water, Eh – redox potential, B – function of the growth rate of bacteria in the well, Γ – function of several structural parameters (well with or without gravel pack, gravel pack characteristics, type and characteristics of screen slots) and the grain-size distribution of the aquifer.

The study areas included:

- The alluvial groundwater source along the Sava River (comprised of 99 radial wells), which provides water supply to Belgrade;
- The Kovin-Dubovac drainage system along the Danube River (comprised of a large number of tube wells);
- The water supply source of Veliko Gradište along the Danube River (two tube wells);
- The water supply source Ključ – water supply system of Požerevac, the Velika Morava River (10 tube wells), etc.

Figure 1: Study areas along the Sava, Danube and Velika Morava rivers (www.Google earth)

Most of the results have been circulated through numerous journals and other publications.

The most significant locality is Belgrade's alluvial groundwater source comprised of 99 radial wells.

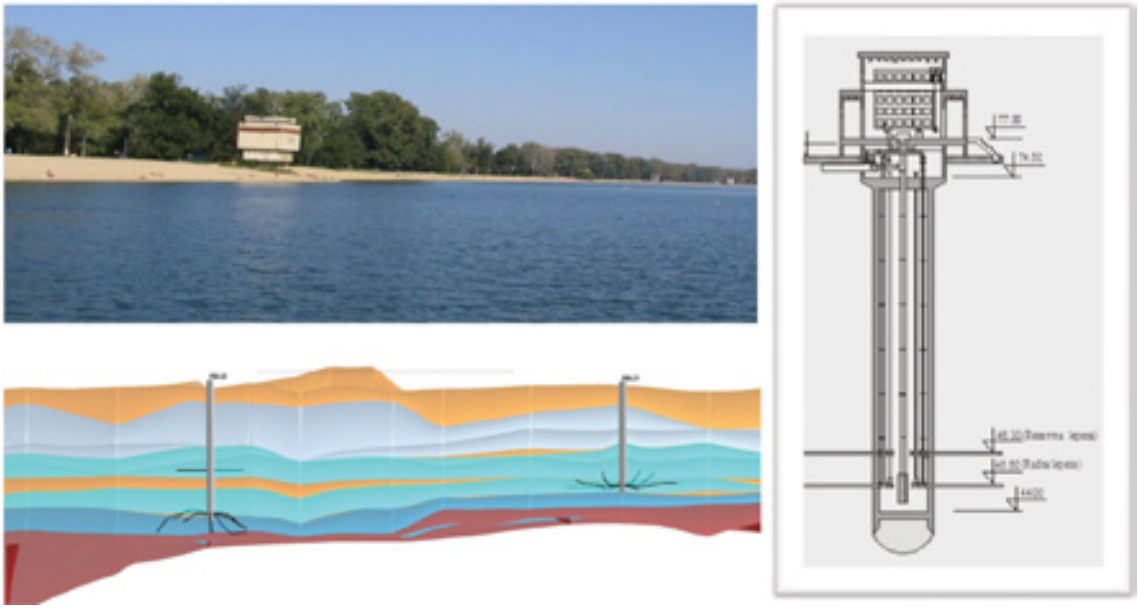

Figure 2: Radial wells, Belgrade groundwater source; well RB23 with horizontal lateral screen drenom (JCI, Belgrade, 2010a)

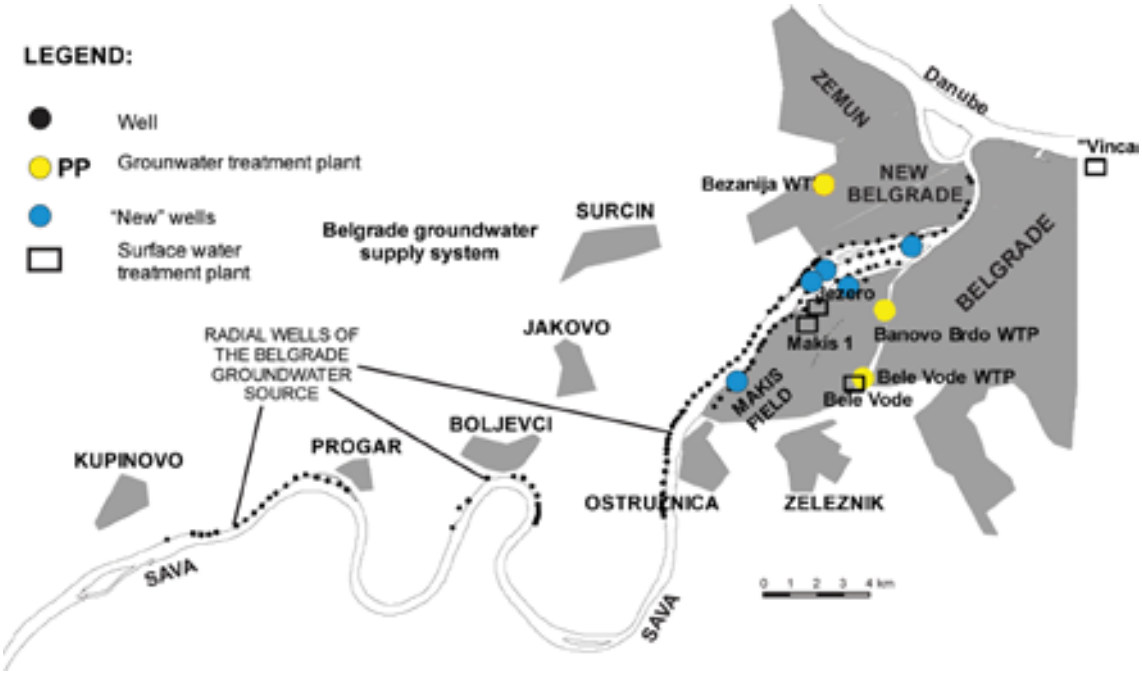

Figure 3: Belgrade groundwater source (JCI, Belgrade, 2010a)

There are four distinct phases of bank filtration (Fig. 6):

Phase 1 – High sorption potential and intensive biochemical activity

Phase 2 – Filtration in predominantly oxic conditions

Phase 3 – Filtration in diminished oxygen/anoxic conditions

Phase 4 – Filtration within the zone of influence of the well screen

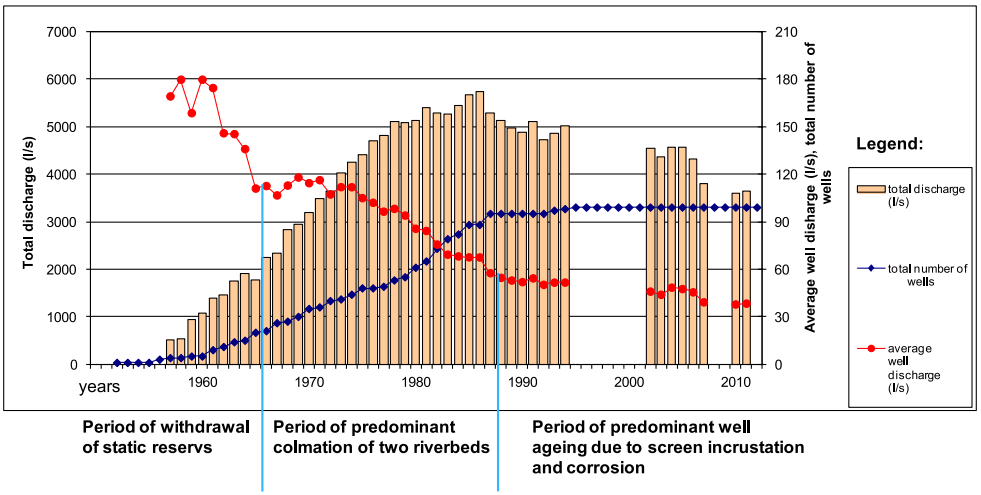

Figure 4: Belgrade groundwater source – decline in discharge of the wells and the entire source (Dimkić et al., 2012)

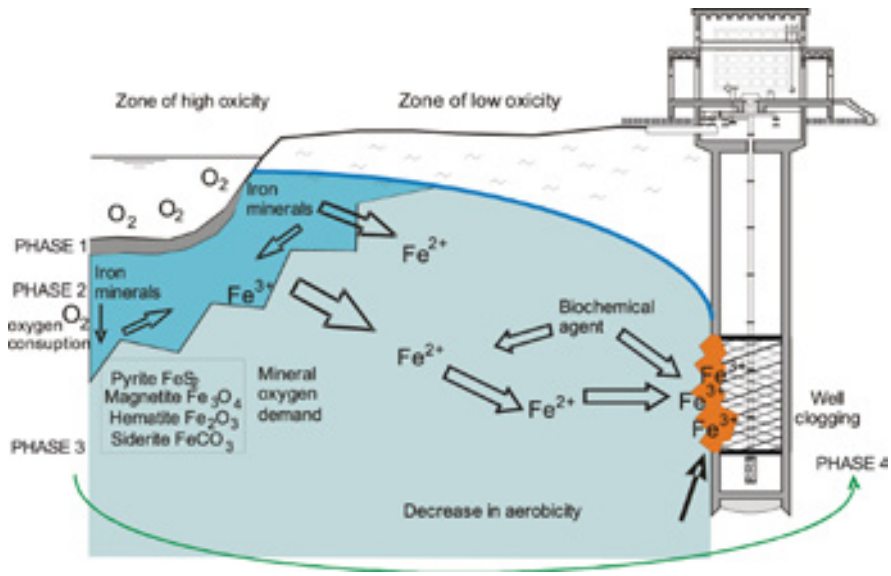

Figure 5: Schematic representation of the conversion of Fe^{2+} to Fe^{3+} between the river and the well

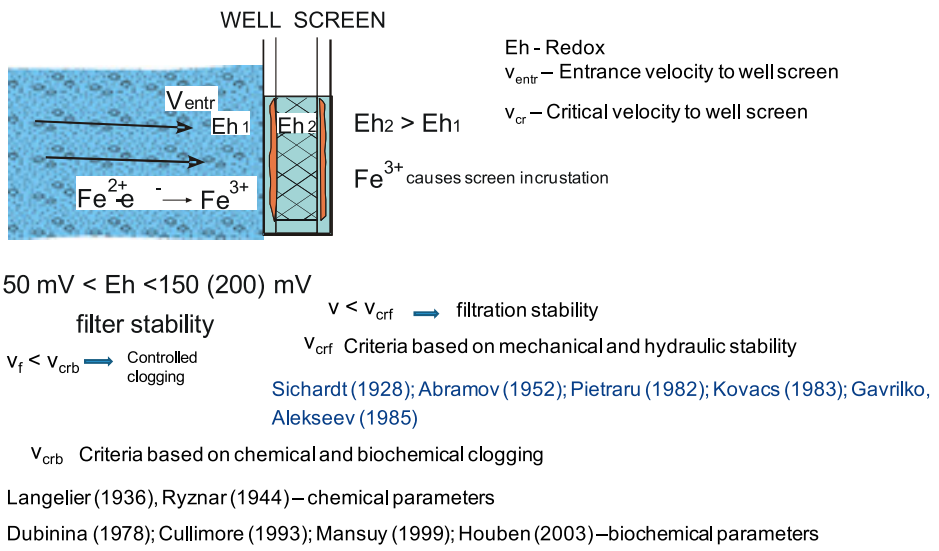

Figure 6: Iron incrustation – well screen entrance velocities

The following expressions apply:

$$LHR = \frac{\Delta S}{v_{ul}}$$

$$KLHR = \frac{\Delta LHR}{\Delta t} = \frac{\Delta S)}{\Delta t \cdot v_{ul}}$$

$$\Delta S = KLHR \cdot v_{ul} \cdot \Delta t$$

$$v_{ul} = \frac{\Delta S}{KLHR \cdot \Delta t}$$

The critical well screen entrance velocity is the velocity that prevents the resistance at the screen to exceed a set value per year (or other period of time).

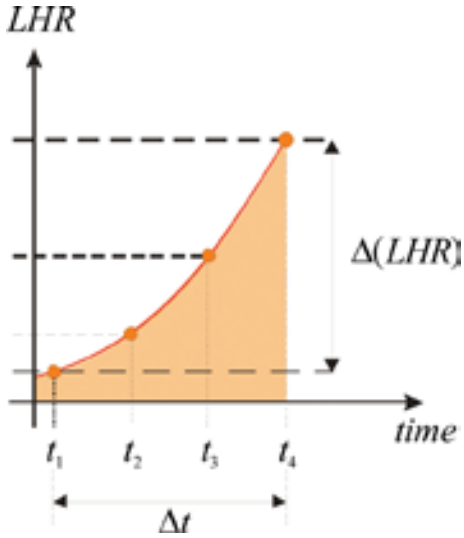

Figure 7: Definition of LHR (local hydraulic resistance) and KLHR (kinetics of increase in local hydraulic resistance)

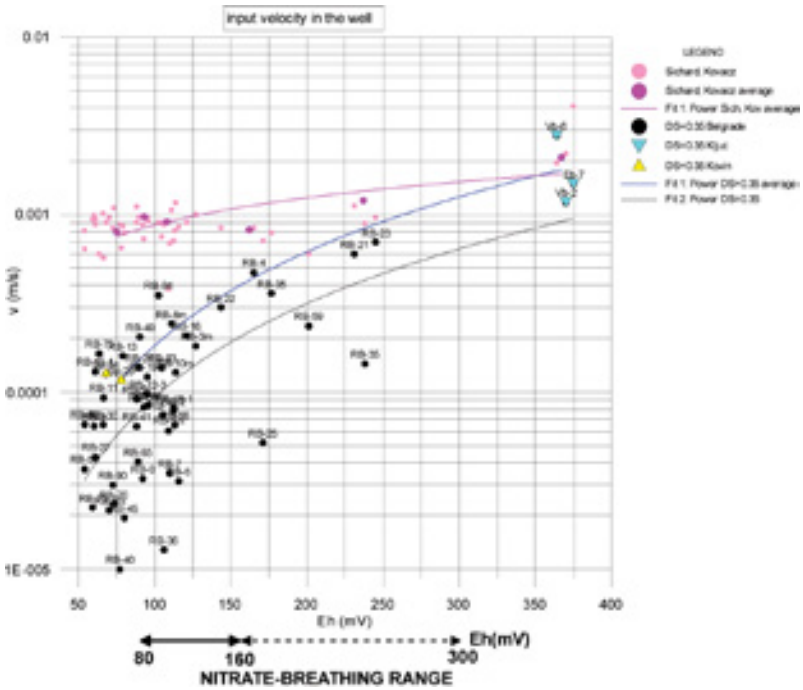

Figure 8: Recommended well screen entrance velocities for several alluvial groundwater sources in Serbia (Dimkić M., Pušić M., 2014)

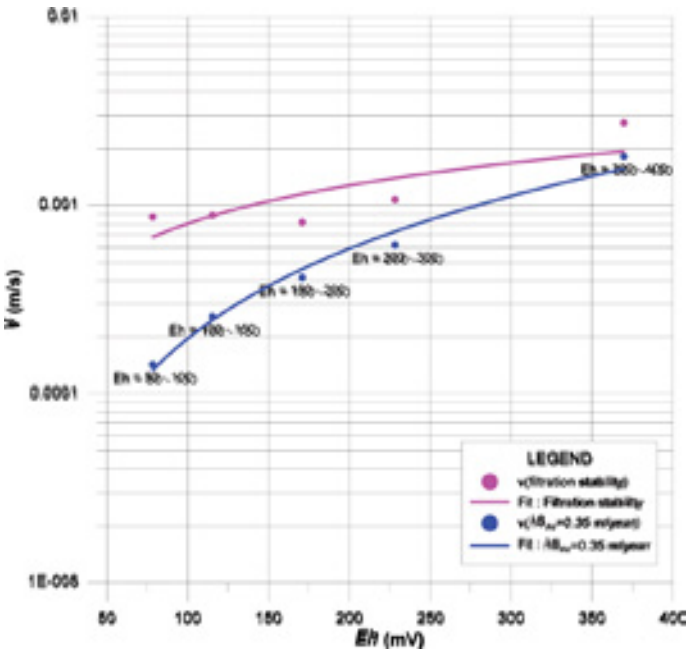

Figure 9: Well entrance velocities as a function of groundwater redox potential at a controlled annual increase in local drawdown of ΔS = 0.35 m/year (Dimkić M., Pušić M., 2014)

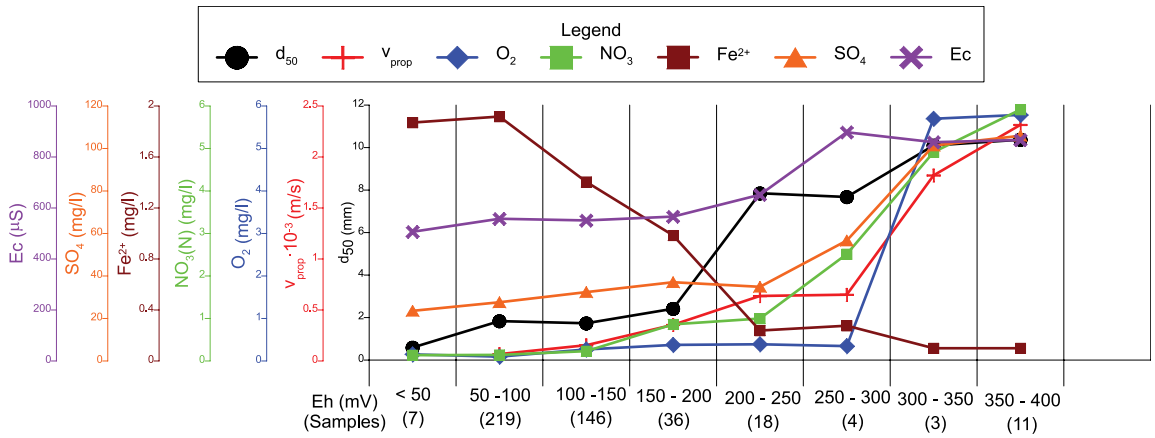

Figure 10: Average values of selected well parameters in all study areas, by redox potential segment. (Dimkić M., Pušić M., 2014) (Legend: Eh – redox potential, d50 – aquifer grain size (50% of the grain-size distribution curve), vprop – recommended entrance velocity, O_2 – oxygen concentration in water, NO_3 – concentration in water, as N, Fe^{2+} – bivalent iron concentration in water, SO_4 – concentration in water, and Ec – water conductivity).

The correlation presented here between the increase in hydraulic losses at the well screen due to iron incrustation and biochemical parameters is the first or among the first attempts to correlate:

resistance at well screens – water chemism (Eh, Fe^{2+}, NO_3, i dr.) – types of bacteria and their activity – types of internal screen encrustations.

Detailed research is ongoing.

With regard to well design or replacement of radial well laterals, it is certainly necessary, inter alia, to:

- determine the potential or targeted well discharge capacity with a sufficient degree of accuracy, and
- establish critical screen entrance velocities based on biochemical indicators (above all Eh, Fe^{2+}, etc.), and then determine the size and structural elements of the well screens (or radial well laterals).

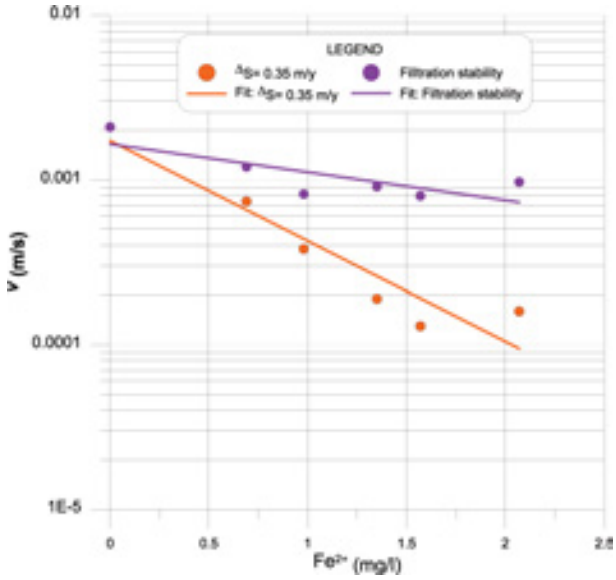

Figure 11: Well entrance velocities as a function of Fe^{2+} concentration for a controlled annual increase in local drawdown of ΔS = 0.35 m/year (Dimkić M., Pušić M., 2014)

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NOTES

APPLICATION OF A 3D MODEL TO DETERMINE DESIGN CRITERIA FOR RADIAL WELLS AT BELGRADE'S GROUNDWATER SOURCE

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Abstract: Jaroslav Černi Institute for the Development of Water Resources has developed software that models 3D groundwater flow and relatively easily and faithfully simulates radial well laterals and riverbed configurations and permeability. This software is a valuable tool for determining the capacities of groundwater abstraction sites and radial wells. It is especially useful in the case of aquifers that comprise a semi-permeable interbed between the water-bearing layer tapped by the well laterals and the overlying strata. A comparative hydrodynamic analysis is conducted of two wells at Belgrade's groundwater source. There is a semi-permeable interbed at the location of one of the wells (RB-16), but not at the other (RB-46). Maximum permissible entrance velocities at the laterals are controlled by previously-determined correlations with the oxic state of the aquifer and the rate of clogging of the well laterals. The design of radial wells that takes these parameters into account guarantees stable operation and longevity.

Keywords: groundwater, well capacity, design

INTRODUCTION

In the past, radial wells have generally been considered in the light of individual analyses of hydraulic criteria, the filtration stability of the aquifer (Abramov, 1952, Gavrilko,1968, Johnson, 1972, Kovacs, Ujfaludi, 1983, Vuković, Pušić, 1992) and the near-well region, and well ageing predominantly caused by iron incrustation (Cullimore, 1999, Dimkić, Pušić, 2014, Dimkić et al, 2011b, 2011c, Houben, Treskatis, 2007, Mansuy, 1998, McLaughlan, 2002). A lack of suitable software has prevented a more comprehensive hydrodynamic analysis of groundwater flow for radial-well design purposes. Jaroslav Černi Institute for the Development of Water Resources (JCI) has developed 3D software for simulating groundwater flow, which enables hydraulic quantification of the elements of radial well laterals (Vidović et al., 2014, Dotlić, 2015). This software relatively easily and faithfully simulates radial well laterals and riverbed configurations and permeability. Maximum permissible entrance velocities at the laterals are controlled by pre-determined correlations with the aquifer's oxic state, via the redox potential (Eh) and the rate of clogging of the laterals via bivalent iron concentrations (Dimkić, Pušić, 2014, Dimkić et al, 2011a, 2011b, 2011c).

The City of Belgrade uses groundwater from the alluvial aquifer of the Sava River, by means of 99 radial wells. The beginning of radial well construction dates back to the 1950s. Even though the quality of the well water was consistent, there were problems with well capacity decline and ageing of laterals. The initial capacity of more than 150 L/s has dropped to an average of less than 40 L/s today. The initial number of laterals was eight and is presently less than five per well. A specific feature of the aquifer's origin is polycyclic sedimentation. The consequences of the presence of interbeds in the final sequences of sedimentation are: lower-than-expected well discharge capacity and longer groundwater travel time from the river to the well. The sediment grain size is in the range from gravelly sands to clayey silt.

The application of a 3D model in the design of radial wells for Belgrade's groundwater source is comprised of two steps and several sub-steps.

The first step is the development and calibration of a model of the considered well and the respective part of the source (or aquifer). Model development begins with hydrogeological schematization of the aquifer layers, generally based on the outcomes of drilling in the extended zone of the well. Special attention is devoted to the analysis of semi-permeable layers and the possibility of quantifying their hydraulic role in the groundwater flow

to the well. The presence of two observation wells in the zone of the well laterals is extremely useful; one of them taps the water-bearing layer below and the other above the previously-mentioned interbed. The piezometric head difference between the two observation wells is clearly indicative of the filtration characteristics of the interbed and the magnitude of hydraulic resistances as groundwater percolates through the interbed.

The radial well laterals and the riverbed configuration are specified in the model on the basis of in-situ measurements. The laterals are first filmed by an underwater camera and the length of the laterals and their vertical and horizontal displacements recorded. The riverbed is scanned by an echo sounder or similar instrument, from a suitably-outfitted ship.

The model is calibrated by simulating periodic pumping tests, conducted under normal operating conditions of the site, by temporarily placing the well off-line. Special-purpose monitoring of the relevant part of the groundwater abstraction site (which contains the analyzed well, neighboring wells, the river and all nearby observation wells) is undertaken for a certain period of time before, during and after the well is disconnected from the system. Occasional prolonged well testing is extremely useful for defining the rate and nature of well ageing. At Belgrade's groundwater source, well ageing is predominantly caused by clogging of radial well laterals due to iron incrustation. The obvious consequence of that process is a decline in well capacity.

The second step in 3D modeling is a hydrodynamic analysis of the groundwater under present or design conditions. The ultimate goal is to define well capacity and the natural and man-made factors that limit its capacity.

The natural factors are hydrogeological conditions, which include the spread and characteristics of the aquifer and its various strata, the configuration and characteristics of the riverbed, and the river stage regime. Of special relevance to well capacity is the permeability of the riverbed and of the semi-pervious interbed (or interbeds).

Additional factors include the positions, lengths and characteristics of the laterals of the analyzed well, and the locations of neighboring wells in the considered part of the site. Well density largely dictates (limits) the initial capacity of the wells.

Well ageing falls under the technoeconomic category as it affects well longevity and the cost of maintenance. Well entrance velocities, which determine capacity, need to ensure a pre-defined rate of ageing (or capacity decline). The initial sustained water level in the well is defined accordingly, to ensure enough time (as specified) for undertaking well rehabilitation measures.

The results of a hydrodynamic analysis of two wells at Belgrade's groundwater source, whose characteristics differ, are presented below.

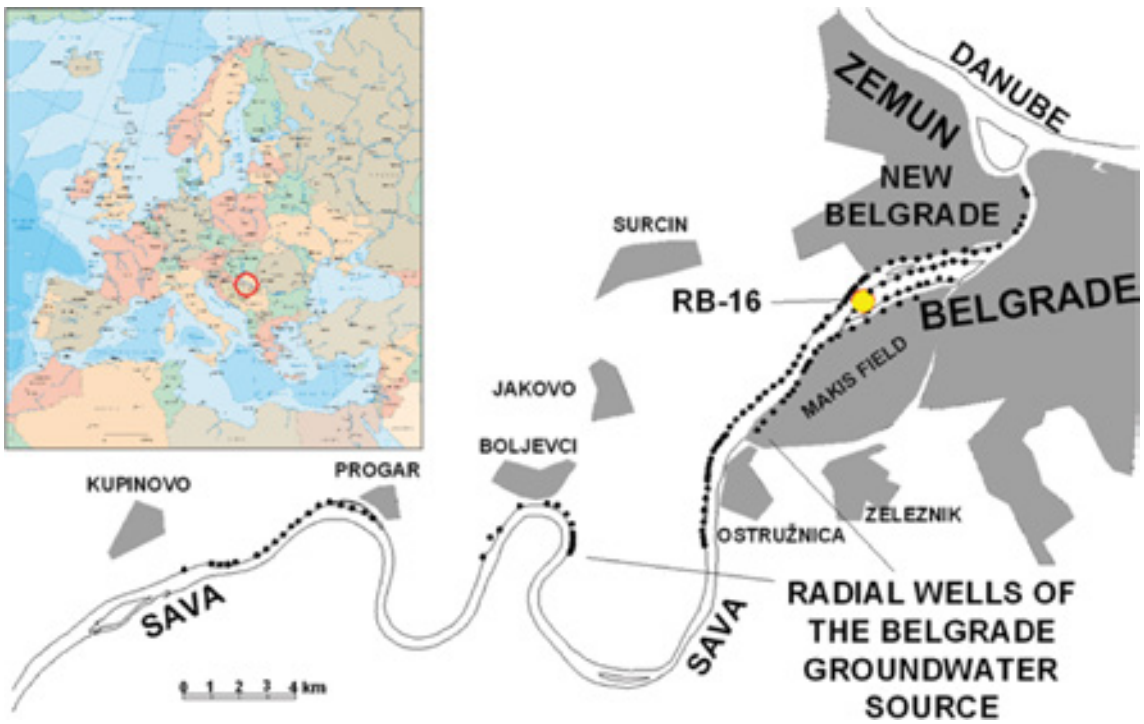

Figure 1: Location of Belgrade's groundwater source and study wells RB-16 and RB-46.

RELEVANT CHARACTERISTICS OF WELLS RB-16 AND RB-46

Belgrade's groundwater source is situated along the lower course of the Sava River, in the vicinity of its confluence with the Danube.

Well RB-16 is located on the edge of a river island – Ada Ciganlija, whereas well RB-46 is on the left bank of the Sava, upstream from the former well, Fig. 1 (Dimkić et al., 2007b).

In hydrogeological terms, these two wells differ because in the case of well RB-16 there is a sequence of semi-permeable sediments, which can hydrodynamically be schematized as a single semi-permeable interbed, Fig 2. There is no such inter-layering at the location of well RB-46.

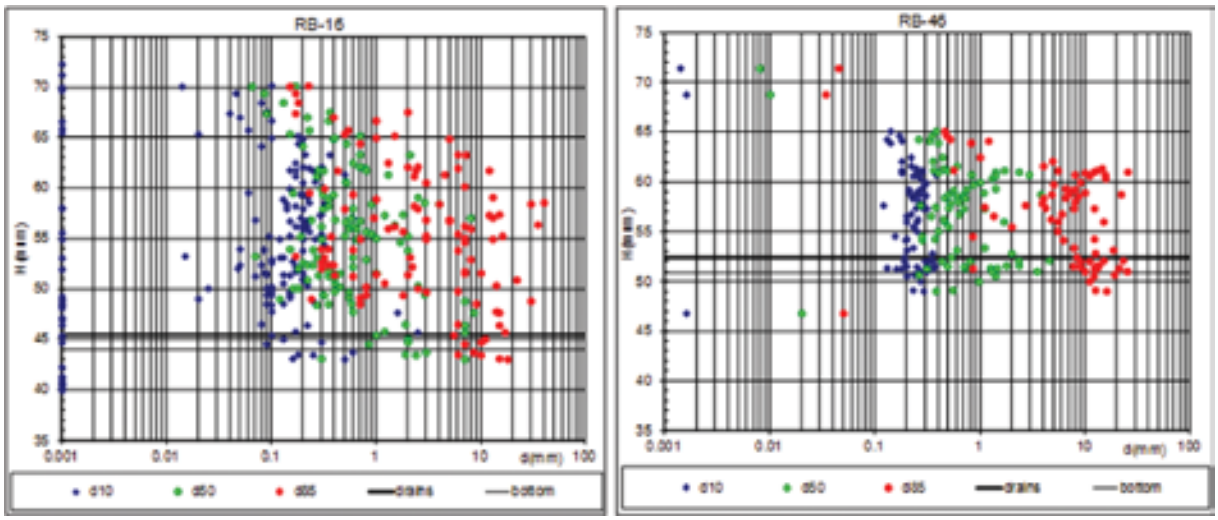

Figure 2: Vertical sections of select grain-size distribution fractions in the zones of wells RB-16 and RB-46. The horizontal line denotes the elevation of the laterals.

The discharge history of the two wells is shown in Fig. 3. The times of construction and initial capacities differ to a large extent. Following numerous rehabilitations, the existing laterals of well RB-16 were replaced by four new laterals in 2007. Since then, the capacity of this well has been relatively consistent (~100 L/s). Well RB-46 was built much later (1983) and its initial capacity was modest by comparison. Several rehabilitations of its laterals have been conducted over time. The initial number of laterals was eight and is now five. Their total length is about 40 m.

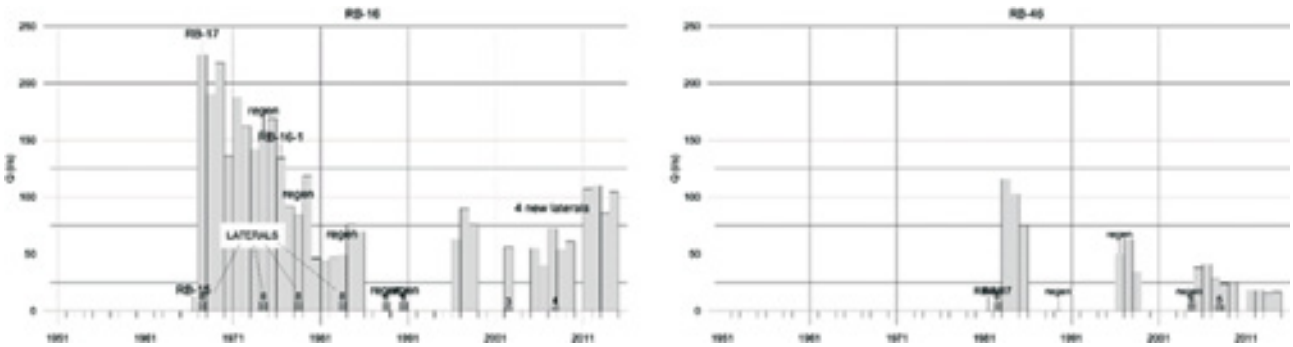

Figure 3: Gauged capacities of wells RB-16 and RB-46 over time. Dark bars denote the number of functional laterals after rehabilitation.

Well ageing, expressed via the increase in hydraulic resistance at the laterals (KLHR), differs between the two wells. The oxic states, expressed via the redox potential (Eh), and bivalent iron concentrations are also different, as shown in Table 1.

	Q av. [L/s]	KLHR av. [m/(L/s)/y]	Eh av [mV]	$[Fe^{2+}]$av [mg/l]	Number of laterals	Length of laterals [m]
RB-16	81	0.1	137	0.6	4	179
RB-46	22	2.3	109	1.6	5	101

Table 1. Several parameters of wells RB-16 and RB-46

RESULTS

Given below is a basic interpretation of the results of model simulations of the two selected wells. Model testing with the specially-developed software provided reliable and accurate information about groundwater flow to the wells.

The effect of the semi-permeable interbed on groundwater flow is reflected in the piezometric head difference between the upper and lower water-bearing layers. In close proximity to well RB-16, a pair of observation wells registered a difference of about 10 m. Taking this parameter as the basis for model calibration, the piezometric head was mapped as shown in Fig. 4. Even though there are three schematized layers at RB-46 as well, the middle layer is not a distinct hydraulic barrier for groundwater flow. The piezometric head difference between the upper and lower water-bearing layers at this well is of the order of 1 m, even though the thickness in the region of well RB-46 is from 10 to 13 m.

Figure 4: Piezometric head difference between the upper and the lower water-bearing layer at well RB-16 (left) and well RB-46 (right).

Zones of different rates of groundwater flow to the well were simulated on the model, Fig. 5, as lines of the corresponding percent contribution to the well's discharge. The basis for this was a simulation of the vertical fluxes through the middle layer of the model.

Figure 5: Zones of different contributions to the groundwater flow to wells RB-16 and RB-46.

The travel time through the middle layer of the aquifer was simulated on the basis of the vertical flow distribution and the thickness of the interbed. Figure 6 shows the results. By combining these with the previous results, it

was possible to estimate the concentrations and total participation of substances in well discharge, depending on the location of the pollution source.

Figure 6: Travel time (in months) through the middle layer (interbed) of the aquifer at wells RB-16 and RB-46.

Model testing also provides the capacities of the well laterals and the entrance velocity distribution along them, as shown in Fig. 7. It is apparent that the discharge of lateral 1 of well RB-16 is low. Its characteristic is a vertical bend of about 6 m, due to improper emplacement. This lateral penetrates the semi-permeable interbed and goes to the water-bearing layer above it. The low discharge is attributable to considerable clogging, which is indirectly apparent in the underwater video.

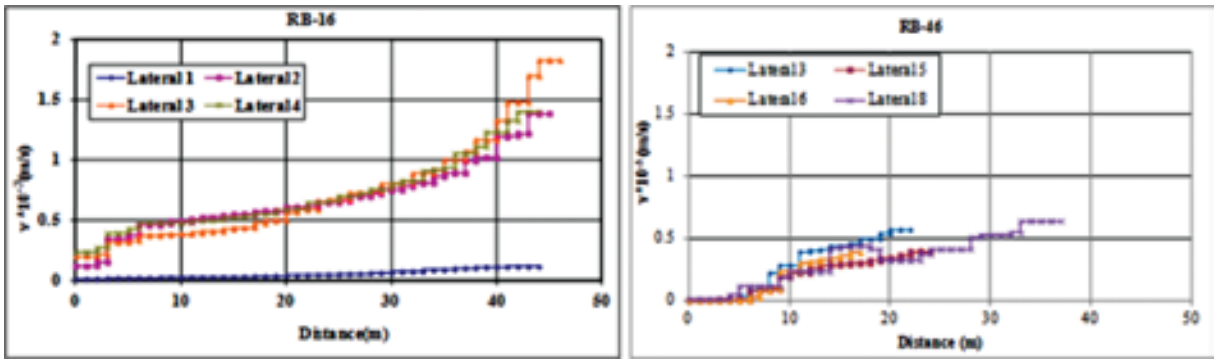

Figure 7: Distribution of groundwater flow to the laterals.

Riverbed permeability is of key importance for the capacity of an existing or future well. The characteristics of the colmating layer vary over both space and time. They depend on the river's discharge regime and the predominant nature of groundwater flow. If an operating well causes continuous infiltration of water from the river into the aquifer, this can result in riverbed colmation to such an extent that normal operation of the well becomes impossible. In such a case the well would receive water from the riparian zone, which would reduce well discharge dramatically.

The travel (residence) time between the river and well RB-16 under "normal", calibrated model conditions differs depending on the travel route, but is not shorter than two years. This fact is part of the answer to the question why the quality of the well water is consistently high, regardless of the time-varying quality of the river water.

Sizing of well discharge capacity is not only a matter of initial permissible entrance velocities at the well laterals. Sustainable operation also needs to be considered. The authors of this paper have been studying well ageing processes at Belgrade's groundwater source for years and, based on numerous analyses, have established a correlation between the rate of well ageing and the biochemical characteristics of the groundwater. Consistent with well maintenance procedures and rehabilitation frequency at this source, the adopted sustainable rate of increase in local hydraulic resistance (LHR) is 0.35 m/year. This criterion was used to derive maximum permissible velocities at the wells, depending on the groundwater redox potential (Eh) and bivalent iron (Fe^{2+}) concentrations, Fig. 8.

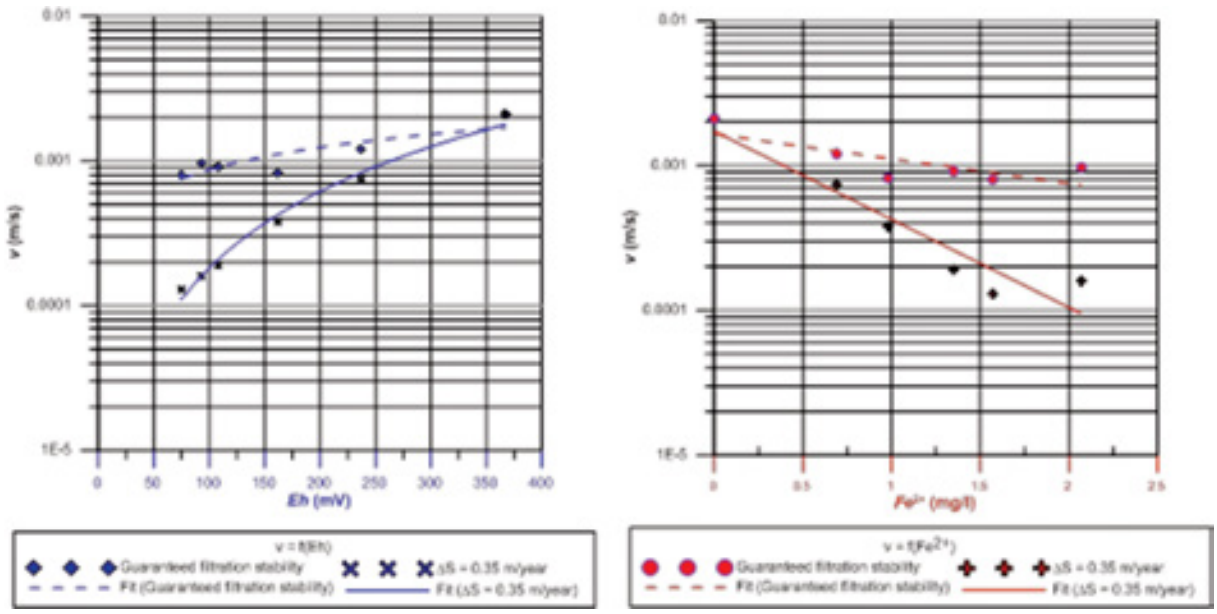

Figure 8: Permissible entrance velocities at the well as a function of Eh and Fe^{2+} (Dimkić, Pušić, 2014).

Considering the existing configuration (number and length of laterals) of well RB-16 and using the plots shown in Fig. 8, the resulting well capacities are Q = 51 L/s and Q = 118 L/s. The corresponding discharge of well RB-46, based on both criteria, is Q = 19 L/s. Since well RB-16 has new laterals, it is deemed that its real discharge is consistent with long-term sustainable capacity. If new laterals were installed for well RB-46, the achievable stable capacity would be 70 to 80 L/s.

CONCLUSION

The capacity of the radial wells at Belgrade's groundwater source declines predominantly due to trivalent iron incrustation of the well laterals. The total annual rate of decline is about 100 to 150 l/s. Given the need to reduce the damage, a well capacity simulation methodology has been developed to support the design of new wells or the replacement/rehabilitation of laterals. The present paper shows the results of mathematical modeling of two wells, through the following steps: quantification of the capacity of the well's location, determination of maximum permissible capacities of the laterals, and prediction of the hydraulic effects of a long-term increase in well discharge.

The maximum permissible capacity of the location of well RB-16 was found to be between 100 and 110 L/s. The decline in capacity and incrustation of this well are very slow, such that periodic rehabilitation of the laterals is recommended instead of replacement.

The capacity of well RB-46 has declined considerably due to biochemical clogging, to the present discharge rate of 22 L/s. The capacity of the location is about 80 L/s, such that new laterals are needed to withdraw this amount of water. Applying the new method discussed above, via correlations with the redox potential and bivalent iron concentrations, the maximum permissible (critical) entrance velocity at the laterals is about 2*10-4 m/s. This well needs eight new laterals to ensure effective operation and longevity.

The determination of critical entrance velocities at the laterals via the aerobic state and bivalent iron concentrations in the groundwater, in the manner presented in the paper, is of capital importance for Belgrade's groundwater source, but also other groundwater abstraction sites that suffer from well screen incrustation.

ACKNOWLEDGEMENTS

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NOTES

BANK FILTRATION SYSTEMS: A GIFT OF NATURE EXPLOITED SINCE THE 19TH CENTURY

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Abstract: River bank filtration plays a very important role in the supply of Hungarian drinking water. On a country level, about 31.2% of the total drinking water supply comes from bank filtration, while the capital city Budapest is completely supplied through bank filtration systems. Some of the water supplies have been in operation for more than 130 years, demonstrating the effectiveness of the water production process. The riverbed and nearby aquifers vary along the rivers (e.g. thickness of gravel, filtration properties, etc), so hydrogeological surveys are important to characterise and define a river-bank filtration protection area. Hydrogeological flow and transport modelling, combined with an interpretation of environmental isotope data were carried out to map and define some Hungarian drinking water protection areas. This paper presents and evaluates the results of the hydrogeological modelling at the Budaújlak and Margit island drinking water protection areas (DWPAs) in Central Budapest. These studies show that the abstraction wells of Budaújlak produce about 92-98% water originating from the Danube with a negligible groundwater component at the given Danube water level. A correspondingly high Danube water origin was found in the abstraction wells at the northern part of the city in the Balpart II water supply unit. However high pollution signals (eg. nitrate) could be detected locally in some monitoring wells which are further inland from the river bank. The number of the Hungarian drinking water supply companies has been drastically reduced over the past few years through consolidation, and the larger regional suppliers are now considering providing potable water from distant, even cross-border sources. Bank filtration is a proven, economic option for delivering clean, potable drinking water without the need for any additional purification systems in more than sufficient volumes, also stated in the national River Basin Management Plan of Hungary. Implementation of a comprehensive water governance plan is needed, including the use of aquifers of larger rivers in the wider Pannonian Basin region, to ensure long term sustainability for the coming century and beyond.

Keywords: bank filtration, Danube, water governance

INTRODUCTION

The role of river bank filtration as an integral part of the Hungarian water supply network has been important for more than 100 years. The total abstraction through river bank filtration (about 231M m3/year) accounts for 22.6% of the total groundwater abstraction, while the drinking water supply through bank filtration (about 223 Mm3/year) accounts for 31.2% of the total drinking water abstraction in Hungary (VGT2, 2015). The water resource processed by bank filtration comprises a larger fraction of surface water with a short residence time in the aquifer, and a smaller fraction of so-called background groundwater, e.g. the shallow groundwater of the background hills. According to the strict Hungarian definition, a river bank filtration system must comprise a minimum of 50% surface water origin. However, in general the surface water origin is higher than 90% (VGT2, 2015). Although the contribution of background groundwater can, in some cases, be higher than 50% of the total water resource, these water supplies are generally called bank filtered, since they operate as bank filtration systems. The main functioning drinking water protection areas (DWPA) utilising river bank filtration systems are along the Danube (figure 1), with smaller DWPAs or DWPAs partially supplied through bank filtration along the Hernád, Ipoly and Mura rivers. Additional DWPAs have been delineated and are retained as potential future river bank filtration systems along the Danube, Rába, Dráva and Tisza rivers. In total 92 river bank filtration DWPAs were registered in 2015, out of which 51 are in operation, while 41 are prospective DWPAs (VGT2, 2015).

The time which elapses between the infiltration of the surface water through the river bed and the well can vary between a few days up to few hundred or even one thousand days, depending on the location of the well relative to the river bank (Hunt, 2009), on the hydraulic conductivity of the aquifer, and on the production rate. The average transition time in Hungary is in the order of a few tens of days.

The drinking water for the capital city Budapest is completely supplied through river bank filtration systems. This water abstraction reached a maximum between the beginning of the 80's and beginning of 90's, up to 350-370 Mm^3/year, with an approximately average abstraction of 200 Mm^3/year from the middle of 2000. The drinking water abstraction of Budapest seems to have stabilised around 166-167 Mm^3/year from the beginning of 2010. The operational territory of the Budapest Waterworks runs from Szentendre island located north of Budapest, to Csepel island in the south, crossing the densely populated and built-up urban sprawl. Figure 2 illustrates the middle part of this system (discussed in this paper) showing the contour lines of the DWPAs together with the abstraction and monitoring wells.

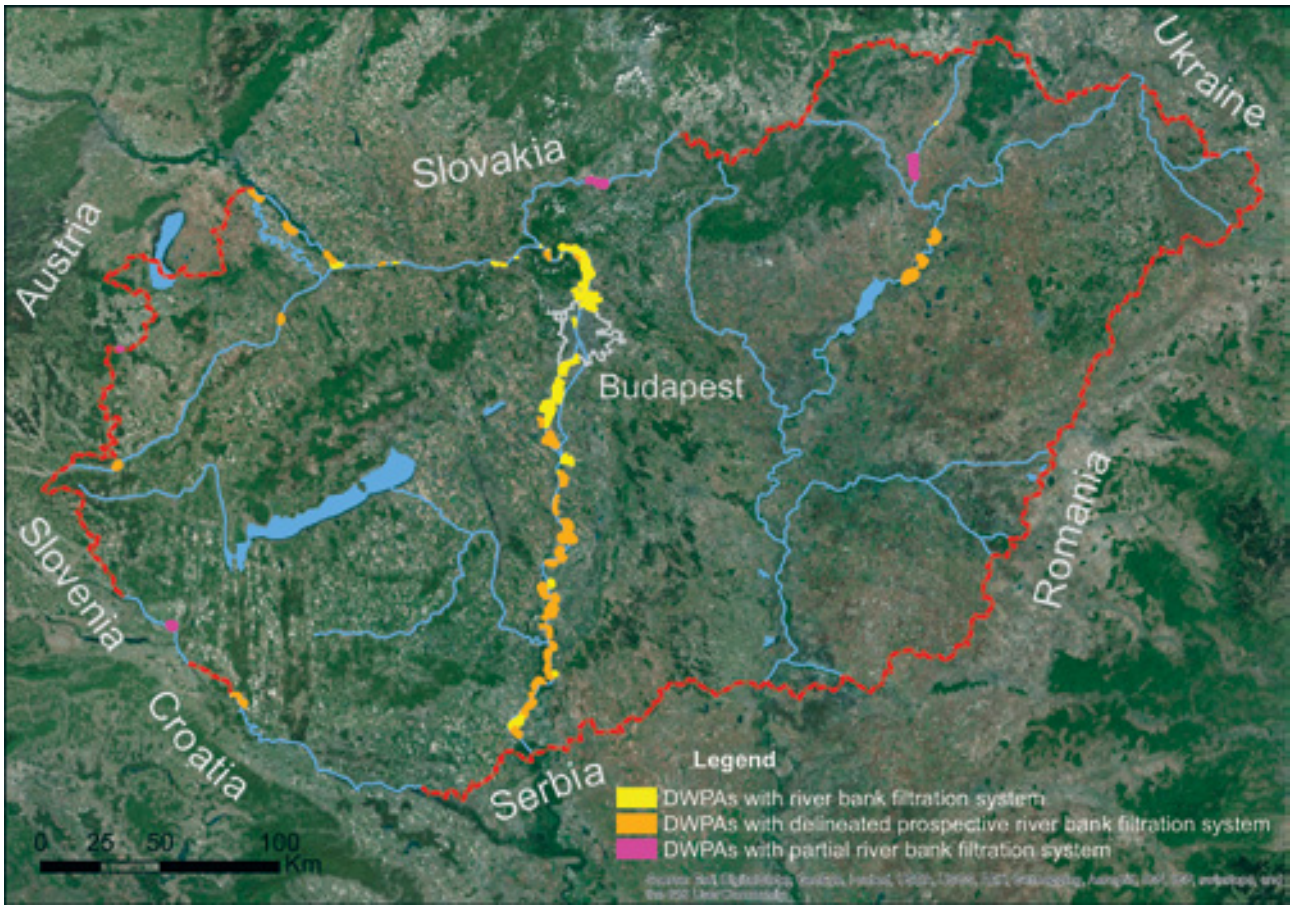

Figure 1: Drinking water protection areas (DWPAs) with river bank filtration systems

RESULTS AND DISCUSSION

In order to be able to ensure a long term, safe water supply, it is very important to know the residence times of water passing through the bank filtration systems, and to model different scenarios which may result from flood events or the potential effects of climate change. The best tool for this is hydrodynamic flow and transport modelling combined with hydrogeochemial and/or environmental isotope data interpretation. Several studies have described the characteristics of the different river bank filtration systems and presented the flow paths and residence times of some of the Hungarian bank filtration DWPAs (Deák et al., 1992, Deák et al., 1996, Fórizs et al., 1999, Balassa et al., 2003, Kármán et al. 2013). Surveys related to bank filtration DWPAs carried out at the Geological and Geophysical Institute of Hungary (and its predecessor Geological Institute of Hungary) include 2D and 3D hydrogeological modelling, and hydrogeochemical and isotope data interpretation.

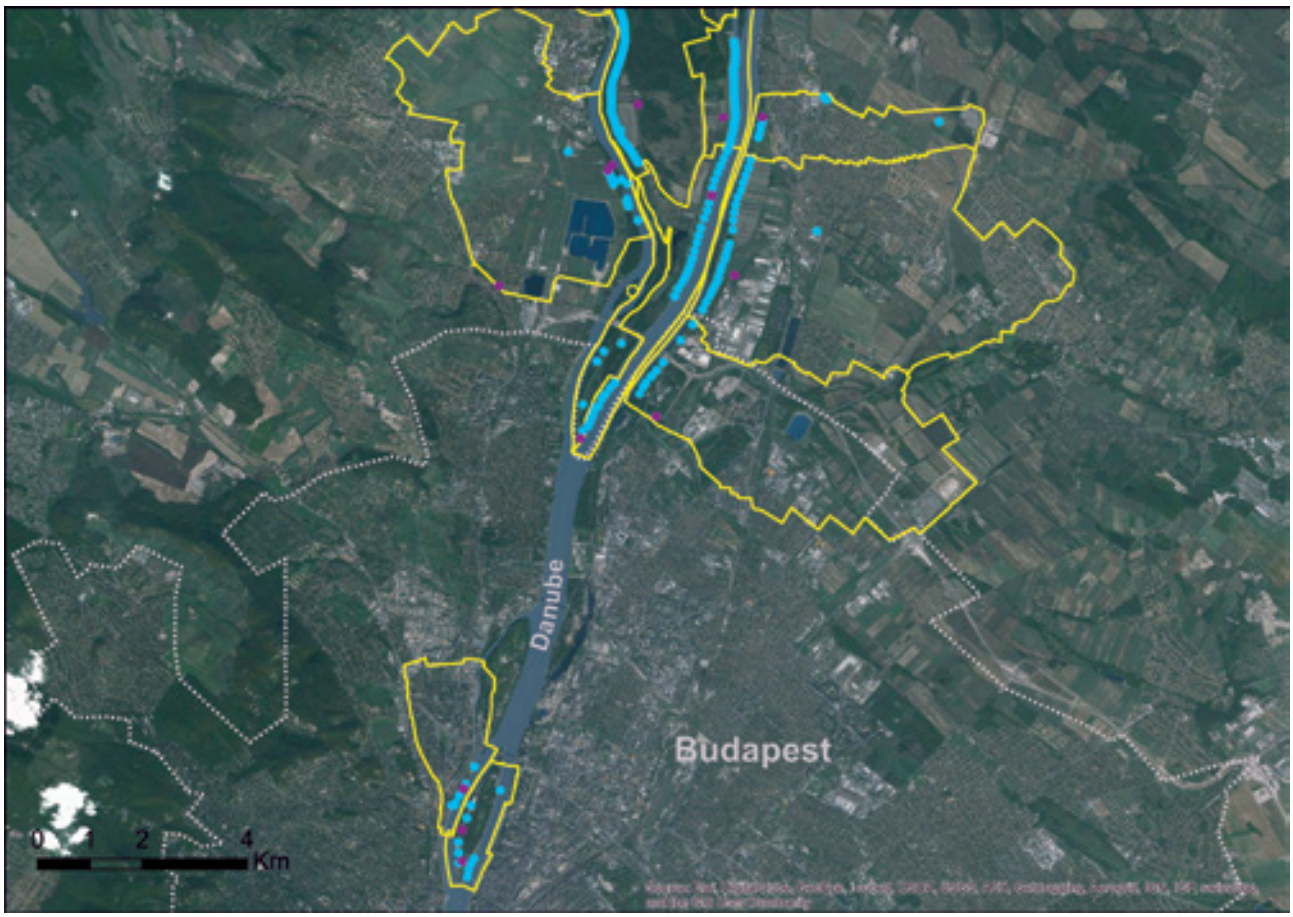

Figure 2: Drinking water protection areas (DWPAs with yellow contours) in the middle part of operational territory of the Budapest Waterworks showing the abstraction (blue dots) and monitoring wells (purple dots)

A hydrogeological model was developed for the second waterworks in Budapest, the Budaújlak water supply, within the framework of the hydrogeological evaluation of alluvial deposits of large Hungarian rivers. Budaújlak has been in operation for more than 130 years, and is one of the oldest water supply systems in Budapest. This study focusses on one of Budapest's drinking water protection areas with a river bank filtration system, and was carried out following the requirements of a diagnostic examination of vulnerable DWPA. As shown in figure 3. the flow paths (marked with blue) reach the abstraction wells within 20 days. The half year (purple), five years (green) and fifty years long (dark orange colour) flows are shown in figure 3, showing that the south western part of the protection zone is within less than half year (partly around one month) travel time from the surface, which would require fast intervention in the case of an unexpected contamination of an operating abstraction well.

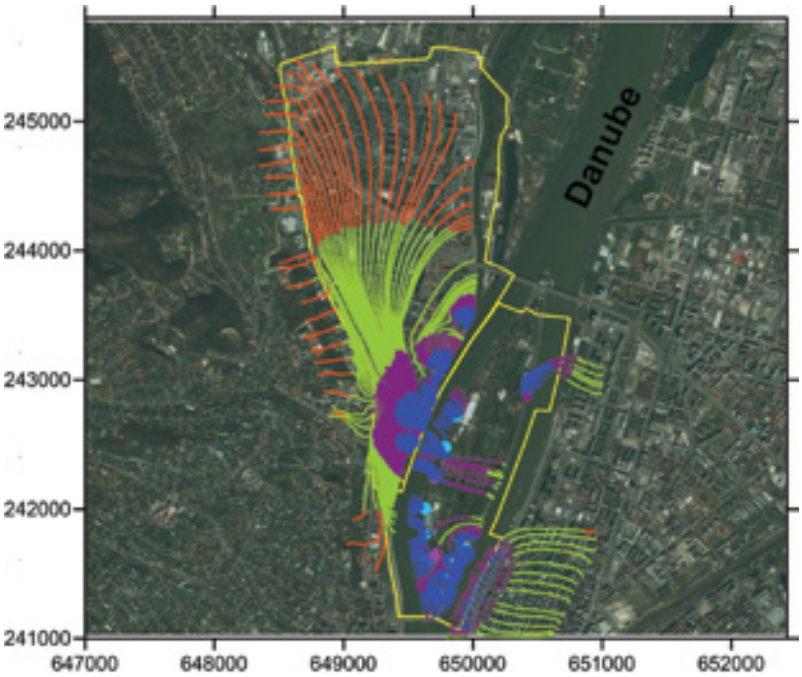

Figure 3: Modelled flow paths at the Budaújlak and Margit island drinking water protection areas (DWPAs) in central Budapest. (Colours represent 20 days (blue), half year (purple), five years (green) and fifty years (orange) long flow paths lines)

The chemical composition of the water supplied by the Budapest Waterworks is determined by the chemistry of the Danube. However, similar to other river bank filtration type DWPAs, the effect of mixing with background waters could be traced by the higher chloride, nitrate or total hardness content compared to the water composition of the Danube. Although the differences between the Danube and background water composition can be clearly detected, the concentrations of the parameters mentioned above are low in spite of the very densely populated and built-up neighbourhood. This shows there is no ongoing anthropogenic activity which could harm the quality or composition of the drinking water under the current production rates and river composition.

In addition to chloride which is a conservative ion, an internationally recognised parameter which can be applied in determining the origin of drinking water in the Danube river bank filtration systems is stable oxygen isotopes as there is a significant difference between the $\delta^{18}O$ values of the Danube water and the background groundwater. The $\delta^{18}O$ values of the Danube vary along its flow path (Deák et al., 1996, Pawellek et al., 2002, Miljevic et al, 2008, Wyhlidal et al., 2014) according to the characteristics of its tributaries and related catchment areas. The mean $\delta^{18}O$ value of the Danube water in Hungary is -11.0% (Deák et al., 1996), while the multi-annual mean of the infiltrating precipitation is -9.3% (Deák et al., 1996).

Kármán (2013) performed lumped parameter calculations at the Szentendre island and in Szigetköz in order to calculate the flow time between the river bed and the abstraction wells. She interpreted $\delta^{18}O$ isotope data using analyses of water samples from the Danube, the background monitoring wells and the bank filtration abstraction wells. Initially four to five samples per week were collected both from the river and the wells. Later, the Danube was sampled daily after a time. Kármán et al (2013) studied the $\delta^{18}O$ data distribution according to a low, a medium and a high Danube level. The changes in the $\delta^{18}O$ data reflected the changes in the Danube level as could be expected. The higher the Danube level, the more negative the $\delta^{18}O$ values.

Our studies from 2003 show the abstraction wells of Budaújlak produce 92-98% Danube water (figure 4) at a given Danube water level. A similarly high Danube water origin can be seen in the abstraction wells at the northern part of the city at the Balpart II water supply unit. However high pollution signals (eg. nitrate) were detected in some monitoring wells which are further inland from the river bank. A higher background water component can also be shown by the more positive $\delta^{18}O$ data (green diamond symbols) of the monitoring well (figure 4). In the case of smaller islands within larger rivers, the direct river bank filtration system might draw its background water component from the other side of the island pumped through the gravel aquifer. This means that in a similar case no difference in the water composition of the different components can be tracked, based on the $\delta^{18}O$ data.

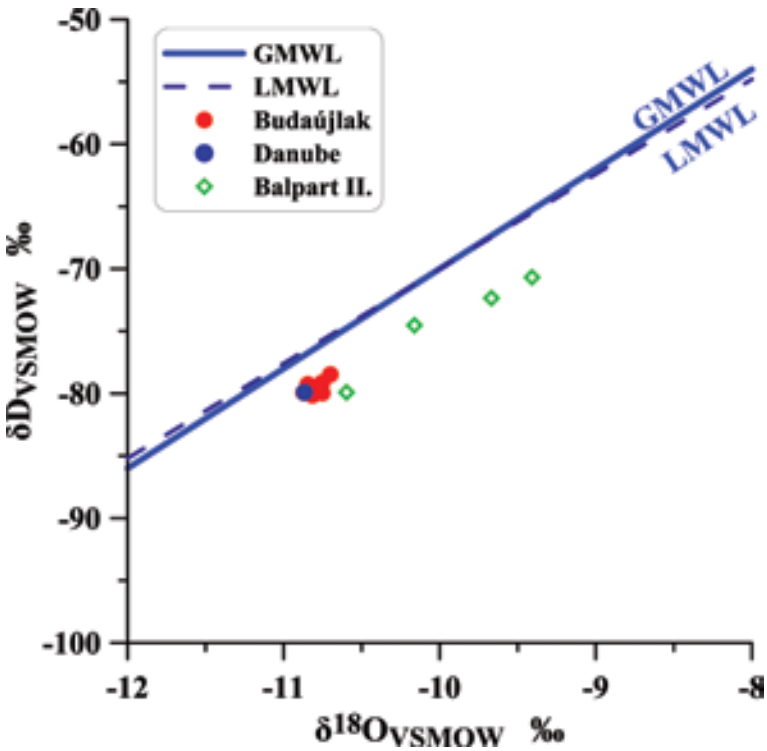

Figure 4: Stable isotope data distribution at two DWPAs in Budapest

CONCLUSION

River bank filtration systems proved to be an efficient source for good quality and sufficient drinking water supply even in densely populated areas. Special attention should be paid to maintaining the quality and morphology of the river bed and to protecting the ultrafiltration properties of the river banks. Any intervention plan (for example for flood protection) must first be checked to ensure it will protect the status and functioning of the DWPA. This means river bed sweeping shall be avoided in cases where it poses a risk to the thickness of the filtration system, and shall also be installed (as needed) in places where they do not enhance the clogging of the riverbed.

Bank filtration systems can guarantee drinking water supplies not just to avoid over-exploitation of groundwater, to handle water scarcity, but also in case of anthropogenic contamination (eg. increasing toxins in surface waters) or in the case of groundwater with high natural background levels (eg. arsenic). Dimkić et al. (2011) concluded that the high arsenic and organic matter content characteristic for the Pleistocene porous intergranular aquifer complex of the south-eastern part of the Pannonian Basin (Hungary, Serbia, Romania, Croatia) would require sophisticated complex water purification plants which do not exist at the moment, although different arsenic removal technologies have been tested with good results (eg. SUMANAS). A regional drinking water supply system was proposed for Vojvodina Province (Serbia), to provide water from an alluvial aquifer of the Danube through bank filtration and/or artificial recharge. The number of the Hungarian drinking water supply companies has been drastically reduced in the last years through consolidation, and the larger regional suppliers consider providing potable water from distant, even cross border sources. However, the supply of potable water from the alluvial aquifer of the Danube can also be an economically realistic option, as has been stated in the national River Basin Management Plan of Hungary (VGT2, 2015).

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NOTES

QUALITY ASSESSMENT OF DEEP-WELL RECHARGE APPLICATIONS IN THE NETHERLANDS

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INTRODUCTION TO DEEP-WELL RECHARGE

Artificial recharge of aquifer systems may be performed for various reasons. These include, among others, the subsurface storage of water for drinking and agricultural purposes, the natural subsurface water treatment, and the disposal of wastewater.

The general driver for subsurface storage of water is the increasing demand for drinking water in areas where the government has forced the water supply companies to restrict their groundwater pumping. This is usually enforced in order to prevent the drawdown of groundwater tables, to restore wetlands in selected areas and to prevent seawater intrusion. Moreover, recent benchmarks of drinking water prices in the Netherlands push water supply companies to lower their costs. Aquifer storage applications (e.g. ASR), if operating without quality deterioration, are thus becoming an interesting option also in the Netherlands. The main financial advantages compared to surface water storage consist of (1) an increased security of water supply, (2) reduced well maintenance, (3) little land occupation, (4) reductions in costs of water storage and evaporation losses, and (5) during water purification, storing the treated water in the subsurface can decrease the peak factor allowing the facility to have a smaller capacity (Pyne, 2005).

Deep well injection consists of separate injection and recovery wells and aims at water quality improvements by aquifer passage (Stuyfzand and Timmer, 1999). Processes such as filtration, sorption, and biodegradation are responsible for the water “recycling” during its passage through the aquifer. The intentional use of the natural attenuation processes to improve water quality has been referred to as natural aquifer treatment (Maliva and Missimer, 2010). Water quality improvements may consist of denitrification, biodegradation of organic micro-pollutants like chlorination by-products (Pavelic et al., 2005) and pharmaceuticals (Overacre et al., 2006), and removal of pathogens (Page et al., 2010). The environmental profits of this natural purification method are many, the most important being a reduced application of undesired chemicals like coagulants, active carbon, ozone, and chlorine. These beneficial aspects make deep well recharge an interesting option for drinking water production using reclaimed water or polluted surface water, especially in areas with limited space restricting open recharge applications (e.g. infiltration basins).

INJECTION IN FRESH AQUIFERS FOR DRINKING WATER PRODUCTION

Since the early 70’s, numerous deep well injection and aquifer storage experiments have been carried out in the Netherlands to acquire insight in 1) the feasibility of recharging confined aquifers with surface water through wells and 2) the water quality changes upon interaction of the injected water with the native groundwater and aquifer sediments (Stuyfzand, 1998). The target aquifers are usually composed of Pleistocene or Miocene

sands with a grain size of 300-500 µm and a permeability of 30-50 m/d. In most cases the native groundwater is fresh, anoxic, calcite saturated and with relatively high concentrations of Fe(II), Mn(II) and ammonium. Most formations contain low amounts of very reactive iron-sulfides (pyrite). Calcium-carbonate is typically present in marine deposits and Pleistocene sediments while small amounts of iron-carbonates that contain manganese and/or magnesium (siderite, ankerite) are often present.

Hydrogeochemical Processes Affecting Water Quality

Upon injection of aerobic water, the water quality is mainly altered by oxygen consumption by sedimentary electron donors like pyrite, sedimentary organic matter, and exchangeable Fe(II), NH_4^+, and Mn(II). The induced acidity is partly buffered by HCO_3^- in the groundwater and, if present, by the dissolution of carbonate minerals. Carbonate dissolution further affects the water quality due to the possible release of Fe(II) and Mn(II) in the groundwater. Heavy metal release may also result from cation exchange (Ca^{2+} in the injected water displacing Fe(II) and Mn(II) from the exchanger). If oxygen is present then the released Fe(II) is further oxidized and precipitates in the form of Fe-hydroxide (ferrihydrite). If however the oxygen front is lagging behind (at larger distances from the injection well) then Fe(II) remains dissolved and may contaminate the abstracted water. The kinetics of Mn(II) oxidation are very slow resulting in dissolved Mn(II) contamination being more persistent, even in the presence of oxygen. The generalized evolution of quality changes in the water abstracted from a well downstream of the injection well is depicted in Figure 1.

The situation differs in aquifer storage recovery (ASR) applications where the water is abstracted back from the same dual-purpose well. Iron and manganese which become mobilized during injection may show a retarded breakthrough due to adsorption in the oxidized zone around the ASR well. Adsorption is taking place on the newly formed iron-hydroxides and on the original cation-exchangers, mainly composed of sedimentary organic material and clay minerals (Appelo et al., 1999). Eventually, Fe(II) and Mn(II) desorb from the outer sorption zone due to decreasing pH conditions and reach the ASR well. Mn(II) especially has a higher tendency to desorb due to its higher pH requirements (pH > 7.5, Buamah et al., 2008) to remain adsorbed on the exchange sites of the Fe-hydroxide surfaces. In the presence of Mn-containing carbonates, drinking water standards may be exceeded (with respect to manganese) even sooner due to additional dissolution of these minerals during recovery (Antoniou et al. 2012).

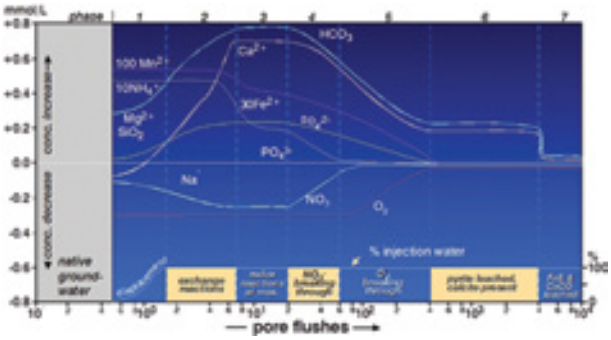

Figure 1: Generalized evolution of the quality changes of oxic injection water in an anoxic, calcareous aquifer, as a function of the number of pore flushes of the soil in between injection and abstraction well. The X-axis also gives the retardation factor for species with a negative change, and the leach factor for species with a positive change (Stuyfzand, 1998).

Measures to Prevent Contamination

Field observations and reactive transport modelling have suggested an increasing sorption capacity with subsequent injection-recovery cycles due to a gradual build-up of Fe-hydroxide precipitates. Moreover, a buffer zone can be implemented around the ASR well by halting recovery and restarting injection as soon as drinking water standards are exceeded (Antoniou et al., 2015). This approach shifts the reactive zone further away from the ASR well and can substantially increase the recovery efficiency (ratio between recovered and injected volume) of the ASR plant. However, if Mn-containing carbonates are present then aquifer pre-treatment or source water pre-treatment may be required to prevent the dissolution of these carbonates during recovery phases.

The use of pH-buffering agents such as NaOH and Na_2CO_3 can increase the alkalinity and pH of the aquifer around the ASR well and prevent the dissolution of carbonate minerals as a response to under-saturated source waters or acidifying water-aquifer interactions. Additionally, increased pH will enhance the sorption of Fe(II) and especially Mn(II) on the Fe-hydroxides formed during injection. The effects of dosing a pH buffer have been experimentally tested with positive results in real scale ASR pilots in Virginia and South Carolina which suffered from Fe(II) and Mn(II) concentration exceedances in the recovered water (Ibison et al., 1995; Pyne et al., 2013).

Pre-treating the aquifer was tested by means of column experiments where ASR was realistically simulated in an anoxic setting using real aquifer sediments (Antoniou et al., 2014). It was concluded that treating the aquifer sediments with permanganate can prevent the mobilization of Fe(II) and Mn(II) and greatly improve the recovery efficiency. This is the result of 1) the partial depletion of sedimentary electron donors due to increased oxidation, 2) the extended precipitation of Mn-oxides (by-product of the oxidation reactions) with a high sorption capacity and 3) the increased pH conditions due to proton consumption. Care should be taken as to prevent the reduction of the Mn-oxides by the inflowing native groundwater during an extended recovery phase, as this may lead to undesirable results.

INJECTION IN BRACKISH/SALINE AQUIFERS

Amsterdam Water Supply Dunes

In 1994 the Amsterdam Water Supply started an experiment to investigate the option of a deep-well recharge system in the Amsterdam dune catchment area, to replace or expand the open recharge system with basins, which is in operation since 1957 (Van Duijvenbode and Olsthoorn, 2002; Olsthoorn and Mosch, 2002). Artificial recharge is needed to combat overexploitation of fresh groundwater in the area since the beginning of the 20th century, which caused groundwater table declines, upconing of brackish/saline water and the disappearance of natural groundwater dependent vegetation. Pre-treated Rhine river water was injected by four wells screened in the semi-confined aquifer 30 to 60 m below mean sea level. The water was recovered by a series of extraction wells 400 m away. Prior to injection, the already pre-treated (by coagulation and rapid sand filtration) Rhine river water was additionally slowly filtered through fine aeolian dune sand (Figure 2). This filtration process served to reduce the Membrane Filtration Index (measuring the clogging rate of a 0.45 µm membrane filter – indicative of the physical quality of the water and its ability to be injected) which, especially in summer, rose due to biological activity in the open supply channel.

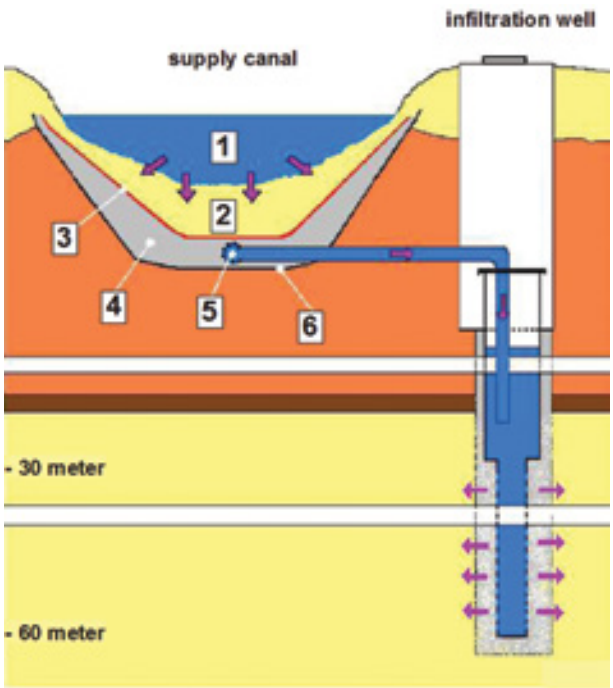

Figure 2: Cross-section showing the deep injection system (from: Van Duijvenbode & Olsthoorn, 2002). 1: pre-treated river water, 2: fine Aeolian dune sand that polishes the water to make it suitable for injection, 3: nylon fabric, 4: gravel pack, 5: drainage system, 6: impermeable plastic sheet to prevent the inflow of the local iron-rich groundwater.

The sand filter was cleaned once a year to limit the development of hydraulic resistance due to the continuous infiltration of water with moderate quality. Hydraulic resistance developed also in the injection wells mainly due to the accumulation of biomass and iron flocks in the gravel pack. This resistance disappeared by the automatic backwashing, switching on as soon as the water level inside the well exceeded a certain threshold. The removal of clogging which developed on the borehole wall (chemical clogging) required occasional well surging using compressed air. Currently the extra infiltration capacity in the dune aquifers is not needed and the well infiltration system has stopped.

Nootdorp

Aquifer storage of freshwater in brackish or saline aquifers can be an efficient technique to bridge freshwater shortages in coastal areas. The main challenge in such setting is dealing with the buoyancy effects which may cause salinization at the bottom of the ASR well during recovery, making part of the fresh water irrecoverable. A study was performed in an area dominated by greenhouse horticulture where a high irrigation water demand was up to recently covered by storage of rainwater in basins/tanks, use of surface water, and desalination of brackish groundwater (Paalman et al., 2012). The experiment aimed at reducing freshwater losses by applying deep injection and shallow recovery using multiple, individually controlled well screens (Zuurbier et al., 2014). The recovery efficiency was substantially increased (40%) compared to a conventional fully penetrating well (15-30%).

Noardburgum and Zevenbergen

The production of fresh drinking water from brackish groundwater by reverse osmosis (BWRO) is becoming more attractive, even in temperate climates. The drivers in this case may consist of environmental problems like the pollution and salinization of aquifers, drawdown of water tables in phreatic aquifers, effects of climate change like reduced base flows that render surface waters less fit for drinking water production, and increasing costs to produce drinking water from heavily polluted, fresh groundwater. In the Netherlands, the injection of the waste saline concentrate into a more saline, confined aquifer is considered as an ideal disposal solution for this reverse osmosis by-product. An aquifer should meet a number of hydraulic and geochemical requirements in order to qualify as a suitable disposal aquifer (Stuyfzand and Raat, 2009). The native groundwater should preferably have a lower quality (in terms of salinity and critical compounds) than the injected concentrate. The BWRO concept is based on the Freshkeeper® approach (Grakist et al., 2002; Kooiman et al., 2004) which stops and reverses salinization of aquifers and water wells by intercepting the intruding brackish groundwater, preventing thus the underground mixing of fresh and brackish water (Figure 3).

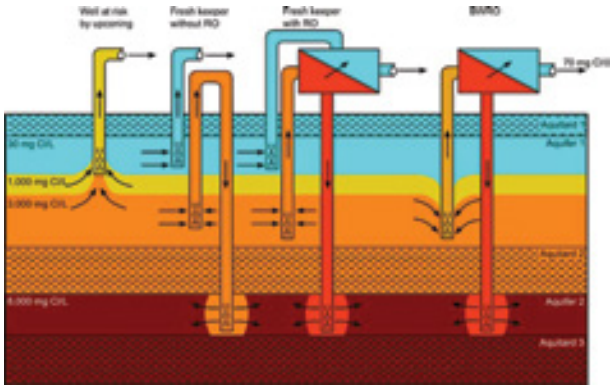

Figure 3: Schematic of (from left to right) a fresh well salinizing by upconing, the fresh-keeper without reverse osmosis (RO), the Freshkeeper with RO, and brackish water with RO (Stuyfzand and Raat, 2009).

Two pilots were initiated in 2009 to test the BWRO concept in the Netherlands (Noardburgum and Zevenbergen). The simultaneous abstraction of upper fresh and lower brackish groundwater led to a lowering of the fresh-brackish water interface confirming that instead of lowering production, brackish groundwater should be pumped and used (Raat et al., 2012). At both locations, concentrate injection was technically feasible, as long as the RO recovery levels were not higher than 50% (Zevenbergen) or 70% (Noardburgum). At higher levels, clogging of the injection well due to mineral precipitation could become an issue.

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NOTES

ENVIRONMENTAL FATE AND BEHAVIOR OF ACESULFAME IN LABORATORY EXPERIMENTS

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Abstract: Biodegradation, sorption and transport behavior of the artificial sweetener acesulfame were tested in different aqueous matrices to evaluate the potential of acesulfame to be used as a tracer. For practical application, detailed knowledge on the environmental fate and behavior of acesulfame is needed. Batch experiments yielded low sorption for several soils and Kd of acesulfame was estimated to be < 0.1 cm^3/g. Biodegradation in a fixed-bed reactor was not observed at environmental concentrations of 9 µg/L in two aqueous matrices (compost and soil extract) over a period of 56 days. The latter confirmed older observations made by (Scheurer et al., 2010) for drinking water. Only in diluted effluent of a wastewater treatment plant biodegradation started after 17 days of operation and acesulfame completely faded within 28 days. Results were confirmed by subsequent amendment of acesulfame to the fixed-bed reactor and a prompt and rapid degradation without a new phase of adaptation. The latter is surprising and puts reasonable doubt on the assumption that acesulfame behaves in general conservative in the environment. However, all flow-through column experiments indicated conservative behavior of acesulfame. Laboratory experiments demonstrated conservative behavior of acesulfame under conditions typical for riverbank filtration and groundwater. Results are in accordance with literature and indicate conservative behavior of acesulfame under conditions relevant for bank filtration, i.e. persistence versus biodegradation and negligible sorption. However, there are hints that there seem to be certain settings which favor an adaptation of the microbial community and facilitate a rapid biodegradation of acesulfame.

INTRODUCTION

Acesulfame is widely used in beverages and low-calorie food, is excreted after consumption and is directly discharged into surface water by untreated domestic wastewater or transported to wastewater treatment plants. Consequently, acesulfame has been detected in surface waters. Concentrations up to 10 µg/L have been reported for smaller streams, while in big rivers like the Rhine or the Danube, concentrations range from approximately 0.5 to 3 µg/L (Bayerisches Landesamt für Umwelt, 2009; Scheurer et al., 2009; Scheurer et al., 2010; Scheurer et al., 2011; Storck et al., 2015a; Storck et al., 2015b). State-of-the-art SPE-HPLC-MS/MS analysis allows the determination of low concentrations of acesulfame in aqueous samples down to 10 ng/L and make acesulfame a potential tracer for a wide range of environmental applications. Some examples for applications are the detection of sewer leakages and the determination of the proportion of wastewater in raw water sources like groundwater or riverbank filtrate. However, for a quantitative approach and for mixture calculations to evaluate reactive subsurface transport processes, stability and conservative behavior of acesulfame under different environmental conditions must be investigated. Acesulfame is a small molecule, mostly present as an anion and hydrophilic in the aquatic environment. Degradation and transport studies yielded so far ambiguous results on the stability of acesulfame (Buerge et al., 2011; Engelhardt et al., 2013). The aim of this study was to investigate the fate and behavior of acesulfame at realistic environmental concentrations in laboratory experiments and to reproduce the results in simulations.

METHODS

Acesulfame was analyzed by high performance liquid chromatography-electrospray tandem mass spectrometry (HPLC-ESI-MS/MS) after solid-phase extraction (SPE) (Scheurer et al., 2009; Scheurer et al., 2010). Reporting limit of acesulfame was 10 ng/L. Sorption of acesulfame was determined in batch experiments according to

modified OECD TG 106 (Organisation for Economic Co-operation and Development, 2001) with air dried soil and compost at acesulfame concentrations of 1 and 20 µg/L for 2 to 96 h. Biodegradation of acesulfame under oxic conditions was studied over a period of 56 d at a level of approximately 9 µg/L with a fixed-bed reactor designed to simulate river bank filtration (Karrenbrock et al., 1999; Knepper et al., 1999b; Knepper et al., 1999a). Behavior of acesulfame was studied under eutrophic conditions (diluted extracts of A: soil and B: compost) and with different microbial composition (C: diluted waste water treatment plant effluent) to cover a broader spectrum of environmental conditions. Reactive transport of acesulfame was studied in laboratory column flow through experiments. Silty sandy gravel sediments (S I and S II) for the experiments were excavated from areas with oxic (OX – S I) and anoxic (AN – S II) redox setting at a site with artificial groundwater recharge and bank filtration. Three columns (C) were fed with different water matrices pumped directly from a site with artificial groundwater recharge and bank filtration: C1-OX: surface water from River Ruhr, C2-OX: aerobic groundwater, C3-AN: anoxic groundwater. The columns were operated for 7 month to allow adaptation of the microbial community and to avoid short-term effects. Long-term break through curves of acesulfame were recorded at background concentration levels of the water used for percolation (surface water, aerobic and anoxic groundwater). Moreover, acesulfame was added to the column inflow both as a short-term pulse-type injection (duration 1 minute) and a permanent amendment (duration 1 day). Acesulfame behavior was compared with those of the conservative tracer sodium chloride. Experimental data were modelled with software CXTFIT (Tang et al., 2010; Toride et al., 1995) which gives a solution to the convection-dispersion-equation. Only the increase of concentration by the amendment of tracer was considered.

RESULTS AND DISCUSSION

Sorption to all substrates was very small (< 2%) and equilibration was achieved within < 2 hours. Based on maximum sorption losses of 2 % Kd values for the soil material < 0.1 cm^3/g were estimated (Koc < 1.1. cm^3/g, log Koc < 1.41) and for compost material < 0.23 cm^3/g (Koc < 11.2 cm^3/g, log Koc < 1.05). Low sorption of acesulfame to soil and compost material fits the hydrophilic properties of acesulfame (Ziesenitz and Siebert, 1988), its low sorption to activated carbon (Scheurer et al., 2010) and the marginal retardation on a unsaturated column fed discontinuously with wastewater (Buerge et al., 2011). In the fixed-bed reactors, DOC concentration, SAC and development of gas bubbles in the filter bed indicated biological activity and biodegradation of DOC in the reactors. Acesulfame was stable under eutrophic conditions (compost and soil extracts) and was biodegraded under oligotrophic conditions (WWTP effluent) within 28 days. Acesulfame was added again to the reactor with WWTP effluent and a rapid degradation within 7 days was observed. Stability of acesulfame observed in the fixed-bed reactors with compost and soil extracts is in accordance with results by (Scheurer et al., 2010) with surface water from the Rhine river as a matrix running 90 days (after this long period, oligotrophic conditions can be assumed in the fixed-bed reactor). Moreover, long-term storage experiments of acesulfame in tap and surface water at environmental concentrations (results not shown) did not result in concentration losses. Therefore, oligotrophic conditions seem not to be the only trigger for the biodegradation of acesulfame.

Laboratory column experiments to investigate reactive transport of acesulfame with a short pulse injection of acesulfame and NaCl to the inflow (C2-OX and C3-AN) yielded similar mean residence times for acesulfame (1 to 1.9 h) and NaCl, with earlier breakthrough of acesulfame and a long tailing of NaCl. The recovery of the added acesulfame was 83 % under anoxic conditions (C3-AN) and 95 % under oxic condition (C2-OX). During three different situations representing winter and summer season and low and high river discharge, acesulfame behaved conservative in all column experiments (C1-OX, C2-OX, C3-AN) with different background concentrations. Experiments with a continuous amendment of acesulfame and NaCl to the inflow and longer residence times yielded again similar breakthrough for both parameters (C2-OX: 29 h for acesulfame and 27 h for NaCl, C3-AN: 28 h for both parameters). The recovery of acesulfame was determined for both columns at approximately 93 %, whereas the recovery of the electrical conductivity was 98 % in C3-AN and almost 100 % in C2-OX. Recovery of added acesulfame during pulse–type column experiments and permanent amendment exceeded 83 %. This means low sorption and confirms results from batch experiments. Long-term observations at different acesulfame concentration levels yielded similar concentrations in column inflow and outflow and thus no biodegradation, even after a long period of adaptation. The experimental break through curves can be modeled by the variation of dispersion parameters without biodegradation.

CONCLUSIONS

Negligible sorption of acesulfame observed even at high organic carbon content (compost) and stability in column studies are consistent with observations at oxic bank filtration sites (Scheurer et al., 2010) and imply conservative behavior of acesulfame. However, in a further fixed-bed reactor experiment with the diluted

effluent of a waste water treatment plant and a prompt and rapid degradation was observed. Results were confirmed by subsequent amendment of acesulfame to the fixed-bed reactor resulting in a prompt and rapid degradation without a new phase of adaptation. The latter is surprising and puts reasonable doubt on the assumption that acesulfame behaves in general conservative in the environment. Batch experiments yielded low sorption for several soils and Kd of acesulfame was estimated to be < 0.1 cm^3/g. However, all flow-through column experiments indicated conservative behavior of acesulfame: Recovery of added acesulfame during pulse–type column experiments and permanent amendment exceeded 83 %. This means low sorption and confirms results from batch experiments. Long-term observations at different acesulfame concentration levels yielded similar concentrations in column inflow and outflow and thus no biodegradation, even after a long period of adaptation. Laboratory experiments demonstrated conservative behavior of acesulfame under conditions typical for riverbank filtration and groundwater. However, there are hints that there seem to be certain settings which favor an adaptation of the microbial community and facilitate a rapid biodegradation of acesulfame.

ACKNOWLEDGEMENT

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ANALYSING DISPERSIVE MIXING NEAR LOSING STREAM REACHES USING ANTROPOGENIC TRACERS

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Keywords: Anthropogenic gadolinium, trace substances, dispersion, losing stream

INTRODUCTION

Bank filtration is a technique to increase natural groundwater resources and can positively alter the quality of infiltrated surface water. In this context it is important to gain insights into the impact of hydromechanical dispersion as a key parameter for the description of groundwater flow and transport processes.

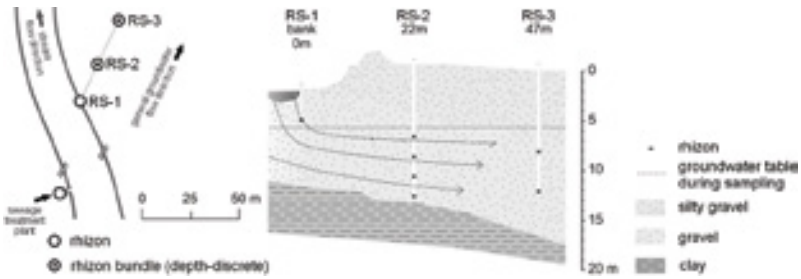

Figure 1: Schematic plain view (left) and hydrogeological cross-section (right) of the test site with conceptualised depictions of the rhizon samplers (simple and as depth-discrete bundles), of the groundwater table as well as of streamlines

The investigated site is located in a subalpine catchment area and the river permanently infiltrates into an unconfined porous aquifer. The test site is characterized by a relatively high hydraulic conductivity (≈1.5-5.5 10^{-2} m s^{-1}) of the aquifer and short distances between stream and rhizon samplers (<1-47 m). Due to the high hydraulic conductivity range, mechanical dispersion is, therefore, considered to play an exceedingly dominating part in the impact of hydrodynamic dispersion with diffusion being insignificant.

As shown from 12-hours composite water samples, the discharge of treated sewage from a sewage treatment plant (STP) upstream of the sampling site leads to weekly-periodic transient concentrations of anthropogenic gadolinium (Gd_{anth}) in the stream.

This weekly-periodic transient signal originates from the application of gadolinium-based contrasting agents in ambulatory magnetic resonance imaging. They are being excreted in non-metabolised state in the catchment after a few hours (Bellin et al., 2008) if the patient enters within that timeframe – even if only being applied outside the catchment's borders. The conservative behaviour and source-specificity of Gd_{anth} enabled qualitative evaluation of the impact of hydromechanical dispersion in the aquifer, because the transient time series were found with diminished amplitude in the close vicinity (<50 m) of the stream along a transect in depth-discrete sampling points (see Figure 2). The transect was oriented parallel to the general groundwater flow direction.

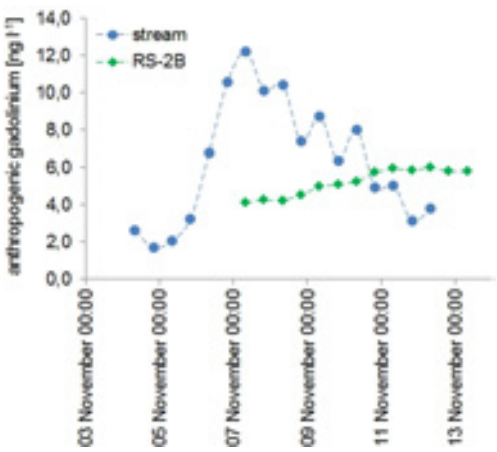

Figure 2: Anthropogenic gadolinium concentration time series in the stream and at a selected sampling point (RS-2B) representing decreasing temporal concentration variation

METHODS

Sampling

By direct push drilling customised rhizon samplers (Rhizon flex, Rhizosphere Research Products, Netherlands) with a filter length of 15 cm and a mean pore diameter of 0.15 µm were installed in the aquifer in various depths. Samples were taken from the rhizons by connecting a vacuumed glass bottle to its end. For both surface water as well as groundwater samples the integrating temporal interval of the composites was chosen as 12 hours. Samples were taken over a ten day period during a quasistationary discharge regime.

Sample analysis

For the analysis of the concentrations of rare earth elements (REE) the samples were pretreated with H_2O_2 and UV-C radiation, further preconcentrated using a SeaFAST 2 (Elemental Scientific, USA) before being analysed with a triple-quadrupole mass spectrometer (8800 ICP-QQQ, Agilent Technologies, USA; LOQ 0.1 ng l^{-1}, SD 0.04 ng l^{-1}). Concentrations of Gd_{anth} could subsequently be derived by interpolation of the geogenic background using the concentrations of samarium and terbium (Bau et al., 1996).

RESULTS AND DISCUSSION

The results generally indicate a rapid diminishment of the temporal variation of Gd_{anth}'s weekly-periodic transient concentrations even along comparatively short flow paths. Its impact is reflected in the ratio between the respective sampling point's and the stream's maximum Gdanth concentration ($R_{sample/stream}$) during the 10 days of sampling. This ratio shows a decreasing trend with increasing distance from the stream and increasing sampling depth.

With the exception of sampling point RS-1A directly beneath the stream and RS-2A, the topmost sampling point further downgradient, $R_{sample/stream}$ was generally below but close to 50%. At sampling point RS-1A and RS-2A it was relatively high at 87% and 70%, respectively. In rhizon RS-2 $R_{sample/stream}$ was, thereafter, rather steadily decreasing with depth from 49% at RS-2B, 46% at RS-2C and 43% at RS-2C. A similar decreasing trend and similar ranges of $R_{sample/stream}$ was observed even further downgradient (47 m distance to the stream) with 47% at RS-3A and 45% at RS-3B.

Assuming the spatial extent of recharge from the losing stream reach to be small in comparison to the length of the flow path and mixing only to take place between water parcels, which infiltrated in the same recharge area, this decrease can be attributed to hydromechanical dispersion. Thus, the reduction in the concentrations temporal variation with increasing distance to the stream and sampling depth depicts the comparatively strong heterogeneity of – most importantly the hydraulic conductivity field of – the glacial sediments in the test site resulting in dispersion. Aside from that, the decrease in temporal variation to merely slightly transient concentrations sampled 22 m and 47 m away from the stream are indicative of the spatial limit of applicability due to their propagation limit.

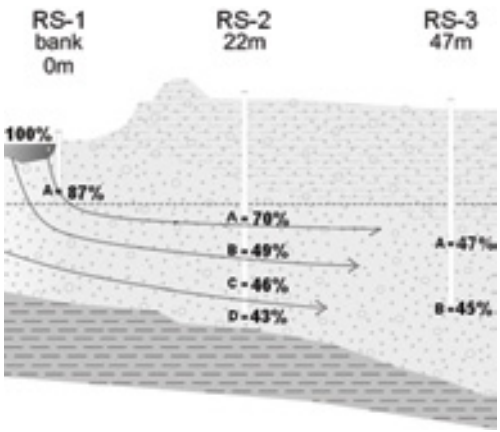

Figure 3: Ratio between stream and respective sampling point maximum Gd_{anth} concentration

CONCLUSIONS

Gd_{anth} concentration time series in losing streams reaches and the adjacent aquifer can be resorted to for a qualitative evaluation of the impact of hydromechanical dispersion in such a setting – especially due to Gd_{anth}'s weekly transient temporal appearance. Compared to conventional groundwater sampling the spatial resolution of hydrochemical gradients is enhanced by rhizon sampling and enables a more depth-discrete and, therefore, more precise observation of transport. Due to the extremely low limit of quantitation, the applicability of the source-specific tracer anthropogenic gadolinium is extended to sites with surface waters impacted by very low sewage loads.

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ANTHROPOGENIC GADOLINIUM: A MULTI-PURPOSE TRACER

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Keywords: gadolinium, anthropogenic tracer, river bank filtration, multi-purpose tracer

INTRODUCTION

Since the first approval (in 1988) of gadolinium (Gd) complexes as contrast agents in magnetic resonance imaging (MRI), their increasing use has resulted in rising levels of Gd input into aquatic environments (Bau and Dulski, 1996; Reiser and Semmler, 2013). These Gd complexes are very stable and pass unmetabolized through human kidneys (Bellin and Van Der Molen, 2008). Depending on which complex is administered and the kidney function of the individual patient, the biological half-life in the body after injection is between 1.5 and 30 hours (Idée et al., 2008 and references therein). Passing through sewage systems and conventional sewage treatment with almost no degradation, these complexes are released into surface waters resulting in an anthropogenic Gd (Gdanth) anomaly, which make Gdanth a capable tracer for surface water – groundwater interactions (Kümmerer and Helmers, 2000). The objective of this study is to assess the suitability of using Gdanth for investigating bank filtration processes with different spatial and temporal resolution.

EXPERIMENTAL

Study site

The site investigated lies within a subalpine headwater catchment in Western Europe covering approximately 4.3 km². The investigation area and the lower parts of the catchment are mainly used for agriculture, predominantly as pasture land for livestock farming, while the headwater area is covered by forest. There are scattered settlements consisting predominantly of isolated farms and small villages.

There are two rivers (R1 and R2) within the investigation area. The river beds are partly colmated; discharge measurements showed that the river R1 is infiltrating into the aquifer but infiltration from the R2 river is negligible. The average discharge rate for the river R1 is 8.7 $m^3 s^{-1}$ and is influenced by an upstream effluent of a sewage treatment plant (STP) with a discharge rate of 0.2 $m^3 s^{-1}$.

The aquifer consists of Pleistocene sediments comprising mainly coarse carbonate gravels, which cover the underlying molasse basin to a thickness of up to 60 m. The channel-like form of the aquifer is a result of glacial erosion of the molasse basin; the two rivers have incised into quaternary gravel deposits and created the present-day topography. The main groundwater body (Aquifer 1) is joined by a second groundwater body (Aquifer 2) in the north (Figure 1).

During a one week sampling campaign, samples from all groundwater observation wells (GW) were taken. Additionally, a time series of samples from R1 and extraction wells (W1 and W2) were taken. The infiltration area around GW1 was further investigated during a second sampling campaign over a 10-day period. To account for temporal variations of Gd_{anth} concentrations a continuous 12-hours composite sampling was conducted. All samples were taken in acid-washed PP vials, filtered through 0.22 µm or 0.15 µm, respectively, and acidified with HNO_3.

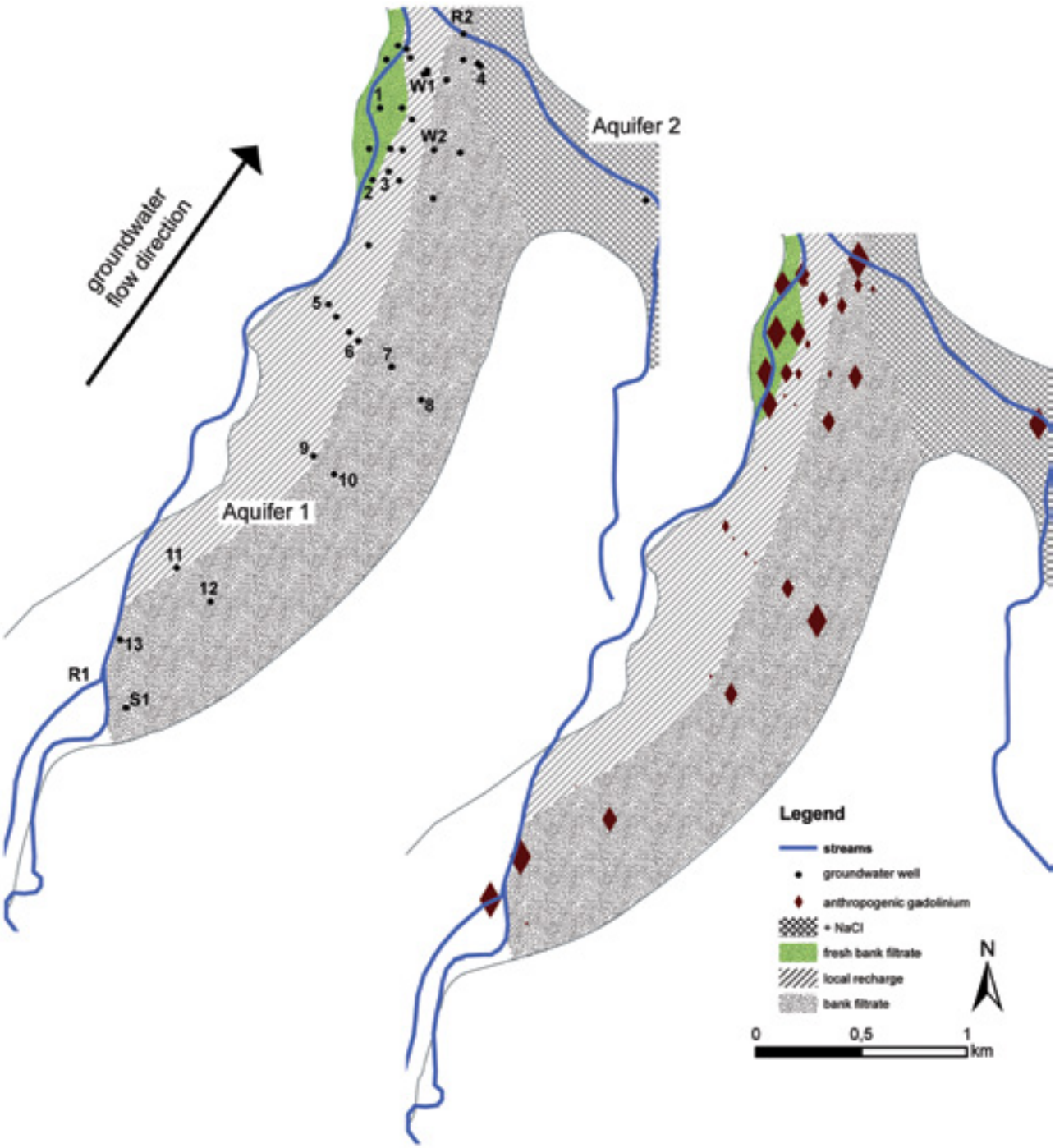

Figure 1: Scheme of the investigated study site after Bichler et al., 2015. Size of the dark red diamonds related to the concentrations of Gd_{anth}. High Gd_{anth} concentrations indicate a high proportion of bank filtrate.

Lab analysis

Rare earth element (REE) analysis was conducted using an on-line pre-concentration system (SeaFAST 2, Elemental Scientific Inc., USA) in combination with an Agilent 8800 Triple Quad-ICP-MS (ICP-QQQ, Agilent Technologies, Japan; LOQ 0.1 ng L^{-1}, SD 0.04 ng L^{-1}). The SeaFAST system uses a resin with ethylenediaminetriacetic acid and iminodiacetic acid functional groups to specifically pre-concentrate REEs as they are exclusively trivalent cations, while major cations and anions are washed out (Hathorne et al., 2012). Since measurements with this column-based pre-concentration step require degradation of the anthropogenic gadolinium complexes, H_2O_2 (31%, ROTIPURAN Ultra, Carl Roth, Germany) was added to the samples (5% v/v) and they were then exposed to UV-C light (254 nm, 4x15 W m^{-2}, Narva, Germany) for 24 hours. For this pre-treatment the samples were transferred into acid-prewashed polymethylpentene (TPX) centrifuge tubes as they are UV-C light-transmissive, and the tubes were sealed with acid-prewashed HDPE stoppers.

The background concentrations of geogenic gadolinium (Gdgeo) needed to be estimated in order to be able to calculate the Gdanth concentrations of the measured gadolinium concentrations. The concentration of Gdgeo was therefore interpolated using the samarium (Sm) and terbium (Tb) REEs, normalised to the upper continental crust (UCC) (Taylor and McLennan, 1985), as described by Bau and Dulski (1996):

$$\mathrm{Gd_{geo}} = \left(0.33\,\frac{\mathrm{Sm_{measured}}}{\mathrm{Sm_{UCC}}} + 0.67\,\frac{\mathrm{Tb_{measured}}}{\mathrm{Tb_{UCC}}}\right)\mathrm{Gd_{UCC}} \quad (1)$$

$$\mathrm{Gd_{anth}} = \mathrm{Gd_{measured}} - \mathrm{Gd_{geo}} \quad (2)$$

RESULTS AND DISCUSSION

The spatial distribution of Gdanth in groundwater reveals that Aquifer 1 has two groundwater zones with high influence and one zone in between with less influence of bank filtrate. This zone based likely on local recharge, while in both other zones major parts of bank filtrate occur. Gdanth shows strong horizontal gradients over short distances (e.g. GW6 to GW7, GW9 to GW10 and GW11 to GW12) indicating low transverse mixing between both groundwater zones.

The Gd_{anth} concentration in the river is a direct function of the discharge (dilution of the STP effluent). Samples from the time series show less temporal variation of Gd_{anth} concentrations at W2 (RSD: 20%) compared to R1 (RSD: 63%) suggesting both dispersive mixing processes and almost constant flow paths within Aquifer 1. End member mixing analysis indicates a proportion of bank filtrate of at least 63% for the infiltration zone around GW1 and a proportion of 43% in the eastern part of Aquifer 1 (Bichler et al., 2015). However these results may realistic, the errors of these estimations exceed them due to the temporal variability of the R1 end member.

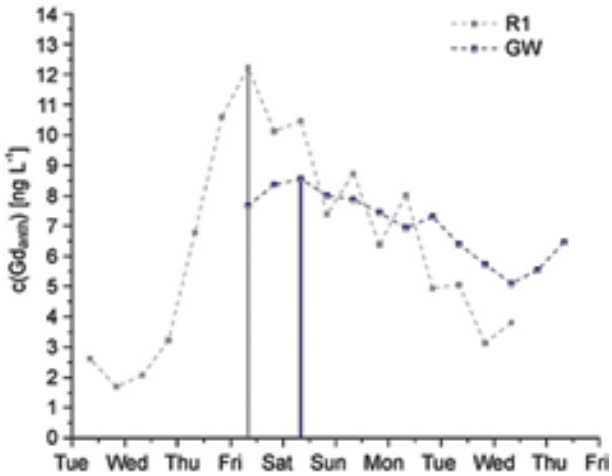

Figure 2: Temporal variability of Gd_{anth} in stream water (SW) and groundwater (GW, location close to GW1) directly affected by the stream. Vertical lines point out the Gd peak shift.

A weekly signal of Gd_{anth} concentrations, a result from the predominant use of MRI diagnostics between Monday and Friday, can be observed in both 10 day time series of river water (R1) and groundwater close to the river. In comparison with the river, the time series of the groundwater shows a Gd peak shift and a dampening effect (Figure 2). The lower amplitude of the signal in groundwater indicates that even with a transient signal in the river end member, mixing analysis might gain reliable results with the estimation of a mean or median value (Bichler et al., 2015). The peak shift reveals a mean travel time of 1 day and demonstrates that the transient signal is propagated from river water into groundwater with short travel times.

CONCLUSIONS

The source-specificity in combination with low detection limits of Gd_{anth} concentrations allows for investigating the spatial distribution of river bank filtration as well as the quantification of bank filtrate in groundwater. Both are essential to estimate the potential of infiltrating surface water to compromise raw water sources (Hoehn and Scholtis, 2011). The temporal variability of Gd_{anth} concentrations within the stream contribute to the high uncertainties in end member mixing analysis. The long-term median, however, does allow for reliable results (Bichler et al., 2015). Investigating the temporal variations of Gd_{anth} concentrations both in surface water and riverine groundwater gained qualitative and quantitative information on dispersion, mean travel time, and mixing. It reveals that Gd_{anth} is a multi-purpose tracer for investigating river bank filtration on small and larger scales.

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In order to comply with the legal requirements only generic names have been used throughout this publication and all data has been anonymized.

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MANAGED AQUIFER RECHARGE (MAR) FOR THE MANAGEMENT OF STORMWATER ON THE CAPE FLATS, CAPE TOWN

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Keywords: WSUD, Managed Aquifer Recharge, Stormwater Management, Cape Flats Aquifer, MIKE SHE.

INTRODUCTION

The city of Cape Town in South Africa, has shown consistent economic and population growth in the last few decades and that growth is expected to continue to increase into the future. These projected economic and population growth rates are set to place additional pressure on the city's already strained water supply system (DWAF, 2009; CoCT, 2013). Thus, given Cape Town's water scarcity, increasing water demands and stressed water supply system, coupled with global awareness around the issues of sustainable development, environmental protection and climate change, alternative water management strategies are required to ensure water is sustainably managed. Water Sensitive Urban Design (WSUD) is an approach to sustainable urban water management that attempts to assign a resource value to all forms of water in the urban context, viz. stormwater, wastewater, potable water and groundwater. WSUD employs a wide range of strategies to improve the sustainable management of urban water such as the water reuse, developing alternative available supply sources, sustainable stormwater management and enhancing the aesthetic and recreational value of urban water (Brown et al., 2008; Wong and Brown, 2008).

Managed Aquifer Recharge (MAR) is one WSUD strategy which has proven to be a successful reuse strategy in a number of places around the world. MAR is the process where an aquifer is intentionally or artificially recharged, which provides a valuable means of water storage while enhancing the aquifers supply potential (Dillon et al., 2009). This paper investigates the feasibility of implementing MAR in the sandy, unconfined Cape Flats Aquifer (CFA) in Cape Town. The main objectives of this study are to assess if MAR is a viable strategy for stormwater management in Cape Town by aiding the prevention or mitigation of the seasonal flooding that occurs on the Cape Flats and to improving the supply potential of the aquifer for fit-for-purpose or bulk water supply to the city of Cape Town. Two scenarios are tested in this study. First, a pumping scenario examines the concept of artificially drawing down the aquifer during the summer months to create additional storage for winter stormwater. The second examines the infiltration of stormwater or treated wastewater into the CFA during the wet winter months to increase the supply capacity of the CFA during summer months.

STUDY SITE

The Cape Flats is a coastal sand plain in Cape Town, South Africa. The Cape Flats extends over an area in excess of 400 km^2, situated between False Bay to the South, the Tygerberg Hills in the North, Table Mountain in the West and the hills Brackenfell in the east (DWAF, 2008). The topography of the Cape Flats is unique as the change in elevation over the Cape Flats itself is low, ranging from 0 m to 45 m above mean sea level, but the surrounding topography is marked by significant changes in elevation reaching a height of 1080 m above sea level at its highest point (DWAF, 2008). Due to the topography of Cape Flats and the surrounding mountains, the hydrology of the study site is unique, with the mountainous areas such as Table Mountain receiving significantly more rainfall (>1000 mm.a^{-1}) than the lower altitude Cape Flats (600 mm.a^{-1}) (Schulze et al., 2008). As a result, many of the rivers that flow over the Cape flats originate in these mountainous areas. Due to its flat topography, the Cape Flats have associated with wetland or seasonal wetland conditions. However, with the rise in urban development on the Cape Flats, many wetlands were removed with the result that most rivers on the Cape Flats are canalised to ensure the rapid removal of stormwater. This canalisation has effectively created artificial rivers, as most of the natural rivers that flow over the Cape Flats are non-perennial (Rebelo et al., 2011).

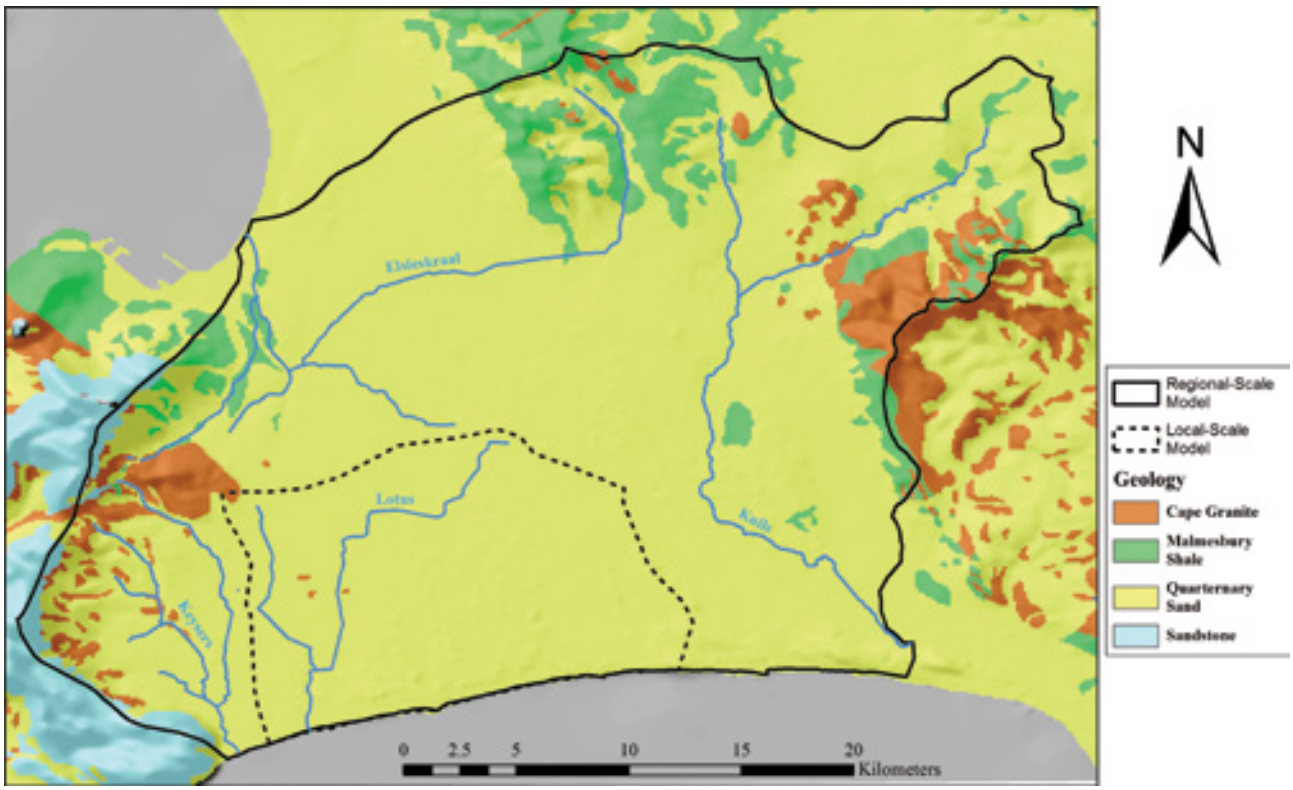

Figure 1: The geology and hydrology of the Cape Flats.

METHODOLOGY

The fully-integrated MIKE SHE model is used in this study to simulate both surface water and groundwater hydrology. Two MIKE SHE models were developed; a regional model with a resolution of 500 m and a local-scale model with a resolution of 60 m (Figure 1). The regional-scale model was setup and calibrated for a four year period from 1980 to 1984 using groundwater levels and streamflow data. The benefit of this regional-scale modelling using an integrated hydrological model is that both groundwater and surface water processes can be simulated. The regional-scale model provided insight into the regional groundwater and surface water flow processes and surface-groundwater interaction over the CFA.

In order to simulate MAR strategies in greater detail a finer model resolution is required, therefore a smaller local-scale model was developed for the central and Southern parts of the CFA. The site selection process for identifying areas suitable for testing MAR at a local-scale on the CFA required information from a number of sources, such as aquifer information from hydrogeological surveys and regional hydrogeological modelling results. Since this study seeks to test MAR as a flood mitigation strategy it is also important to consider where flooding is problematic on the Cape flats. The informal settlement of Sweet Home was selected as a site for testing MAR as is listed as one of the areas most impacted by winter flooding. The results from the regional MIKE SHE model provide the main basis for the selection of a local-scale site for testing MAR on the CFA – the most important of which are the maps of groundwater levels, groundwater head elevation and recharge. A significant limiting factor to MAR is finding locations where there is sufficient storage capacity within the aquifer for infiltrated or injected stormwater. Therefore, the local-scale model area incorporates both the Sweet Home settlement and the areas in the South of the CFA that may hold potential for artificial recharge. Furthermore, this local-scale model was then validated to data for the period from 2000 to 2015, showing the models performance was consistent over two different time periods and different input data.

RESULTS

It is important to identify the areas of the CFA that are most appropriate for MAR. The method demonstrated by Murray et al. (2007) the was used to calculate the MAR potential of the CFA (Figure 2). This method assumes that half the difference between the “top of the aquifer” and the mean groundwater level is available for additional groundwater storage. The mean groundwater levels were calculated using a 15 year MIKE SHE simulation of groundwater levels. The top of the aquifer was derived by simulating the groundwater levels using

an artificially high rainfall dataset. This dataset consisted of the doubling the daily rainfall for 2007, which was the wettest year between 2000 and 2015 and running the model with that data for 15 years. The results of this mapping indicate that the highest MAR potential exists in the Southern parts of the CFA, showing between 5000 m^3/ha per year to over 8000 m^3/ha per year.

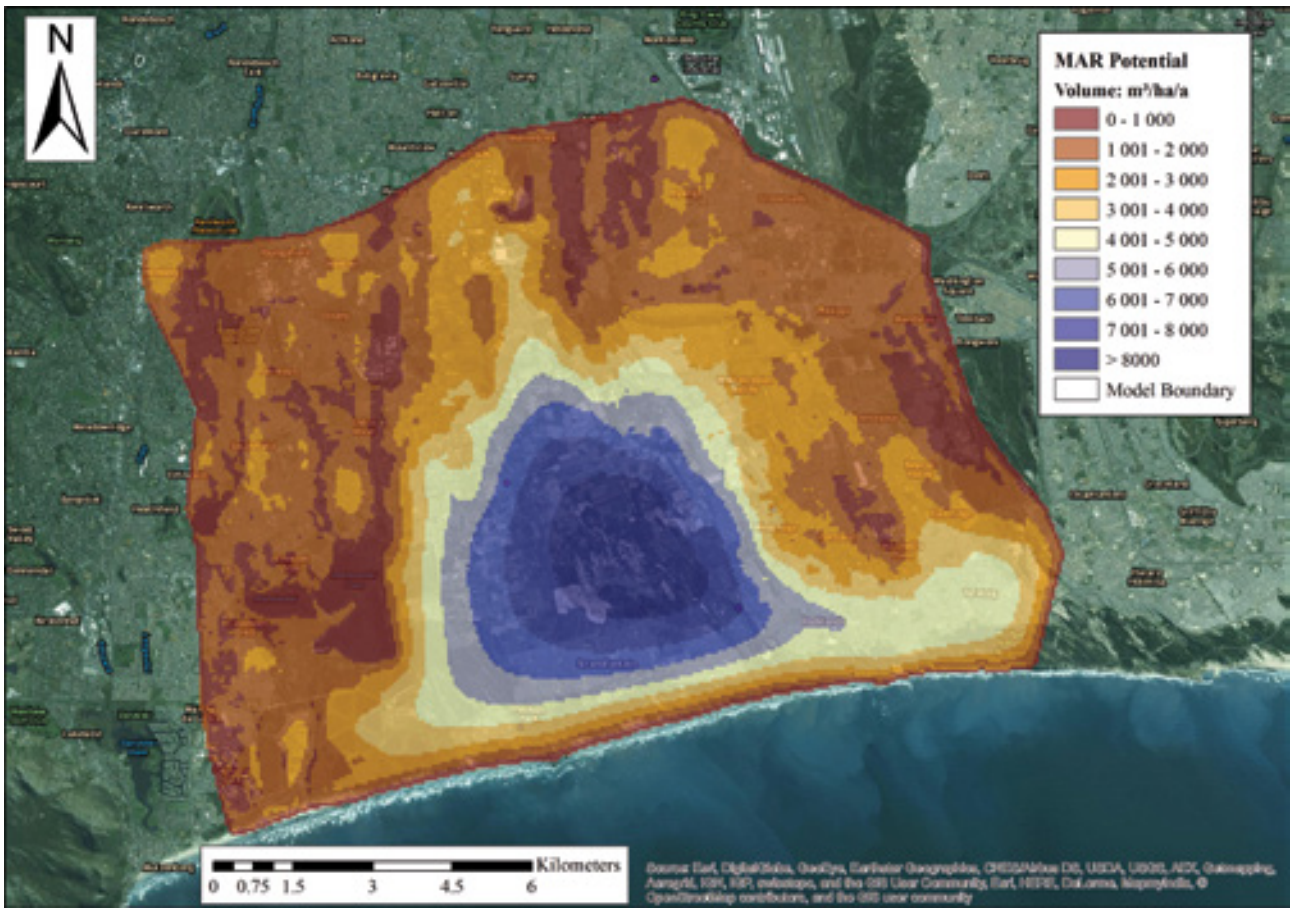

Figure 2: The MAR potential of the CFA

The pumping scenario examined three deferent wellfield arrangements (9, 18 and 27 boreholes) at two different pumping rates (3 ℓ/s and 5 ℓ/s). The pumping simulation was carried out in the vacinity of the informal settlement of Sweet Home as shown in red in Figure 3. Regular seasonal winter flooding occurs at Sweet Home, however the causes of flooding are not well understood. Many of informal settlements lack formal drainage systems and are often located in low-lying areas that are prone to flooding. Thus, flooding is often attributed to a number factors including elevated groundwater levels. Simulated groundwater levels for the Sweet Home area are seldom at or near the ground surface. The groundwater levels are typically between 1-2 meters below ground level. However, the areas adjacent to Sweet Home are seasonal wetlands and these areas show groundwater levels that are at or near ground level. This suggests that the flooding at Sweet Home might be largely due to poor drainage, however elevated groundwater levels in the vacinity may exacerbate the effects of flooding in Sweet Home. The results of the pumping scenarios indicate that substancial draw downs from the baseline groundwater level can be achieved that would yeild additional storage for winter stormwater (Figure 4). Pumping using 27 boreholes at 5 ℓ/s demonstrates a near maximum pumping rate as some of these boreholes occationally run dry when the aquifer is depleted. In some instances, by pumping at a higher rate the equivilent drawdown can be achieved using less boreholes (i.e. 9 boleholes at 5 ℓ/s ≈ 18 boreholes at 3 ℓ/s). For this study it was assumed that a minimum of a 1 meter of draw down was required to suitably mitigate flooding in an area prone to inundation due to high groundwater levels. As a result only the 18 boreholes at 5 ℓ/s and the 27 boreholes at 3 ℓ/s and 5 ℓ/s demonstrate this. However, the 18 boreholes at 3 ℓ/s and 9 boreholes at 5 ℓ/s do show some success, only exceeding the 1mblg mark in wet years such as 2006, 2007 and 2008.

The recharge scenario simulated the recharge of stormwater or treated wastewater into the southern section of the CFA where the MAR potential is the highest. The volume of infiltrated water was assumed to be equivalent to a similar MAR scheme located in Atlantis, which is 50 km north of the city of Cape Town. The Atlantis MAR scheme is proven system and has been in service for over 30 years (Murray et al., 2007). An infiltration basin of 180 000 m2, which as similar size to that used in Atlantis, was used to simulate the infiltration of

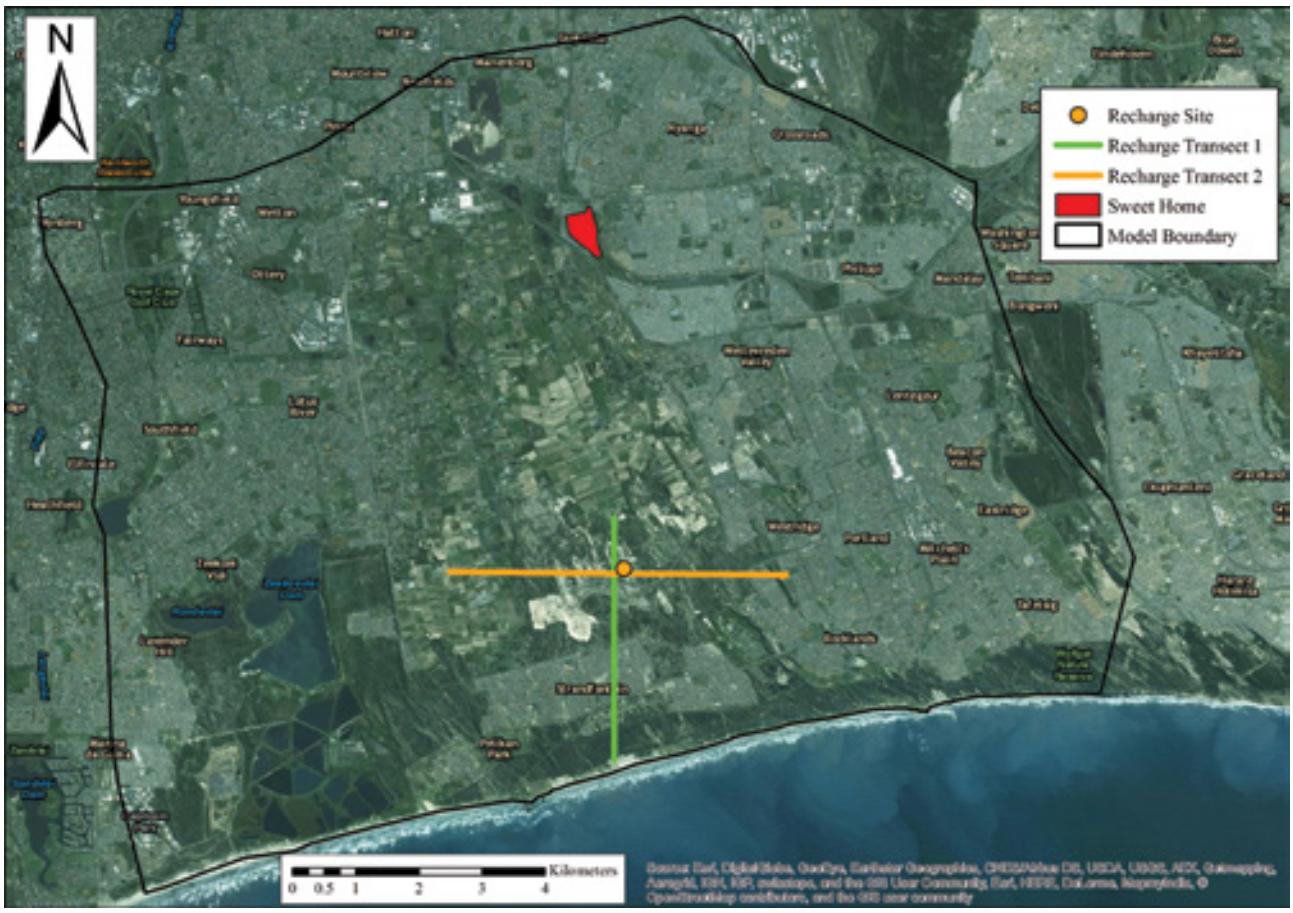

Figure 3: The location of Sweet Home and the recharge scenarios and transect profiles

7500 m³/day or 2 737 500 m³/year of stormwater or treated wastewater. Figures 7 and 8 show the change in mean head elevation over transect 1 and 2. The mounding of the recharged water is clearly visible and extends for 3500 m to 4000 m. At its maximum, the increase in head elevation is approximately 4 m which is within the relatively conservative range of 50 % of total aquifer storage recommended by Murray et al. (2007). Much of the recharge area has an available aquifer capacity of approximately 11 m in the central and southern sections of the CFA.

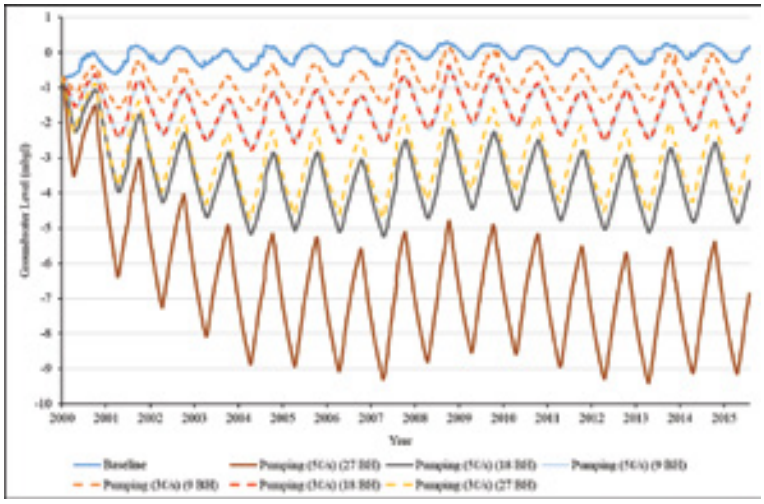

Figure 4: Groundwater levels for the three borehole scenarios at 3 ℓ/s and 5 ℓ/s, measure as meters below ground level (mbgl)

DISCUSSION AND CONCLUSIONS

The pumping scenarios show that pumping may be a viable option to reduce flooding on the Cape Flats. The results indicate that a wellfield of 18 boreholes pumping at 5ℓ/s or 27 boreholes pumping at 3ℓ/s and 5ℓ/s are able to provide sufficient drawdown to sustain groundwater levels at 1 m below the ground surface. The recharge scenario suggested that there was sufficient increases in the mean groundwater head elevation suggesting an increase in the storage of the aquifer. This increase in storage is within the limits set by Murray et al. (2007), however this estimate is relatively conservative and further investigation may yield greater storage potential. An integrated model such as MIKE SHE is a valuable tool for evaluating the feasibility of the MAR scenarios and gave insight in to the feasibility of the application of MAR as a stormwater management strategy and its potential to contribute towards improving Cape Town's water security into the future.

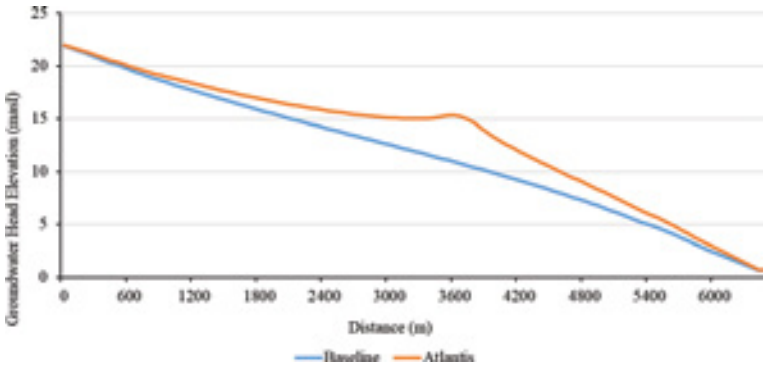

Figure 7: The change in mean head elevation for transect 1 which runs in a North-South direction.

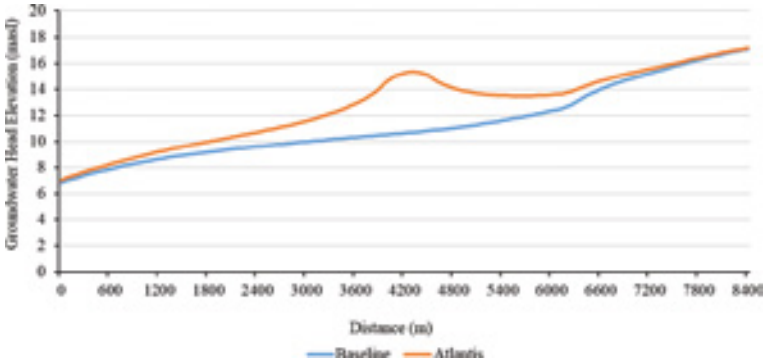

Figure 8: The change in mean head elevation for transect 2 which runs in a West-East direction.

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NOTES

KNOWLEDGE-BASED PLANNING OF GROUNDWATER TREATMENT TRAINS FOR AN EFFICIENT DRINKING WATER SUPPLY SYSTEM IN URBAN AREAS

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Abstract: A knowledge-based planning of the proper treatment trains was applied to the drinking water supply system of Milan city, involving the application of statistical tools and experimental tests. As first step, multivariate statistical techniques were applied to groundwater monitoring data in order to identify specific contaminations of the captured groundwater and their spatial distribution. Starting from 88 quality parameters, 16 significant factors were extracted by Factor Analysis, identifying different kinds of groundwater contamination in the studied area. Then, Cluster Analysis allowed to recognize 8 typical compositions of captured groundwater and their distribution in DWS units. According to these results, different treatment processes were chosen to be adopted in DWS units and their performances were experimentally evaluated on specifically selected water samples. Heterotrophic denitrification has been tested at pilot-scale to treat water affected by nitrate contamination: results allowed to obtain the optimal operating parameters, such as organic carbon supply and volumetric loads, in order to comply with regulation limits. Activated carbon adsorption was tested at lab-scale for the removal of various VOCs (volatile organic carbon) and pesticides in different water mixtures: variable removal efficiencies were obtained towards different contaminants, depending on their physical-chemical properties and the occurrence of competition phenomena (as in the case of perchloroethylene, PCE, and trichloroethylene, TCE, simultaneous adsorption). Air stripping was tested at pilot-scale and it was found to be a suitable solution for removing the most volatile organic compounds (i.e. PCE). According to observed results, an air stripping step before adsorption phase could be a valid solution to increase the lifetime of GAC beds.

Keywords: drinking water; multivariate statistics; activated carbon; VOCs; biological nitrate removal

INTRODUCTION

Drinking water supply (DWS) in industrialized and densely populated metropolitan areas is often assured through multiple DWS units that intercept various punctual and diffuse pollution plumes.

In such a complex context, planning the appropriate treatment trains could be a hard task. The first step is the knowledge of raw groundwater composition and its variability, which could be efficiently supported by data mining techniques (Selle et al., 2013; Olsen et al., 2012). In literature different statistical tools are reported for the analysis of water quality data; among these, data driven techniques such as Principal Components Analysis (PCA), Factor Analysis (FA) and Cluster Analysis (CA) are reported to be effective and unbiased methods to extract meaningful information from a dataset (Papaioannou et al., 2010). The use of multivariate statistics for water quality assessment is widely reported in literature (Olsen et al., 2012; Papaioannou et al., 2010; Page et al., 2012), however, their application as supporting tool for planning and management of DWS systems is not conventional.

The second important challenge of the planning of a DWS system is the selection of the appropriate treatment schemes, based on the knowledge of available technologies and their removal potential considering technical and non-technical factors (Hamouda et al., 2009). Since knowledge acquisition is often case specific, experimental and pilot studies are needed in order to obtain representative information about technical and economic efficiency of the alternatives (Joksimovic et al., 2006).

The present work considers the case study of the Milan city DWS system. The system provides about $230 \cdot 10^6$ m^3/y of drinking water, collecting groundwater from 3 aquifers by 522 wells spread in the city area and organized in clusters of about 20 wells, each one conveying water to a DWS unit. This study applies a knowledge-based concept to the planning of the proper treatment train to have in the DWS units. As first step, a multivariate statistical analysis is applied to available groundwater monitoring data to identify specific contaminations of the captured groundwater and their spatial distribution. As second step, an experimental testing of some treatment processes is performed at laboratory and pilot-scale to assess optimal operating conditions. Specifically, activated carbon adsorption, air stripping and heterotrophic biodenitrification were evaluated respectively to address the removal of organics (i.e. VOCs and pesticides) and of nitrate.

METHODS

Monitoring data of groundwater quality collected during 2007-2012 by the Milan city DWS service were analyzed through a data-driven statistical analysis approach constituted by a sequence of Factor and Cluster Analysis (Afifi and Clark, 1996). The analyzed dataset was constituted by 8,477 cases (corresponding to different capturing wells) and 88 parameters: 6 physical-chemical parameters, 7 ionic species, 18 metals and transition metals, 19 VOCs, 23 pesticides and 15 PAHs (polycyclic aromatic hydrocarbons). All the data analysis was performed through the IBM SPSS Statistics 21 statistical package.

As far as the experimental setup is concerned, a series of lab-scale batch experiments was performed to assess organics removal in groundwater samples by adsorption on activated carbon (AC). A commercial activated carbon (Cecacarbon GAC 1240) was tested through bottle-point isotherm measurements (ASTM D5919-96): different doses (from 1 to 35 mg L^{-1}) of AC were dosed in 1 L pyrex bottles and kept mixed on a magnetic stirrer at ambient temperature (20-25 °C) for 48 h before measuring the residual concentration of VOCs and pesticides in the liquid phase.

Air stripping was tested through a pilot-scale steel column (0.15 m diameter, 1.8 m height, 3.2 min HRT, 15.8 m^3 m^{-2} h^{-1} air flow rate), analyzing inlet and outlet concentrations of VOCs and pesticides.

Finally, heterotrophic denitrification was tested in a pilot-scale biofilter consisting of a PVC column (0.33 m inner diameter, 2.40 m height, 21 min EBCT, 0.38 porosity) filled with expanded clay media (Biolite®). After a start-up period of about 50 days, aimed at allowing biomass colonization, the biofilter was fed up-flow with groundwater extracted by a supply well at a flow rate of 0.6 m^3 h^{-1}. Average influent NO_3^- concentration during the experimentation was 8.9±0.65 mg N L^{-1}. Nutrients availability was assured by dosing CH_3COONa and KH_2PO_4 and the reactor was periodically backwashed in order to remove excess biomass. The process was evaluated by monitoring NO_3^-, NO_2^-, VSS (Volatile Suspended Solids) and TOC (Total Organic Carbon) in water at biofilter inlet and outlet for 10 weeks.

Regarding analytical methods, the concentrations of VOCs, pesticides, nitrite and nitrate ions and VSS were measured according to EPA 524.3-09, APAT-IRSA 5060/03, EPA 300.1 and APHA 2540 methods, respectively; TOC was measured photometrically by a kit method (LCK 380, Hach Lange).

RESULTS AND DISCUSSION

FA was applied to groundwater quality dataset in order to reduce the number of variables and to identify sets of parameters with the same pattern of variability. Starting from the 88 analyzed parameters, 16 relevant factors were extracted, explaining the 57.6% of data variance and identifying different kinds of contamination in the studied area. Among factors summarizing parameters usually present in natural groundwater, such as physical-chemical parameters or alkaline metals, 13 of the extracted factors could be attributed to pollution of anthropic origin, such as fertilizer's constituents (nitrate, sulphate and chloride), PAHs, pesticides, heavy metals (Sb, Cd, V, Se, As and Cr) and VOCs.

Hence, CA was performed to recognize typical compositions of captured groundwater and their distribution in DWS units: 98.8% of groundwater samples were grouped in 8 clusters, each having similar factor scores and, thus, similar contamination characteristics. CA results (reported in Figure 1) showed that the majority of cases belongs to cluster G (59.6% of total samples), grouping groundwater samples displaying average values for all the extracted factors, therefore identifying groundwater of average quality. Other 2 main clusters can be distinguished: cluster E (15.3% of total samples), grouping groundwater samples affected by nitrate and pesticides contamination, and cluster H (11.6% of total samples), grouping samples having high concentration of chromium, even higher of the Environmental Quality Standard of 50 µg L^{-1}. The remaining clusters (A, B, C, D and F) identified groundwater affected by local contaminations, mainly due to the presence of groups of 2-3 pesticides and/or VOCs at relevant concentration.

Therefore FA and CA results provided useful indications for identifying the most proper technologies to be adopted locally for treating groundwater in the studied DWS system.

Concerning nitrate, pesticides and VOCs different types of treatments were experimentally tested: 1) heterotrophic denitrification, for nitrate removal, 2) activated carbon adsorption, for both pesticides and VOCs removal, and 3) air stripping for the removal of the most volatile VOCs.

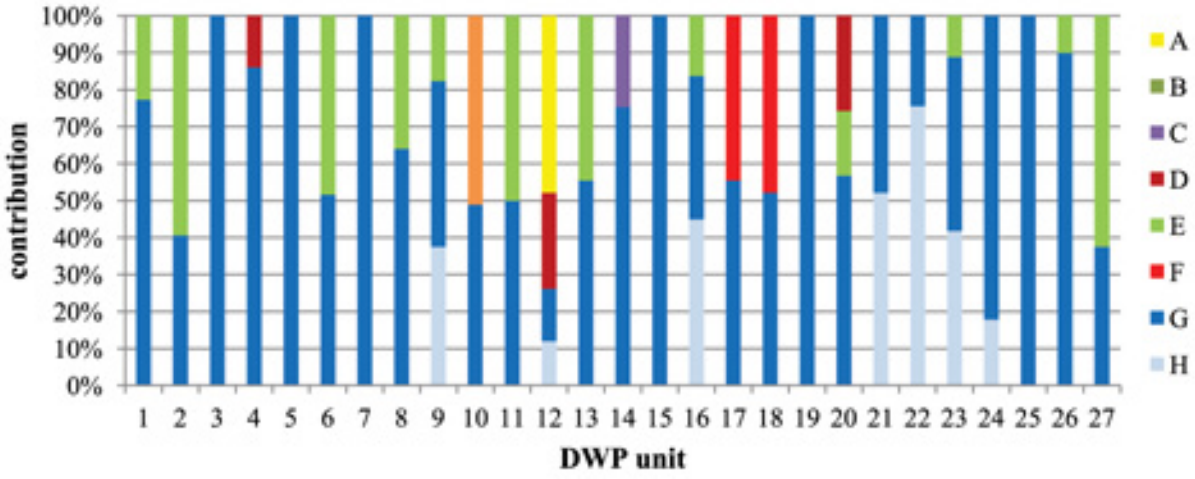

Figure 1: Distribution of the 8 clusters in DWS units (contributions <10% are not reported).

Nitrate removal. Groundwater belonging to cluster E showed a nitrate concentration above the Italian quality standard for drinking waters (i.e. 50 mg L^{-1}). The suitability of a heterotrophic denitrification treatment was then experimentally assessed using a pilot-scale biofilter, evaluating the main aspects of the process: 1) nitrate removal efficiency, 2) residual nitrite concentration in the effluent, and 3) risk for bacterial regrowth in the distribution network triggered by the release of biomass and the availability of readily biodegradable organic carbon. All these aspects were evaluated with respect to the main process parameters, namely organic carbon availability and nitrogen volumetric load.

Figure 2 shows NO_3^- and NO_2^- concentration profiles along the biofilter, observed during the pilot scale testing for different carbon dosage conditions, expressed as volumetric load (BV, in kg N m^3 d^{-1}). Results showed that high nitrate removal efficiencies (i.e. >86%) and complete denitrification could be achieved by supplying carbon source over 90% of the stoichiometric request (estimated according to Henze et al., 2008), corresponding to 21±1.5 mg C L^{-1}. On the other hand, C limiting conditions (corresponding to a C dosage <90% of the stoichiometric request) resulted in unsatisfactory nitrogen removal efficiencies of the order of 46%±32% (mean±standard deviation) and nitrite concentrations in the effluent of 1.4±2.20 mg N L^{-1}.

In order to assess the risk of bacterial regrowth in distribution networks, the release of organic carbon and biomass during pilot tests was also evaluated: residual TOC and VSS in the effluent were equal to respectively 4.6±1.5 mg C L^{-1} and 3.2±1.57 mg VSS L^{-1}. No significant differences (p-value>0.05) among the tested carbon dosage conditions were found in TOC and VSS effluent concentrations.

The effect of the volumetric load on denitrification process was evaluated considering the process efficiency along the biofilter height. Under C limiting conditions, none of the tested BV provided nitrate removal efficiencies higher than 60%, resulting in the highest nitrite concentrations in the effluent (up to 6.2 mg N L^{-1}). In carbon oversupply conditions, removal efficiencies were strongly affected by the treatment cycle duration (t_{TR}), which was modified by varying the biofilter backwashing frequency: for t_{TR} of 24 and 72 h and volumetric loads between 0.64 and 1.07 kg N m 3 d 1, a complete nitrate removal and nitrite concentrations below the regulation limit (0.5 mg L^{-1}) were obtained; on the other hand, at t_{TR} of 48 h, nitrate removal efficiency >90% were obtained only for BV up to 0.80 kg N m^{-3} d^{-1}. Moreover, nitrite concentrations in the effluent below the regulation limit were observed at t_{TR} of 48 h only when BV was set to 0.64 kg N m^{-3} d^{-1}. This behavior may be probably attributed to transitory or less stable conditions achieved at the intermediate tTR of 48 h; however, available data are not robust enough to draw conclusions and further investigations are needed.

Finally, no significant removal was observed for the 3 VOCs (PCE, TCE, vinyl chloride) and 9 pesticides (2,6-dichlorbenzamide, 3,6-dichloropiridazine, atrazine, atrazine desethyl, atrazine desisopropyl, bromacile, hexazinone, terbuthylazine desethyl, tris-2(chloroethyl)-phosphate) which were initially present in the inlet water. Therefore, additional treatments, such as activated carbon adsorption or air stripping, should be designed for groundwater requiring the removal of these organics.

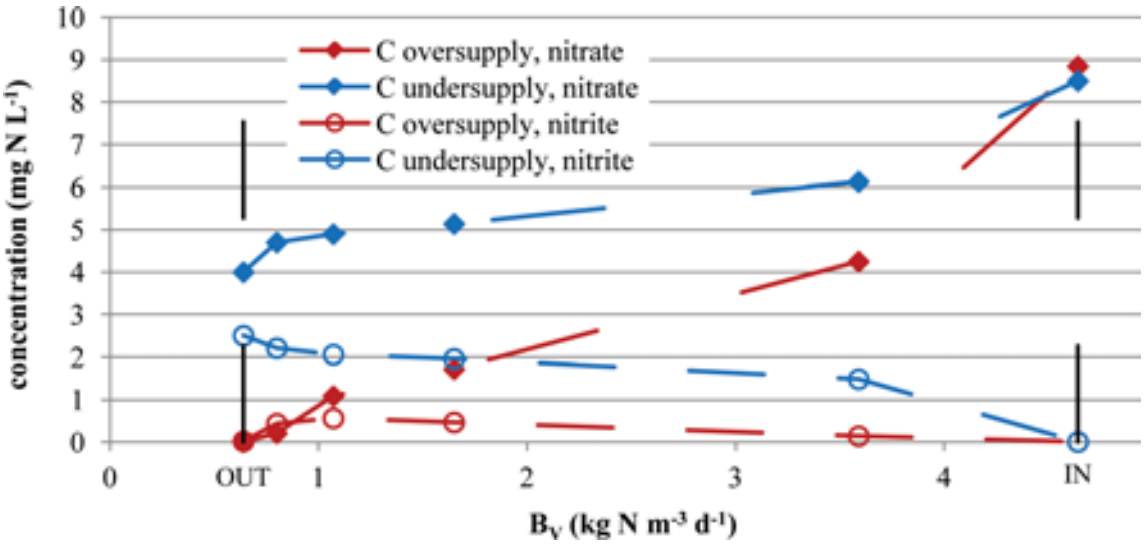

Figure 2: Average nitrate and nitrite concentrations observed along the biofilter for tested operating conditions.

Activated carbon adsorption. Since the presence of VOCs and pesticides affected most of the captured groundwater, adsorption equilibrium batch tests were carried out selecting groundwater samples from 2 DWS units (DWS8 and DWS11), representative of diffuse and average contamination (clusters G and E, respectively) and one DWS unit (DWS14) representative of an organic micropollutants hotspot (tris(2 chloroethyl)phosphate, PCE, and 2,6 dichlorobenzamide of the order of 0.4, 242.4 and 0.7 μg L^{-1}, respectively - cluster C). Figure 3 shows the maximum removal efficiency observed during batch experiments (obtained at the highest AC dose) for various pollutants: it can be noticed that pesticides, present at initial concentrations <0.7 μg L^{-1}, were satisfactorily removed in all the groundwater samples, with removal efficiencies higher than 80%. On the other hand, VOCs showed different affinity towards activated carbon: the highest removal efficiencies were observed for PCE and TCE (>93% and >72%, respectively), while the other VOCs showed a lower affinity towards activated carbon, depending on their physical-chemical properties (such as solubility, molecular weight and structure, vapor pressure). It must be pointed out that the majority of the VOCs, except PCE, TCE and chloroform, were present in raw water at low concentrations, never being >1.0 μg L^{-1}; for most of these contaminants, removal efficiencies could be limited by the low initial concentration. The same was not verified concerning chloroform, being present at relatively high concentration (12.9, 15.6 and 29.2 μg L^{-1} in samples from DWS8, DWS11 and DWS14, respectively) but removed with low efficiencies (η<0.4). The low affinity of AC for chloroform should be carefully considered in designing a full-scale GAC system, in particular when final disinfection is obtained by means of chlorine-based products, since trihalomethanes would be formed. In fact, the concentration of trihalomethanes can be easily increased, considering the initial concentrations of chloroform in captured groundwater and its possible transformation during disinfection phase.

Isotherms were then computed from experimental data on PCE and TCE. Isotherms have an important role in the study of adsorption processes, allowing to evaluate the affinity between a solute and an adsorbent and to preliminary design full scale operations (Foo and Hameed, 2010). Residual liquid concentration (C_e, expressed in μg L^{-1}) vs. solid phase concentration (q_e, expressed in μg mg^{-1}) data obtained for PCE and TCE in the different water samples are reported in Figure 4: it should be pointed out that no significant differences were observed in PCE removal in water samples coming from the three DWS units, despite the different initial concentrations (29.1, 16.2 and 242.4 μg L^{-1} respectively in DWS8, DWS11 and DWS14). On the contrary, TCE concentrations at the DWS14 unit are significantly different from those obtained for the other two DWS units: despite the comparable initial concentrations in all groundwater samples (2.5-4.3 μg L^{-1}), TCE removal efficiency was significantly lower in samples from DWS14, in which the PCE initial concentration was higher than in samples from DWS8 and DWS11. This behavior suggests that adsorption of compounds as TCE, having lower affinity towards activated carbon, may be affected by the presence of competitors for adsorption sites in water matrix, being in this case PCE.

These results suggested that adsorption onto activated carbon is a suitable process for the removal of organic micropollutants. Nonetheless, when poorly adsorbable organics are present, an upgrade of the process is required, in order to increase the bed lifetime, for example, adopting higher EBCTs or a two-stage in-series configuration.

Air stripping. In some cases, especially for DWS units treating groundwater with high levels of VOCs (such as clusters C, D and F), air stripping could be a suitable solution both as stand-alone treatment or as a pre-treatment before adsorption onto activated carbon. Stripping efficiency was evaluated using a pilot-scale aeration column, fed on groundwater containing various VOCs, mainly PCE and TCE at average initial concentrations of 16.2 and 2.4 μg L^{-1}, respectively. Significant removal was observed for PCE and TCE, on average 36%±11% and 18%±13%, respectively. PCE removal was higher than TCE removal, since a lower air-water ratio is required as expected by their Henry's constant values. Moreover, results for TCE showed a significant correlation between removal efficiency and initial concentration (ρ=0.713, p value=0.001, N=10), while the same behavior was not observed for PCE. Results suggested that the adoption of an air-stripping step before GAC could be a valid solution, especially in presence of PCE at high concentrations: as a matter of fact, the preliminary removal of PCE could reduce competition for adsorption sites, increasing the adsorption of the other organic micropollutants and reducing the frequency of GAC regeneration. However, the choice and the proper design of such a layout must be also based on economic evaluations, considering the costs related to both the treatment phases, depending on the specific water composition.

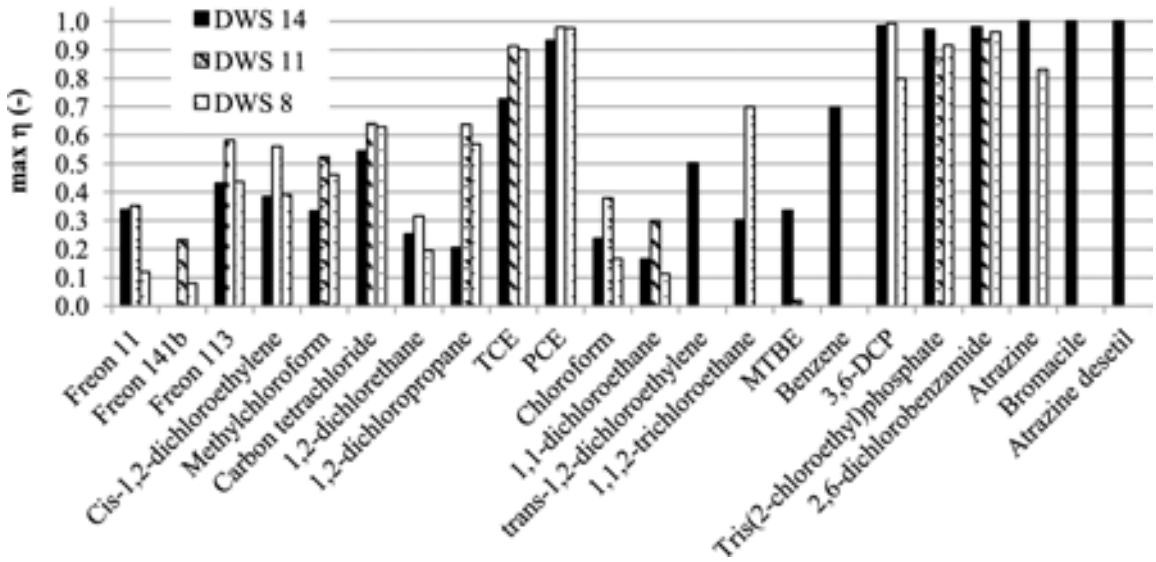

Figure 3: Maximum removal efficiency (η) for various VOCs and pesticides observed during adsorption batch experiments in three DWS units (DWS14, DWS11 and DWS8 belonging to clusters G, E and A respectively).

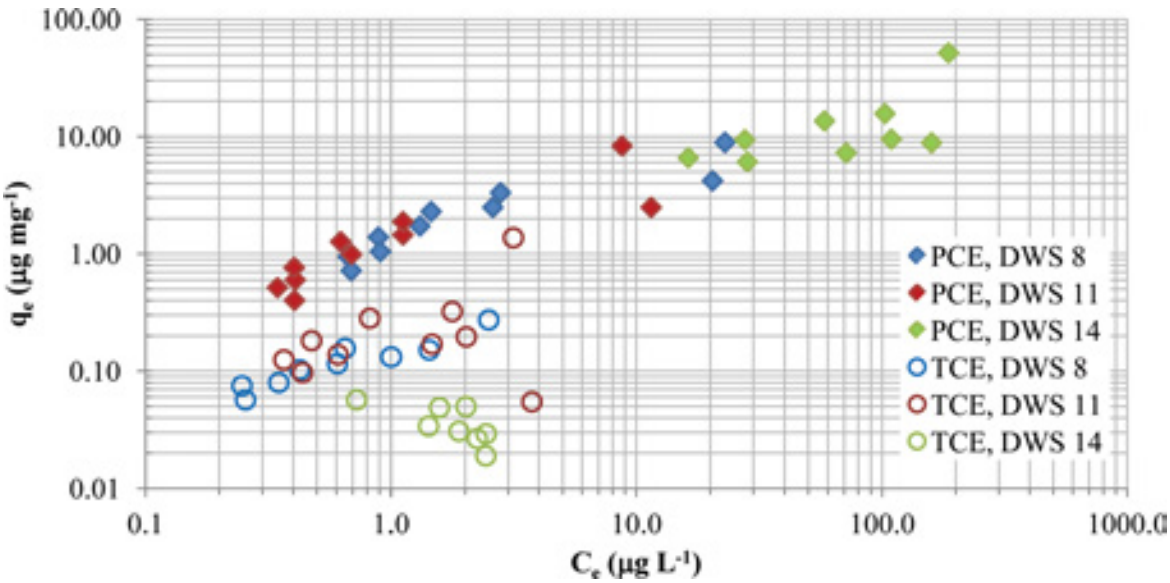

Figure 4: Equilibrium solid phase (q_e) vs. residual liquid concentration (C_e) for PCE and TCE observed in three tested water samples.

CONCLUSIONS

Data mining applied to groundwater quality data permitted to identify the main kinds of contamination affecting the DWS system of Milan city, defining typical water composition contributing to each DWS unit. According to these results, different treatment processes were selected to be adopted in DWS units and their performances were experimentally evaluated. Experimental tests were performed on the most representative groundwater samples to obtain information generalizable to a high number of DWS units.

Heterotrophic denitrification resulted to be effective for nitrate abatement despite the significant organic contamination due to pesticide and VOCs. Carbon supply over 90% of the stoichiometric requirements and volumetric loads ≤1.07 kg N m^{-3} d^{-1} were found to assure effective and complete denitrification.

Adsorption onto activated carbon was effective for the removal of several VOCs and pesticides. However, variable efficiencies were highlighted towards contaminants due to: 1) their physical-chemical properties, and 2) the influence of water composition, which magnifies competition phenomena. An air stripping step before GAC resulted to be a successful solution to remove the most volatile compounds (e.g. PCE), favoring the following adsorption of low adsorbable compounds (e.g. TCE).

ACKNOWLEDGEMENTS

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AN APPROXIMATE SOLUTION FOR DELINEATION OF WATER SOURCE PROTECTION ZONES IN SAND AND GRAVEL AQUIFERS

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Abstract: The paper presents a simple method for delineation of approximate time-of-travel water source protection zones (WSPZs) for a well in a homogeneous and isotropic sand and gravel aquifer with a one-dimensional and uniform ambient groundwater flow. The exact solution for WSPZs is available, but it is given in an inconvenient implicit form and requires computational effort to delineate such protection zones. The approximate solutions presented in the paper are on the other hand explicit and thus easy to calculate. They are given in a dimensionless form as a function of a single variable – dimensionless residence time $\tilde{T}$. The approximate solution proposes three typical shapes for time-of-travel WSPZs: a circular and centric WSPZ for $\tilde{T} < 0.1$, a circular and eccentric WSPZ for $0.1 < \tilde{T} < 1.0$, and a boat-shaped WSPZ for any $T > 1.0$. The approximate solutions are conservative as they enclose the exact WSPZs.

Keywords: simple method, modeling, aquifer, delineation, water source, protection zone

INTRODUCTION

Groundwater is widely used in many countries as a source of water supply of the population, industries and other users. Due to growth of water consumption and deterioration of water resources, the protection of groundwater sources is becoming increasingly important. In response to these problems, many countries enforce water source protection as a mandatory measure for drinking water sources. The protection is typically enforced through establishment of one or more water source protection zones (WSPZs) around the water intake, in which different land use regimes and protective measures are adopted in order to minimize the risk of pollution.

The delineation of the WSPZs can be very complex due to the complex nature of the geological formations that make up the aquifer. The U.S. EPA (1987) suggests that one of the following WSPZ delineation methods should be used: (i) arbitrary fixed radius method, (ii) calculated fixed radius method, (iii) simplified variable shapes method, (iv) analytical method, (v) hydrogeologic mapping, or (vi) numerical flow/solute transport modeling. The methods listed are in order of sophistication, with the arbitrary fixed radius method being the simplest but least reliable way to obtain a WSPZ. More sophisticated methods provide more reliable and accurate results, but field data requirements, time requirements, needs for highly trained personnel and financial resources needed are often constraints to apply these methods.

During the last 20-30 years, rapid development of computer hardware and user friendly software packages for groundwater flow modeling have made the application of more sophisticated WSPZ delineation methods increasingly more popular. Nevertheless, building three dimensional, transient, multi-aquifer models for every project is not possible due to limited available resources, and often times not necessary for many hydrogeological settings. Simple methods, although admittedly less accurate, are useful to come up with initial assessments of the WSPZs, and therefore should not be immediately dismissed. The application of simple methods is particularly important if the modeler has decided to gradually build the model and increase its complexity, which is a practical and economic approach to delineation of the WSPZs. Another advantage of simple models and elementary analytic solutions is that they build modelers' intuition (Haitjema, 2006), thus building modelers' skills to evaluate and verify computer models and results obtained.

This paper presents a methodology for a rapid and simple assessment and delineation of the WSPZs in sand and gravel aquifers.

METHODS

The research has been carried out for the case of a confined sand and gravel aquifer of a constant thickness H (m), which is homogeneous and isotropic, with a uniform filtration coefficient k (m/s) and a constant effective porosity n (-).The ambient groundwater flow in the aquifer is one-dimensional and uniform, with a discharge rate of Q_o (m^2/s). A perfect well is located in the aquifer which pumps at a constant rate Q (m^3/s). A Cartesian coordinate system is originated at the center of the well, with the x-axis oriented in the direction of the ambient groundwater flow (Figure 1). The Dupuit-Forchheimer assumption ($q_z = 0$) applies in the entire domain.

The time-of-travel WSPZ is an area around the abstraction well that contains groundwater that will enter the well within a specified time period T (s). The boundary of the area is an isochrone of equal residence time T. The isochrones are analytically solved using a solution provided by Bear and Jacobs (1965) for the advancing fronts created by the artificial replenishment of an aquifer through an injection well at a rate Qi = −Q.

Based on the assessment of the shape of the exact time-of-travel WSPZs, approximate WSPZs are proposed as simple and conservative solutions, as described in the following sections.

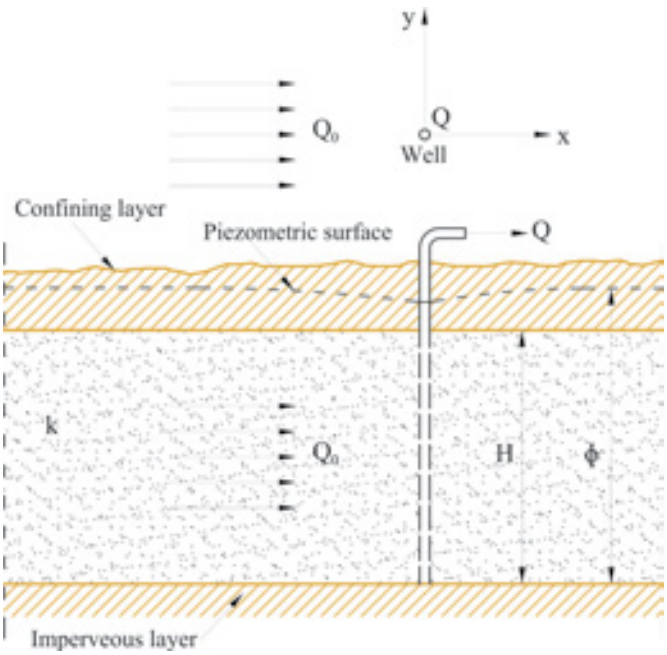

Figure 1: A perfect well in a confined aquifer with a uniform ambient flow field

RESULTS AND DISCUSSION

Exact Solution of WSPZs

Adapting the solution of Bear and Jacobs (1965) for an extraction instead of an injection well yields:

$$e^{-\tilde{x}-\tilde{T}} = \cos(\tilde{y}) - \frac{\tilde{x}}{\tilde{y}} \cdot \sin(\tilde{y}) \,, \qquad (1)$$

where:

$$\tilde{x} = \frac{x}{L_s}, \; \tilde{y} = \frac{y}{L_s}, \text{ and } \tilde{T} = \frac{T}{T_o}. \qquad (2)$$

Variables $\tilde{x}$ and $\tilde{y}$ are dimensionless coordinates of the time-of-travel WSPZ, where L_s (m) is the distance from the well to the well's stagnation point (Haitjema, 1995):

$$L_s = \frac{Q}{2 \cdot \pi \cdot Q_o}. \qquad (3)$$

Variable $\tilde{T}$ is a dimensionless residence time, where T_o is a reference time which can be defined as the travel time from the well to the stagnation point of the well in case the flow due to the well itself is ignored:

$$T_o = \frac{n \cdot H \cdot Q}{2 \cdot \pi \cdot Q_o^2}. \qquad (4)$$

For an infinitely long residence time T ($\tilde{T} \rightarrow \infty$), the time-of-travel WSPZ becomes the catchment area, inside which all groundwater will eventually reach the well. The analytical solution for the catchment area is derived from (1):

$$x = \frac{\tilde{y}}{\tan(\tilde{y})}. \qquad (5)$$

Figure 2 shows the contours of time-of-travel WSPZs constructed for a number of selected values of variable $\tilde{T}$.

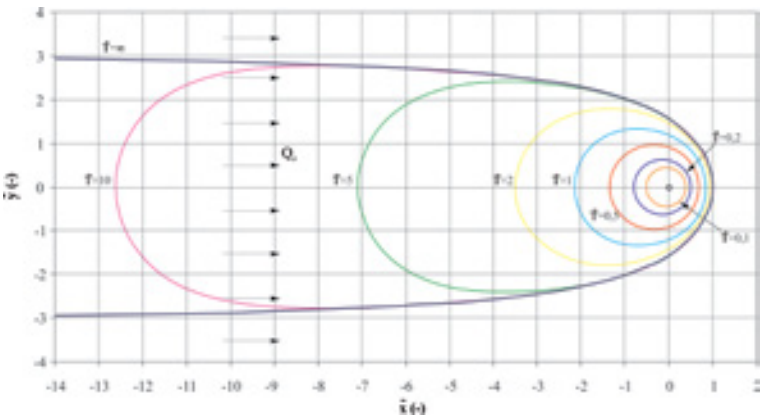

Figure 2: Contours of time-of-travel WSPZs for a range of values of $\tilde{T}$

For small values of variable $\tilde{T}$ (roughly for $\tilde{T} \leq 0.1$), time-of-travel capture zones tend to have a near circular shape that appear centric with respect to the well. For $0.1 < \tilde{T} \leq 1.0$ the WSPZs still resemble circles, but are shifted into the direction from where the uniform flow is coming. For $\tilde{T} > 1.0$ the contours of the WSPZs become more and more elongated and cannot be reasonably approximated by circles.

Approximate WSPZs

Three basic shapes of the WSPZs are proposed for the approximation of the exact solution, de-pending on the value of variable $\tilde{T}$ (Ćerić, 2000):

- a centric circular WSPZ for $\tilde{T} < 0.1$,
- an eccentric circular WSPZ for $0.1 < \tilde{T} < 1$, and
- a boat-shaped WSPZ for $\tilde{T} > 1$.

Centric circular WSPZ. The diameter of a centric circular WSPZ was developed based on the assessment of the time-of-travel WSPZ in an aquifer in which there is no ambient groundwater flow, or it can be ignored. The diameter (R) is defined as follows (U.S. EPA, 1987):

$$R = \sqrt{\frac{Q \cdot T}{n \cdot \pi \cdot H}} \,. \tag{6}$$

Diameter R (m) follows from the calculated fixed radius method which uses an analytical solution that is based on the volume of water that will be drawn to the well in the specified time interval T (the so-called volumetric method). Dividing (6) by L_s the diameter is obtained in the following dimensionless form:

$$\frac{R}{L_s} = \sqrt{2 \cdot \frac{T}{T_o}} \text{ , or } \tilde{R} = \sqrt{2 \cdot \tilde{T}} \,. \tag{7}$$

Due to existing ambient groundwater flow Q_o, the diameter in expression (7) underestimates the exact WSPZ from the upgradient side, so it is necessary to introduce a correction factor $\eta > 1$ to get a fully protective circular WSPZ. The approximate solution is given in the following form:

$$\tilde{R} = \eta \cdot \sqrt{2 \cdot \tilde{T}} = 1.1543 \cdot \sqrt{2 \cdot \tilde{T}} \,. \tag{8.}$$

Figure 3 shows examples of approximate WSPZs calculated from (8) for selected values of $\tilde{T} < 0.1$ (thick lines) which are plotted against the corresponding exact WSPZs (thin lines) calculated from (1). The approximate solution in (8) is conservative in the entire domain ($0 < \tilde{T} < 0.1$).

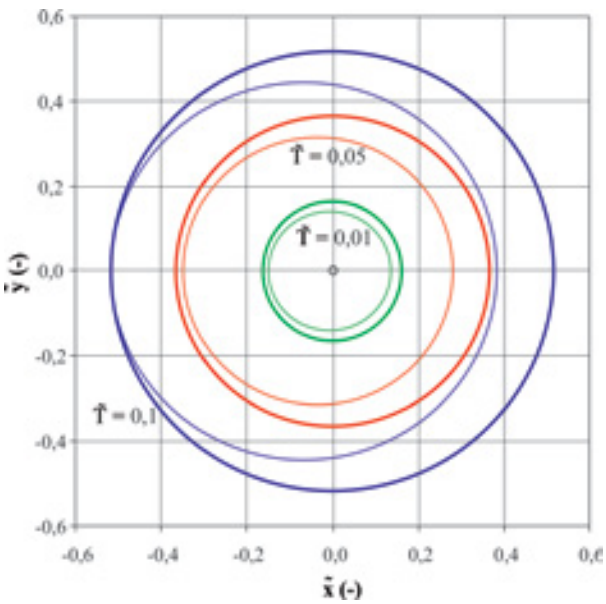

Figure 3: Approximate centric circular WSPZs

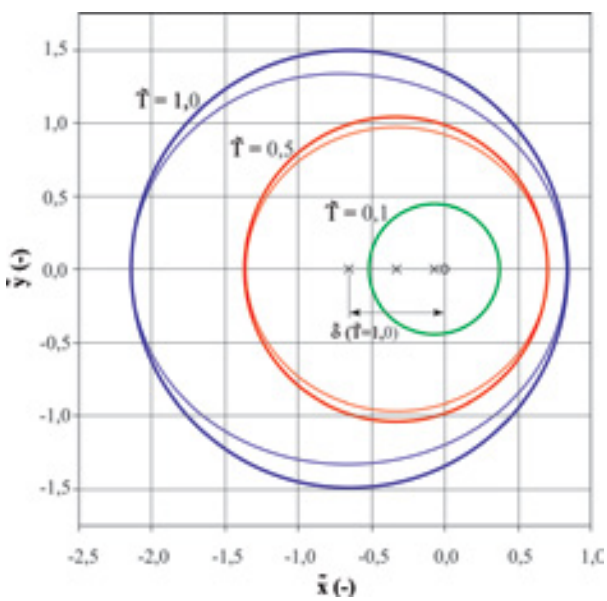

Figure 4: Approximate eccentric circular WSPZs

Eccentric circular WSPZ. For the purpose of defining eccentric circular WSPZs, the distances from the well to the furthest upgradient (L_u) and downgradient (L_d) points of the exact time-of-travel WSPZ are defined in a dimensionless form as follows:

$$\tilde{L}_u = \frac{L_u}{L_s}, \ \tilde{L}_d = \frac{L_d}{L_s}. \tag{9}$$

Expressions (9) may be derived from (1) in the following form:

$$\tilde{L}_u = \tilde{T} + \ln(1 + \tilde{L}_u), \ \tilde{L}_d = -\tilde{T} - \ln(1 - \tilde{L}_d). \tag{10}$$

The diameter ($\tilde{R}$) and eccentricity (shift from the center of the well, $\tilde{\delta}$) of the approximate WSPZ are defined in a dimensionless form as follows:

$$\tilde{R} = \frac{\tilde{L}_u + \tilde{L}_d}{2}, \ \tilde{\delta} = \frac{\tilde{L}_u - \tilde{L}_d}{2}. \tag{11}$$

As both terms in (11) are implicit in terms of $\tilde{T}$, they are approximated by the following expressions:

$$\tilde{R} = 1.161 + \ln\left(0.39 + \tilde{T}\right), \ \tilde{\delta} = 0.00278 + 0.652 \cdot \tilde{T}. \tag{12}$$

The approximate eccentric WSPZs in (12) always enclose the exact WSPZs (Figure 4), and are conservative in the entire domain $0.1 < \tilde{T} < 1$.

Boat-shaped WSPZ. For $\tilde{T} > 1$ the exact WSPZ can reasonably be approximated by the boundary of the catchment area, which is given by (5). Expression (5) is explicit in terms of $\tilde{y}$ and thus easy to evaluate. The approximate WSPZ is terminated at distance L_u. Since variable $\tilde{L}_u$ is implicit in (10), the solution is for convenience of calculation approximated by the following explicit expression:

$$\tilde{L}_u = \tilde{T} + \ln\left(\tilde{T} + e\right), \tag{13}$$

where $e \approx 2.71828$ is the base of the natural logarithm. Variable $\tilde{L}u$ calculated by (13) is conservative for $\tilde{T} \leq 2.85$, and a fairly good approximation of the exact solution for $\tilde{T} > 2.85$ (Figure 5).

CONCLUSIONS

The paper presents a method for delineation of approximate time-of-travel WSPZs for a well in a homogeneous and isotropic sand and gravel aquifer with a one-dimensional and uniform ambient groundwater flow. The exact solution for WSPZs can be obtained analytically in a dimensionless form based on a number of key aquifer properties. However, the exact solution is given in an inconvenient implicit form and requires computational effort to delineate a WSPZ.

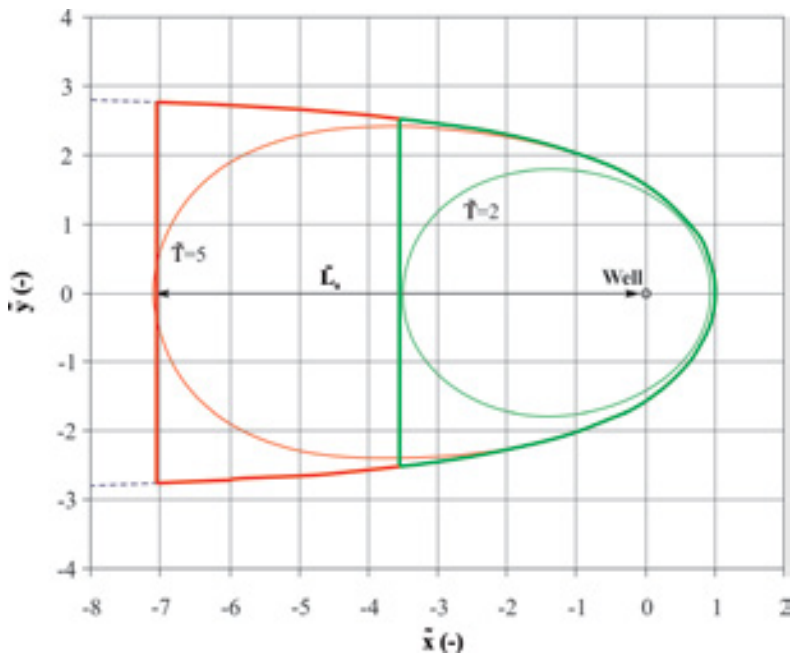

Figure 5: Boat-shaped WSPZs

The approximate solution that is presented in this paper proposes three typical shapes for time-of-travel WSPZs: a circular and centric WSPZ, a circular and eccentric WSPZ, and a boat-shaped WSPZ. The approximate solutions, which are presented in a dimensionless form, are estimated on the basis of a single variable – dimensionless residence time $\tilde{T}$. All approximate solutions are explicit and thus easy to calculate. They are conservative as they enclose the exact WSPZs.

In addition to being simple and easy to calculate, the proposed method for delineation of approximate time-of-travel WSPZs provides modelers with some rules of thumb with respect to the shape and size of the WSPZs in sand and gravel aquifers. However, these rules of thumb should be used with caution especially in realistic groundwater flow problems in aquifers with hydrogeological features that are significantly different from the conceptual model used in this research.

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NOTES

ANALYSIS OF THE OCCURRENCE OF PHARMACEUTICALS IN RIVERS AND CORRESPONDING ALLUVIAL WATER SUPPLY SOURCES

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Abstract: Alluvial groundwater sources in Serbia are under the direct influence of surface water, which are contaminated in the most cases with untreated waste water, such that the alluvial springs are exposed to the growing number of pharmaceuticals which are detected using new and modern analytical methods. The paper analyzes the occurrence of selected pharmaceuticals in major rivers of the Republic of Serbia and the correspondent wells between 2009 and 2014. Total of 167 samples of 24 studied pharmaceuticals and metabolites were analyzed, of which 10 were detected in surface water, and 7 in groundwater. Carbamazepine, 4-AAA and 4 FAA were the most often detected pharmaceuticals in surface water and groundwater. In addition Lorazepam, Diclofenac, Azithromycin and Bisprolol were detected in surface water and groundwater with relatively low frequencies of occurrence, while Trimethoprim, Sulfamethoxazole and Metoprolol occur only in surface waters with low frequency. Based on the data of occurrence of pharmaceuticals it is fully shown the general state of the Danube, Sava, Tisa, and Velika Morava River in the Republic of Serbia, as well as alluvial groundwater close to surface water sampling. The objective of the research is to determine the general state of affairs with regard to the occurrence of pharmaceuticals and to identify significant effects of river-water purification through bank filtration which represent very important self - purification mechanism and a set of natural processes which are used to obtain high quality groundwater.

Keywords: Pharmaceuticals, surface water, groundwater.

INTRODUCTION

The occurrence of pharmaceuticals in surface water, groundwater in Serbia has not yet been sufficiently studied, pharmaceuticals occur in surface water and groundwater, according to several papers that present the results of a number of studies conducted in Serbia (Grujić et al., 2009; Petrović et al., 2014; Radović et al., 2015), such that there is the need for further research and testing of the fate of pharmaceuticals in rivers and groundwater. Sufficient information about the occurrence and detection frequency of pharmaceuticals in Serbia's rivers would provide a fuller picture of the average concentrations, as well as the fluxes of pharmaceuticals in major rivers. Due to growing production of an increasing number of pharmaceuticals, and as a result of population growth (Daughton, 2003) and incomplete removal at WWTPs (Radjenovic et al., 2009; Miège et al., 2009; Jiang et al., 2013; Luo et al., 2014), and the data on the occurrence of pharmaceuticals in watercourses, it is necessary to assess the effects and mechanisms of natural self-purification processes that take place in groundwater, which are ultimately quantified by transport models that assess the fate of pharmaceuticals in groundwater and define numerous processes that lead to self-purification. The most prominent among them are sorption to the porous medium and degradation of micro pollutants (Dimkić and Kečkarević, 1990, Dimkić et al., 2010). The results are related to the determination of the rates of removal of pharmaceuticals through

bank filtration. Currently under way are experiments and in-situ tests aimed at determining the potential of pharmaceuticals, whose detection rates are the most, pronounced to sorb to the riverbed and aquifer material (Kovačević et al., 2013.)

SAMPLING LOCATIONS AND SAMPLE COLLECTION

During the study period (2009 – 2014), a total of 167 samples were analyzed: 58 surface water samples, and 109 groundwater samples. Surface water (SW) samples were collected from the Danube River (six locations), the Sava River (one location), the Tisa River (one location), and the Nišava River (one location). Surface water was sampled mid-stream, at a depth of about one meter. Groundwater (GW) samples were collected from wells in the immediate vicinity of the studied rivers. In the case of free-flowing or pumped wells, measurements were conducted by submerging a peristaltic pump to the level of the well screen or horizontal collector, whereas in the case of observation wells the pump was submerged to the screen after removing a minimum of three water volumes from the observation wells by means of a peristaltic pump. All surface water and groundwater samples were collected using 1-liter bottles. The samples were stored unpreserved in refrigerators and were later frozen up to the time of analysis, generally several days after sampling.

Figure 1: Map of Serbia showing sampling locations.

METHODS

A previously developed multi-residual method was used to analyze the selected pharmaceuticals and two Metamizole metabolites and the limits of detection and the quantification of the selected pharmaceuticals were addressed in previous research (Grujić et al., 2009; Radović et al., 2015). The water samples were prepared applying the method of extraction on the solid phase, which has been developed and optimized at the University of Belgrade/Faculty of Technology and Metallurgy (TMF)/Laboratory of Mass Spectrometry/ Department of Analytical Chemistry. The said method includes sample purification, as well as extraction and preconditioning of pharmaceutical traces. Calibration was performed applying the standard addition method (Conely et al., 2008).

RESULTS OF MONITORING OF PHARMACEUTICALS IN SURFACE WATER AND GROUNDWATER

Of the 25 analyzed pharmaceuticals, 10 were detected in the studied surface waters and 7 in groundwaters, Table 1.

Detected pharmaceuticals 2009 – 2014	LOD (ng/L)	Surface water		Groundwater		Rate of removal by bank filtration
		Frequency of occurrence (n=58)	Min/max (ng/L)	Frequency of occurrence (n=109)	Min/max (ng/L)	
Trimethoprim	1	12%	4/223	n.d.	n.d	100%
Sulfamethoxazole	4	3.4%	11/23	n.d.	n.d	n.c.
Azithromycin	3	3.4%	20/56	6.5%	18/83	n.c.
Carbamazepine	1	53.4%	4/68	37.6 %	3/41	68%
Lorazepam	1	3.4%	20/34	0.9 %	14	n.c.
Diclofenac	2	3.4%	18/53	2.75%	13/18	n.c.
4-FAA	1	55.1%	7/248	26.6%	14/150	74%
4-AAA	1	63.8%	12/520	22%	12/128	90%
Detected pharmaceuticals 2011 – 2014	LOD (ng/L)	Frequency of occurrence (n=24)	Min/max (ng/L)	Frequency of occurrence (n=84)	Min/max (ng/L)	Rate of removal by bank filtration
Metoprolol	1	4.1%	35	n.d.	n.d.	n.c.
Bisprolol	1	4.1%	6	3.5%	5/6	n.c.

* (n.d. – not detected, n – number of samples, n.c – not calculated – low frequency of occurrence, ½ LOD value adopted for samples in which the selected pharmaceuticals were not detected, for average concentration calculations)

Table 1. Detection frequency, LOD – limit of detection of pharmaceuticals, concentrations in surface water and groundwater, and rate of removal by bank filtration

Carbamazepine, 4-AAA and 4 FAA were the most often detected pharmaceuticals in surface water and groundwater. The detected concentrations for Carbamazepine were from 4 to 68 ng/L. Carbamazepine was detected in a large number of groundwater samples; its concentrations were found to be somewhat lower than in surface water (3 to 41 ng/L). The high frequency of carbamazepine occurrence in surface water and groundwater is attributable to its relatively low affinity for sorption, as well as its persistence (or low degradability), relatively poor removal at wastewater treatment plants, and widespread and continuous administration (as an antiepileptic).

Among benzodiazepines, only Lorazepam was detected in one surface water sample (20 ng/L) and one groundwater sample (14 ng/L).

Two Metamizole metabolites (4-AAA and 4-FAA) were detected in more than half of the surface water samples, which is consistent with reports of a 71-100% detection frequency. Detected concentrations of 4-AAA in surface water were from 12 to 520 ng/L. The frequency of detection in groundwater was lower than in surface water; 4-AAA concentrations detected in groundwater in Serbia were from 12 to 128 ng/L. 4-FAA concentrations in surface water were found to be from 7 to 248 ng/L. The frequency of 4-FAA detection in groundwater was lower than in surface water; the concentrations in groundwater were found to be from 14 to 150 ng/L. The lower concentrations of Metamizole metabolites in Serbia are attributable to much lower loading, in view of the population relative to river basin size, even though most of the wastewater is not treated.

Among antibiotics, Sulfamethoxazole was detected in concentrations from 11 to 23 ng/L, and Azithromycin in concentrations from 20 and 56 ng/L. The detection frequency was low. With regard to groundwater, only Azithromycin was detected in concentrations from 18 to 83 ng/L. Trimethoprim was detected only in surface water, in concentrations from 4 to 223 ng/L. Trimethoprim was not detected in groundwater in Serbia and Doxycycline and Erythromycin were not detected in the surface water and groundwater samples. The occurrence of antibiotics, in this case of Azithromycin, Sulfamethoxazole and Trimethoprim, in surface water in Serbia is a problem that might cause the flora and fauna to become resistant.

Diclofenac was detected for the first time in surface water in Serbia, in concentrations from 18 to 53 ng/L, and in groundwater in concentrations from 13 to 18 ng/L. Metoprolol was detected in one surface water sample, in a concentration of 35 ng/L. Bisprolol was detected in one surface water sample relatively low concentration of 6 ng/L, and in 3 samples from groundwater in concentration between 5 and 6 ng/L. The low concentration and low frequency of occurrence made this finding irrelevant. None of the other pharmaceuticals was detected in the surface water or groundwater samples.

CONCLUSIONS

Based on the research reported in this paper, the rates of removal of detected pharmaceuticals through bank filtration in all the study areas were: 100% for Trimethoprim and 69% for Carbamazepine. The rates of removal of 4 – FAA was 70% and that of 4-AAA as much as 90%,. Other pharmaceuticals were either not detected or the detection frequency was too low to quantify the rates of removal through bank filtration. The conclusion is that the reduction in concentrations at the studied production and observation wells depends on the method of groundwater abstraction, which is in turn associated with the anisotropy of the medium, such that each study area represents a specific environment with different groundwater flow conditions. This is extremely important in the study of the effects of bank filtration on the fate of pharmaceuticals. Currently under way are experiments and in-situ tests aimed at determining the potential of pharmaceuticals, whose detection rates are the most pronounced, to sorb to the riverbed and aquifer material.

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NOTES

MATHEMATICAL MODELING OF SORPTION AND DEGRADATION OF PHARMACEUTICALS: CASE STUDY OF BELGRADE GROUNDWATER SOURCE WELL RB-16

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Abstract: The paper discusses the application of a 3D mathematical model that analyzes the transport of select pharmaceutical from the Sava River to a corresponding radial well at Belgrade's groundwater source, which is situated in an anisotropic setting with a semi-permeable layer below which groundwater is tapped. The occurrence of 24 pharmaceuticals in the Sava River and the corresponding well (Rb-16) was monitored from 2009 to 2014. The pharmaceuticals selected for the present study are Carbamazepine and Metamizole metabolite 4-AAA. Transport was analyzed based on experimental data (sorption isotherms) and the results of an in situ tracer test that included injection of the selected pharmaceuticals to record the time delay of the pharmaceutical relative to a NaCl tracer. The average concentration of Carbamazepine was found to be nearly identical in the Sava River and well Rb-16. The transport analysis showed that sorption of Carbamazepine was relatively low and that this pharmaceutical did not degrade under the studied conditions, so it was not possible to accurately determine the degradation half-life. On the other hand, the Metamizole metabolite 4-AAA was detected in the Sava River with an average concentration of 20 ng/L but there was no positive detection in well Rb-16. As such, the experimental data and information collected in situ on the sorption coefficient were used to determine the minimum half-life. The objective of the research was to apply an existing hydrogeologic model and a pharmaceuticals transport model to determine the site-specific residence time and degradation half-life.

Keywords: Pharmaceuticals, sorption, degradation, model.

INTRODUCTION

Belgrade's groundwater source is situated along the Sava River, for the most part within city limits, making the source vulnerable to anthropogenic pressures. Drinking water is treated at five plants. The rate of groundwater abstraction from the Sava alluvion is currently about 4.5 m^3/s and the design capacity of the treatment plant for mainstream river water is 3.5 m^3/s (Dimkić et al., 2011b). As such, about one half of the drinking water supply relies on alluvial groundwater of the Sava River. In Serbia in general, about 50% of drinking water originates from groundwater, of which 50% comes from alluvial aquifers (Dimkić et al., 2007). Riverbank filtration ensures additional purification as groundwater flows through the aquifer, which can be considered an extensive physical and biochemical reactor. This is an extremely important aspect from the perspective of river water treatment and mitigation of accidental pollution risks.

Periodic testing has been undertaken to study the effect of the transport of a substance along with groundwater from the river to the well and to obtain input data for quantifying self-purification processes. Experiments were also conducted to determine the sorption isotherms and an NaCl tracer test was undertaken to determine the delay time relative to the tracer. The present paper presents model simulation results of the transport of Carbamazepine and Metamizole metabolite 4-AAA from the Sava River to well Rb-16. Based on

a hydrogeologic model previously developed by the Jaroslav Černi Institute for the Development of Water Resources (JCI) and the sorption coefficient data obtained experimentally and in situ, the degradation half-life s of the two pharmaceuticals were assessed and a spatial and temporal analysis conducted of transport along with groundwater from the river to the well. A total of 11 samples of surface water (the Sava River) and six samples of groundwater from well Rb-16 at Belgrade's groundwater source were analyzed during the study period (2009-2014). Surface water (SW) was sampled mid-stream, at a depth of about one meter. Groundwater (GW) samples were taken directly from well Rb-16. All surface water and groundwater samples were collected using 1-liter bottles. The samples were stored unpreserved in refrigerators and frozen on the same day, until the time of analysis, generally several days after sampling. Well RB-16 is located on the right bank of the Sava River, on a river island called Ada Ciganlija, within the city proper. The well is outfitted with four relatively new laterals (installed in 2007). The old laterals have been shut off and decommissioned. The laterals tap the lowest water-bearing layer, at a depth of about 30 m.

METHODS

Analytical method

A previously developed multi-residual method was used to analyze the selected pharmaceuticals. The limits of detection and the quantification of the selected pharmaceuticals were addressed in previous research (Grujić et al., 2009). The water samples were prepared applying the method of extraction on the solid phase, which has been developed and optimized at the University of Belgrade/Faculty of Technology and Metallurgy (TMF)/ Laboratory of Mass Spectrometry/Department of Analytical Chemistry. The said method includes sample purification, as well as extraction and preconditioning of pharmaceutical traces. Calibration was performed applying the standard addition method (Conely et al., 2008). The validation method, recovery rate, matrix effect, and quantification are described in detail in previous research (Grujić et al., 2009). A method optimized in previous research was used to conduct adsorption experiments. It was found that the optimal ratio of sediment mass to water solution volume of a certain concentration was 1 g : 20 ml, as well as that the optimum contact time between the sediment and the solution was 24 h. Eight concentrations were selected to monitor adsorption equilibrium variation and generate the adsorption isotherms: 10, 25, 50, 75,100, 250, 500 and 1000 $ngml^{-1}$ (µg/L, ppb). Each adsorption isotherm was defined as needing to have six to seven points.

Numerical method

WODA (Well Outline and Design Aid) is a simulator of variably saturated well-driven groundwater flow in an anisotropic discontinuous environment with miscible displacements, heat transfer, variable density, sorption, degradation, etc. It was developed by the Numerical Analysis Group at JCI. WODA does not have its own graphical user interface, but it can work with groundwater models constructed using a Lizza interface. Lizza was co-developed by JCI and the Bioengineering Research and Development Center - BioIRC, Kragujevac, Serbia. It supports full 3D modeling, stationary and non-stationary modeling, and saturated and non-saturated environment calculations, as well as handling of mass and heat transport (Dimkić et al., 2009, 2010a, 2011a).

RESULTS AND DISCUSSION

Analyses were performed from 2009 to 2014 to determine the average concentrations of Carbamazepine and 4-AAA in the Sava River and well Rb-16, relative to the river discharge at the time of sampling. The results showed that Carbamazepine was detected in roughly the same concentrations in the river and the well (about 6 ng/L on average), such that it was not possible to accurately determine the degradation half-life with the transport model. Therefore, the conclusion was that Carbamazepine did not degrade in groundwater or, in other words, that its degradation half-life was much longer than the groundwater travel time from the river to the well under the considered site conditions (Ternes et al., 2007). On the other hand, the detected concentrations (in the range from 6 to 28 ng/L) were so low that averaging errors were likely. River discharge during the study period varied from 300 m^3/s to 2100 m^3/s and diluted pharmaceuticals of anthropogenic origin, such that generally higher concentrations were detected at low discharges. The Metamizole metabolite 4-AAA measured a concentration of 20 ng/L, which was dependent on discharge, but was not detected at well Rb-16. Consequently, a value of ½ LOD (limit of detection), or 0.9 ng/L, was assumed when the transport model inputs were defined.

Spatial data related to well RB-16 were analyzed and organized with the goal of creating a hydrogeologic model of the terrain, a simplified 3D model of the water-bearing medium – alluvial sediments. The hydrogeologic model served as a basis for developing a hydrodynamic model of groundwater flow in the region of well

RB-16. This model included schematized layers of the alluvial complex of the Sava River. The Sava River and Lake Sava were specified in the model using prior cross-sectional measurement data. The effect of the interbed on groundwater flow is reflected in a piezometric head difference between the upper and lower water-bearing layers. The conclusion was that the hydrogeologic characteristics of the interbed (position, areal extent, thickness, filtration rate) were extremely important aspects of the discharge capacity of both the well and the location as a whole. A model with three schematized layers provided representative, averaged values of filtration parameters of the porous medium and the permeability of the riverbed, where for Layer 1 (water-bearing layer) the horizontal hydraulic conductivity was found to be about 3 E-04 m/s, vertical hydraulic conductivity roughly 2 E-06 m/s, and effective porosity 1.5E-01. For Layer 3 (also a water-bearing layer), the vertical and horizontal hydraulic conductivities were about 6.5 E-04 m/s and the effective porosity 1.2E-01. Layer 2 (semi-permeable layer) acts as an isolator, whose horizontal hydraulic conductivity was determined to be about 4.46E-04 m/s, vertical hydraulic conductivity some 3.00E-07 m/s, and effective porosity 7.0E-02. The specific yield of all three layers was about 7.E-05 l/m. Riverbed conductivity K/d of the Sava was 4.00E-07 m/s and that of Lake Sava 3.00E-07 m/s.

The table below show linear sorption coefficients based on a water-bearing sediment sample and riverbed sample from the location of Belgrade's groundwater source (Kd_1), analyses of different fractions of the water-bearing layer in the Danube alluvion and riverbed sediment collected at the Kovin – Dubovac location (Kd_2), and the results of in situ testing at Kovin – Dubovac (Kd_3).

	Kd_1 (cm^3/g)	Kd_2 (cm^3/g)	Kd_3 (cm^3/g)
Layer 1	1.56	1.05	0.15
Layer 2	10.6	3.94	3.94
Layer 3	1.56	1.05	0.15
Calculated half-life	$t_{1/2}$ min ≈ 600 days	$t_{1/2}$ min ≈ 320 days	$t_{1/2}$ min ≈ 130 days

Table 1. Experimentally-derived linear sorption coefficients Kd of different layers

Since the model comprised three layers, a different sorption coefficient was specified for each. Layer 2 was the semi-permeable interbed and its sorption coefficient was set as equal to that of the riverbed.

Experimentally-derived data were specified as the boundary conditions in the transport model and served as a basis for defining the degradation half-life of 4-AAA. For the Sava River, the boundary condition was the average concentration of 4-AAA relative to the river discharge, and the degradation half-life was determined by steady - state simulations, where the experimentally-derived sorption coefficient Kd was specified in the existing hydrodynamic model and the half-life was up to the time the value equal to the average concentration at well Rb-16 was reached. When the parameters based on the first experiment with the sample from the water-bearing layer at Belgrade's groundwater source and the Sava riverbed were specified under steady - state conditions, the minimum degradation half-life of 4-AAA was about 600 days. When the experimental data derived for different fractions of the water-bearing layer at Kovin – Dubovac, and for the second layer the data on the Danube's sediment were specified, the calculated minimum degradation half-life was about 320 days. According to the sorption coefficient derived from in situ testing, the minimum half-life was some 130 days. Figure 1 shows simulation results under nonstationary conditions, with a 4-AAA breakthrough curve without sorption or degradation on the way from the river to the well, whereas Fig. 2 shows the time difference between the occurrences of 4-AAA, relative to the specified sorption coefficients obtained from the analyses of different samples.

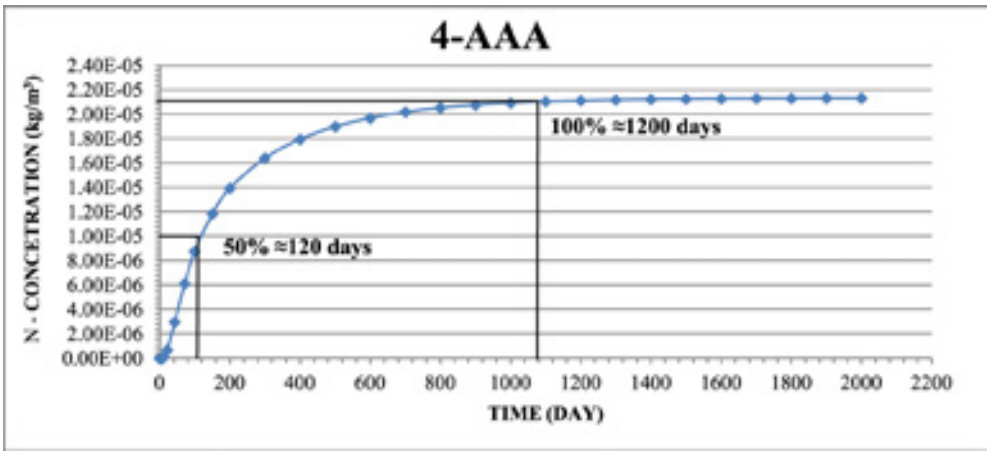

Figure 1: Breakthrough curve of 4-AAA concentrations between the river and the well, without degradation or sorption.

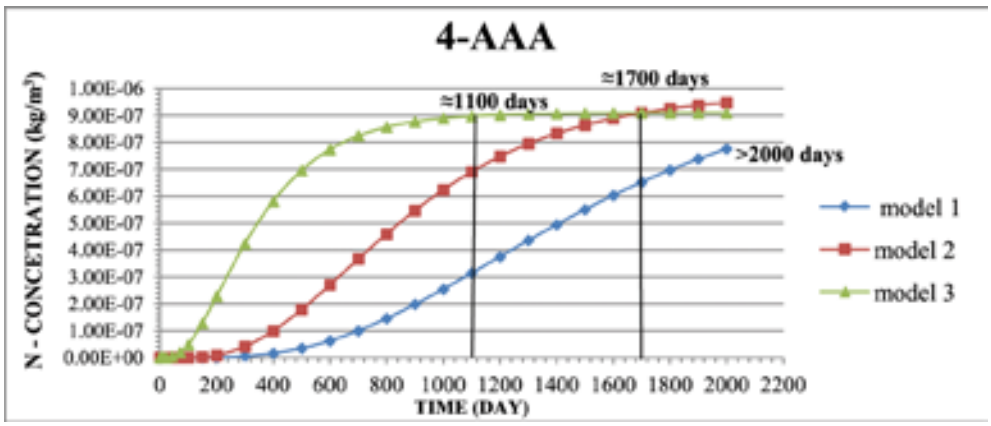

Figure 2: Breakthrough curve of 4-AAA concentrations with specified degradation half-life and sorption in different transport models.

CONCLUSIONS

The results indicated that the degradation half-life was directly related to the sensitivity of the analytical methods used to determine the concentrations of the pharmaceuticals, due to very low concentrations and limits of detection, as well as to the data used to develop the hydrogeologic model (boundary conditions). Another important factor was information relating to the sorption coefficient. Considerably different results were obtained with the various samples used to experimentally determine the sorption isotherms. The in situ test data yielded a sorption coefficient that closely reflected natural conditions. According to the experimental data, the degradation half-life was 2-3 times longer, which would have a considerable effect on the travel time. Such data are extremely important for delineating sanitary protection zones and predicting potential impacts of pollution from anthropogenic sources.

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NOTES

TRACER TEST AND BEHAVIOR OF SELECTED PHARMACEUTICALS

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Abstract: Study of the behavior and transport of pharmaceuticals in groundwater is significant for understanding the processes of natural attenuation and potential use of filtration through the aquifer to evaluate the most effective way to remove micropollutants that occur under anthropogenic influence. Due to insufficient data on the characteristics of the subsurface structure and mechanism and the behavior of studied pharmaceuticals during groundwater transport, tracer experiments can be a very effective method for the characterization and examination of the behavior of pharmaceuticals in relation to the transport of a non-reactive tracer. Tracer experiments provide information about effective parameters and data for breakthrough curves of pharmaceuticals in relation to the breakthrough curve of the non-reactive tracer, based on which transport parameters can be determined and used for further modeling and forecasting. The quantification of the effects of sorption during a field tracer test has not been sufficiently studied, such that the implementation of a tracer test is very useful for collecting better and more precise data. This paper presents the results of field research on the location of the drainage system Kovin-Dubovac, during which a tracer test was conducted and the behavior of selected pharmaceuticals (Trimethoprim, Carbamazepine, Diclofenac and Metamizole metabolites 4-AAA and 4-FAA) monitored. The objective of this paper is to show and analyze the results of a tracer test during which the tracer NaCl was injected, and to correlate the obtained characteristics of the subsurface and the breakthrough curves of selected pharmaceuticals, so that the effects of sorption can be quantified.

Keywords: Pharmaceuticals, tracer, sorption.

INTRODUCTION

In the case of intergranular aquifers, the simulation and prediction of groundwater flow and transport of substances, in this case pharmaceuticals, require detailed knowledge of the nature and spatial distribution of the aquifer. In most cases, such data may not be easy to collect and thus necessitate detailed research and experiments. Pharmaceuticals belong to the group of emerging contaminants in the environment. Dimkić conducted tracer tests and monitored the behavior for heavy metals and phenols near Žičko Polje, as reported in (Dimkić et al., 2008). The need for conducting a tracer test arose from a lack of experimental data on the behavior of pharmaceuticals in groundwater.

A tracer test is a very powerful tool for characterizing the subsurface. There is a large variety of application possibilities: tracer testing can be used for conventional subsurface investigations that yield effective transport parameters (transport velocity, porosity, and dispersivity), which may describe non-reactive as well as reactive (contaminant) transport processes within an aquifer, like in the present study. Information on the subsurface structure (preferential flow paths and structural anisotropy) can be obtained as well (Käss, 1998). Tracer tests also help generate a database (tracer breakthrough curves and their respective derived statistical transport parameters), which can be used to test forward transport predictions obtained from deterministic or stochastic model approaches and reduce prediction uncertainty within stochastic modeling frameworks, or to develop and apply inverse stochastic flow and transport modeling methods (Ptak, 2004).

The tracer test reported in this paper was conducted under forced gradient conditions, induced by groundwater pumping because of the duration of the test and other limiting factors. In this test the convergent flow field approach was used: groundwater was pumped out of an extraction well, the tracer was injected continuously into the injection piezometer over a limited period of time, and breakthrough curves were plotted at the extraction site based on the example from (Ptak and Schmid, 1996). NaCl was used as the tracer for many practical reasons: nontoxic, readily available, affordable, good solubility for injection, low detection limits, low natural background concentrations, negligible effect on transport properties (density, viscosity, pH, etc.), stable or well-characterized low and very slow degradation, thermal or radioactive decay acceptable, and no sorption processes on the tracer substance. During this test, the concentrations of selected pharmaceuticals (Trimethoprim, Carbamazepine, Diclofenac and Metamizole metabolites 4-AAA and 4-FAA) at an extraction well were monitored and then a sampling and analysis program was established to define breakthrough curves.

MATERIALS AND METHODS

Experimental Setup

During the tracer test, the nonreactive tracer NaCl and reactive pharmaceuticals were injected into the injection piezometer, approximately 8.5 meters from the monitoring well and about 20 meters deep. A continuous-flow peristaltic pump was set up in the monitoring well at 6 L/s. Also, monitoring of groundwater levels was conducted with CERA divers. The flow was monitored by a Thompson overflow, the volumetric method and ultrasonic flow meter Nivus PCM Pro. The NaCl tracer was mixed and dissolved in 1000 liters of water extracted from the monitoring well. The pharmaceuticals, obtained from Sigma Aldrich, were dissolved in 1 liter of methanol, then mixed with 100 liters of water and injected into same piezometer as the NaCl tracer. During the experiment, only specific conductivity was monitored as the parameter for calculating the concentration of the NaCl tracer. Samples of the reactive compounds were collected periodically and frozen for further investigation.

New Boreholes

A new piezometer borehole was drilled by the conventional method with the use of flasks. During drilling, water was sampled at every three meters and then a composite sample was collected from pelite fractions for further examination. Each core was crated and transferred to the Jaroslav Černi Institute for the Development of Water Resources for further investigation, mapping and sampling for detailed analysis. The purpose of drilling was to form an injection piezometer near a drainage well of the Kovin Dubovac drainage system where testing took place. Particle size distribution was determined by sieving the materials using sets of sieves according to JUS L.J9.010 with the following mesh sizes in mm: 0.063; 0.090; 0.125; 0.250; 0.500; 0.710; 1.0; 2.0; 4.0; 8.0; 11.2; 16.0; 22.4; 31.5; 63.0; and 125.0. Based on the previously obtained data, hydraulic conductivity was calculated using the USBR empirical equation, where $d_{ef} = d_{10}$.

$$K = 0.36 \cdot d_{ef}^{2,3} \quad (1)$$

The hydraulic conductivity was calculated based on the particle size distribution curve; K amounted to 7 x10^{-4} m/s.

Sampling and Analysis

All groundwater samples for pharmaceutical analyses were collected in 1-L bottles from the well discharge and kept refrigerated without preservatives. Once prepared, the collected samples were kept at 4°C until they arrived at the laboratory and were processed within 48 h.

In situ monitoring was carried out with a probe immersed at the point of outflow from the well. Electrical conductivity was observed continuously during the experiment with an HQ40d multi-parameter probe. Before the test started, baseline quality was monitored to determine the initial state. Based on the results, the average electrical conductivity before the test was 649 µS/cm. A previously-developed multi-residual method for analysis of the most commonly administered pharmaceuticals and two Metamizole metabolites was employed (Grujić et al., 2009). Water samples were prepared by extraction on the solid phase; the method was developed at the University of Belgrade, Faculty of Technology and Metallurgy (TMF), Laboratory for Mass Spectrometry, Department of Analytical Chemistry and Metallurgy. This method relates to the purification of the sample as well as traces of the extraction and preconcetrations of pharmaceutical traces. Calibration was performed using the standard addition method. A Surveyor LC system (Thermo Fisher Scientific, Waltham, MA, USA) was used to separate the analytes in a reverse-phase Zorbax Eclipse® XDB–C18 column, 75mm×4.6mm ID and 3.5mm particle size (Agilent Technologies, Santa Clara, CA, USA). A pre-column, 12.5mm×4.6mm ID and 5mm particle

size (Agilent Technologies), was also used. Mass spectra were obtained using the LCQ Advantage quadrupole ion trap mass spectrometer and applying the electrospray ionization technique (Thermo Fisher Scientific). All compounds were analyzed in the positive ionization mode. For LC–MS2 analyses of pharmaceuticals in the positive ionization mode, the mobile phase was composed of methanol (A), deionized water (B) and 10% acetic acid (C), and the gradient varied as follows: 0.0min, A 14.5%, B 85%, C 0.5%; 35.0 min, A 99.5%, B 0.0%, C 0.05%; 46.0 min, A 99.5%, B 0.0%, C 0.5%. The initial conditions were re-established and held for 10 min. The flow rate of the mobile phase was 0.6 ml/min. The injection volume was 10ml. The optimal source working parameters for monitoring all the ions were as follows: source voltage (4.5 kV), sheath gas (25 au, i.e. 25 arbitrary units, from a scale of arbitrary units in the 0–100 range defined by the LCQ Advantage system) and capillary temperature (290 °C).

RESULTS AND DISCUSSION

After successful dissolution of NaCl in a 1000-liter injection tank, injection of the NaCl tracer started at 15:07 h and lasted for 52 minutes. The average specific conductivity in the injection tank was 74.3 mS/cm. At the beginning of the test 50 kg of NaCl was dissolved in the tank. The amount of pure Cl^- that was poured into the tank was 35.7 kg, calculated on the basis of plots of electrical conductivity as a function of Cl^- concentration. The maximum concentration of the NaCl tracer was established 201 minutes after the beginning of the test, which is consistent with the data obtained by analyzing the filtration properties of the aquifer and the average hydraulic conductivity of $7x10^{-4}$ m/s. The figure below shows the breakthrough curve of the NaCl tracer.

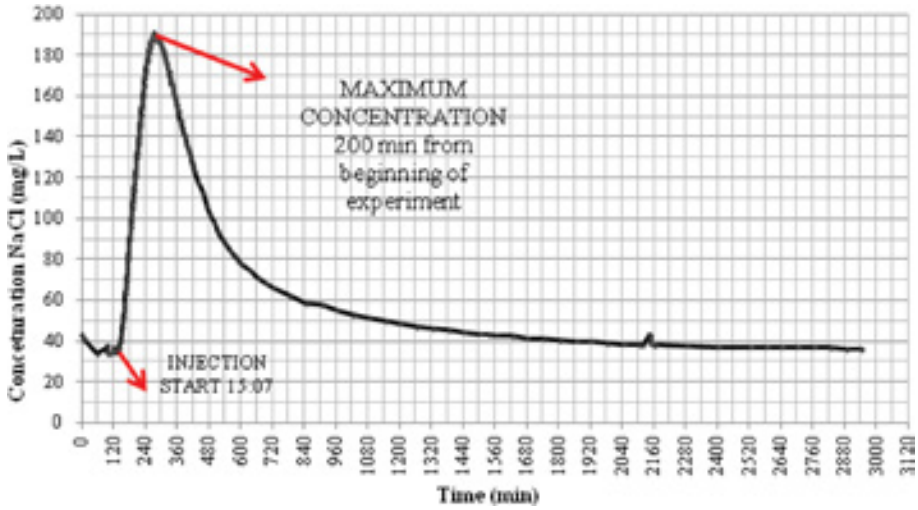

Figure 1: Breakthrough curve of the NaCl tracer

Following successful injection of the NaCl tracer, injection of the pharmaceuticals was initiated. The initial concentrations in a 100-liter injection tank were: Trimethoprim 2.5 mg/L, Carbamazepine 1 mg/L, Diclofenac 1 mg/L, and Metamizole metabolites 4-formylamino antipirine (4–FAA) 0.1 mg/L and N-acetyl-4-aminoantipyrine (4–AAA) 1 mg/L. Injection was continuous and lasted for approximately 36 minutes. Then sampling started based on the established program. The following equation was used to calculate Kd of all the pharmaceuticals:

$$Rd = \frac{v_{NaCl}}{v_{pharmaceutical}} = 1 + \frac{\rho_b}{n} Kd \qquad (2)$$

where: Rd is retardation coefficient; v_{NaCl} is the velocity of the NaCl tracer; $v_{pharmaceutical}$ is the velocity of the pharmaceutical; ρ_b is the bulk density; n is the porosity; and Kd is the linear sorption coefficient.

The velocities of the NaCl tracer and the pharmaceuticals were calculated based on the results of the tracer test (n-porosity and ρb – bulk density were calculated from the grain size curve and theoretically).

The next figure shows the representative breakthrough curve for Diclofenac. Based on the results of the test, the conclusion was that Diclofenac, for example, reached its maximum concentration after 315 minutes or, in other words, that the delay of Diclofenac with respect to the NaCl tracer was approximately 1.56 times.

Analytes	Kd [cm^3/g]
Trimethoprim	1.2
Carbamazepine	0.15
Diclofenac	0.1
4-formylamino antipirine(4–FAA)	0.4
N-acetyl-4-aminoantipyrine (4–AAA)	0.15

Table1. Linear sorption coefficient of the analyzed pharmaceuticals

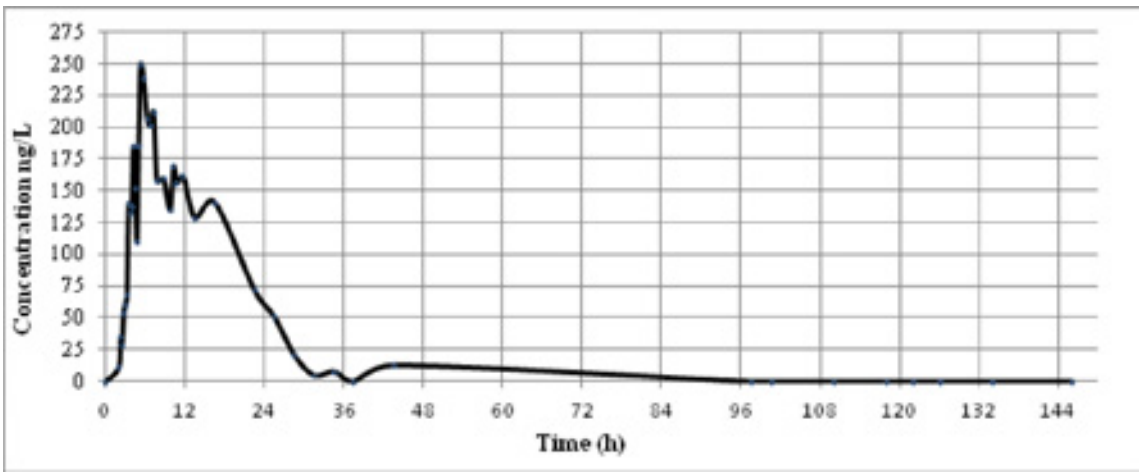

Figure 2: Breakthrough curve of Diclofenac

CONCLUSIONS

Based on the results of the tracer test, the sorption capacity of the selected pharmaceuticals under experimental conditions could readily be calculated. It is very important to note that sorption of the selected pharmaceuticals, with relatively small calculated partition coefficients compared to the data reported in the literature, represents a significant factor that influences the behavior of pharmaceuticals in groundwater during filtration. However, much of the literature contains results for laboratory conditions and such results cannot be used in practice to calculate real transport parameters. Groundwater represents a huge bioreactor in which numerous processes take place under different conditions, so that even a very small extension of the transport time seriously affects the removal of these compounds in groundwater. This makes it possible to design appropriate safeguards for existing and future drinking water sources and thus protect public health.

ACKNOWLEDGEMENTS

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CHARACTERIZATION OF MINERAL ENCRUSTATIONS IN WATER SUPPLY WELLS AND INTERACTIONS WITH TRACE ELEMENTS

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Abstract: The results of characterization of encrustations formed in public water supply wells that tap shallow alluvial aquifers of the Sava (Belgrade groundwater source) and Velika Morava rivers (Trnovče groundwater source) are presented in the paper. Special attention is devoted to analyses of trace metals in encrustations. Trace element concentrations of As, Pb, Ni, Zn, Cd, and Co are assessed. Sampled encrustations were analyzed using energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), X-ray powder diffraction (XRPD) and inductive coupled plasma (ICP-OES) instruments. Based on the redox conditions in which they are formed and the differences in the dominant mineral species, all the samples are divided into four groups: (1) Fe&Mn low-crystallinity (oxy)hydroxides from Trnovče groundwater source, (2) predominantly older, more crystallyine iron encrustations - goethite, (3) sulfide-rich & goethite encrustations, and (4) iron encrustations with large amounts of SiO_2. The last three groups of encrustations were sampled from radial wells at Belgrade groundwater source. The results show a considerably affinity of iron encrustations for trace metals. In neutral groundwater, anions (such as AsO_4^{3-}) have a high sorption affinity for iron encrustations. Pb concentrations are the highest in the first group of encrustations, owing to the ability of Mn-oxides to retain cations of large ionic radii. Recent low-crystallinity sediments that contain Mn in addition to iron exhibit high reactivity and high coefficients of correlation with trace metals. Iron sulfide encrustations sampled from anoxic S-rich settings feature high sorption capacity.

Keywords: encrustation, trace elements, alluvial aquifers, water supply wells

INTRODUCTION

Well clogging decreases well discharge capacity (Misstear et al. 2006, Houben and Treskatis, 2007, Dimkić and Pušić 2008, Dimkić et al 2011) and increases maintenance costs, but can also affect water quality. In order to study well clogging, two different alluvial sources were selected in the present research Trnovče groundwater source was chosen as an example of extremely rapid clogging and formation of considerable incrustations on well screens and well pump discharge pipes (Majkić-Dursun et al. 2012, Majkić-Dursun et al. 2015a). The Belgrade Groundwater Source was selected because of its importance for the public water supply of Serbia's capital and long-term research of ageing processes. The radial-wells at this source tap the alluvium of the Sava River, while those tube wells at Trnovče tap the alluvium of the Velika Morava River. Special attention is devoted to analyses of trace metals in encrustations (As, Pb, Ni, Zn, Cd, and Co).

Encrustations have the ability to affect mobility and trace metal availability, mostly due to the sorbability of trace metals to the surface of Fe-(oxy)hydroxides (Cornell and Schwertmann 2003, Houben and Treskatis 2007). Fe-(oxy)hydroxides are able to sorb both ions and cations. Apart from anions, iron Fe-(oxy)hydroxides have a affinity for sorption of trace metals: Al, Ni, Zn, and Co (Houben 2003, Houben and Treskatis, 2007, Lynch et al. 2014), whereas those that in addition to iron have significant proportions of Mn-oxides, due to the formation of tunnel structures, exhibit a better affinity for retaining large-radius cations (Pb and Ba) (Houben 2003, Houben and Treskatis, 2007). The sorption capacity of recent, fresh Fe- (oxy)hydroxide encrustations is ten times greater than that of hardened recrystallized iron encrustations (Shuman 1977 in Lynch et al. 2014). Meta-stable iron-sulfide minerals (e.g. amorphous FeS, mackinawite $FeS_{0,9}$, greigite Fe_3S_4) are also highly reactive. Trace metals (Pb, Zn, Co) can be adsorbed or deposited along with iron-monosulfides (Billon et al 2001). Apart from reducing well discharge capacity, well incrustation can affect the quality of the water withdrawn from the well.

MATERIAL AND METHODS

Encrustations from the radial well laterals at Belgrade groundwater source were sampled by specially-trained divers, who removed the encrustations from the inside of the laterals. At Trnovče groundwater source, encrustations were sampled from tube wells during the course of mechanical regeneration, prior to applying chemicals. The samples were placed in sterile jars and immediately refrigerated to prevent oxidation. To maintain the phase ratios, the samples were dried at room temperature. For analytical purposes, the samples were ground into powder in an agate mortar. Semi-quantitative chemical analyses of the encrustations were performed applying the SEM-EDS technique (SEM model JEOL JSM – 6610LV). The powdered samples were sputter-coated with 24-carat gold. The limit of detection for the semi-quantitative chemical analyses was 0.1wt. %. The main shortfall of this method was the high spectrum baseline, which rendered the determination of micro-components in the sample rather difficult. The same instrument was used for imaging. X-ray powder diffraction (XRPD) analyses of the selected samples were conducted using a Philips PW-1710 automated diffractometer (equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter), including a Cu-tube operated at 40 kV and 30 mA. Data were collected in the 2σ-range between 4 and 80°, with a counting time of 0.25 s per step and a step size of 0.02° 2 σ. A fixed 2° divergence and 0.2 mm receiving slits were used. Trace metals were determined using ICP–OES. Prior to analysis, samples were digested using EPA method 3051, as the sample preparation method. After digestion, trace metals were analyzed applying the ICP-OES (EPA 6010 C) method.

A total of 23 encrustation samples were analyzed, of which six came from tube wells at the left bank of the Velika Morava River near the Trnovče village that tap a mixed oxic-anoxic medium (Majkić-Dursun et al 2015a) and 17 were collected from radial wells that capture groundwater from a largely anoxic medium (Majkić-Dursun et al 2016). Those radial wells are located in the Sava River alluvial (2 radial – wells chosen from Sector Ušće – Novi Beograd, 3 wells from Sector Ada Ciganlija, 3 from Makiško polje, 5 radial wells from Sector Progar-Boljevci, and 4 from Sector Surčin-Donje Polje). The samples from radial wells of Belgrade groundwater source, Rb-79, Rb-88, Rb-69 and Rb-83 (all from Sector Progar-Boljevci), because of a specific feature that requires detailed analysis of mineral origin, were excluded from the trace metal concentration analysis.

RESULTS AND DISCUSSION

The encrustations removed from wells that tap the mixed oxic-anoxic medium of the alluvial sediments of the Velika Morava River (Trnovče groundwater source) were found to contain, in addition to iron, a considerable percentage of manganese (Majkić-Dursun et al 2015b). These recent “amorphous” poorly-crystalline encrustations were assigned to Group 1 (Fe&Mn (oxy)hydroxides). Largely iron oxides and hydroxides of different levels of crystallinity become incrusted in anoxic to mildly oxic-anoxic environments, where groundwater carries substantial amounts of bivalent iron and no sulfate reduction occurs. Their “hardness” mostly depends on the residence time in the well screens, as well as on the presence of inhibitors (e.g. phosphate concentration). In the present research such encrustations were assigned to Group 2 (older, more crystalline iron encrustations such as goethite). Encrustations are almost never monomineralic. In S-rich environments characterized by anoxic conditions, the most frequently occurring were iron sulfides (metastable greigite), and among iron minerals goethite. Encrustations that contained iron sulfides, along with goethite, were assigned to Group 3. Samples collected from sanded and corroded wells exhibited a significant SiO_2 content (SiO_2 66.53 compound % in radial well Rb-14-1) and were allocated to Group 4. Goethite was detected in the sanded wells, where SiO2 that originated from the gravel pack or the alluvial medium itself had the largest share.

Trace element concentrations in the groundwater of the sandy-gravel alluvial sediments of the Velika Morava (Trnovče groundwater source) and the Sava (Belgrade groundwater source) were found to be low. Depending on initial concentrations, as well as the ability of incrusted minerals to sorb anions and cations, their ultimate concentrations in well encrustations can be elevated. The results of this research show that anions (e.g. AsO_4^{3-}) sorbed very well to low-to-medium crystallinity encrustations (ferrihydrite and goethite). At Trnovče, for example, the concentration of arsenic in the encrustations ranged from 0.607 to 1.55 g/kg (Group 1), whereas the concentrations in Group 3 encrustations were from 0.033 to 0.85 g/kg. Given that As does not sorb to SiO_2, the total As concentrations in the encrustations that contained a significant proportion of sand were even lower, from 0.025 to 0.26 g/kg. In view of the fact that the pH levels of the groundwater withdrawn from the two groundwater sources was close to neutral (pH ≈ 7), the results are consistent with those reported in the literature and corroborate that in neutral conditions Fe (oxy)hydroxides sorb more anions (AsO_4^{3-}) than cations. The concentrations of cations in the samples of well encrustations are shown in Fig. 1. Cobalt concentrations were found to be the highest in S-rich encrustations from wells at Belgrade groundwater source, as opposed to predominantly Fe encrustations (Group 2).These results are consistent with the claim that iron sulfides can accommodate considerable amounts of trace metals in their crystal lattice, where the sorption affinity order is Co>Ni>Hg>As>Pb>Zn (Belzilile and Leber 1986 in Houben and Treskatis 2007).

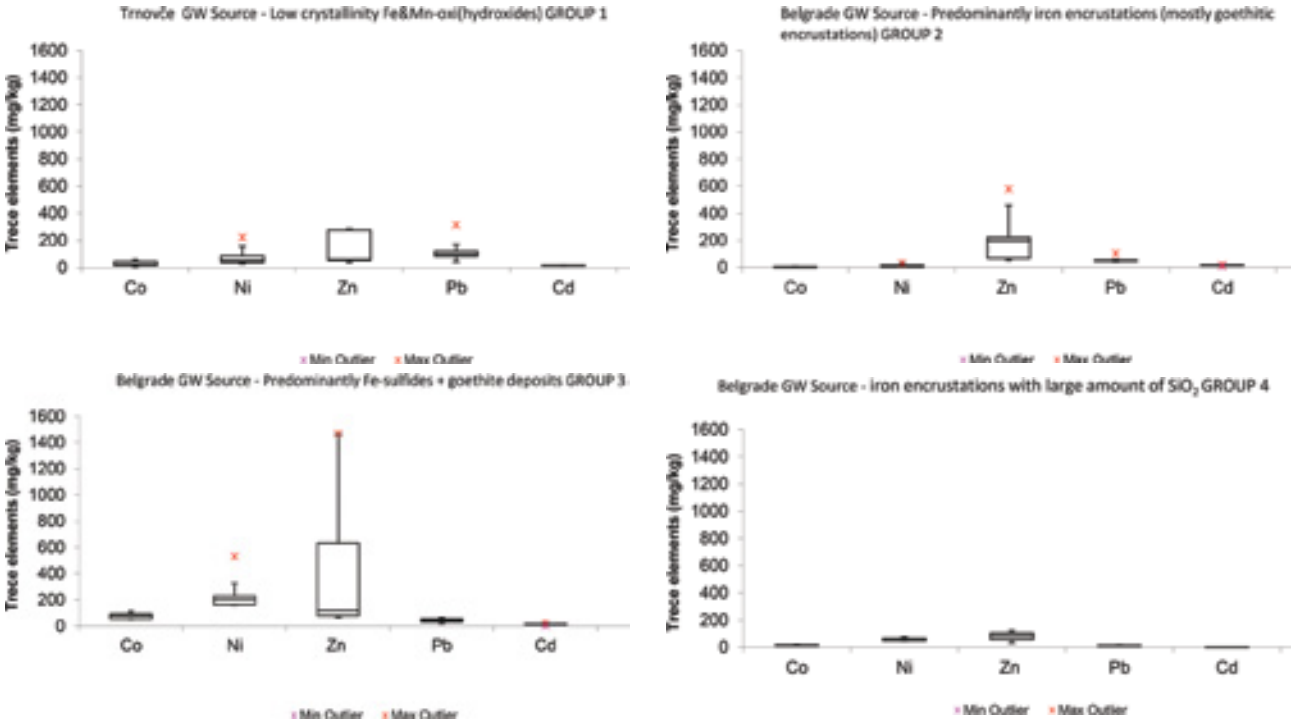

Figure 1: Concentrations of trace elements (mg/kg) in encrustations at Trnovče groundwater source and Belgrade groundwater source

According to the analyses of the encrustations sampled at Belgrade groundwater source, iron sulfide encrustations (Group 3) exhibited considerably higher concentrations of Ni (average 0.258 g/kg) than Group 2 Fe encrustations (average 0.0143 g/kg), which is attributable to a higher sorption affinity of Ni to iron sulfides. Ni concentrations in recent poorly-crystalline encrustations from Trnovče (Group 1) were about 0.050 g/kg on average, except in those sampled from well Bnz-1 where it was found to be 0.223 g/kg and requires further analysis. Pb concentrations were the highest in poorly-crystalline Fe and Mn (oxy)hydroxide encrustations from Trnovče (Group 1). With regard to these samples, a significant correlation was established between Mn and Pb concentrations (r^2= 0.877), and between Fe and Pb (r^2=0.718). Lead concentrations in Group 3 encrustations were from 0.018 to 0.064 g/kg, and in Group 2 encrustations from 0.044 to 0.103 g/kg. Zn concentrations were the highest in Fe sulfide encrustations, attributable to the fact that it is a chalcophile element. Cd concentrations were found to be low (average about 0.015 g/kg) and uniform in the first three groups of encrustations, and extremely low (close to the limit of detection, LLD) in Group 4. Figure 4 shows that the concentrations of sorbed trace elements were generally the lowest in Group 4 encrustations.

CONCLUSION

The results of mineral and semi-quantitative chemical analyses indicated four main types of iron encrustations, with varying degrees of crystallinity and manganese/sulfide content. Group 1 encrustations (low-crystallinity iron and manganese encrustations) was typical of mixed oxic-anoxic environments, whereas anoxic settings featured older more crystalline form such as goethite encrustations (Group 2), and Group 3 iron-sulfide encrustations dominated by metastable greigite, along with goethite. Samples collected from sanded and corroded wells exhibited a significant SiO_2 content (Group 4). Iron encrustations were found to have a high affinity for sorption of trace elements. The concentrations of sorbed arsenate (AsO_4^{3-}) in some of the encrustations were considerable; the highest concentrations were detected in samples of iron encrustations (Group 2). The amount of sorbed metals depended on several factors (iron concentration, degree of crystallinity, proportion of manganese minerals able to form tunnel structures, previously sorbed trace elements, sorption affinities, and initial concentration of trace metals in groundwater). The origin of trace metals should be analyzed in future research.

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SORPTION BEHAVIOR OF SELECTED PESTICIDES IN ALLUVIAL AQUIFERS

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Abstract: There are approximately 1000 registered products for plant protection with over 300 different active ingredients in Serbia. Due to their extensive use in agriculture, they may be detected in all environmental mediums. Therefore, they're monitored in air, water and soil, but also in food and tissues. Concentrations of 15 pesticides in surface and groundwaters in Serbia have been monitored from the year 2009 to 2014, in sampling campaigns conducted by the Jaroslav Černi Institute for the Development of Water Resources. The results showed that the selected pesticides were detected in almost 34% of surface water samples, and in 33% of groundwater samples. All of the detected pesticides had very low concentrations in both surface and groundwater samples (lower than 0.1 µg/L), with a few exceptions. The most frequently detected pesticides were carbendazim and atrazine. These two pesticides have been selected for further analyses of sorption behavior in the sediment, with one additional pesticide for these experiments: carbofuran. In this paper, sorption coefficients for Danube sediment samples collected in Kovin-Dubovac area were analyzed. Sorption coefficient in these samples was highest for carbofuran, and lowest for atrazine. Lack of information on organic matter content and pH of the sediment used in sorption experiments lead to the further research of sorption behavior dependence on various factors of the three selected pesticides in literature data. Regression analysis with a large number of literature data was carried out, with regression equations as results. These results were compared to the ones gained in sorption experiments.

Keywords: pesticides, sorption coefficient, multiple regression analysis

INTRODUCTION

The consequence of growing agricultural production is the increased use of pesticides for plant protection, which leads to the potential contamination of soils, sediments and water resources. The behavior of a pesticide in the environment depends on its structure and physicochemical properties. Other important aspects affecting pesticides' environmental fate are the form, intensity and frequency of application (Meiwirth, 2003). Characteristics of a region, such as climate, geology, morphology and hydrology also have an important impact on the fate of these chemicals.

The research of sorption behavior of a pesticide is of great importance, due to its effect on other processes determining their fate in the environment, such as transport, degradation, volatilization and bioaccumulation (Gao et al., 1998; Krishna and Philip, 2008). Pesticides that are not effectively retained in the soil by sorption processes may reach the groundwater. Shallow groundwater tables are especially vulnerable for pesticide contamination (Meiwirth, 2003). Pesticide sorption processes greatly depend on the soil's organic matter, particle-size characteristics, but also pH values of the soil (Gao et al., 1998; Krishna and Philip, 2008; Meiwirth, 2003, Weber et al., 2004).

Several surface and groundwater sampling campaigns were performed from the year 2009 to 2014, by the Jaroslav Černi Institute for the Development of Water Resources. The samples were collected from Danube, Sava, Tisa and Great Morava and corresponding wells and piezometers. Total of 188 samples (74 surface

water samples and 114 groundwater samples) were analyzed in the laboratory at the Faculty of Technology and Metallurgy in Belgrade. Out of 15 targeted pesticides, only 6 of them were detected, including one that was detected in only two samples, with concentrations under the limit of quantification. The most frequently detected pesticide was carbendazim, which was detected in more than 29% of the surface water samples, and more than 16% of the groundwater samples. The second most frequently detected pesticide was atrazine, that was banned several years ago, but can still be detected because of its persistent nature. It is important to emphasize that the detected pesticides had very low concentrations, below 0.1 µg/L, with a few exceptions in Morava river samples, when concentrations were 0.165 µg/L (atrazine, May 2010) and 0.269 µg/L (carbendazim, June 2011).

The main focus of this paper is the sorption behavior of the two most frequently detected pesticides: atrazine and carbendazim. The sorption experiment of these two pesticides has been conducted on the alluvial sediment of the Danube river, in the Kovin-Dubovac area. The reason for choosing this area is the fact that it has a lot of agricultural fields. Also, during the sampling campaigns, 46 both surface and groundwater samples were collected from this area with very low concentrations of selected pesticides. It is possible that these low concentrations are a consequence of sorption processes on aquifer materials. The sorption experiment was also performed for carbofuran, even though it was detected in only a few samples. This pesticide was chosen, due to its rare detection and also the fact that the detected concentrations were very low, which can be a result of sorption processes.

Due to the fact that information on the soil properties responsible for sorption of pesticides are not available for the selected sediment, except the particle-size (from 63 µm to 1 mm in diameter), some further analyses have been conducted. In this paper, multiple linear regression of sorption coefficients has been performed, using the literature data to set correlation to pH, texture and organic matter content.

MATERIALS AND METHOD

Sorption Experiments

Adsorption experiments for the three selected pesticides were conducted at the Faculty of Technology and Metallurgy in Belgrade. In this paper, the experiment was carried out for the sediment material collected from the Danube river, for the particles with 63µm to 1mm in diameter. This particle-size is specific for sand particles. This is highly important, because the results of the adsorption isotherms on these particles will give a good perspective on the sorption behavior of selected pesticides in the alluvial aquifer sand.

Adsorption experiments were performed using the previously optimized 1 g: 20 ml rate of sediment mass and water solution volume, and the optimal time for the sediment/solution contact was 24h. Sediment samples were dried prior to adsorption experiments at a room temperature, in the dark. Specific volume of the standard pesticide solution was added to 1 g of sediment mass, and then the deionized water was added to the volume of 20 ml, so the solution concentrations in contact with the sediment were 10, 25, 50, 75, 100, 250 and 500 ng/mL. After the addition of soil samples, the reaction mixtures were agitated in a shaker at 300 rpm for 24 h, and then centrifuged for 10 minutes at 4000 rpm. The solution was decanted, and the pH value of the solution was adjusted to the optimal value for determination of selected pesticides (pH=6). Simultanously with the samples, for every value on the adsorption isotherm, the specific standard was prepared, and for every sediment sample, a blank probe was conducted. Decanted solution was extracted on Oasis HLB cartridges. Cartridges were preconditioned with 5 mL of methanol-dichloromethane (1:1) mixture and 5 mL of deionized water. Eluate was evaporated in a stream of nitrogen in a water bath at 25˚C. Sample, standard and blank were reconstructed with 1 mL of methanol and analyzed using an optimized and validated method on HPLC-MS2 for these pesticides (Dujaković et al., 2010).

The sorption of pesticides is most frequently described using linear, Langmuir or Freundlich isotherms for equilibrium (Dimkić et al., 2008; Köhne et al., 2009; Weber et al., 1991). The linear sorption isotherm is based on the following equation (equation 1):

$$A = K_d \cdot C_e \tag{1}$$

Where A is the amount of pesticide sorbed at equilibrium, ng/g; K_d is the linear sorption coefficient, mL/g; C_e is the equilibrium solute concentration, ng/mL.

The Langmuir sorption isotherm is described using an equation with two parameters (equation 2):

$$A = A_{max} \frac{b \cdot C_e}{1 + b \cdot C_e} \tag{2}$$

Where A_{max} is the maximum sorption capacity at the given conditions, ng/g; b is the Langmuir constant related to energy of adsorption, mL/ng.

The Freundlich sorption isotherm is dependent on the two parameters expressed in the equation (3):

$$A = K_f \cdot C_e^{1/n} \quad (3)$$

Where K_f is the Freundlich isotherm constant and n is the Freundlich exponent.

Multiple Regression Analysis

Multiple regression analysis is a valuable tool for predicting an unknown value of a variable from the known value of two or more variables. In this paper, multiple regression analysis was performed for predicting the linear sorption coefficient from the main characteristics of solid materials that have an influence on sorption behavior of pesticides: pH, solid material texture and organic matter content. Literature data for linear sorption coefficient of atrazine, carbendazim and carbofuran were used, choosing only those values where data on previously mentioned parameters of soil were available.

RESULTS AND DISCUSSION

The results obtained in sorption experiments showed high affinity of pesticide carbofuran for sediment particles, resulting in high concentrations of this pesticide on solid material at equilibrium. Atrazine and carbendazim showed very low affinity for the sediment used in the experiments.

Linear, Langmuir and Freundlich equations were used for describing the sorption behavior of atrazine, carbendazim and carbofuran on the 63 µm to 1 mm particle-size Danube sediment,. The most accurate prediction for all three pesticides had the Langmuir model, with coefficient of determination, R^2, around 0,9. The least accurate was the linear sorption model. Better predictions for all three types of isotherms are possible if the values observed are results of sorption equilibrium for initial concentration of these pesticides in the solution under 250 ng/mL (100 ng/mL for carbendazim) (Table 1). The best equilibrium sorption isotherms are for carbofuran, with coefficient of determination higher than 0.98, which means that all of the presented equation coefficients can be used in modeling of the pesticide transport in alluvial aquifer, containing 63 µm to 1 mm particles.

Multiple linear regression was performed for linear sorption coefficient, due to the fact that models commonly use this type of equation for predicting transport and determining the fate of pesticides in the environment (Köhne et al., 2009). Correlation between soil properties (pH, texture and organic matter content) and linear sorption coefficient was analyzed. Regression analysis for carbendazim showed no significant dependence of linear sorption coefficient on pH, organic matter content or soil texture. Multiple linear regression for atrazine showed dependence of linear sorption coefficient on organic matter content, pH and clay content, which is in agreement with the literature results reported by Weber et al. (2004). Coefficient of multiple correlation was 0.85, but the p-values were higher than 0.05 for pH and clay content, so the regression equation is not presented in this paper.

Pesticide	Type of sorption isotherm	Sorption isotherm parameters	R^2
Atrazine	Linear	$K_d = 0.3941$ mL/g	0.9394
	Langmuir	$A_{max} = 372.97$ ng/g $b = 0.001343$ mL/ng	0.9544
	Freundlich	$K_f = 0.7651$ (ng/g)(mL/g)$^{1/n}$ $1/n = 0.8729$	0.9509
Carbendazim	Linear	$K_d = 2.226$ mL/g	0.9281
	Langmuir	$A_{max} = 653.39$ ng/g $b = 0.002712$ mL/ng	0.9606
	Freundlich	$K_f = 0.6964$ (ng/g)(mL/g)$^{1/n}$ $1/n = 1.272$	0.9512
Carbofuran	Linear	$K_d = 15.68$ mL/g	0.9847
	Langmuir	$A_{max} = 21971.54$ ng/g $b = 0.0007801$ mL/ng	0.9866
	Freundlich	$K_f = 19.09$ (ng/g)(mL/g)$^{1/n}$ $1/n = 0.958$	0.9858

Table 1. Sorption isotherm parameters and R^2 values for atrazine, carbendazim and carbofuran for initial concentrations in the solution lower than 250 ng/mL (100 ng/mL for carbendazim).

Multiple linear regression performed for carbofuran showed that the linear sorption coefficient is dependent on pH and organic matter content. Regression equation for carbofuran, calculated using the literature data (Hsieh and Kao, 1998; Liyanage et al., 2006; Yazgan et al., 2005) (equation 4):

$$K_d = 0.4611 \cdot (pH) + 0.2529 \cdot (\%OM) - 2.7029 \pm 0.7448 \quad (4)$$

Coefficient of multiple correlation is 0.73, p-values are lower than 0.0001 for all parameters in the equation. The resulting equation cannot be compared with the result gained in the sorption experiments on the Danube river sediment, because there is no information about these parameters for the sampled sediment. Due to these results, it is important to continue the research on sorption behavior of carbofuran and to include the analysis of these parameters in the experiments.

CONCLUSIONS

The sorption experiment presented in this paper showed that among the three selected pesticides, carbofuran has the highest affinity for the sediment used in this study. This conclusion is significant, because it explains the results of surface and groundwater monitoring studies, more precisely, why carbofuran was detected to a lesser extent than carbendazim and atrazine. The other important conclusion is that sorption behavior of atrazine, carbendazim and carbofuran on Danube river sediment can be predicted with linear, Langmuir and also Freundlich sorption isotherm, with determination coefficients close to 1, when initial concentrations of these analytes are below 250 ng/mL (lower than 100 ng/mL for carbendazim). Multiple linear regression analysis showed that the sorption behavior of atrazine and carbofuran are influenced by the pH and organic matter content of the solid material. The linear sorption coefficient of atrazine was also dependent on clay content. The multiple linear regression analysis of linear sorption coefficient for carbendazim could not be calculated only using the pH value, organic matter content and the texture of the solid material. Further research is acquired to establish the parameters on which this sorption coefficient is dependent on. The sorption behavior of these pesticides has to be researched even further. It would be significant to discover what sorption mechanisms are the most important for retaining these pesticides in soil and prevailing them from entering the groundwater and other environmental compartments.

ACKNOWLEDGEMENT

This research was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, under the Project No. TR 37014.

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THE SANITÀ (CAPOSELE) SPRING: A FUNDAMENTAL WATER RESOURCE OF SOUTHERN ITALY

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The Sanità spring is located on the north side of Picentini Mountains, 417 m a.s.l., inside the Caposele village, Campania region, and constitutes the beginning of the Sele river which flows into the Tyrrhenian sea.

The spring was tapped during the beginning of the last century to supply the Puglia region, and one of the most important aqueduct system of Europe was constructed: the "Pugliese Aqueduct". The first part is a tunnel 17 km long, crossing the water divide between Tyrrhenian and Adriatic seas; only by gravitational movement, water reaches localities up to 400 km far from the spring. Spring water reached for the first time the town of Bari in 1920, and the Salento area few years later. After the last great war, further water recourses have been used to satisfy the increasing water demand of Puglia region; in particular, other springs of Picentini Mountains are added to the aqueduct channel.

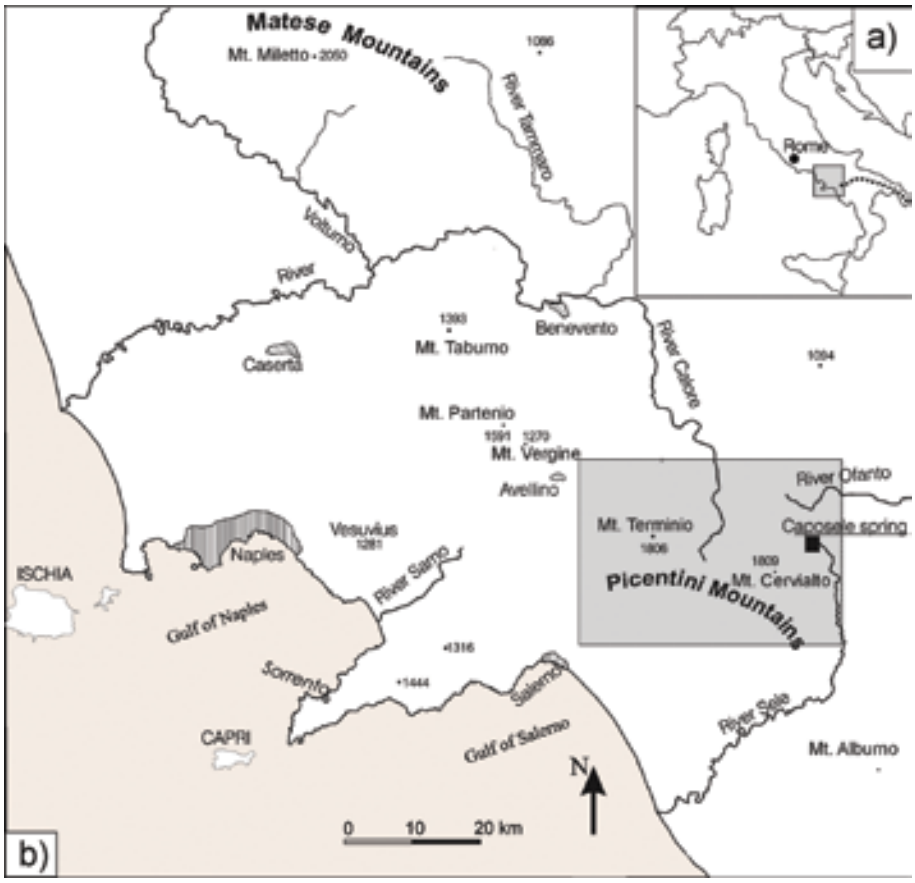

Figure 1: a) Italian peninsula, zone detailed in b) and main channel of the Pugliese Aqueduct (dotted line). b) Map of the western Campania region; rectangular area is detailed in Figure 2.

The Caposele spring catchment is estimated to be 110 km^2, with ground elevation up to 1800 m a.s.l.; it is constituted by calcareous and dolomite sequences of Mesozoic age, bounded by argillaceous sequences of Oligocene age (Figure 2). No man-made modifications or groundwater pmping occurred in the catchment, so that the Caposele spring has a strictly control by the climate.

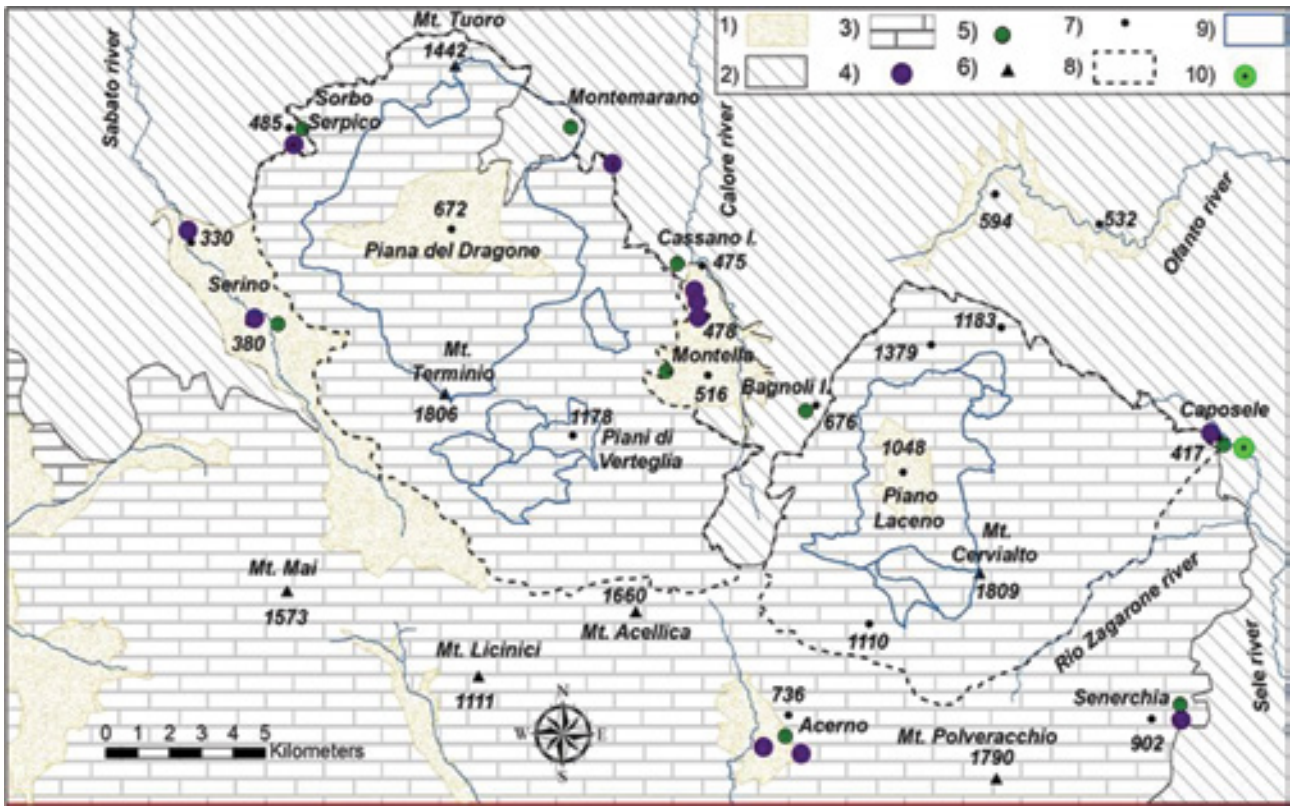

Figure 2: Hydrogeological sketch of north-eastern sector of Picentini mountains (Fiorillo et al., 2015). 1) Slope breccias and debris, pyroclastic, alluvial and lacustrine deposits (Quaternary); 2) argillaceous complex and flysch sequences (Paleogene–Miocene); 3) calcareous-dolomite series (Jurassic–Miocene); 4) main karst spring; 5) village; 6) mountain peak; 7) elevation (m a.s.l.); 8) Cervialto and Terminio groundwater catchment; 9) endorheic area; 10) Caposele river gauge

Systematic spring discharge measurement exist since 1920, and allow to investigate on the long-term behaviour of this spring. The annual mean discharge of Caposele spring is about 4 m^3/sec, and the regime is characterised by absence of peaks in the hydrographs; the flood period occurs in spring-summer time, and the minimum during the autumn-winter time. Thus, the regime is almost opposite of that of rainfall.

The relationship between spring discharge and climate regime has been analysed, providing useful results of aquifer behaviour during droughts. Insufficient recharge due to poor annual rainfall results in flat spring hydrographs (without flood) that indicate a continuously decreasing discharge for the entire hydrological year. Flat spring hydrographs reveal a drought, which is characterised by a prolonged shortage of water that induces a reduction in discharge during the following year as well in this spring (Figure 3).

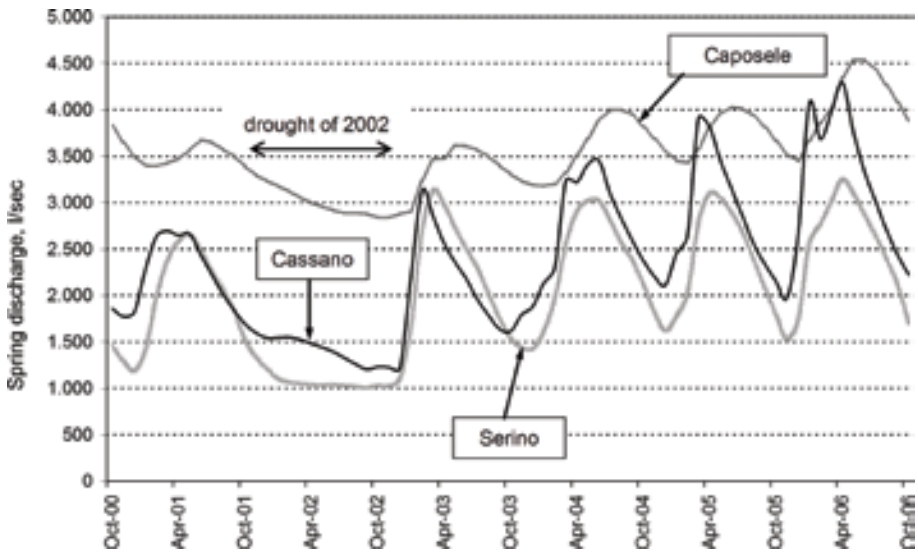

Figure 3: Spring discharges for the period of October 2000 to October 2006. Caposele and Cassano spring hydrographs show the memory effect of the 2002 drought, which is not recorded in the Serino springs (Fiorillo, 2009).

Droughts also appear to be induced by consecutive years with lower than average rainfall. The historical data have shown that each hydrological year depends strongly on the previous

year because the "memory effect" of aquifer. Due to a long historical series and the specific karst spring regime, a flat hydrograph can be forecast as early as winter, thereby providing a useful tool for water management (Fiorillo, 2009).

The recharge processes have been evaluated for the spring catchment, which is characterized by wide endorheic areas. After the estimation of the recharge coefficient (ratio between the output spring and input rainfall), the annual recharge has been used to calibrate a daily scale model, which allows to estimate the amount of effective rainfall, which is retained as soil moisture, the amount reaching the water table (recharge s.s.), and the amount of rainfall, which develops the runoff and leaves the catchment (Figure 4).

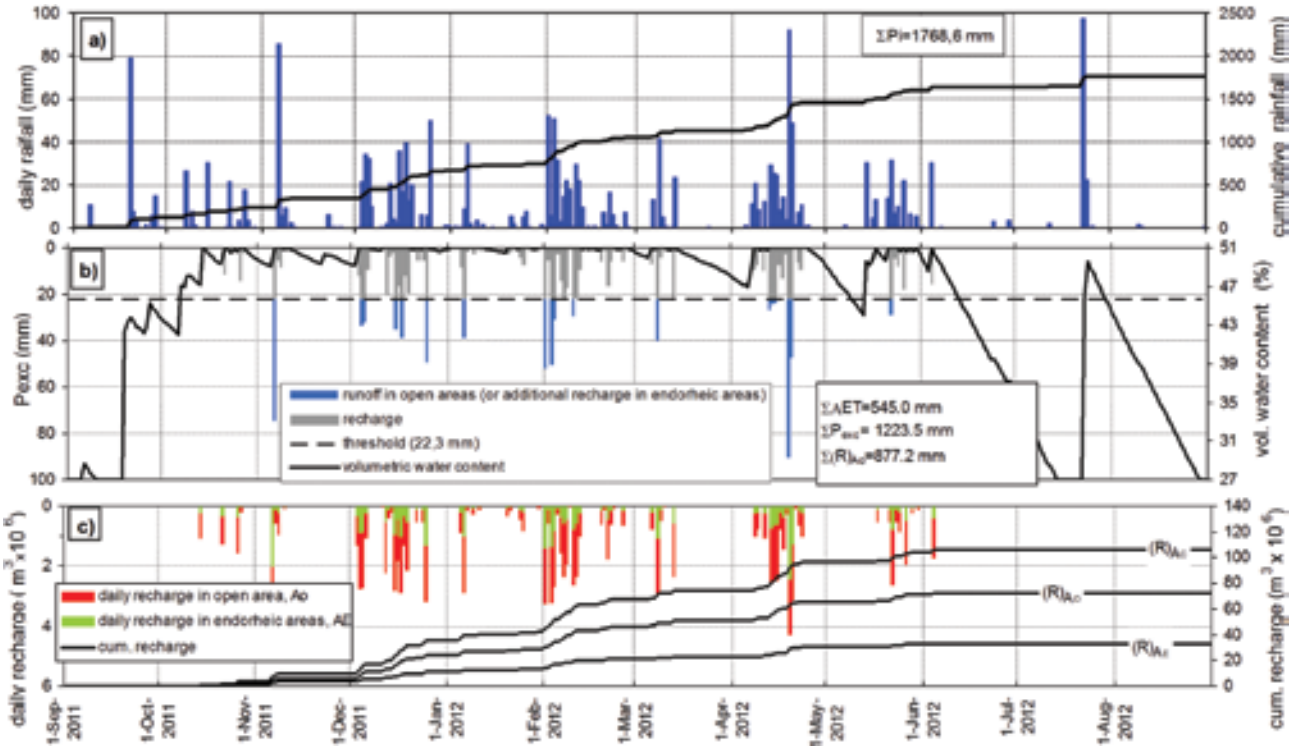

Figure 4: Hydrological characteristics of the 2011–2012 hydrological year, Laceno rain gauge, 1170 m a.s.l. (modified from Fiorillo et al. 2015). a) Daily and cumulative rainfall; b) volumetric water content, Θ, computed from daily hydrological balance (Θmin = 27% and Θmax = 51%) and daily recharge and runoff (histogram); c) daily and cumulative recharge expressed in volume for Caposele spring catchment.

An anomalous behaviour was observed during the Irpinia earthquake of 23 November 1980 (Ms = 6.9); this earthquake caused an anomalous increase in the spring discharge, with maximum values of 7.32 m^3/s on 19 January 1981, and the hydraulic behaviour is still a controversial issue (Fiorillo 2015).

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NOTES

THE UPWELLING WATER FLUX WHICH FEEDS KARST SPRINGS: EXAMPLES FROM SOUTHERN ITALY

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The drainage system of some karst springs has been investigated thank to long term discharge and piezometer measurements. Data come from Serino springs located along the Sabato valley, locally a deep tectonic depression with N-S trend, located in Campania, Southern Italy. The depression is filled by alluvial and pyroclastic materials of Quaternary, argillaceous sequences of Miocene as well, covering a karst substratum located at more than 100 m depth (Figure 1).

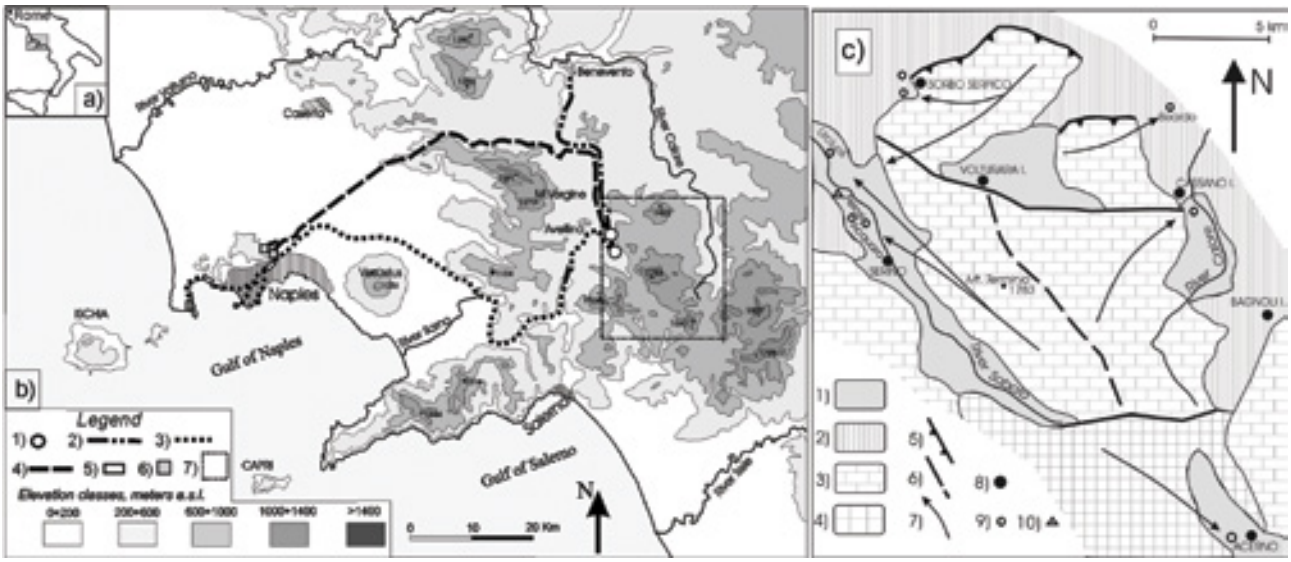

Figure 1: (a) Plan of the Southern Italian peninsula. (b) Plan of the western Campania region. 1) Serino springs; 2) remains of Sannitico aqueducts (Roman, 1st century AD); 3) remains of Claudio aqueducts (Roman, 1st century AD); 4) actual aqueducts; 5) Roman reservoir; 6) actual reservoir, 7) area of C); (C) Hydrogeological plan of the Terminio massif (modified from Celico, 1978). 1) Slope breccias and debris, pyroclastic, alluvial and lacustrine deposits (Quaternary); 2) argillaceous complex and Flysch sequences (Paleogene–Miocene); 3) limestone complex (Jurassic–Miocene); 4) dolomite complex (Triassic–Jurassic); 5) reverse fault; 6) normal fault (probable, if dashed); 7) groundwater flow direction; 8) village; 9) main spring; 10) Serino rain gauge (from Fiorillo et al., 2007).

The Serino springs are distinguished in two main groups: Urciuoli and Acquaro-Pelosi springs.The first group is formed by a single outlet zone, with mean discharge of 1120 l/sec; the second group is formed by two main spring zone, with a mean of 800 l/sec. Considering the local climate conditions, the hydraulic connection between Serino springs and the Terminio massif (a karst area located on the East of Sabato valley, involving wide endorheic areas) has to be assumed, as water volume discharged by springs needs a wide catchment (>50 km^2). This connection would occur by the karst substratum of the Sabato valley, a complex geological structure, joined with Terminio karst system.

The hydraulic head measured in several piezometers of Sabato valley (Figure 2) show that the piezometric level in the alluvial deposits depends on the depth of the well (up to 100 m below the ground level), indicating an increase of the hydraulic head with depth (Figure 3). These characteristics highlight the general upwelling of the water flux in the deposits of the Sabato valley, and has been detailed described. In particular, the hydraulic head varies during the hydrological year, its range is higher for deeper wells, and reverse hydraulic conditions occur during droughts.

This hydraulic mechanism appears common with several karst springs of southern Italy, where spring outlets come from "isolated" carbonates blocks, hydrogeologically joined with wide karst areas.

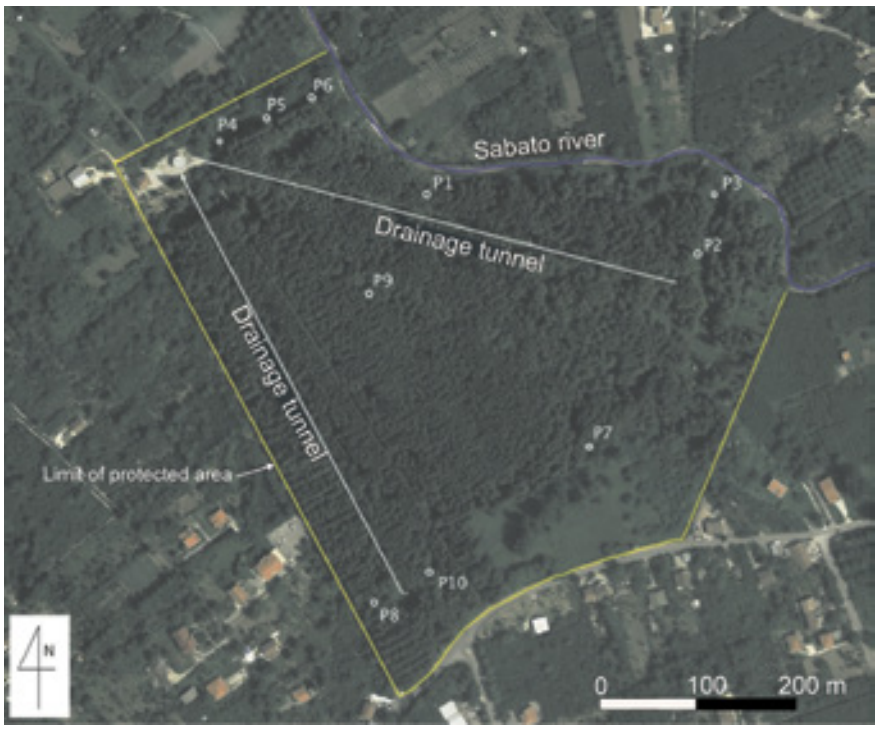

Figure 2: Piezometers location in the area of Acquaro and Pelosi spring drainage systems.

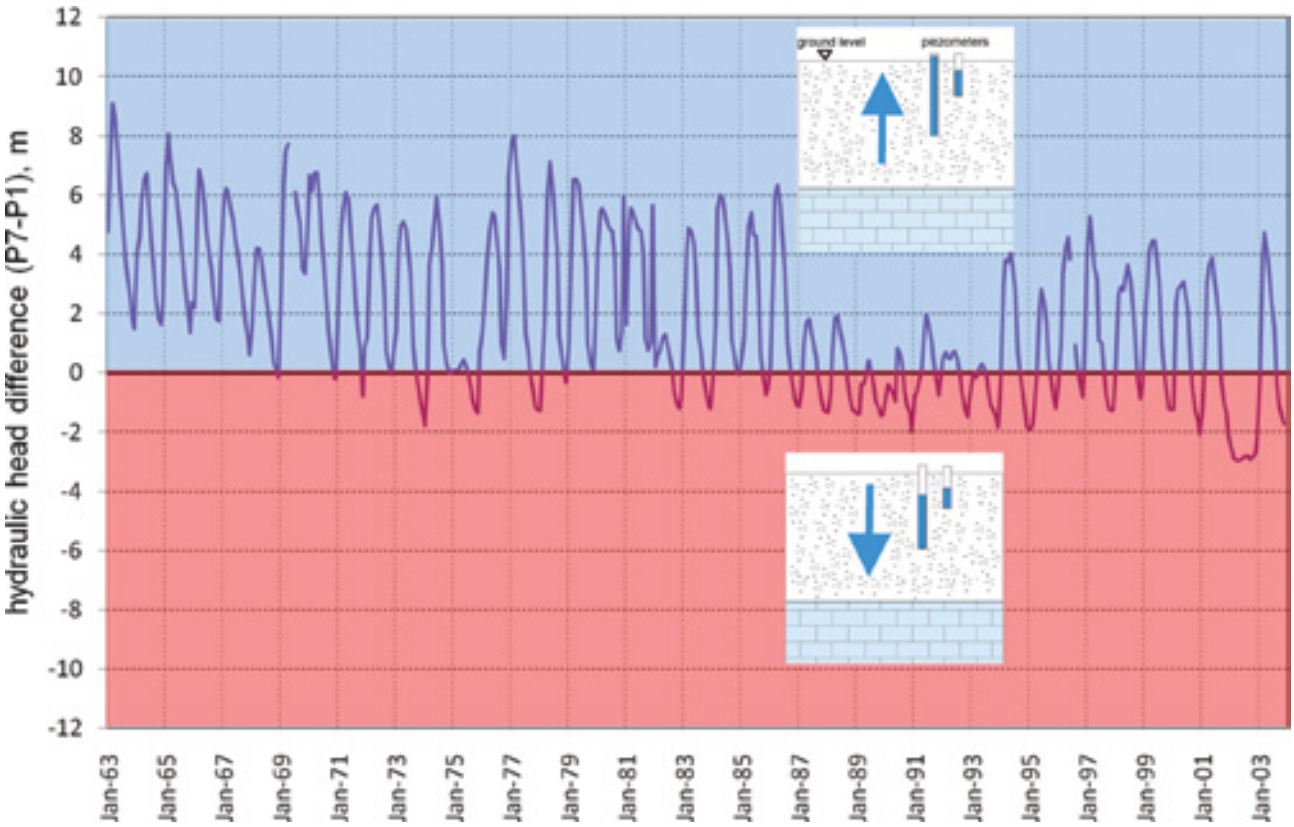

Figure 3: Hydraulic head difference between Piezometer P7 (93.40 m depth) and Piezometer P1 (51.20 m depth), located at similar ground level. Positive values indicate an upwelling flux; negative values indicates an downward water flux.

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THE ROLE AND IMPORTANCE OF HYDROGEOLOGY IN THE CREATION OF RIVER BASIN MANAGEMENT PLANS AT A REGIONAL SCALE

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Keywords: Hydrogeology, river basin management plan, water framework directive

EXTENDED ABSTRACT

During the last decades of the 20th century, along with a wide promotion of the term and concept of "sustainable development," an attempt has been made at many levels - international, national and local - to regulate the water management issues. Many conventions, protocols and agreements from that period emphasised the importance of sustainable and balanced exploitation of water resources. For the European countries, the Water Framework Directive (WFD) adopted by EU in 2000 was the most important. The aim of this Directive is to preserve, protect and improve the environment and the quality of water by also promoting reasonable and rational use of natural resources. To implement these goals, WFD prescribes the creation of Programmes of Measures and River Basin Management Plans (RBMP), which have to be prepared for larger and smaller river basins alike. In other words, international coordination between the states that share large river basins is necessary, as the case is with the Danube RBMP (coordinated by ICPDR, 2009) and the Sava RBMP (coordinated by ISRBC, 2013).

In case of groundwater an RBMP should estimate the current situation concerning the current exploitation of water resources, pressures on the groundwater quality and quantity, organisation of a monitoring network, as well as the necessary measures to maintain or remedy the current chemical status and the long-term sustainable use of water resources including measures of protection of dependent ecosystems and safe water management in protected areas, in particular.

Every RBMP includes a section pertaining to groundwater (WFD CIS, 2003, 2007). In the regional plans, such as those prepared for Danube and Sava, only transboundary groundwater bodies or groups of groundwater bodies have been recognised by concerning countries, to be delineated and analysed in general. As regards the next, more detail level, and the creation of RBMP for entire catchments and inner groundwater bodies, their characterization requires much more attention. After the definition of geometry of groundwater bodies, hydrogeological assessment of pressures on their quantity and quality is an essential step in defining the measures necessary to ensure their sustainable development (the optimal extraction rate, protection against pollution, operational or surveillance monitoring, etc.)

Delineation of aquifer catchment area should be the very first step in the hydrogeological analysis of groundwater bodies (Đurić et al. 2004). In the case of karst, these areas usually comprise autogenic and allogenic (attached) aquifer recharge zones. Some examples of delineated groundwater (GW) bodies are shown on Figures 1 and 2. These maps represent GW bodies or group of GW bodies that have been determined within RBMP of the Sava River in Bosnia and Herzegovina and the Danube RBMP in Serbia. Two different approaches of GW bodies' delineation can be seen on these examples. In other words, while the entire area of the Republic of Serbia has been covered by GW bodies (including those with almost impermeable rocks), in Bosnia and Herzegovina only those GW bodies containing a certain amount of water have been delineated. Further analytical steps include creation of conceptual models for each groundwater body. Groundwater budgeting is a best method for the assessment of groundwater reserves and availability, and - accordingly - pressure on groundwater quantity. Different methodological conceptions

should be applied to karstic and intergranular aquifers as, worldwide these two types represent most of the aquifers creating groundwater bodies. Such methodologies have recently been applied in DIKTAS (Stevanović et al. 2012a) and CCWaterS (Stevanović et al. 2012b) projects, as well as in the RBMP developed for the Sava basin in the territory of Bosnia and Herzegovina (Stevanović et al. 2015a).

The assessment of the aquifers' geometry, recharge, groundwater flow directions, discharge rate and water extraction rate is thus essential for any further analysis, the application of water management measures, and sustainable development. To develop a proper conceptual model several issues must to be evaluated for each of the delineated groundwater (GW) bodies:

- Permeability
- Recharge
- GW flow direction
- Drainage
- Hydrodynamic condition
- Relationship with surface waters
- Relationship with other aquifers
- Regime of GW
- GW quality

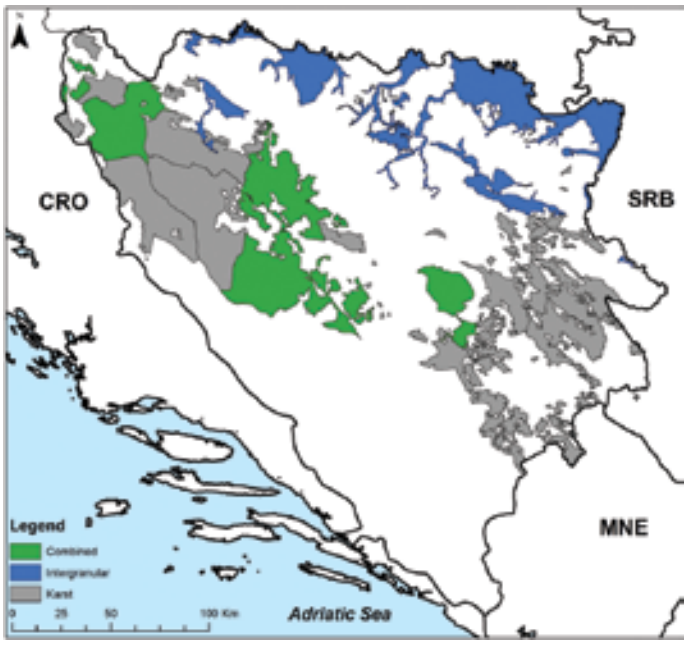

Figure 1: Delineated GW bodies in B&H (Stevanović et al. 2015a)

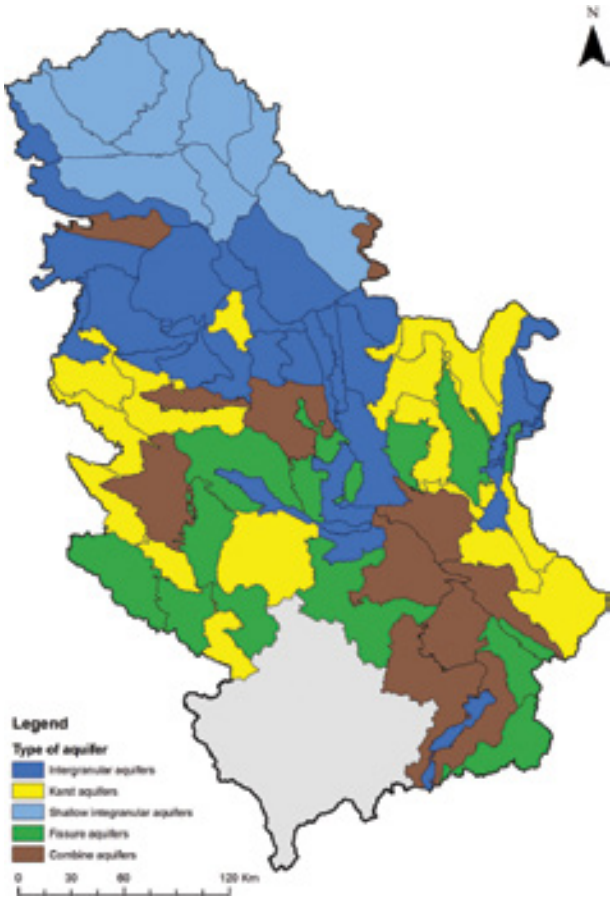

Figure 2: Delineated groups of GW bodies in Serbia (after Official Gazette (2011), modified by Stevanović et al. 2015b)

As stated above, one of the main goals of implementing RBMP, in general is to define the pressures on groundwater quantity and quality. The pressures on quantity are best estimated as a ratio of renewable GW reserves (available reserves) vs. the current extraction rate and demands of water-dependent eco systems (total demands). Different concepts may be applied to define the level of pressures, but the most common (WFD CIS, 2007) is the following: the use of less than 15% of available groundwater can be valued as "no pressure", between 15-30% as "potentially under pressure", and the use of over 30% of available water resources as "under pressure"(UK Techn. Adv. Group, 2005a,b). Such an approach was applied in the RBMP of the Sava River in Bosnia and Herzegovina (Fig. 3). In this document, the pressures on quantity have been determined as a ratio of renewable reserves vs. the current extraction reserves, where the use of less than 33% of available groundwater resources can be valued as "no pressure", between 33-66% as "potentially under pressure", and the use of over 66% of available water resources as "under pressure". Another concept was also applied, where the pressures of quantity were determined as a current exploitation vs. total amount of infiltrated water. According to this concept, the pressures of quantity can be determined as in WFD CIS (2007) "no pressure" if the groundwater extraction is less than 15% of infiltrated water, "potentially under pressure" if the percentage is between 15 and 30%, while the current extraction greater than 30% of infiltrated water classified a GW body as a "under pressure" one. However, the methods for groundwater reserves assessment cannot be based on improvisation, and the level of certainty (depending on data availability) should also be defined and presented in reports.

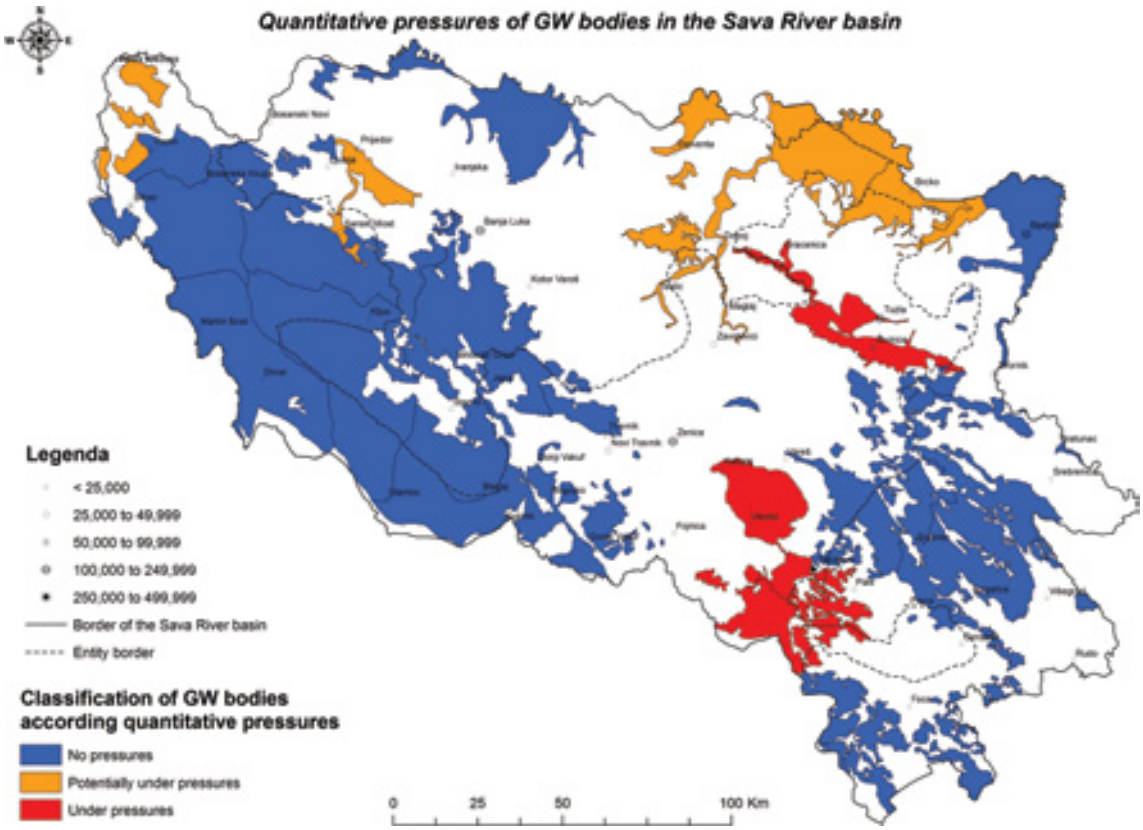

Figure 3: Quantitative pressures of groundwater bodies in the Sava river basin in Bosnia and Herzegovina (Stevanović et al. 2015a)

Along with groundwater chemistry (chemical status), the pressures on (ground) water quality must also consider the aquifer(s) vulnerability. Numerous methods based on GIS technology, as well as tools, have been developed in hydro-geological practice for the purpose of such an assessment (DRASTIC; EPIK; PI; COP, etc.). One of the very few that exist at the national level, but which is nevertheless successfully applied, is the "IZDAN" method (Milanović et al., 2010, Fig. 4), while the "SODA" method was developed recently and applied in the RBMP prepared for the Sava basin in the territory of Bosnia and Herzegovina (Stevanović et al. 2015).

In addition to vulnerability maps for the present aquifers (GW bodies), the hazard maps should also be created, based on punctual and diffuse pollutants. The latter could be developed at a regional level, based on CORINE land cover map (2006) already created for the entire territory of Europe (Fig. 5). Combination of the two inputs: vulnerability – hazard, results with Risk maps which may consider punctual or diffuse pollution risks. Finally, by introducing an adequate grading system of risks, the final maps will show the level of risk for each GW body, and in the cases of diffuse threats - the risk for every single pixel on the created map, analogue to the concerning land/aquifer surface. Considering above mentioned methodology, the pressures on groundwater quality can be assessed based on given vulnerability, hazard and/or risk maps. Such an example was used in the River basin management plan for the Sava River basin in Bosnia and Herzegovina, where two risk maps

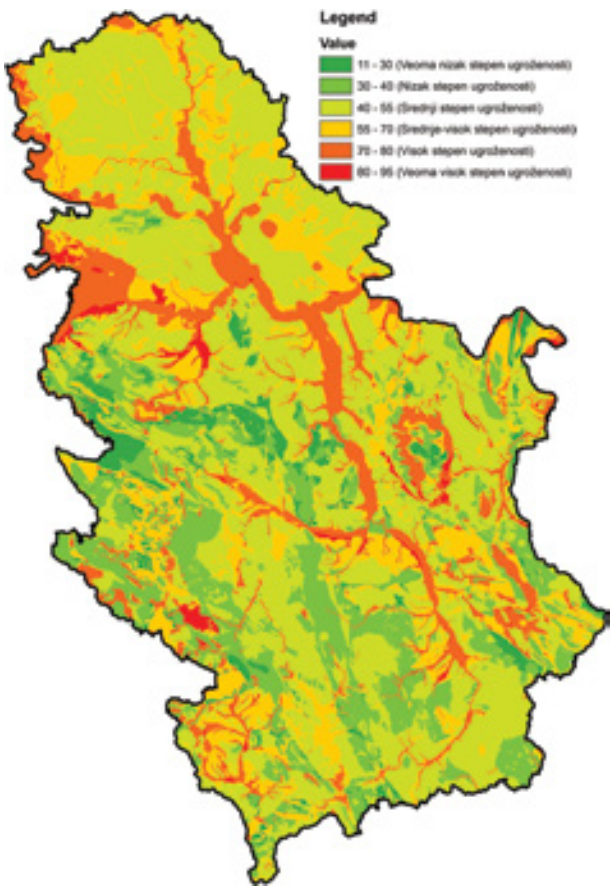

Figure 4: Aquifer Vulnerability Map for the Republic of Serbia (Milanović et al. 2010)

was created, based on punctual and diffuse pollutions. That means that each of groundwater bodies had two risk categories, while the worst category was used as a final one.

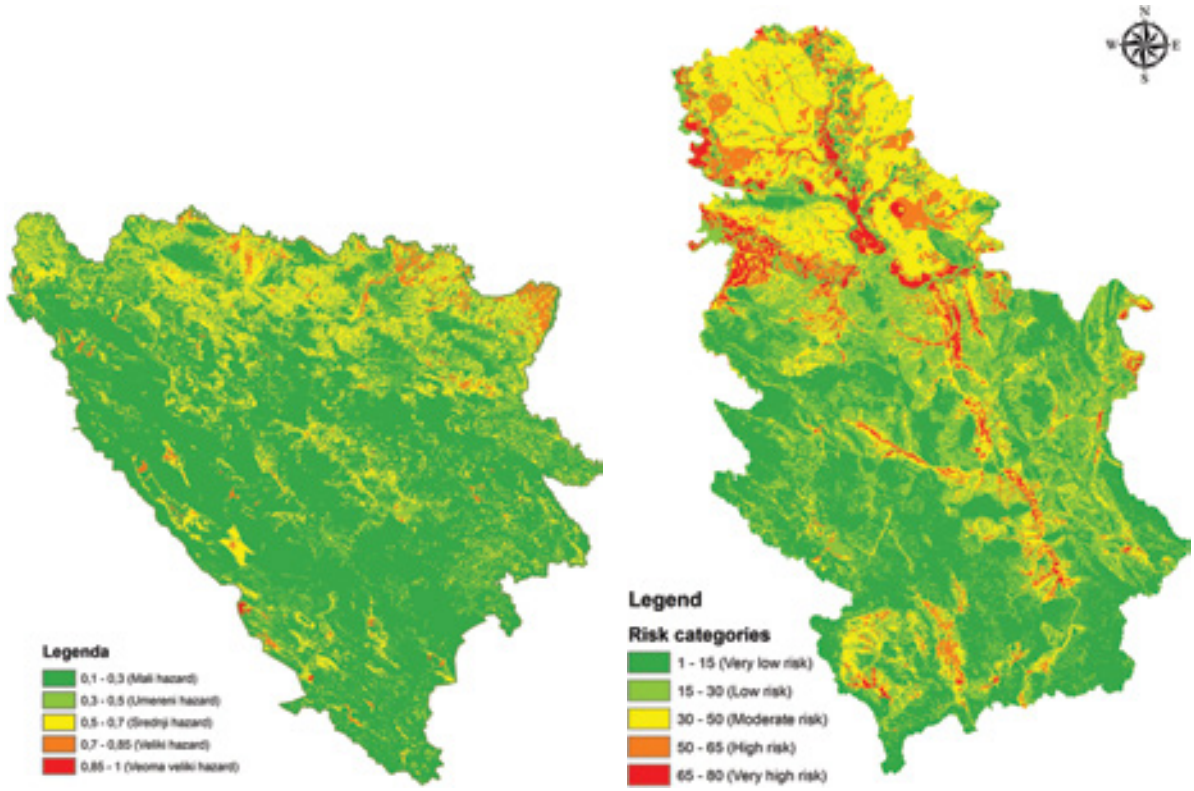

Figure 5: left - Diffuse Hazard Map for the territory of Bosnia & Herzegovina based on CORINE land cover map (the hazard raising from green to red colors, map created by V. Marinović, 2015); right - Diffuse Risk Map for the territory of Serbia (Stevanović et al. 2015b)

Finally, the programme of measures and the type of monitoring (network density, observed elements, observation frequency) should directly result from assessed pressures. Basic measures that should be applied for maintaining the optimal qualitative and quantitative characteristics of groundwater are incorporated into Annex VI of Water Framework Directive. Those measures include precise determination of the amount of water that can be exploited and control, treatment and remediation measures for two types of pollutions: punctual and diffuse. At the end, the main goal of applying this programme of measures would be achieving (or maintaining) good qualitative and quantitative status of groundwater. This is another reason why highly correct and professional hydrogeological studies ought to be undertaken. In most EU countries and the SE Europe, the use of GW for potable water supply is dominant and thus great attention must be paid to ensure the sustainability of this source in the future.

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NOTES

AN ATTEMPT TO UNDERSTAND THE HIGHER SULFATE CONCENTRATION IN GROUNDWATER OF KUWAIT USING GEOCHEMICAL MODELLING

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Abstract: The higher concentration of major ions in groundwater or anthropogenic influences result in the dissolution of salts present in the host matrix. In this scenario, higher concentrations of sulfate ions were witnessed in the groundwater of Kuwait. Hence, a study was attempted to understand their higher concentration of sulfate in groundwater by collecting samples spatially representing the two major aquifer systems of Kuwait. The concentrations were noted around the oil field and, further the variation of the state of saturation of sulfate minerals in water with pO2 was carried out in different aquifers. Later the geochemical data was subjected to statistical analysis and the results revealed that the higher concentrations of sulfate were mainly due to oxidations of hydrogen sulfide from the oil fields and also due to the influence of weathering of gypsum and anhydrite in the aquifer matrix.

Keywords: aquifer, anthropogenic, oxidation, oilfields.

INTRODUCTION

Kuwait is situated to the northeast of Saudi Arabia at the northern end of the Arabian Gulf, south of Iraq. The low-lying desert land is mainly sandy and barren. The natural water resources of Kuwait are practically limited to groundwater resources. These resources are brackish in nature in the central and southwestern part of the country. Groundwater becomes more saline toward the north and northeastern parts of the country following the general direction of the groundwater flow towards the Arabian Gulf. Apart from salinity, there are also reports of higher sulfate and nitrate concentration in the groundwater of this region. Fresh groundwater, where the total dissolved solids (TDS) range between 300 and 1500 mg/l, has limited occurrence in Kuwait. In fact, it is uniquely present at the northern parts of Kuwait at Al-Raudhatain and Umm Al-Aish depressions, where it occurs in the form of freshwater lenses floating on the top of Kuwait Group's brackish water. The importance of these lenses as the country's only secured freshwater reserve and its fragile stability calls for thorough management schemes for its utilization. With the exception of these northern depressions in general, the TDS in the northern groundwater field of Kuwait varies between 300 and 4500 mg/l and the sulphate concentration ranges between 100 and 2600 mg/l. The primary mineral sources of sulphate ions include evaporate minerals such as anhydrite, gypsum, and sulphates of magnesium and sodium. It may also be due to the leaching of fertilizers in hard rock aquifers of Madurai district of Tamilnadu, India, which ranges from below detection limit (BDL) to 100 mg/l (Thivya et al., 2013). It is also commonly found in minor concentration due to the breakdown of organic substances from weathered soil/water (Miller, 1979; Craig and Anderson, 1979). Dissolved sulphate (SO42-) is derived from the dissolution of gypsum or the oxidation of sulphide minerals such as pyrite. These two minerals are present in the groundwater of northern Jabal Hafit in the eastern part of Abu Dhabi as thick beds streaks in the limestone strata and are sufficiently soluble to cause water in contact with them to have a higher sulphate concentration (Murad et al., 2012). The present study is aimed at delineating the source of sulphate through geochemical modeling approach in two main aquifers, namely, the Kuwait Group of aquifers and the Dammam Formation aquifer.

METHODOLOGY

Groundwater samples were collected from the two main aquifers of Kuwait, namely, the Kuwait Group and Dammam formation aquifers. Twenty one groundwater samples were collected (Fig. 1) representing the entire country from the KG aquifer and 12 samples from the Dammam aquifer. The samples were analyzed for in situ physicochemical (electrical conductivity, pH, temperature, dissolved oxygen, Eh) and hydrochemical parameters (major-ions and minor-ions) in the laboratory. Modeling approaches were used to understand the groundwater quality issues of Kuwait and to predict the dynamic changes in the groundwater quantity and quality. Two approaches were adopted for geochemical modeling: i) inverse modeling (PHREEQC), based on mass-balance that uses the chemical composition data of the water and the rock with the objective of quantitatively identifying the geochemical reactions; and ii) direct modeling, on the basis of some well-known initial conditions of the water-rock system that predicts the characteristics of the resulting solution through a hypothetical chemical reaction. The saturation indices of the groundwater samples from Kuwait Group of aquifers and Dammam formation for calcite and dolomite were calculated based on the hydrochemical data of water samples using the computer model WATEQF. The accuracy of the saturation index for predicting the equilibrium of carbonate minerals depends largely on the accuracy of the field measurements of pH and alkalinity (Nordstrom and Ball, 1989). Inclusion of uncertainties in the process of identifying inverse models is a major advance. Considering all of these advantages in PHREEQC, this model was used in the present study to calculate the inverse modeling and variation of solution composition along its flow path with the SI of different minerals in the study area.

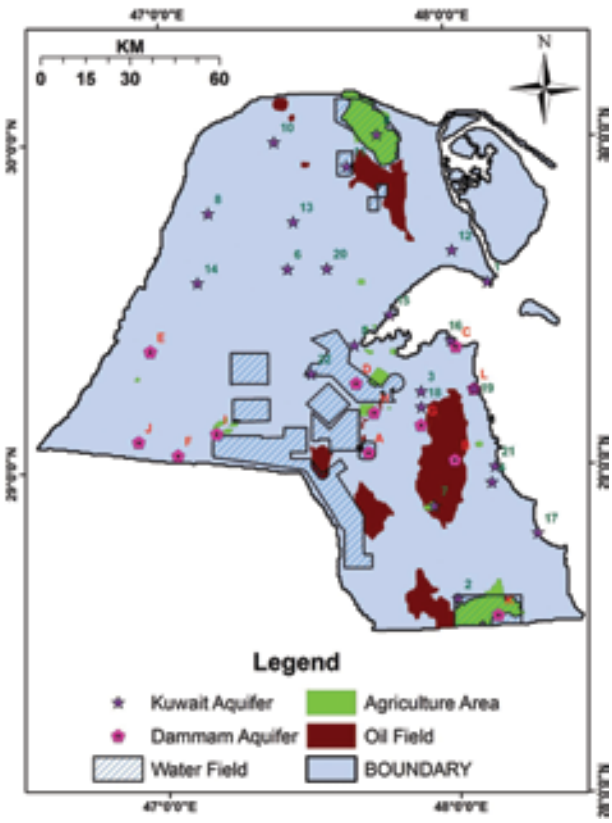

Figure 1: Sampling location map of the study area, the samples of the KG aquifer are provided numbers and that of Damman aquifer are provided in alphabets.

RESULTS AND DISCUSSION

The results of a chemical analysis of samples indicated that most of the groundwater was chemically Na-Ca-Cl-SO_4 type. The chloride bromide ratio indicated that a majority of the Kuwait Group and Dammam Formation aquifers showed the influence of evaporate dissolution. The sulfate concentration was higher in the Kuwait Group of aquifers compared to the Dammam Formation aquifer. The summary of the samples analyzed are reflected in table 1, and it is inferred from the table that the anions show the following order of dominance $Cl>SO_4>HCO_3>NO_3$ and that of cations is Na>Ca>Mg>K irrespective of the aquifer.

	EC (µs/cm)	Cl (mg/l)	Br (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	HCO_3 (mg/l)	pH
						Kuwait Aquifer					
Average	17586	6077	7.78	39.87	2338	3691	91.8	752	322	113	7.26
Minimum	519	6.8	0	0	120	56	4	39.2	4.13	57	6.57
Maximum	92000	44121	102	98.12	6097	22856	515	2888	2547	211	7.83
						Dammam Aquifer					
Average	18598	7911	10.3	34.14	1383	4171	125	1216	264	105	7.22
Minimum	3460	351.5	0	0.88	0	327	8.2	260	92.8	21.2	5.74
Maximum	120700	66000	107	149	2700	35000	1030	8720	1001	323	8.13

Table 1. The maximum, Minimum and Average values of major ions present in groundwater of both aquifers.

pO_2 and Sulfate Concentrations. Partial pressures of O_2 (pO_2) and CO_2 (pCO_2) indicate that oxidation of H2S, coupled with dissolution of calcite and dolomite, were the primary reactions affecting water quality. The relationship of pO_2 to the saturation states of these sulfate minerals indicate that there is an inverse relationship in both the aquifers (Fig. 2), which is due to the fact that the decrease of pO_2 increases the concentration of SO_4. Shallower waters of the region are characterized by a large concentration of sulphate, an equally striking feature of many of the waters associated with oil is the presence of alkali carbonate.

Between the sulphate and carbonate zones is a zone characterized by waters carrying the hydrogen sulphide. Sulphate is abundant in the shallow waters everywhere, whereas sulphide is found only near hydrocarbons (Rogers, 1917), it is reasonable to suppose that the sulphate has been derived under special conditions through oxidation of sulphide. It is supposed that sulphate is reduced to sulphide or vice versa when it moves from a low to higher formation, which passes of as hydrogen sulphide (Bischof, 1851), and that an equivalent portion of oil and gas is oxidized to CO_2 and carbonate through an equation as follows:

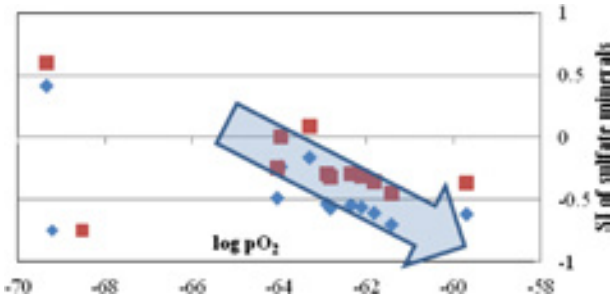

Figure 2: Relationship of log pO_2 with sulfates in Dammam Aquifer

$CaSO_4 + CH_4 = CaO + H_2S + CO_2 + H2O$

or

$CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O = CaCO_3 + H_2S + H_2O$

These reactions are hypothetic. These H_2S are oxidized to sulfate rich groundwater as follows

$H_2S + 5O_2 \leftrightarrow 2H_2O + 2SO_4$

In the saline-water zone near the down dip limit of freshwater could result in the precipitation of gypsum. It is also inferred the pH of the samples are neutral to alkaline in nature hence the formation of H_2SO_4 is neglected. Alternatively, just as sulphate by reduction yields sulphide, so sulphide under other conditions may oxidize to sulphate.

$H_2S + 2O_2 \rightarrow 2H+ + SO_4^{2-}$,

or by biological mediation

$H_2S + 1.33\ CO_2 + 1.33\ H_2O \rightarrow 2H+ + SO_4^{2-} + 1.33\ CH_2$ (organic matter),

The earlier reactions produce H^+ concentration, which reduces the pH of the groundwater. But in reality the pH of the groundwater containing high sulphate are not acidic. Similar to the Kuwait aquifer, saturation states of sulfate minerals were also reflected in the Dammam formation aquifer (Fig. 2). When the concentration of the sulfate is lesser in this aquifer at higher log pO_2 values, it is also inferred that Damman formation aquifer has comparatively higher values of pO_2 than Kuwait group aquifers. This shows that the variation in pO_2 values have also resulted in the increase of SO_4 concentration of the KG aquifer. There are two different trends noted in the plot of Kuwait group aquifers; this is due to variation in the sources of sulfate in different oil fields. This relationship of pO_2 is also reflected in the saturation index of the sulfate minerals: There is a decrease in saturation of sulfate minerals with increase in pO_2 values.

Statistical Analysis. Pearson's correlation coefficient between ion pairs is the best method of measuring the correlation, because it based on the method of covariance (Swan and Sandilands, 1995). The correlation coefficient gives the information about the degree of correlation and as well as the direction of correlation. The Pearson's correlation coefficient value lies between +1 to -1 and the degree of correlation is said to be perfect correlation if the coefficient value is near ±1. For values ranging between ±0.75 and ±1, it is said to be high degree of correlation, similarly moderate degree of correlation for values between ±0.25 and ±0.75 and low degree of correlation for values between 0 and ±0.25.

Correlation Matrix (Kuwait Group Aquifer). The statistical correlation of the hydrochemical ionic species (Pearson's correlation coefficient based on the method of covariance) of the groundwater of Kuwait Group of aquifers shows good correlation between different ions. Cl shows good correlation with Ca and Mg indicates leaching of secondary salts or dolomite dissolutions. HCO_3 shows significant correlation with Ca, indicating predominance of chemical weathering. pH shows negative correlation with other variables, which indicates pH governed dissolution. Na shows strong correlation with Cl, which indicates saltwater intrusion. Br has a good correlation with Cl, Na, K, Ca, Mg, which also indicates seawater influences into the system. NO_3 is not showing any correlation with others ions except good correlation with SO_4, which indicates the influence of oil field gas (Rogers, 1917) or that of similar sources.

Correlation Matrix (Dammam Formation Aquifer). In general, most of the ions are positively correlated with Cl^-, especially Na^+, Mg^{2+}, K^+, and NO_3 show strong correlation, along with negative representation of pH and Ca^{2+}. The negative relation is also significant with Br and SO_4; this may be due to the fact that composition of most of the groundwater from the saline plumes differs from those of anthropogenic sources. The positive correlation between Cl^-, Na^+, Mg^{2+}, K^+, NO_3^-. It is also inferred that in this aquifer there is no correlation between the SO_4 and NO_3 ions, which was exhibited in the Kuwait aquifer. The major ion exhibiting correlation with other ions is mainly possible due to the impact of leaching of the secondary salt. The relation of pH with Ca^{2+} indicates the dominance of the ion exchange process (Chapelle and Knobel,1983), which shows strong correlation with Cl^-, indicating that such ions are derived from the same source of saline waters (Kim et al., 2003a; Thilagavathi et al., 2012; Singaraja et al., 2013).

Factor Analysis. The factors with Eigen values larger than 1.0 were selected and rotated iteratively by the Varimax method (Davis, 2002). The purpose of factor analysis is to interpret the structure within the variance, covariance matrix of a multivariate data collection. The technique that it uses is extraction of the Eigen values and Eigen vectors from the matrix of correlations and co-variances. The interpretation is based on rotated factors, rotated loadings, and rotated Eigen values Factor loadings are sorted according to the criteria of (Liu et al., 2003), i.e. strong, moderate and weak, corresponding to absolute loading values of >0.75, 0.75 to 0.50 and 0.50 to 0.30 respectively.

Kuwait Group aquifer factor analysis rendered three significant factors explaining 92.31% of the total variance of the dataset. The association of the ion in Factor 1 representing EC, Cl, Br, Na, K, Ca, and Mg indicates seawater intrusion into the system (Rogers, 1919). Factor 2 indicates the enrichments of NO_3 and SO_4, which is due to influence of oil field (Rogers, 1917). The spatial distribution of the NO_3 and SO_4 in groundwater shows that they fall above the regions represented by oil fields.

Dammam formation aquifer factors with Eigen values greater than 1 are taken into account. Following this rule, two independent factors were extracted, which explained 95.96% of the total variance of the original data set, sufficient enough to give a good idea of data structure. Factor 1 accounted for 77.24% of the total variance with positive loadings on Ca^+, K^+, Na^+, Mg^+, Cl^-, HCO_3^-, NO_3, pH, and EC. This association strongly suggests that factor 1 represents a salinization (salinity) variable and influence of the anthropogenic factor during the process of seawater intrusion aided with infiltration of untreated domestic sewage (Steinich et al., 1998) or industrial effluent (Davidova et al., 2001), The nitrate content in the groundwater of Damman aquifer are lesser and, moreover, the associates of this ion indicate an anthropogenic influence of this factor. Factor 2 accounts for 18.72% of total variance, with strong positive loadings on SO_4, and HCO_3. Sulphate decreases with increasing depth and practically disappears at a certain distance above the oil zone (Rogers, 1917). The decrease of sulfate in the waters as the oil measures are approached and its absence from the waters most closely associated with the oil are believed to be the result of chemical reaction with constituents of oil and gas. The sulphate is probably reduced to sulphide or hydrogen sulphide, which may either escape as gas or undergo oxidation to free sulphur and so be lost by precipitation. The reduction of sulphate is presumably attended by the oxidation of an equivalent portion of hydrocarbon material to carbonate or carbon dioxide (Bischof, 1851). Hence, clear associations of these two ions are represented in this factor. Alternatively, the Dammam aquifer is a marine formation and, hence, free sulphur has been found in a number of marine muds, where it is formed by oxidation of hydrogen sulphide derived from the sulphate in the sea water (Buchanan, 1916). Under more strongly oxidizing conditions, or in the presence of certain bacteria, the sulphur becomes thiosulphate, sulphite, and finally sulphate. It may be noted that the oxidation of hydrogen sulphide to sulphur or sulphate results in the evolution of much heat (Becker, 1888) and if the earth temperatures in oil regions are higher than elsewhere, as suggested by Koenigsberger and Muhlberg (1911), some of the excess heat may be contributed by this reaction. The Dammam formation aquifer is consisting of limestone and anhydrites of Rus formation (Mukhopadhyay et al., 1996) may also inferred to undergo weathering. Hence, this factor could be mainly due to weathering processes/dissolution processes.

CONCLUSION

The study on the groundwater of the region with reference to the higher sulfate in groundwater indicates that there are greater associations of sulfate in the Kuwait aquifer than in Dammam Aquifer. This fact is reflected from the correlation analysis, which is also supported by the higher concentration of sulfate around the oil fields. Thus, it is inferred that the H2S evolved from the reservoirs is oxidized in the Kuwait group aquifer; as the log pO_2 values in Dammam formation aquifer are higher, the sulfate concentrations and saturation states of sulfate minerals are higher in this Kuwait aquifer. Further the oxidation of this sulfide takes place resulting in the increase of higher sulfate concentrations. Also, the contour shows that it is higher near the oil fields and shows correlation with sulfate in the Kuwait aquifer. Hence, it is inferred from the study that the sulfate in groundwater is mainly due to the oxidation of the sulfide from the oil field and to a certain extent by the

dissolution/weathering of $CaSO_4$ minerals present in the aquifer matrix. It is also evident from the PCA analysis that apart from these processes there are other hydrogeochemical processes responsible for the groundwater chemistry of the region like seawater intrusion and rock water interaction in Dammam aquifer along with ion exchange process.

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QUALITY GUIDED WATER ABSTRACTION AT KARST AQUIFERS: HYDROGEOLOGY MEETS MICROBIOLOGY

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BACKGROUND AND AIM OF RESEARCH

Water resources from alpine and other mountainous karst aquifers play an important role for drinking water supply in many countries. World-wide approximately 25% of the population are fed by water resources from karst aquifers (Ford, Williams, 2007). These karst regions cover 12.5% of the land surface (Martin & White, 2008). As regulated in the WFD (Water Framework Directive, EC,2000), karstic catchments require a sustainable protection. The increasing impact to such regions and different land use in the watersheds of karst springs are important reasons to establish early warning systems and quality assurance networks in water supplies. Microbial fecal pollution belongs to the most endangering contaminants in alpine karst aquifers. However, until recently, microbial fecal pollution could only be detected by traditional standard approaches based on individual grab sampling and time demanding cultivation procedures in the laboratory. Hardly any information on the pollution dynamics, origin of pollution as well as associated health-risks (in case of exposure) could be given. Due to this lack of knowledge, a joint effort between the disciplines of microbiology and hydrogeology was undertaken to open the “black box” of microbial pollution and its dynamics by developing new techniques and strategies which guide resources and water quality management at catchments of alpine karst water aquifers. Therewith a sustainable framework provide which supports decision making at all required time scales of information (e.g. from near-real-time spring water abstraction management, within the resolution of minutes, up to catchment protection practices, within the time frame of months to years) can be established.

The aim of the paper is to show i) the dynamic of microbial fecal pollution indicators and chemo-physical parameters with high resolution time at the scale of hydrological events, ii) to demonstrate the usability of the Spectral Absorption Coefficient at 254nm (SAC254) as a real-time pollution proxy for optimised spring water abstraction management, iii) the establishment of new molecular fecal source tacking technologies to guide target-oriented catchment protection, and finally, iiii) to discuss strategies for translating the observed fecal pollution hazards into associated health-risks to assess the required level of water treatment (disinfection) for a sustainable drinking water supply according to health-based quality targets.

HYDROGEOLOGICAL SETTINGS AND METHODS

Investigations took place at three karst springs (LKAS2, LKAS6, LKAS8) in the northern Calcareous Alps. The mean discharge ranges from 250 to 5300 litres per second, according to different mean altitude of the catchments and different catchment size. The lithology is characterized by Triassic limestones, forming wide plateaus and steep slopes (Mandl et al., 2002). Land-use is dominated by alpine pastures, krummholz and alpine forests, touristic activities and wildlife.

In-situ measurements of different chemo-physical parameters at karst springs were adapted to the local contamination scenario. Online and near real-time availability of data is obligatory. Time increments of the measurements were set to 15 minutes, considering the high dynamics in quantity and quality of these springs. As fecal pollution cannot be detected directly in near-real-time, proxy parameters are necessary to establish on-line monitoring. All investigations were carried out at event scale.

These investigations lay the foundation for advanced microbiological analysis and hazard and risk assessment, the basis for catchment protection based on the Dominant Process Concept (DPC) - elaborated by the combination of process-orientated hydrogeological mapping and hydrological modelling – and a state-of-the-art multi barrier protection system of drinking water resources.

MICROBIOLOGICAL METHODS

Microbiological sampling was performed automatically by networking via LEO-satellites. Single manually samplings were done for checking purposes. Several microbiological standards including E. coli, enterococci, C. perfringens, HPC37°C, HPC22°C, as well as aerobic spore formers and pathogens (Cryptosporidium parvum, Giardia) were investigated (Farnleitner et al. 2010). Alternative parameters including ruminant-associated (BacR), and human-associated (BacH), and total (AllBac) Bacteroidetes faecal markers quantified by qPCR as well as automated enzymatic ß-D-glucuronidase and ß-D-galactosidase measurements were investigated (Ryzinska et al., 2013). Regular catchment surveys were performed as well.

RESULTS AND DISCUSSION

The Conceptual Design is based on three interacting levels characterizing the backbone of the concept: (1) Is there a problem with fecal pollution? (2) If yes, what is the reason for it? (3) What is the actual health risk in relation to the faecal source(s) contributing to the observed pollution? The suggested framework (see Fig. 1) is also referred to as “bottom-up approach” because it starts at the most general level (i.e. total faecal pollution monitoring) and it becomes more specific as it proceeds to the right-end-side of the diagram.

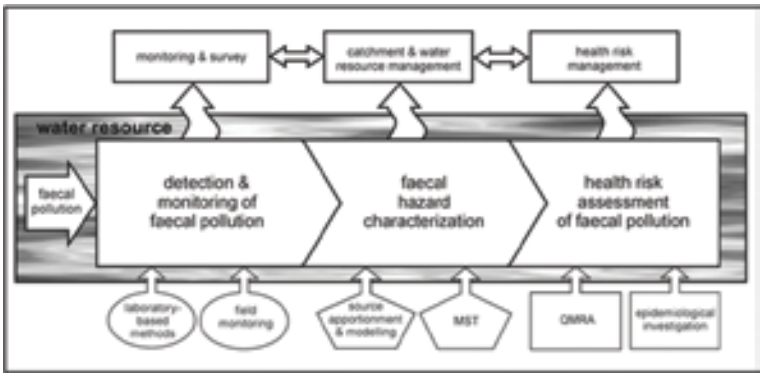

Figure 1: The suggested framework for integrated fecal pollution analysis and management (“3-step approach”). Note that any of the 3 steps of analysis is important for catchment protection and spring water quality management. The methods needed to realize the suggested “3-step approach”, as shown at the bottom of Fig. 1, are presented in the results section. Abbreviations: MST= microbial source tracking, QMRA= quantitative microbial risk assessment

In a first step standard fecal indicator (SFIB) bacterias in particular E. coli. were investigated in animal and human fecal sources (Farnleitner et al., 2010) and found to be reliable as indicator for fecal pollution in the investigated alpine catchment. The event triggered detection of fecal pollution is based on automated event sampling, including microbial parameters. This method was chosen, because as previously described (Stadler at al., 2008) event sampling and monitoring allows a worst case view to pollutant transport in karst aquifers. Further investigations showed that the spectral adsorption coefficient at 254 nm can operate as proxy parameter for microbial contamination (Stadler, et al, 2010). This parameter can be measured in-situ and is therefore available in near-real time. Quality management of karst springs needs this high time resolution of critical parameters. Pollution-hypothesis guided microbial source traking (MST) was proved to be a valuable approach for faecal hazard characterisation during times of microbial fecal input to sensitive aquifers (Farnleitner et al., 2011) Hypotheses on relevant faecal pollution sources were generated directly at the catchment and reviewed by subsequent testing using host-associated genetic Bacteroidetes markers at the springs. Quantitative source apportionment for E. coli contamination by genetic faecal markers could be realised by hydrology guided sampling and multi-parametric statistical analysis. To enable a reliable health risk assessment of fecal pollution comprehensive quantitative microbial risk assessment (QMRA) has to be carried out. For example, the occurrence of fecal pollution from ruminants guided the QMRA towards the assessment of zoonotic pathogens in the LKAS2 area (Farnleitner et al., 2014). Additional information came from catchment surveys, spring-water quality investigations and evaluation of storage and discharge dynamics of the aquifer.

The realised framework for integrated fecal pollution analysis allows state-of-the-art microbial water resource safety management including target-oriented catchment protection, optimized near real-time spring abstraction management and risk-based definition of treatment/disinfection requirements. The temporal resolution of the applied methods is of complementary nature in order to support the respective management decisions at the appropriate time scale. This concept is alienable to other water resources as the selected parameters and methods can be adapted to the respective situation or requirements and can be included in water safety plans.

Future developments based on the Dominant Process Concept (DPC) enables the focusing of dynamic pollutant transport to the karst system. This concept is elaborated by the combination of process-orientated hydrogeological mapping and hydrological modelling (Reszler et al., 2014). High resolution precipitation data and their spatial distribution in the catchment are essential to describe transformations like changing of land-use and climate change effects and other scenarios. In this way DPC can be assumed as the first step towards transport modelling at catchment scale.

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NOTES

ON THE NEED TO DELINEATE THE CATCHMENT AREA OF THE TRANSBOUNDARY KARST AQUIFER OF SOUTH-WESTERN SERBIA AND NORTHERN MONTENEGRO

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Keywords: transboundary aquifer, karst, water management, southwestern Serbia, northern Montenegro

The occurrence of several countries sharing one river basin is not rare. There are many rivers in the world that flow through two or more countries; the Nile basin, for example, is shared by 10. After the dissolution of former Yugoslavia, the Danube River basin became transboundary and common for 14 European states. As UNDP stated, there are 263 watersheds in the world that cross the political boundaries of two or more countries (UNDP). Transboundary watersheds represent about one half of the earth's land surface, while 40 % of global population lives in the aforementioned areas. These facts underscore how much water connects us all but also highlight the potential for conflict – and for cooperation. Throughout history, there have been numerous examples of non-equitable use of common water resources which led to conflicts between the upstream and downstream countries. The primary objective of sustainable water management would thus be to define the optimal water extraction rate for each of the riparian countries, taking into consideration the local hydrological and hydrogeological characteristics, water demands (potable and industrial), the guaranteed ecological flow, and the minimal flow which impacts the water-dependent eco systems i.e. downstream users and flora and fauna.

Like river basins, but in an "invisible" way, aquifers of all sizes and origin could also be shared by different countries or by different jurisdictions within a country (Margat & Van der Gun, 2013). Functions of a transboundary aquifer do not differ from those of other aquifers as well as its behaviour, however administrative borders that cross them may have strong influence on the way of the development and management of their groundwater resources. Complexity of aforenamed situation kept transboundary aquifers without proper management plans, while attention to these aquifers only began a few decades ago and most activities carried out so far are of a preparatory or enabling nature, real interventions on the ground are still relatively rare. Climate change, which is already altering the global water cycle at an unprecedented rate, adds further complexity to these challenges through its impacts on the timing, intensity and variability of rainfall, droughts and flooding.

Due to the shortage of drinking water in some areas of Serbia and the negative influence of prolonged drought cycles, more attention should be paid in the coming years to groundwater saving and equitable use, especially in the case of sensitive karstic aquifers. If we bear in mind the invisibility of groundwater and the unpredictability of groundwater circulation (especially in karst), the problem of transboundary aquifer management becomes even more complex. The first step in such analysis should be the characterisation of the aquifer and accurate estimation of aquifer geometry and available reserves, as well as climate conditions. Considering climate change and its possible impact on water resources, there is abundant evidence that this vital resource is extremely vulnerable and sensitive to climate change (Anđelić, 2012). In addition, possibilities are limited for quantifying hydrogeological variables and for estimating their impact on water resource while the whole process remains complex and uncertain.

The dissolution of former Yugoslavia and the creation of several new countries resulted in many "national" aquifers becoming transboundary. This was also the case with the karst aquifer in the southwest Serbia and the northern Montenegro. One of the most important karst aquifer in this area (Fig. 1) is formed in rather well karstified Triassic (T2,3 and T23) limestones of the Babine plateau, near the Prijepolje city. Plateau area of approximately 60 km2 is located on the very border of Serbia and Montenegro. It is covered with evergreen forests of pine and spruce and fir with some smaller areas of beech forest as well as rangeland and pastures.

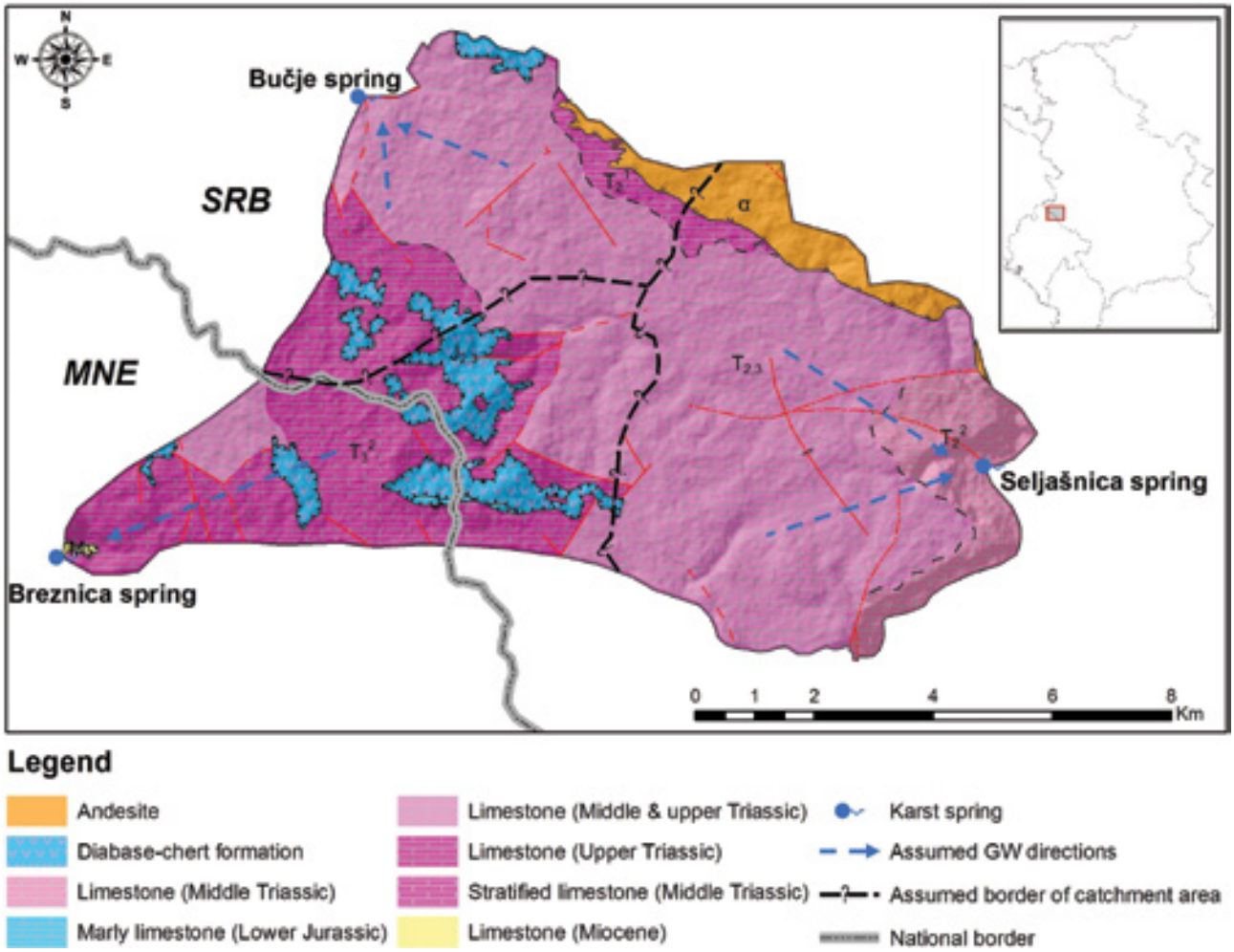

Figure 1: Geological map of catchment area of karst springs near the national border of Serbia and Montenegro

Karstic aquifer has been recharged by precipitation in the form of snow and rain, and mean annual value is around 800 mm. Infiltration of the precipitation is almost complete due to relatively good distribution of dolines and existence of few ponors over the plateau. There is a presumption that groundwater flow is developed in three general directions: east, northwest and southwest (Fig. 1). Three large and several smaller springs are located in the place of the contact of the karstified rocks and impermeable rocks (magmatic and metamorphic rocks). The plateau is scarcely populated and with very poorly developed road network. Previously stated facts help us to conclude that so far aquifer is with no significant anthropogenic influence and currently almost hazard free.

The karst plateau Babine in the East is drained by the large karst spring of Seljašnica. This direction of groundwater flow was under influence of the strong neotectonic movements that caused increased karstification and created the conditions of emerging of groundwater on the surface. The nature of the resurgence is dual: 1. Upper outlet - from the Popova pećina cave (on the right side of the small gorge) and 2. Lower outlet - from the spot 50 m below (on the left side of the gorge), both are in the area of the village Seljašnica. Annual discharge of this dual system varies between 300-3500 l/s. Furthermore, on the eastern side of the Babine plateau few more springs exist with average discharge around 5-10 l/s, separately.

The karst plateau is also discharged by Bučje spring (Q=100-800 l/s) and few smaller springs in the northwestern part of the area. The Bučje spring has larger differences between maximum and minimum of discharge. Thus, delineation of the catchment area of this spring and the catchment area of the Seljašnica karst spring is complicated and with recharge area of karstic aquifer that depends on the season.

Situation is even more complicated if one take in consideration that groundwater originated from the Babine karst area is also discharged towards SW by Breznica karst spring (Q=50-1200 l/s). The Breznica karst spring has been tapped for the water supply of the city of Pljevlja (Montenegro).

Previous historic data of discharge of stated karstic springs shows similarities of balance of karstic aquifer as well as maximum discharge quantities. The differences in the minimum discharge implies that groundwater emerging at the Seljašnica karst spring originate from the most developed part of this karst aquifer.

As stated above, Fig. 1 shows presumed catchment areas for Seljašnica, Bučje and Breznica karst springs. Those areas have been delineated on the basis of mean annual discharge of each karst spring, mean annual recharge rate from precipitation, geological settings, DEM and topographic maps. Based on this method, Seljašnica karst spring's catchment area has been roughly estimated on 39 km^2, Bučje spring's catchment area on 23 km^2, while Breznica spring has a catchment area of 28 km^2. It should be noted that this areas are in fact the topographic watersheds, while hydrogeological watersheds do not have to be the same as topographic ones, particularly in karst. Thus, detailed hydrogeological research in this area should be crucial for obtaining proper results of the size of catchment areas which can give us precise information about how much water, generated in Serbia is discharging in neighbouring Montenegro.

Karst aquifer formed in the limestones of the Babine plateau so far sustain the need of the consumers, for water supply as well as for industrial processes. However, one has to be prepared for the potential increase of the demands. Thus, a precise delineation of the transboundary aquifer catchment area should be carried out, as this would also enable the defining of water budget elements and groundwater reserves as the necessary step toward optimal and sustainable exploitation on both sides. However, there is also an assumption that the same aquifer may be connected, by deep siphonal circulation, with the ascending spring near town Rudo in Bosnia and Herzegovina, which additionally emphasises the need for hydrogeological research and tracing tests in this area.

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NOTES

A NEW H2020 PROJECT – KINDRA: KNOWLEDGE INVENTORY FOR HYDROGEOLOGY RESEARCH

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Abstract: The KINDRA project (EC Framework Programme H2020, Grant 642047) aims to produce an inventory of recent (post-2000) knowledge of hydrogeology research conducted in Europe. The project coordinator is Sapienza University of Rome and project participants include the European Federation of Geologists and several European geological associations, in addition to numerous institutions.

The main objective of KINDRA is a singular inventory of knowledge, comprised of a database of research results, activities, projects and programs concerning groundwater. The outlined requirements of the project are to: (i) identify keywords and categories for a simple and efficient classification system, and (ii) establish groundwater terminology that will be readily recognizable within the framework of general water resources (Petitta et al., 2015). The new terminology, as well as the methodology for classifying groundwater research results and activities (Hydrogeological Research Classification System: HRC-SYS) and the European Inventory of Groundwater Research (EIGR), have been developed during the first two years of the project and constitute the main initial outcomes of KINDRA. The extraction of keywords from the Water Framework Directive (WFD), Groundwater Directive (GWD), and the most recent Blueprint to Safeguard Europe's Water Resources (BWR, European Commission, 2012) was a major step towards the classification of groundwater research under KINDRA. About 100 keywords have been identified and defined. Still, this was not sufficient because the compiled keywords did not cover all the relevant areas of hydrogeology research. As a result, the list of keywords was supplemented by those from journals that report results of groundwater research.

KINDRA has identified three main categories for the purposes of classifying hydrogeology research and knowledge:

1. Horizon 2020 social challenges,
2. Operative activities, and
3. Areas of research.

Each of the main categories comprises five groups that facilitate insight into the main areas of research. The compiled inventory will be a very useful tool for integrated management of water resources. The approach promotes proper development of groundwater management and policies, as recommended in the Blueprint Document (EC, 2012).

It is important to note that a survey has shown that public water supply in Europe largely relies on groundwater. The only exceptions are Spain, Ireland and Ukraine, where the groundwater share is less than 30% (Figure 2).

Figure 1: Participating countries of the KINDRA project (Hartai Eva, Inventory of Information Sources, D1.4 - ppt presentation, Seville 2016)

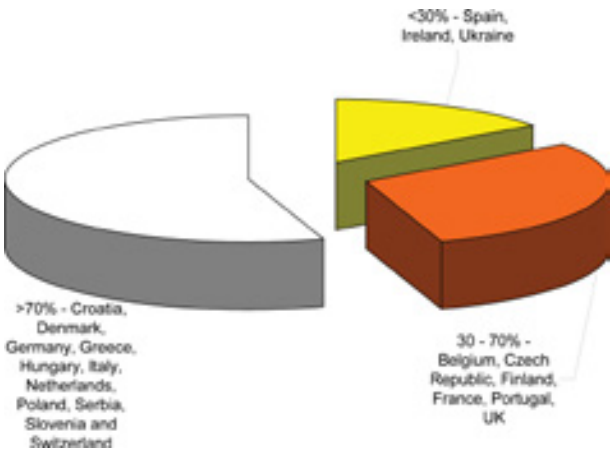

Figure 2: Share of groundwater in public water supply in Europe (after Hartai Eva, Inventory of Information sources, D1.4 - ppt presentation, Seville 2016, supplemented)

NOTES

EFFECT OF PRE-OXIDATION ON THE LEVEL OF RESIDUAL AL IN THE DRINKING WATER TREATMENT PROCESSES

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Abstract: The results show that after the pre-oxidation treatment with three different oxidant (potassium permanganate, sodium hypochlorite and ozone). Pre-oxidation can reduce the residual Al and turbidity of effluent to improve its quality. The turbidity removal was increased by 3.7%, achieving 90.72%; the level of residual Al was 0.186 mg/L in total and 0.177mg/L as the soluble kind, and pre-oxidation decreased the total and soluble Al by 14.68% and 15.31%, respectively. This may be attributed to the improved activity of the coagulant and degradation of organic matters by pre-oxidation. Three-dimensional fluorescence analysis showed that pre-oxidation treatment can degrade the tryptophan and reduce the soluble microbial products; therefore, the negative impact of protein-like substance was alleviated.

Keywords: pre-oxidation; residual Al; drinking water treatment processes

INTRODUCTION

Aluminum is considered as an element that is related to human health risk such as Alzheimer's disease (Kawahara and Kato-Negishi 2011). Due to the worldwide application of aluminum salts as coagulant in drinkingwater treatment processes, the level of residual Al in water is of concern and thus the control of residual Al in drinking water treatments has received much attention. The total aluminum in water consists of the particle and soluble species. The soluble aluminum includes the hydrolysates of Al and the complexes formed by them and organics, phosphas phosphate and groups such as OH-. Therefore, the concentration of residual Al is affecte by pH, water temperature, characteristics of organics, coagulant dose, type of filter media and so on.

Pre-oxidation is a common treatment to enhance the coagulation efficiency yet there was not much information about the effect of pre-oxidation on the level of residual Al in the drinking water treatment processes. In this study, three pre-oxidants (chlorine, ozone and potassium permanganate) was compared in pilot study.

MATERIAL AND METHODS

Source water was extracted from Huairou Reservoir in North China, and its qualities are as follow: turbidity 2.10-2.40 NTU, water temperature 16-19°C, pH 8.45-8.65. The processes used in the pilot study is illustrated as following:

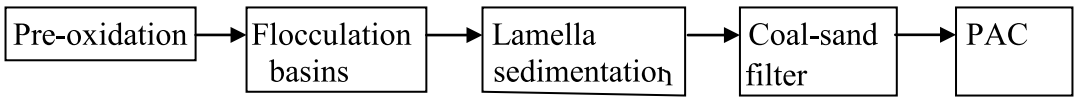

Figure 1: The processes used in the pilot study.

Chlorine, ozone and potassium permanganate (1.0 mg/L) were applied as pre-oxidants, respectively. The coagulant used in this study was polyaluminium chloride. Samples were withdrawn after each process and divided into sub-samples: the first was for the turbidity and pH measurements; the second was quenched by Na_2SO_3 and measured for Al concentration, and the soluble kind needs to be filtered through a 0.45-μm filter in advance; the remaining sample was used for EEM analysis.

RESULTS AND CONCLUSIONS

According to the results of pre-experiments, the optimum dose of PAC in this study was determined to be 30 mg/L and applied in all the following experiments.

As shown in Figure 2, pre-oxidation with potassium permanganate, chlorine and ozone positively affected the removal of turbidity in the outflow of each drinking water treatment process (Figure 2).

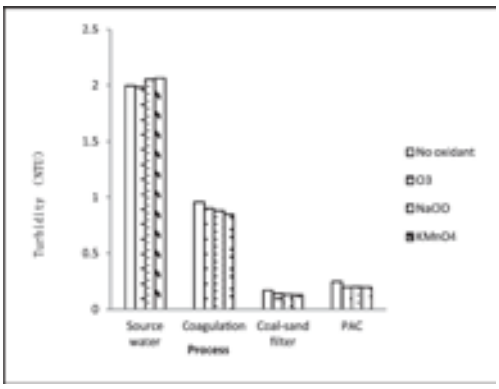

Figure 2: Effect of pre-oxidation on the turbidity in the outflow of drinking water treatmnet processes.

As shown in Figure 3a, the introduction of pre-oxidants contributed to the decrease in the level of residual Al (both total and soluble kind) in the outflow of each process. Without any pre-oxidation, the concentration of residual total Al after coagulation, coal-sand filter and PAC was 0.594, 0.305 and 0.218 mg/L, respectively; pre-oxiation with potassium permanganate, chlorine and ozone decreased the total Al residue to 0.567, 0.572 and 0.570 after coagulation, to 0.264, 027 and 0.288 mg/L after coal-sand filter, to 0.185, 0.191 and 0.195mg/L after PAC, respectively. Similarly, pre-oxidation also facilitated the control of residual soluble Al (Figure 3b).

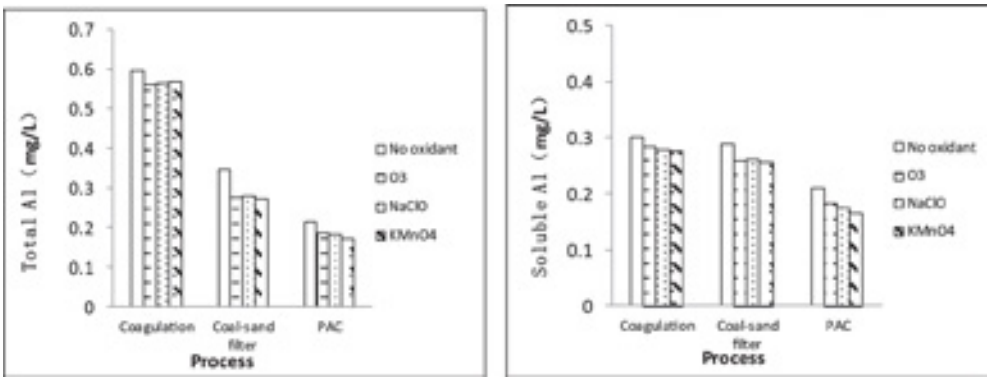

Figure 3: Effect of pre-oxidation on the residual Al in the outflow of drinking water treatmnet processes.

As shown in Figure 4, coal-sand filter and PAC mainly contributed to the removal of particle Al and soluble Al,respectively. The application of pre-oxidation can enhance the removal of residual Al of each process, yet the main species of Al that each process was able to remove was not changed.

As shown in Figure 5, the pre-oxidation degraded the tryptophan-like proteins (TryP) and soluble microbial products (SMP). Rather than humic substances that were suggested the main kind of DOM (Alborzfar et al. 1998), dominated the source water. As protein can form soluble complex with Al (Pivokonsky et al. 2006), the higher level of TryP can negtively affect the cross-linking and clustering of coagulant. As a conquence, the hydrolysis and precipitation of coagulant was interfered. And the degradation of TryP and SMP can result in the decrease of residual Al, including the soluble Al complexes and the particle.

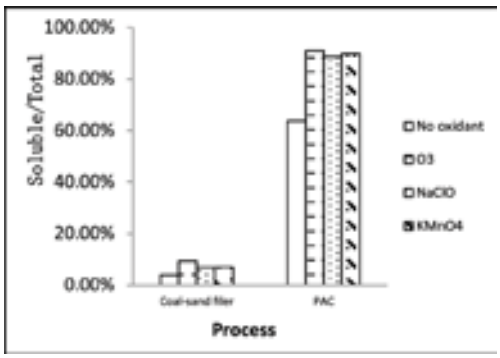

Figure 4: Effect of pre-oxidation on the ratio of soluble Al andthe total Al in the outflow of drinking water treatmnet processes.

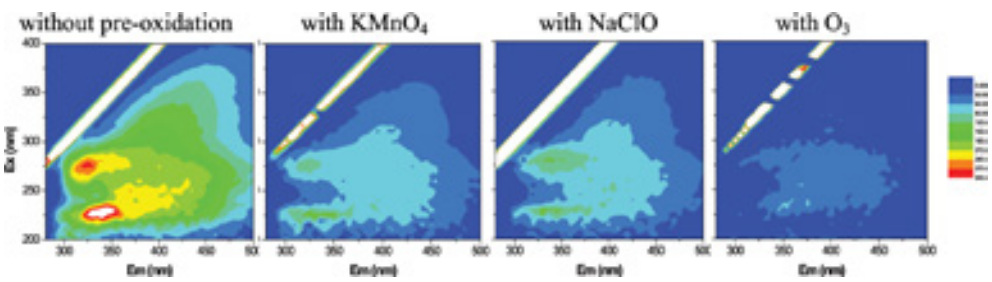

Figure 5: Effect of pre-oxidation on the organics in source water

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NOTES

A SEASONAL IMPACT ON THE TRACE ELEMENTS CONTENT IN SEAWATER OF THE SOUTHEASTERN ADRIATIC SEA – A CHEMOMETRIC APPROACH

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Abstract: Seawater samples from the costal area of the southeastern Adriatic Sea, Montenegro, analyzed in order to determine the concentration and origin of the next ten elements: Fe, Mn, Zn, Ni, Cu, Ni, Co, As, Cd, and Hg during four seasons. The complexity of the obtained data was reduced by Principal Component Analysis (PCA) and Cluster Analysis (CA), chemometric methods well-known and accepted in identifying quality of marine environment. Both PCA and CA analysis were used to discriminate groups of samples according to similarity of chemical composition and to assess the sources of metals and to study the influence of seasonality and anthropogenic activities in the seawater of the southeastern Adriatic Sea.

Two major factors were recognized as the impact on the level of investigated elements in the seawater samples using multivariate analysis: a natural and an anthropogenic factor. In the case of natural impact the element content of Fe, Ni, Mn, and Cu in surface seawater of southeastern Adriatic Sea manly carried by rivers and rainfall erosions of the sea coast, but the anthropogenic impact was in the case of Pb, Hg, and Cd. Varifactors obtained from factor analysis indicate that the parameters responsible for trace elements variations are mainly related to natural impact and natural hydro-geological criteria and regional climate. It was also seen that there was no significant difference between the sampling stations in terms of the level of toxic metal content, but the investigated elements exhibited differences in their distribution related to the investigated seasons.

Keywords: Trace elements, Coastal waters, Statistical Analysis, Climate impact

NOTES

FIELD TESTING OF IHE ADART ARSENIC REMOVAL TECHNOLOGY IN SERBIA

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Abstract: IHE ADART arsenic removal technology, based on low costs adsorbent (Iron Oxide Coated Sand -IOCS) and an innovative in-situ regeneration procedure, was tested at 3 sites in Serbia (Subotica, Zrenjanin & Backi Vinogradi). Groundwater at these sites is characterised by very high arsenic concentration, presence of ammonia, iron, and phosphate, and is some cases natural organic matter (NOM) and methane. Pre-treatment based on aeration and rapid sand filtration is essential to effectively remove ammonia, iron, manganese, and if present methane. Arsenic removal is predominantly achieved in IOCS filters. Consistent production of drinking water with very low arsenic concentration was possible on all testing sites. Regeneration frequency and conditions should be correlated with groundwater composition and specifically phosphate, pH and arsenic concentration. NOM present even at very high concentrations (e.g. Zrenjanin) can be very effectively removed with an anionic ion exchange resins.

Keywords: Arsenic removal, adsorption, low cost adsorbent, IHE ADART, Serbia

INTRODUCTION

Deep groundwater is an essential resource for water supply in Vojovodina, the Northern Province of Serbia. Groundwater used is anoxic with associated presence of elevated concentrations of ammonia, iron and occasionally manganese. Presence of high, to very high concentration of arsenic (≤ 300 µgL), mainly present as arsenite (As(III)), in significant number of groundwater wells was discovered a few decades ago. Several of such wells are used as the only water supply source for towns and villages. Since presence of arsenic in drinking water poses significant health risk to exposed population, including strongly increased risk for development of different forms of cancer, it is necessary to remove it from groundwater, prior to supplying it to the population. In addition to arsenic, phosphate is regularly found in groundwater, with high to occasionally very high concentrations. Further on, high concentration of natural organic matter, and methane are present is large number of wells. Cost effective production of drinking water from such complex groundwater is therefore very challenging.

At present groundwater is in most cases only chlorinated and distributed to the population. In a limited number of cases groundwater is treated through conventional aeration followed by rapid sand filtration, or through pre-chlorination, optional coagulation, and rapid sand filtration. When applied for treatment of complex anoxic arsenic containing groundwater, such treatment requires intensive use of chemicals, generates hazardous oxidation by-products, and produces large volumes of toxic waste. Further on, consistent production of drinking water with As <10 µg/l is difficult.

Adsorptive arsenic removal based on commercial adsorbents is highly effective and relatively simple treatment approach (EPA & AWWA 2005, Jekel & Amy 2006). Due to very high costs of commercial adsorbents, however, this treatment is often not affordable for developing countries and countries in transition. Additionally, owing to its composition (arsenic speciation, presence of phosphate, high pH with high buffering capacity etc.), arsenic containing groundwater in Vojvodina is not an ideal candidate for adsorptive treatment with commercial arsenic adsorbents.

IHE ADART (Adsorptive Dutch Arsenic Removal Technology) is an innovative arsenic removal technology based on adsorption on Iron Oxide Coated Sand (IOCS), a by-product from iron removal groundwater treatment plants, and an in-situ regeneration procedure aimed at development of new nano active iron oxide layer over previously adsorbed arsenic. Potential of IHE ADART technology was extensively tested and verified in laboratory and under field conditions in Hungary, Romania and Jordan (Petrusevski et al 2007).

Objective of the study presented in this paper was to assess suitability of IHE ADART technology under field conditions for treatment of different complex arsenic containing groundwater at several drinking water production locations in Vojvodina (Serbia).

METHODOLOGY

Mobile pilot plant with capacity 50 m^3/day was operated during prolonged period of 6 to 12 months at the main drinking water production sites in Subotica (Izvoriste I) and Zrenjanin. Full scale demonstration plant (capacity 500 m^3/day) was operated in the village of Backi Vinongradi (Municipality of Subotica). Treatment scheme of both pilot and the full scale plant included aeration (plate - Inca aerator or aeration tower), rapid sand filtration (RSF) with quartz sand (0.8-1.2 mm, 2.5 m bed depth) and two stage adsorptive filtration with IOCS as filter media (2.5 m of bed depth). Plants operated continuously at filtration rate of 5 m/h. Regeneration cycles of IOCS filters were carried out when an increase of As concentration in IOCS filters filtrate was observed, with typical duration of 30-60 min, followed by backwashing the filters.

Groundwater composition at testing sites is given in Table 1. Arsenic, present mainly as As(III), was high to very high at all sites. Especially groundwater used for water supply in the village of Backi Vinogardi has extremely high arsenic concentration, and is likely one of the highest in the region. In addition to arsenic, groundwater used in town of Zrenjanin also has very high phosphate, organics and methane, which makes it particularly complex and difficult to treat (Zeng et al 2008).

In samples that were taken at regular intervals, arsenic, iron, manganese and ammonia were measured. In addition to field test kits (Arsenator, Wagtech WTD, UK for arsenic and DR980 portable colorimeter HACH, US for iron and manganese, standard laboratory analytical techniques were applied to confirm field tests and/or measure parameters that were not feasible to measure with field test kits.

	Raw water quality								
	As µg/L	Fe mg/L	Mn mg/L	NH_4 mg/L	PO_4 mg PO_4/l	pH	$KMnO_4$ mg/L	Methane mg/L	Fe/As mg/mg
Backi Vinogradi	110-280	0.6-2.2	0-0.12	0.6-1.1	0.80	7.5-7.7	4.2-7.4	-	1.795
Zrenjanin	65-170	0.2-0.8	0.02-0.70	0.7-1.9	1.4-3.4	7.5-8.40	40-55	11.6	1.055
Subotica	90-135	0.5-0.7	0.04-0.07	0.6-0.8	0.2	7.7	5.6	-	1.333

Table 1. Groundwater composition at testing sites in Serbia.

RESULTS AND DISCUSSION

Initial assessment and optimisation of the IHE ADART technology was conducted at the main drinking water production site in Subotica (Izvoriste I). After common ripening period of a few weeks, highly effective and consistent ammonia removal was achieved through nitrification in RSF. In contrast to ammonia removal through break-point chlorination that is applied at the full scale plant at this site (with very high chlorine consumption), applied aeration-filtration did not require any chemicals.

In addition to ammonia, as expected RSF avery effectively removed iron, as well, and after ripening period also manganese. Arsenic removal efficiency in RSF was, limited to approximately 30% (Fig. 1), as a consequence of raw water composition and specifically low Fe/As ratio (Table 1).

During more than 1 year operation of the pilot different regeneration conditions of (partially) saturated IOCS were investigated, including regeneration cycle duration, pattern and frequency. Optimized regeneration conditions comprising frequent short regeneration applied during the last two months resulted in consistent arsenic removal < 10 µg/L, the maximum acceptable concentration based on the WHO guidelines and the national drinking water quality regulations. Results obtained during last two months of the pilot operation also showed that the arsenic level in IOCS filtrate can be controled: from complete arsenic free water (As < 1 µg/L) with short (30 min) daily regeneration, to arsenic levels between 1-9 µg/L with less frequent short regeneration cycles (e.g. once in 2-3 days). Higher regeneration frequency would only marginally increase operation costs given the low unit costs of ferrous iron salts used for regeneration.

Groundwater quality at the second testing site, the main drinking water production well field in Zrenjanin was very challenging (Table 1). More than 20 pilot plants with different process schemes were employed in the past to investigate options for treatment of this very complex groundwater. Most I had very limited success.

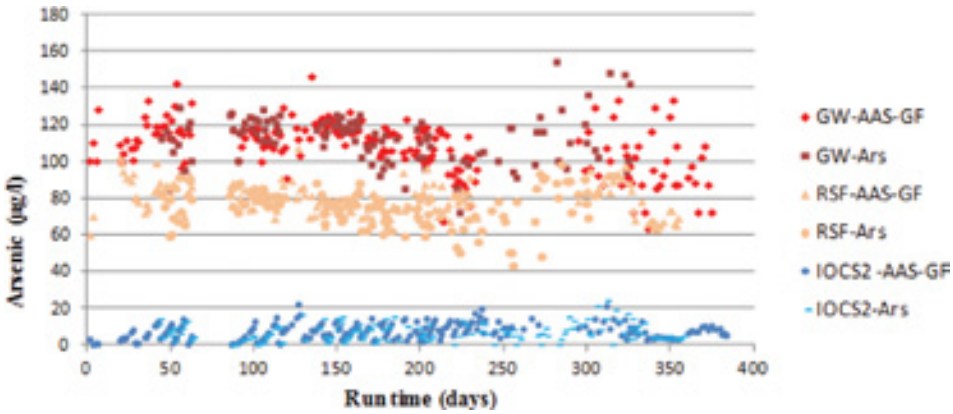

Figure 1: Arsenic concentration in groundwater, and after RSF and IOCS filters, at testing site in Subotica. AAS-GF laboratory analyses, Ars.-results of analyses with field test kit (Arsenator).

Directly after the start of the pilot based on IHE ADART highly effectively removal of iron and ammonia in RSF was achieved. Ripening of RSF filter for ammonia removal was not required, since the pilot was previously in operation in Subotica.

Figure 2 shows arsenic removal achieved with the pilot during the last 70 days of its operation. Arsenic removal in the RSF filter was less effective in comparison to the removal achieved in Subotica, due to even lower Fe/As ration in groundwater, and much higher concentration of phosphate and organics. During the initial 200 days of the pilot operation, optimisation of the IHE ADART took place including different regeneration patterns, and use of two different types of IOCS. During this period arsenic concentration in treated water could not be consistently kept below10 µg/L; typical filtrate concentration was within 5-20 µg/L range. However, once optimization was carried out, treated water with consistently very low arsenic concentration was produced, as can be seen from results of the last 70 days of the pilot operation. The majority of arsenic was removed in the first IOCS filter, while the second IOCS filter had a polishing function only, and produced completely arsenic free filtrate (≤ 1 µg/L). In order to achieve this, frequent (each 1-2 days), but short regeneration cycles were required.

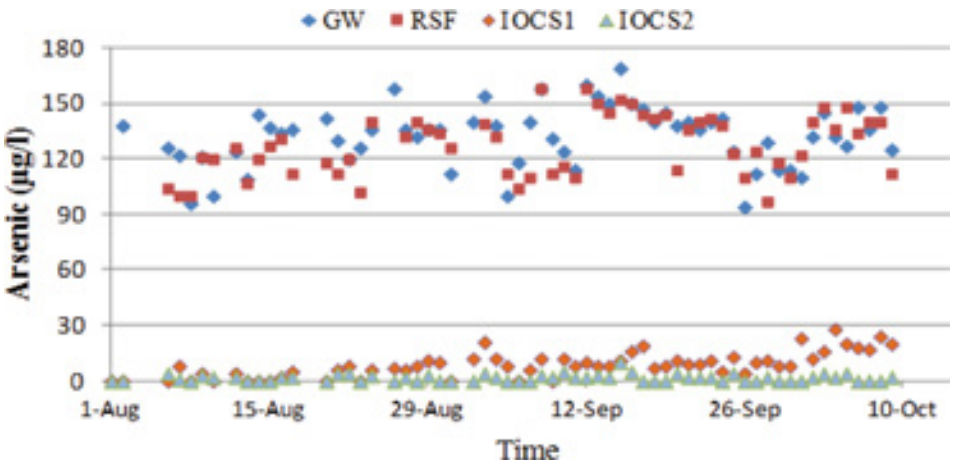

Figure 2: Arsenic removal with IHE ADART pilot plant is Zrenjanin

In a parallel to arsenic, very effective removal of phosphate was achieved in IOCS filters. Given similar chemical properties of phosphate and arsenic, as well as iron oxide nature of the adsorbent, adsorption of phosphate on IOCS was expected. Phosphate removal achieved in the drinking water treatment plant will indirectly lead to generation of domestic wastewater (produced drinking water will after different domestic uses be disposed as wastewater) with much lower phosphate concentration, and associated environmental benefits. At the same time observed effective removal of phosphate, strongly reduces IOCS arsenic adsorption capacity, and introduce the need for frequent regenerations.

In addition to aesthetic aspects (coloured water), high levels of natural organic matter (NOM) also give problems with disinfection (chlorination) given very high required dosages and production of health hazardous chlorination by-products. Conventional aeration-RSF and adsorptive IOCS filtration had very limited effect on removal of NOM that was present at very high concentrations. No signs of NOM adsorption, and associated fouling, were observed on IOCS media. Capability of an anionic ion exchange (IEX) resin to remove NOM was screened, as a simple organic removal option. IOCS filtrate was filtered through IEX filter that operated at filtration rate of 22 m/h with empty bed contact time of 4 minutes. Highly effective NOM removal was achieved to values < 8 mg $KMnO_4$ /L (maximal acceptable NOM concentration according to Serbian drinking water guidelines). Given very high NOM concentration in groundwater, frequent regeneration (once in a few days) of IEX were required to keep NOM level in treated water sufficiently low.

Given the positive experiences at two testing sites, a full scale drinking water production plant was provided for the village of Backi Vinogradi. Irrespective of the highest arsenic concentration in groundwater, practically complete arsenic removal was achieved during 8 months of monitoring period (Fig. 3).

Very high efficiency of IOCS removal can be attributed to applied optimized IHE ADART operational conditions, in combination with somewhat lower treatment capacity (due to limited quantities of groundwater), and with more favourable groundwater composition (phosphate, pH and Fe/As ratio), except for the high arsenic concentration.

Arsenic speciation along the treatment units at all testing sites have shown that As(III) which was predominant in the groundwater (typically ≥ 85%) was practically full oxidized to As(V) by the time the water reached the top of IOCS filters. It is known that iron oxide based adsorbents, including IOCS, have higher adsorption capacity for arsenic present as As(V), which contributes to consistent and efficient arsenic removal.

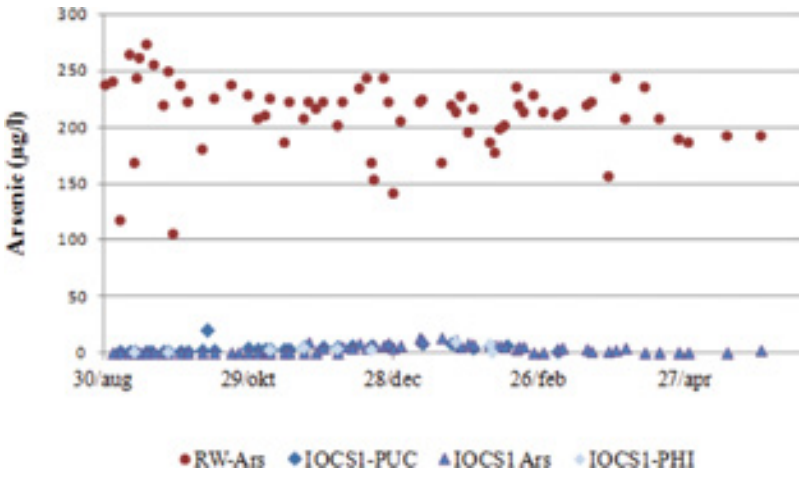

Figure 3: Arsenic concentration in groundwater and filtrate from the 1st IOCS filter at the full scale WTP Backi Vinogradi (Subotica, Serbia). Ars- As analyses conducted with field test kit (Arsenator), PUC and PHI As analyses conducted by laboratories of PUC Subotica and the Public Health Institute of Subotica.

CONCLUSIONS

For successful utilization of IHE AADRT, conventional groundwater treatment (applied as pre-treatment) consisting of aeration and rapid sand filtration is essential to effectively remove ammonia, iron, manganese, and where applicable, methane. Arsenic removal in the pre-treatment was found to be a function of groundwater composition, specifically Fe/As ratio, concentration of phosphate and organics, and was not sufficient to produce low arsenic concentrations in treated water.

Prolonged IHE ARART testing under field conditions at 3 sites in Serbia have shown suitability of this process for drinking water production from very complex ground water characterized by high to very high arsenic concentration.

Optimized regeneration conditions resulted in very low arsenic concentrations at all 3 testing sites. However, regeneration conditions (frequency and the pattern) should be further fine tuned based on groundwater composition.

IEX treatment based on anionic resins can very effectively remove organics from groundwater. Production of drinking water with low concentration of organics from groundwater with very high concentration of organics (e.g., Zrenjanin) requires frequent IEX regeneration.

ACKNOWLEDGEMENT

Results reported in this paper emerged from projects financed by the Innowator programme of the Dutch Government, Public Utilities Companies of Subotica and Zrenjanin (both from Serbia), and WTE Wassertechnik GmbH (Germany). Water Supply Company Vitens and Foundation Water is Our World (both from The Netherlands) provided pilot and full scale plants required for field investigations.

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CHITOSAN COATED WITH FE-MN BINARY OXIDE AS A NEW GENERATION SORBENT FOR THE REMOVAL OF ARSENIC

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Abstract: This paper investigates the use of chitosan coated with Fe–Mn binary oxide, a novel bio-based sorbent, for arsenic removal from synthetic and groundwater matrices. The sorbent was prepared relatively simply by simultaneous oxidation and coprecipitation method. The specific surface area of the chitosan coated with Fe-Mn binary oxide was 1.99 m^2/g. The adsorption kinetics fitted a pseudo-second order model for both As(III) and As(V), suggesting chemical adsorption on the surface of the sorbent and intra-particle diffusion was not the only rate-limiting step in the adsorption process. The adsorption isotherms obtained in the synthetic matrix and groundwater were best fitted to the Freundlich and Redlich–Peterson models. Therefore, a non-ideal non monolayer adsorption model for arsenic on chitosan coated with Fe-Mn binary oxide was proposed.

Keywords: arsenic, sorption, chitosan, Fe-Mn binary oxide, water

INTRODUCTION

In natural water, arsenic is primarily present in two inorganic forms, arsenate [As(V)] and arsenite [As(III)]. Typically, they occur simultaneously in groundwater, with As(III) as the prevalent species (Smedley and Kinniburgh, 2002). As(III) is more toxic, more mobile and more difficult to remove by most arsenic extraction processes than As(V), due to its uncharged form at most pH (Yamani et al., 2012). Among different technologies adsorption is regarded as one of the most promising approaches to remove arsenic from water, due to its simplicity, high efficiency and cost-effectiveness (Qi et al, 2015). Recently, a Fe–Mn binary oxide sorbent has been successfully developed, exhibiting high effectiveness in removing both arsenate and arsenite (Zhang et al., 2007;2012). However, it cannot be used in fixed-bed or other flow-through systems because of its weak mechanical strength and propensity to aggregate, which unavoidably results in extremely high pressure drops and poor hydraulic properties (Li et al., 2012). To overcome these problems, powdered Fe–Mn binary oxide must be immobilized. Chitosan, an aminopolysaccharide obtained by the alkaline deacetylation of chitin (one of the most abundant biopolymers in nature), can be easily formulated into beads and films (Gerente et al., 2007). Moreover, it is inexpensive, biodegradable, biocompatible, and nontoxic to humans and the environment (Sargin et al., 2015). Therefore, the main objectives of this research were to synthesise a new sorbent, chitosan coated with Fe-Mn binary oxide (Chit-FeMn), characterize the novel adsorbent and finally evaluate the adsorption mechanisms of As(V) and As(III) in synthetic and groundwater matrices.

EXPERIMENTAL AND METHODS

The Chit-FeMn was prepared according to a modified method based on Zhang et al. (2007). The key modification was to apply a synthetic chitosan during the particle formation. The specific surface area of the chitosan coated with Fe-Mn binary oxide was determined by nitrogen adsorption using the BET method, by Quantachrome AutosorbTMiQ surface area analyzer. Sorption kinetics were performed with 0.5 g/L of the adsorbent and 0.5 mg/L As(III) or As(V) solution at pH 7.0±0.2. Sorption isotherms were conducted by varying initial concentrations of As(III) and As(V) (0.2–1 mg/L) under a fixed sorbent dose of 0.5 g/L, with a total solution volume of 20 mL in 40-mL glass vials. The vessels were shaken on an orbital shaker at 180 rpm for 24 h at 22±1°C. Sorption isotherms were evaluated in real groundwater samples under similar conditions, by varying the sorbent dose instead of the initial

As concentration. As a real water matrix, groundwater from central Banat region was used (35 µg As/L, 5.1 mg DOC/L, pH 8.2). After the reaction period, all samples were filtered by 0.45 µm membrane filter and analyzed for arsenic. Arsenic concentrations were determined by Graphite Furnace Atomic Absorption Spectrophotometry (Perkin Elmer AAnalyst 700), according to EPA Method 7010. The MDL and PQL of the method were 1.28 and 2.6 µg/L, respectively.

RESULTS AND DISCUSSION

The BET surface area of the synthesized Chit-FeMn was almost 4 times higher (1.99 m^2/g) than the non-impregnated chitosan (0.58 m^2/g). Furthermore, the pore volume of the Chit-Fe-Mn sorbent was approximately 3 times higher (0.005 cm^3/g) than that of chistosan (0.014 cm^3/g). Similar results were obtained in other studies. Gupta et al. (2009) found that the BET surface area of chitosan coated with iron flakes (ICF) was 1.44 m^2/g, while the specific surface area of iron doped chitosan granules was found to be 1.48 m^2/g (Gupta and Sankararamakrishnan, 2010). Based on adsorption kinetics of As on Chit-FeMn, equilibrium is reached after 1080 min (18 h) for As(III) and As(V). Consequently, all other batch sorption experiments were carried out for 24 h, to ensure that sorption equilibrium was reached. Different models were employed to fit the kinetic data, in order to elucidate the sorption mechanism and potential rate controlling steps such as mass transport and diffusion control processes. The pseudo-second order model was found to be more suitable for fitting the kinetic data than the pseudo-first order model, for both As(III) and As(V) (Table 1).

		As(III)	As(V)
Pseudo first order parameters	k_1 (min^{-1})	3.89E-03	3.92E-03
	qe(µg/g)	807	457
	R^2	0.8936	0.8766
Pseudo-second-order parameters	k_2 (min^{-1})	6.71E-06	2.88E-05
	qe (µg/g)	840	833
	R^2	0.9963	0.9996
Intraparticle diffusion parameters	Ki (µg/g $min^{0.5}$)	20.1	13.3
	R^2	0.9581	0.8119

Table 1. Kinetic and diffusion parameters for adsorption of As(III) and As(V) onto Chit-Fe-Mn

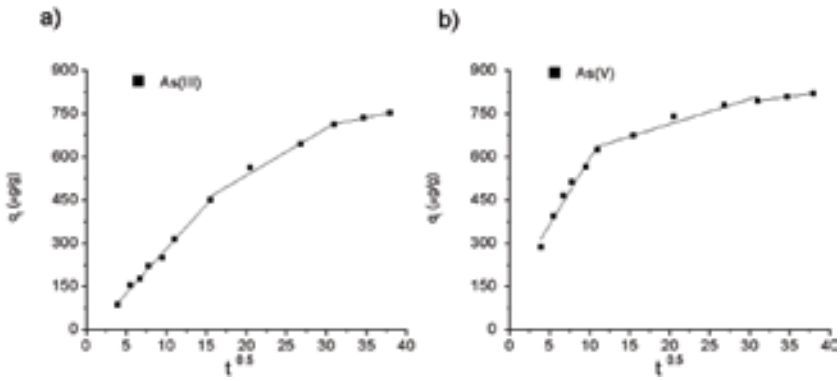

Figure 1: Intraparticle mass transfer plot for a) As(III) and b) As(V) adsorption on Chit-FeMn

This indicates that the sorption process might be chemisorption (Qi et al., 2015). Since the above kinetic models could not identify the rate-limiting step of As(III) and As(V) on Chit-FeMn, the intra-particle diffusion model based on the theory proposed by Weber and Morris was used to analyze the rate-limiting step of adsorption (Fig 1, Table 1). The plots of sorption capacity (q_t) against $t^{0.5}$ do not pass through the origin (the plots for As(III) and As(V) presented multi-linear types in Fig 1a and b), which reveals that the adsorption of As(III) and As(V) on Chit-FeMn is a complex process involving surface adsorption and intra-particle diffusion (all contributing towards the rate of sorption).

		Synthetic matrix		Groundwater
Model	Chitosan Fe-Mn	As(III)	As(V)	Total As
Freundlich	K_F (µg/g)/(µg/L)^n	47.9	40.3	6.43
	1/n	0.71	0.76	0.97
	R^2	0.9613	0.9980	0.9998
Langmuir	q_{max}(µg/g)	4520	4590	4350
	K_L	0.004	0.004	0.001
	R_L	0.20-0.71	0.20-0.71	0.95
	R^2	0.9443	0.9967	0.9997
Redlich-Peterson	K_1 (L/g)	381000	34.6	108
	K_2 (L µg)	7950	23.0	15.8
	α	0.29	0.42	0.034
	R^2	0.9548	0.9981	0.9997

Table 2. Freundlich, Langmuir and Redlich-Peterson isotherm parameters for the sorption of arsenic from real and synthetic matrices on Chit-FeMn

The experimental data for the adsorption of arsenic on Chit-FeMn in synthetic and groundwater samples was fitted with the Freundlich, Langmuir and Redlich-Peterson models (Table 2).

Based on the R^2 values, all the adsorption models fit the experimental data well. Between the Langmuir and Freundlich models, the Freundlich model gives a slightly better representation, possibly due to irreversible adsorption and the heterogeneous nature of the adsorbent (Shan and Tong, 2013). In addition, As(III) uptake by Chit-FeMn involved not only the sorption process but also redox reactions on the surface (Qi et al., 2015). The K_F values derived from the Freundlich models for As(III) and As(V) were smaller for arsenic removed from the groundwater samples, suggesting that the other water constituents affect arsenic removal. In addition, this study confirmed that impregnating Fe-Mn binary oxide onto chitosan could significantly increase the As adsorption capacity of the chitosan beads (the KF values of non impregnated chitosan were 0.000005 and 2.8 (μg/g)/(μg/L)^n g for As(III) and As(V), respectively). The Langmuir model gives maximal sorption capacities of 4.52 and 4.59 mg/g for As(III) and As(V), respectively. Similar results were determined for the groundwater matrix (4.35 mg/g). Gupta et al. (2009) found that the sorption capacity of iron doped chitosan granules (ICB) was 2.32 mg/g and 2.24 mg/g for As(III) and As(III), respectively. The Redlich-Peterson model was employed to better describe the adsorption of arsenic on Chit-FeMn, by representing the adsorption equilibrium over a wide concentration range. The adsorption mechanism is a hybrid model featuring both Langmuir and Freundlich isotherms and does not follow ideal monolayer adsorption. When $\alpha = 1$ the Redlich–Peterson model simplifies to the Langmuir isotherm (Faria et al., 2014). Since the α values obtained from the Redlich–Peterson model for synthetic and groundwater matrices was 0.034-0.42 in this study, it would seem that the arsenic adsorption on Chit-FeMn surface followed a non-ideal non monolayer adsorption model.

CONCLUSION

Chitosan coated with Fe–Mn binary oxide, a novel bio-based sorbent, was prepared by simultaneous redox and the co-precipitation method. The adsorption of arsenic on Chit-FeMn is a complex process involving surface adsorption and intra-particle diffusion all contributing towards the rate of sorption. Arsenic adsorption onto Chit-FeMn follows a non-ideal non monolayer adsorption model. The applicability of the adsorbent for the removal of arsenic from real groundwater samples makes it an attractive filter for arsenic removal units. However, further adsorption experiments should be carried out with different real water matrices, in order to identify the effect of interactions between arsenic and other water constituents.

ACKNOWLEDGMENTS

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NOTES

DRINKING WATER PRODUCTION FROM ARSENIC CONTAMINATED GROUNDWATER IN JORDAN

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Abstract: Objective of the study was to assess suitability of IHE ADART arsenic removal technology based on adsorption on low cost adsorbent Iron Oxide Coated Sand (IOCS) for production of drinking water from the arsenic contaminated groundwater well in Jordan. Operation of full scale drinking water production plant with production capacity of 1000 m^3/day, was monitored during 19 months of continuous operation. The plant consisted of aeration-rapid sand filtration as a pre-treatment for adsorptive IOCS filters, and polishing step with commercial arsenic adsorbents. Ammonia and iron were very effectively removed in RSF, while complete and consistent arsenic removal was achieved in IOCS filters. Regeneration of IOCS filters and polishing filters with commercial adsorbent were not required during the complete monitoring period.

Keywords: Arsenic removal, Jordan, adsorption, low cost adsorbent, IHE ADART

INTRODUCTION

Jordan is historically one of most water stressed countries in the world. Drinking water to majority of population is provided by the Water Authority of Jordan (WAJ). Pressure on water resources increased tremendously in the last decade due to millions of refugees from the region.

Deep groundwater is an essential fresh water resource, extensively used for water supply in this country. Groundwater is in most cases of very good quality, and only requires chlorination before distribution of drinking water to the population. In relatively small number of wells, iron presence in groundwater is detected and water from these wells is treated through conventional aeration filtration, or pre-chlorination, coagulation, sedimentation and filtration.

Recently, a presence of relatively low concentrations arsenic (<40 µg/L) was detected in a number of wells in the Northern part of Jordan. Initially, arsenic containing groundwater was diluted with arsenic-free groundwater from other wells in the region. This practice, however, could not be sustained due to constantly increasing drinking water demand specifically in this part of Jordan, due to large influx of refugees from Syria. There was no experience in Jordan with treatment of arsenic containing groundwater. More over plant operators with general expertise in water treatment are practically nonexistent in this part of Jordan.

Adsorptive arsenic removal is highly effective and relatively simple treatment approach. Iron oxide based composites are at present most effective and most widely used arsenic adsorbents (Mohana et al 2006, Jekel et al 2007). Commercial arsenic adsorbents are expensive, and in general have to be replaced once saturated. As a consequence their use in developing countries is rather limited. IHE ADART (Adsorptive Dutch Arsenic Removal Technology) is an arsenic removal technology based on adsorption on Iron Oxide Coated Sand (IOCS). IOCS is a by-product from water treatment plants removing iron from groundwater and is consequently rather cheap. In addition, (partially) arsenic saturated IOCS can be regenerated in-situ, by creating a new iron oxides nano layers over previously adsorbed arsenic (Fig.1). The potential of IOCS to remove arsenic has been extensively tested under laboratory and field conditions with mobile treatment plants (Petrusevski et al 2007). No experiences were, however, available with long term operation of full scale arsenic removal treatment plants based on IHE ADART. Additionally, the technology requires operators that are experienced in handling chemicals and operation of conventional water treatment units (e.g., filters and pumps).

Objective of the study presented in this paper was to assess suitability of IHE ADART technology as a standalone arsenic removal process, or in combination with adsorptive filtration based on commercial arsenic adsorbent, for drinking water production from the Jaber Balad well in the North of Jordan. The paper will introduce experiences from 19 months long continuous operation of the full scale drinking water production plant Jabber Balad, Jordan.

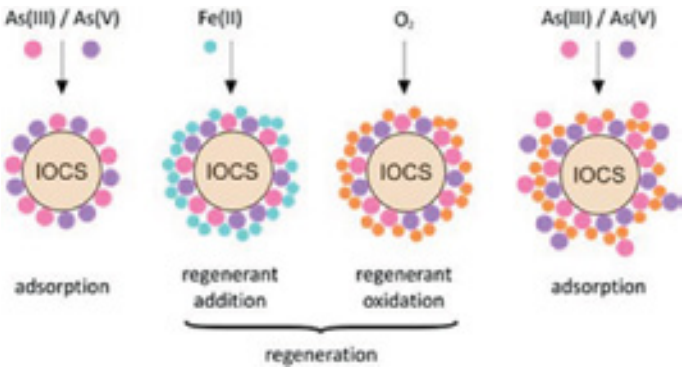

Figure 1: Schematic presentation of IHE ADART technology

METHODOLOGY

Groundwater Composition

Deep groundwater from the Jaber Balad well originates from a limestone aquifer and is consequently well buffered, with slightly alkaline pH. In addition to elevated arsenic concentration, groundwater also contains slightly elevated iron, manganese and ammonia concentrations (Table 1). Concentrations of arsenic, iron, ammonia and pH vary in rather wide range. Abstracted groundwater was found to typically have a few mg/L of dissolved oxygen. Simultaneous presence of ammonia and dissolved oxygen suggests that abstracted groundwater is likely a mixture of aerobic and anaerobic groundwater layers.

As	Fe	Mn	NH_4	PO_4	pH	HCO_3
µg/L	mg/L	mg/L	mg/L	mg PO_4/l		mg/L
10-48	<0.02-0.39	<0.005-0.01	<0.10-0.40	<0.02-0.06	7.4-7.9	270-310

Table 1. Composition of groundwater from the Jaber Balad well.

Arsenic removal groundwater treatment plant with capacity of 1000 m^3/day was provided close to the Jaber Balad well in the North of Jordan (in the vicinity of the border with Syria). Though the main target of the plant was to remove arsenic, presence of ammonia in groundwater introduced need for pre-treatment, prior to IHE ADART technology, in order to avoid the risk of development of nitrification biomass on IOCS and associated reduction of arsenic removal capacity. Consequently, conventional groundwater treatment consisting of aeration and rapid sand filtration (RSF) was provided as pre-treatment. Aeration was achieved by injection of air from oil-free compressors directly into two pressure rapid sand filter vessels (1.6 m in diameter) that operated at filtration rate of 10 m/h. Filters were filled with 2.0 m of quartz sand, size fraction 0.8-1.2 mm. Pre-treated water was fed to 4 adsorptive filters (1.6 m in diameter) installed in a parallel, filled with 2.5 m of IOCS. Adsorptive filters with IOCS operated at filtration rate of 5 m/h with an empty bed contact time of 30 min.

Produced treated water turned out to be essential for water supply of local population and refugees, with practically no alternative drinking water sources. With this in mind and taking into account that there is a lack of experienced plant operators, it was decided to provide an extra polishing arsenic removal step based on commercial adsorbent, i.e., Granular Ferric Hydroxide - GEH (type 102, Wasserchemie GmbH, Germany). Two filters with 1.6 m in diameter were filed with 2.5 m of GEH and were operated in parallel at filtration rate of 10 m/h. Filtrate from GEH filters was disinfected with chlorine gas and transported to the distribution reservoir. Filters were beck washed with water at bed expansion of ≥10%.

Simplified process scheme of the water treatment plant is given in Fig. 2.

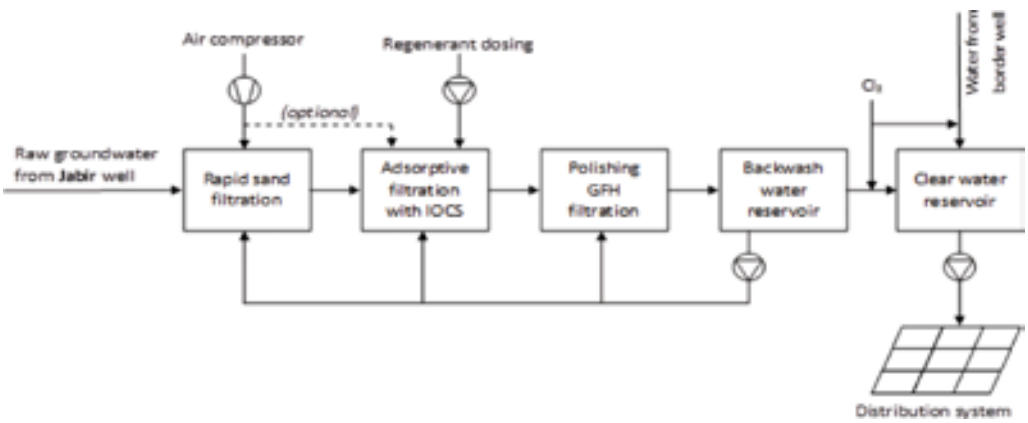

Figure 2: Schematic diagram of the treatment plant at Jabir Balad well

Water Quality Analyses

Arsenic and iron concentrations were monitored on site with an Arsenator, arsenic field test kit (Wagtech WTD, UK) and DR980 portable colorimeter (HACH, US), respectively. Field results were verified in the laboratory with AAS-GF and AAS-flame for arsenic and iron, respectively. The correlation between results obtained in laboratory and test kits was found to be very good.

RESULTS AND DISCUSSION

As expected, after ripening period of approximately 3-4 weeks, required to develop nitrifying biomass on filter sand, very effective and consistent ammonia removal was achieved in RSF(Fig.3).

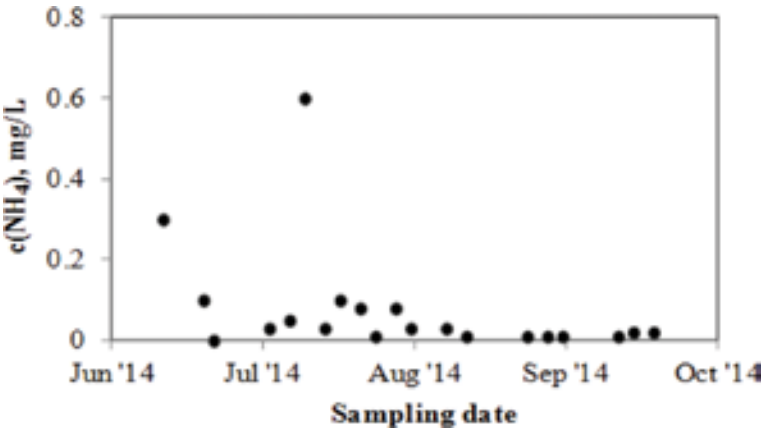

Figure 3: Ammonia concentration in RSF filtrate

Iron concentration in ground-water reduced with prolonged abstraction time from concentration as high as 0.6 mg/L to values below 0.10 mg/L, likely due to drop of groundwater table - consequence of continuous (over) pumping and associated abstraction of groundwater from other aquifer layers. After the start-up of the plant, iron levels in the RSF filtrate (Fig.4) were immediately far below the maximal acceptable concentration based on the Jordanian drinking water quality regulations (<0.3 mg/L). After very short ripening period of a few weeks, iron levels in RSF filtrate were consistently below the detection limit of 0.035 mg/L. It could be assumed that significant part of iron was removed through ferrous iron adsorption on sand, given the extremely short contact time available for oxidation of ferrous iron (aeration with pressure aeration directly above the filter media) in combination with very shallow supernatant layer above the media. As a consequence, backwashing frequency of RSF was very low (once per more than a week).

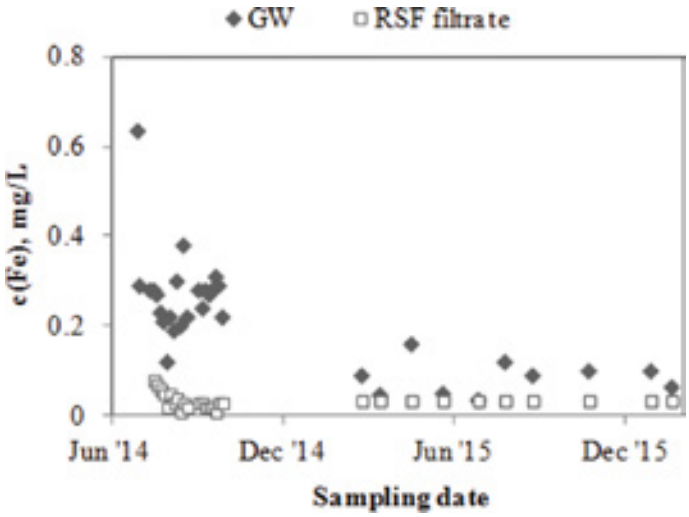

Figure 4: Iron concentration in groundwater and after RSF filters

Arsenic concentration in abstracted groundwater was also find to change significantly with prolonged abstraction time. During the initial few weeks of the plant operation, arsenic concentration increased from approximately 25 µg/L to values as high as 50 µg/L. Prolonged intensive continuous groundwater pumping resulted in slow reduction of arsenic levels in groundwater, likely due to drop of groundwater table, with associated abstraction of groundwater from different layers with lower arsenic concentration.

Throughout the whole monitored period of 19 month, arsenic concentration in IOCS filtrate was found to consistently below the detection limit of 1 µg/L, irrespective of arsenic concentration in groundwater (Fig. 5). Presence of iron in groundwater resulted in limited arsenic removal in the RSF, trough arsenic adsorption on iron flocs, and iron (hydr)oxides formed on sand media. Relatively low effectiveness of arsenic removal in RSF filters is a consequence of low Fe/As ratio in groundwater (on average approximately 4 mg Fe/mg As).

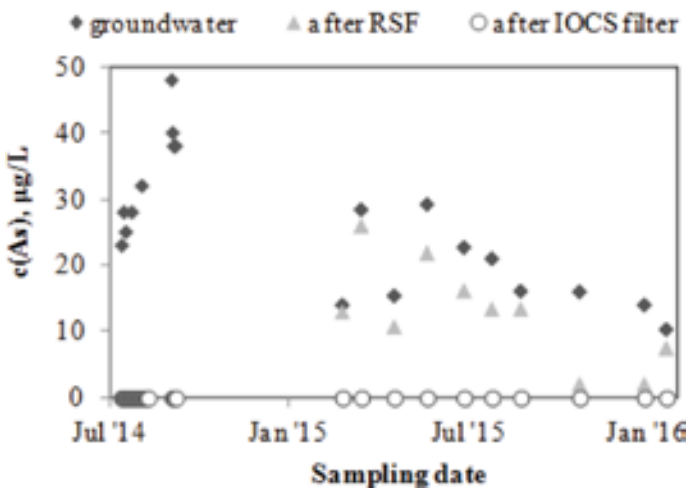

Figure 5: Arsenic concentration in groundwater, RSF and IOCS filters effluent during 19 months of monitoring period

During the reported operational period of 19 months there was no need for regeneration of IOCS media. Within this time, more than 500.000 m^3 of completely arsenic free drinking water was produced and >10 kg of arsenic was removed in IOCS filters. Assuming a conservative IOCS adsorption capacity of 500 mg As/kg IOCS at C_e=10 µg/L, as an extrapolation of results from batch adsorption isotherm experiments, approximately 75% of IOCS arsenic adsorption capacity has been utilized after 19 months of the plant operation. This further suggests that the need for regeneration of arsenic saturated IOCS will very likely be required in the near future.

Given the low adsorbent unit cost, operational costs for arsenic removal at WTP Jaber Balad with IOCS are estimated at ≤ 0.01-0.02 €/m^3 of produced drinking water.

During initial 19 months of the plant operation no GEH adsorption capacity was utilized and as a consequence very long useful life of this expensive arsenic adsorbent is expected. Its main function was, and will remain, a polishing of treated water quality if / when arsenic concentration in IOCS filter filtrate starts increasing (assuming that no timely regeneration is carried out).

As a preventive measure, to avoid possible bio-growth in adsorptive filters due to the very high ambient temperatures (as high as 47°C), IOCS and GEH filters were backwashed once in approximately 10 days.

CONCLUSIONS

Prolonged operation of the full scale WTP Balad Jaber confirmed that IHE ADART arsenic removal technology is highly suitable for production of arsenic free drinking water from arsenic containing groundwater.

For groundwater with relatively low arsenic (≤50 µg/L) and phosphate concentration, a single IOCS adsorptive filtration step with EBCT of 30 min is sufficient to consistently and completely eliminate arsenic from produced drinking water. Polishing arsenic removal filter with GEH for such water can be considered only as an extra safety measure, assuming that available resources will allow it.

Conventional groundwater treatment based on aeration and rapid sand filtration is recommended as pre-treatment for IHE ADART technology when ammonia is present in groundwater. Such pre-treatment will effectively remove ammonia and prevent growth of nitrifying bacteria on IOCS.

ACKNOWLEDGEMENT

Results presented in this paper were collected at the arsenic removal plant for the Jabir Balad well that was constructed with funds provided by Water Authority of Jordan.

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MULTIPARAMETER OPTIMIZATION OF GROUNDWATER TREATMENT BY PREOZONATION AND COAGULATION

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Abstract: Natural organic matter (NOM) present in drinking water sources can cause the formation of disinfection by-products and interfere during treatment with the removal of other contaminants like arsenic. This work studies the effect of pre-ozonation on the coagulation/flocculation process to remove NOM and As from groundwater. Four groundwaters with different NOM (DOC from 3.00±0.16 mg C/L to 6.50±0.62 mg C/L) and As contents (3.69±0.20 µg/L to 18.0±2.10 µg/L) were studied. Results show that treatment choice is highly dependent on the water characteristics and proper treatment conditions can only be selected after site specific study and treatment optimization.

Keywords: groundwater, NOM, As, coagulation, pre-ozonation

INTRODUCTION

Natural organic matter (NOM) are ubiquitous constituents of the groundwaters worldwide and their presence in drinking water sources can cause various negative effects during water treatment and in distribution systems. The formation of disinfection by-products is one of the most important issues related to the treatment of NOM rich water, as they have an adverse effect on human health (Richardson and Ternes, 2014) and tend to interfere with the removal of other contaminants like arsenic (Pallier et al., 2010). Coagulation and flocculation is generally considered the most common and economically feasible processes for NOM removal from water (Matilainen et al., 2010), and also one of the best available technologies for As removal (USEPA, 2000). One possibility to enhance coagulation efficiency is to combine it with pre-ozonation. Ozone is known to affect the coagulation process by significantly altering the nature and content of NOM in water (Matilainen et al., 2010). Therefore, the goal of this study was the optimisation of the ozone dose during pre-ozonation for improving the coagulation efficiency as a treatment of groundwaters which contain NOM and arsenic.

MATERIALS AND METHODS

The effects of the application of pre-ozonation in combination with coagulation/flocculation to reduce NOM and As contents in groundwater were studied. Four groundwaters (municipalities Kulpin-Matrix A, Bački Petrovac – Matrix B, Maglić – Matrix C and Gložan - Matrix D) from Vojvodina region (Republic of Serbia) which differ in NOM and arsenic contents (Table 1) were studied. Pre-ozonation of raw groundwater was performed in a glass column with a 26 cm diameter and a capacity of 2 L. Ozone (applied in doses 0.25, 0.5 and 0.8 mg O_3/mg DOC) was introduced to the water through a diffuser located at the bottom of the column. Tests were carried out on water without correcting the pH (pH 7-7.5). After pre-ozonation, the coagulation experiments were carried out in JAR tests using a FC6S Velp Scientific apparatus, with 0.5 L samples at room temperature (22-25°C). During the experiments, iron(III)-chloride solution was used as coagulant in doses of 150-200 mg $FeCl_3$/L, and polyaluminium-chloride (PACL) in doses of 10-30 mg Al/L, depending on the water type. The optimal doses for each water were determined by a set of preliminary JAR test experiments encompassing a wider range of coagulant doses (0.1-2.0 mmoL/L of coagulant: 50-200 mg $FeCl_3$/L and 2.5-30 mg Al/L; results not presented in this paper). Magnaflok LT27 flocculant was dosed at 0.2 mg/L. Coagulation was carried out with rapid stirring at 120 rpm/min for 2 min, after which flocculation was conducted in slow stirring mode at 30 rpm/min for 25 minutes.

After stirring, samples were settled for 30 min, after which the clear supernatant was withdrawn from each jar and analyzed for DOC, UV254 absorbance, trihalomethane formation potential (THMFP) and As content. DOC concentrations were determined in accordance with standard method SPRS ISO 8245:2007 (SRPS, 2007) with a practical quantitation level (PQL) of 0.5 mg C/L. The UV254 absorbance was determined according to standard procedures (APHA, 2012). THMFP (chloroform; bromodichloromethane; dibromochloromethane and bromoform) was determined according to standard methods (USEPA, 1996a, 1996b). Arsenic concentrations were determined according to EPA method 7010 (USEPA, 2007; PQL of 0.5 µg As/L).

RESULTS AND DISCUSSION

Four groundwaters were selected to represent natural matrices with different characteristics, as presented in Table 1.

Parameter	Unit	Value ±sd			
		Matrix A	Matrix B	Matrix C	Matrix D
DOC	mg C/L	5.28±0.65	5.59±0.23	6.50±0.62	3.00±0.16
UV_{254}	cm^{-1}	0.131±0.002	0.169±0.006	0.224±0.043	0.082±0.016
SUVA	$L \cdot mg^{-1}m^{-1}$	2.45±0.42	3.03±0.01	2.37±0.86	2.76±0.71
THMFP	µg/L	275±39	327±120	330±32	183±37
As	µg/L	8.46±4.46	18.0±2.10	11.8±3.80	3.69±0.20
Bromide conc.	µg/L	423±21	265±19	668±31	76.7±3.6

sd - standard deviation based on 10 measurements

Table 1. Characteristics of the groundwaters

The results shown in Table 1 indicate that based on the dissolved organic carbon contents, water matrix C has the highest content of natural organic matter (6.50 ± 0.62 mg/L DOC), while water matrix D has the lowest value (3.00 ± 0.16 mg /L DOC). The UV absorbance at 254 nm and specific UV absorbance values can be used to characterise the NOM, and with SUVA values from 2.73±0.86 to 3.03±0.01 $Lmg^{-1}m^{-1}$, the presence of hydrophobic and hydrophilic NOM in all tested types of water is indicated. Water matrices A-C have high, mutually similar DOC contents, and after chlorination, they all exhibited high potentials for trihalomethane formation (275±39 to 330±32 mg/L). These test matrices also have high bromide contents, leading to high proportions of brominated trihalomethanes, contributing up to 56-65% of the total THM formed. On the other hand, the lower DOC content (3.00 ± 0.16 mg/L) in groundwater D was reflected in lower potential formation of trihalomethanes (183±37 mg/L). The arsenic content in groundwaters A, B and C was higher than 10 µg/L, which is the maximum allowed level (MAL) controlled by Serbian regulations (Official Gazette SRJ, 1998). In Figure 1, the changes in the NOM related parameters (DOC, UV_{254} absorbance, THMFP) and arsenic contents after the application of coagulation combined with pre-ozonation are presented.

The DOC data presented in Figure 1 show that pre-ozonation slightly improves the coagulation efficiency of PACl and $FeCl_3$, mostly when the doses of ozone are ≥0.5 mg O_3/mg DOC, but strongly dependent on water type. In addition, changes in NOM structure caused by ozone application lead to significantly improved removal of UV_{254} absorbing material during combined preozonation and coagulation treatment for both coagulants and under all ozone doses investigated). This positive effect of pre-ozonation on UV_{254} absorbing material removal can be explained by the fact that ozone reacts mainly with unsaturated bonds in molecules, which are those responsible for the absorption of UV light at 254 nm (Singer et al., 2003). Oxidative degradation of NOM molecules, a reduction of molecular mass and the formation of molecules with hydrophilic characteristics is probably the reason for the lower coagulation efficacy for DOC removal after pre-ozonation, compared to coagulation alone (Matilainen et al., 2010). As a consequence, THMFP values fluctuate depending on the water, coagulant type and ozone dose. The highest improvement in coagulation efficiency for THM precursors removal was observed when the ozone dose of 0.5 mg O_3/mg DOC was applied in pre-ozonation before $FeCl_3$ coagulation of water matrices A and B. Arsenic contents were lowered by as little as 21% in water D and up to 92% in water matrix B, by coagulation alone, with better results obtained when $FeCl_3$ was applied. Pre-ozonation did not improve arsenic removal during coagulation, but arsenic concentrations in all treated waters were below 10 µg/L.

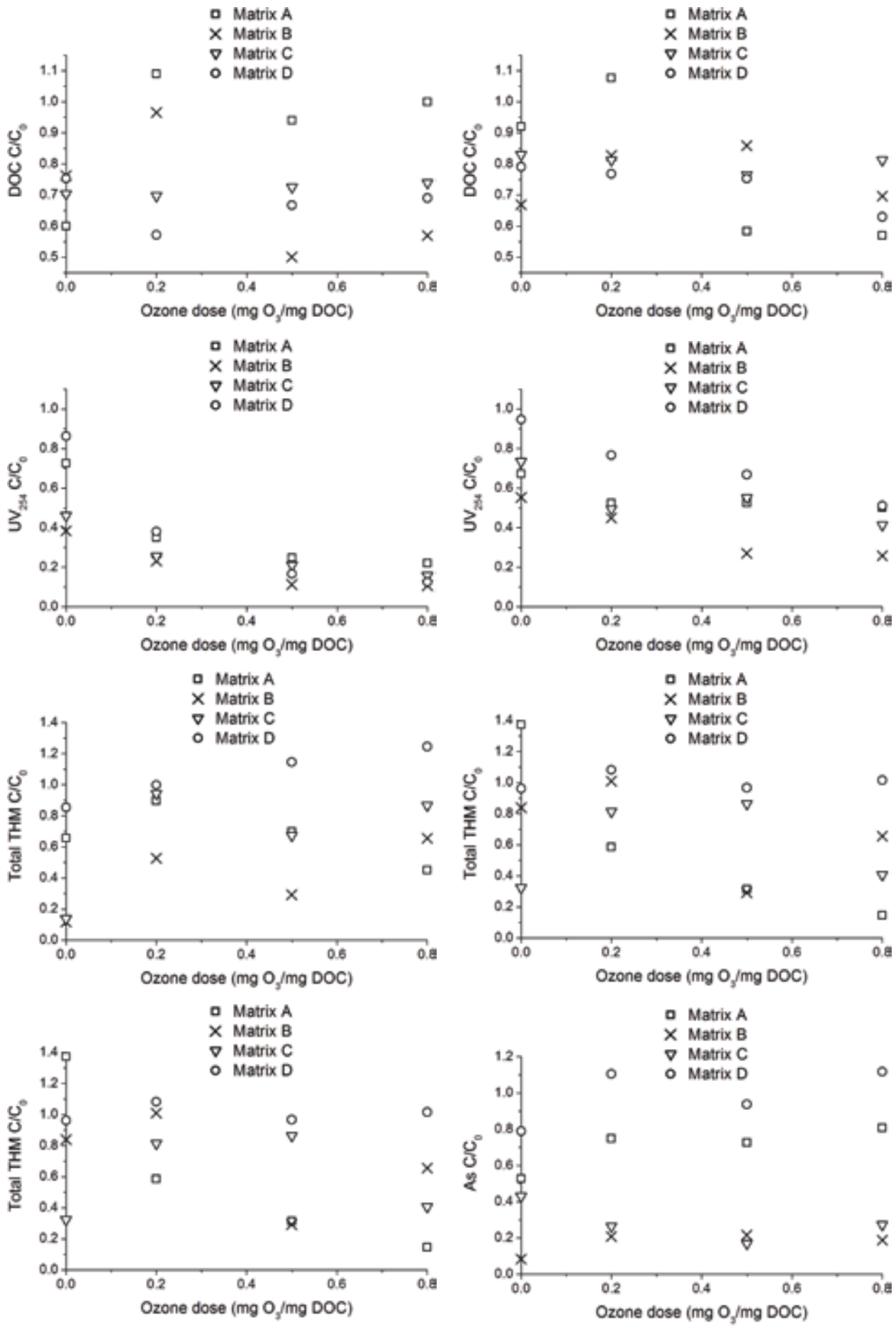

Figure 1: Changes in the DOC, UV254 absorbance, THMFP and arsenic contents after the application of coagulation combined with pre-ozonation

CONCLUSION

This paper presents the results of a study into the influence of pre-ozonation on the coagulation efficiency for the removal of NOM and arsenic from groundwater. The ozone pre-treatment was shown to improve the removal of UV_{254} absorbing material by coagulation, independently of the water investigated and coagulant type used. Depending on the type of water, pre-ozonation has a two-fold impact on coagulation efficiency: positive (at doses ≥ 0.5 mg O_3/mg DOC) or negative. The effects of ozonation within the combined water treatment depend not just on the ozone dose applied, but also on the type of coagulant. In the combined pre-ozonation/coagulation process, NOM removal was greatly improved in the case of $FeCl_3$ coagulant application, whereas ozonation had almost had no impact on PACL efficiency. Coagulation alone was sufficient to remove arsenic to below the MAL of 10 µg/L, and pre-ozonation did not further improve coagulation efficiency. These results confirm that treatment choice is highly dependent on the water characteristics and proper treatment conditions can only be selected after site specific studies and optimization of the selected treatments.

ACKNOWLEDGMENTS

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GROUNDWATER DEFLUORIDATION USING ALUMINUM (HYDR)OXIDE COATED PUMICE: LABORATORY-SCALE COLUMN FILTER STUDIES AND ADSORBENT REGENERATION

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Abstract: The toxic effects of fluoride on human health when consumed in excess amounts in for long periods is well known .This study (i) investigated the effectiveness of aluminum oxide coated pumice (AOCP) for groundwater defluoridation under continuous flow conditions, and (ii) explored the potential for regeneration of exhausted AOCP for its reuse. AOCP was found to be capable of reducing fluoride concentration of 5. 0 ± 0.2 mg/L in model water to ≤ 1.5 mg/L(WHO guideline). In contrast to the regeneration of most adsorbents, it was found that the fluoride adsorption capacity of exhausted AOCP, after the first cycle of regeneration was not only fully (100%) restored, but increased by > 30% under batch conditions and > 50% under continuous flow conditions, suggesting the high potential of the regeneration concept.

Keywords: Fluorosis; Adsorption; Empty bed contact time; Adsorbent usage rate

INTRODUCTION

Millions of people around the world, particularly in developing countries including Ghana, rely on groundwater with excess fluoride, and are exposed to many fluoride-related health hazards including dental and skeletal fluorosis. Due to the lack of known effective treatment of such health effects, groundwater with excess fluoride requires treatment prior to consumption as a preventive measure. Among the available methods, the adsorption process is generally considered the most appropriate for water defluoridation (Chauhan et al., 2007). Additionally, one of the factors that may contribute to the economic viability of any adsorbent is its potential for regeneration for reuse (Tresintsi et al., 2014). The aims of this study were therefore to: (1) investigate the effectiveness Aluminum Oxide Coated Pumice (AOCP) for fluoride removal under dynamic conditions using a laboratory scale fixed-bed adsorption column, (2) investigate the effects of bed depths and empty bed contact times (EBCTs) on the performance of AOCP and determine the contact time for an optimal use of the adsorbent capacity, (3) explore a simple and innovative method for regeneration of exhausted AOCP

MATERIAL AND METHODS

AOCP used for the fixed-bed adsorption experiment was synthesized by an Al coating method. A sufficient amount of 0.5 M $Al_2(SO_4)_3$ used as coating solution was added to completely soak about 3kg of dried pumice in 20L plastic bucket containers, well stirred, drained, dried and subsequently soaked in 3M NH_4OH to neutralize and complete the coating process. Fluoride model water used for the fixed-bed adsorption experiments was prepared using Delft (The Netherland) tap water (with composition (mg/L); Ca = 49.7, Mg = 9.0, SO4 = 78,8, Cl = 72.2, Na = 35, K = 5.5). The tap water and dosed stock solutions of fluoride, HCl and bicarbonate were completely mixed in a model water tank to obtain a final influent fluoride concentration (C_o(mg/L) of 5.0±0.2) and a bicarbonate

concentration of 330.0 ±5 mg/L, similar to that found in groundwater in the Northern region of Ghana. A neutral pH of 7.0±0.2 was used for the experiment. .Laboratory-scale fixed bed column experiments were performed using a PVC pipe of 60mm internal diameter and length of 3.2 m. The column was packed with AOCP (and subsequently with Regenerated AOCP (RAOCP) after regeneration of exhausted AOCP) to a total bed depth of 2.5 m. Fluoride containing model water was filtered through the packed bed column in a down-flow mode at a design flow (Q_d) of 14.1 L/h (equivalent to a filtration rate of 5.0 m/h). At predetermined times, water samples were taken at different bed depths; 0.5m, 1m, 1.5m, 2m and 2.5m, from the top of the filter bed and analyzed for the residual fluoride concentrations (C_t(mg/L). Regeneration was accomplished by re-coating the surfaces of the exhausted AOCP with a new layer of aluminum (hydr) oxides, that created new active sites to restore the fluoride adsorption capacity

RESULTS AND DISCUSSIONS

Effect of Bed Depth and EBCT on AOCP Performance and Usage Rate

The results of fluoride adsorption onto AOCP under continuous flow conditions are presented in the form of breakthrough curves for the five different bed depths (Fig. 1a). AOCP was found to be capable of reducing fluoride concentration of 5. 0 ± 0.2 mg/L in model water to ≤ 1.5 mg/L (WHO guideline). (The breakthrough was attained when the effluent fluoride concentration reached 1.5 mg/L). The number of bed volumes (BV) of water treated before breakthrough, increased with the bed depth till 2m, where maximum of 165 bed volumes were attained, and thereafter slightly declined with further increase of bed depth.

Two of the important design parameters that need to be determined for a fixed bed adsorption treatment system are the EBCT and adsorbent usage rate (i.e., mass of adsorbent/volume of water treated before breakthrough). The EBCT affects the bed life (number of bed volumes (BV) of water treated before breakthrough) of the system and its proper selection is required to fully utilize the adsorbent capacity (Faust and Ally, 1987). The effect of EBCT on AOCP usage rate, which determines how often the adsorbent must be regenerated or replaced and the corresponding bed life, were determined for EBCTs of 6, 12, 18, 24 and 30 min and the results are presented in Fig (1b).

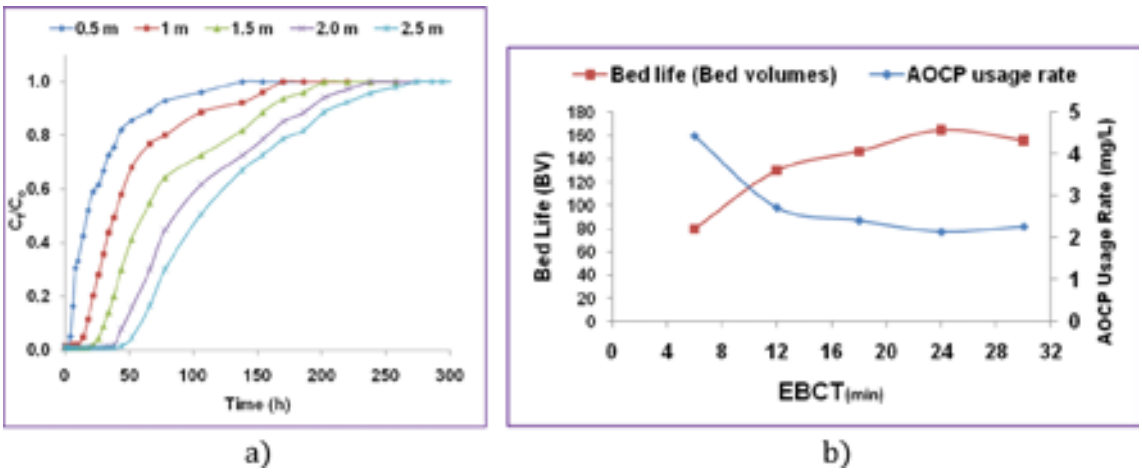

Figure 1: (a) Breakthrough curves for fluoride removal by AOCP for different bed depths and (b) Effect of EBCT on AOCP performance and usage rate.

From Fig (1b), an initial rapid decrease of AOCP usage rate was observed with increasing EBCT from 6 to 24 min, where a minimum value of 2.14 mg/L was attained, and thereafter started to increase. Correspondently, the bed life also increased with increase of EBCT till the maximum value of 165 BV was attained at an EBCT of 24 min. Thus 24 min was considered as an optimal EBCT for optimal use of AOCP adsorption capacity, which could be a useful guide for the design of full scale applications .

Fluoride Adsorption Performance of RAOCP and Comparison With That of AOCP

The fluoride removal performance of the regenerated AOCP (RAOCP) was evaluated under similar batch and column experimental conditions, and the effectiveness of the regeneration procedure was assessed based on the degree of recovery of the adsorption capacity. Other performance measures used for the assessment of the effectiveness of the regeneration method included calculations for RAOCP adsorbent usage rate and

number of bed volumes (BV) of water treated before breakthrough, and comparison of these indicators with that for AOCP. Batch equilibrium experimental data for fluoride removal with RAOCP were also fitted in the well-known Langmuir and Freundlich isotherm models, for estimating the adsorption capacity (graphs not shown).

A comparison of the adsorption capacity of RAOCP with that of fresh AOCP under similar batch conditions applied in our previous studies, based on the Langmuir q_{max} (Salifu et al., 2013), revealed an increase of 34 % after the regeneration, which suggests the effectiveness of the applied regeneration procedure. A comparative plot of the breakthrough curves for RAOCP and AOCP is presented in Fig. 2 (shown for two representative bed depths).

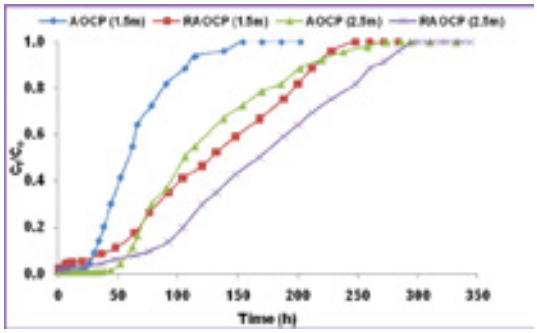

Figure 2: Comparison of breakthrough curves for fluoride removal with RAOCP and AOCP for two representative bed depths.

The breakthrough curves for RAOCP at all bed depths were found to be less steep than that of AOCP, which indicates a slower exhaustion of RAOCP (Maliyekkal et al., 2006), and suggests an improved fluoride removal performance after the regeneration process. An increase of 54%, 58% and 57% of fluoride adsorption capacity , service time and volume of treated water before breakthrough, respectively, for RAOCP were observed, which further revealed a considerable improvement of fluoride removal performance under the dynamic conditions after the regeneration of exhausted AOCP. A reduction of 33% of the adsorbent usage rate for RAOCP, and an increase of 57% for the bed life were observed, which were also indications of improved adsorption efficiency and performance after the regeneration.

A review of literature on regeneration of adsorbents reported by others, reveals that generally, the adsorption capacity/efficiency for most adsorbents are either fully (100%) restored or experiences a marginal loss (about 5 - 10%) or a considerable loss (up to 20%) of capacity after the first cycle regeneration (Ghoral and Pant, 2004; Maliyekkai et al., 2006). In contrast, however, it was found in this study that the adsorption capacity of exhausted AOCP after the first cycle regeneration was not only fully (100%) restored, but attained a considerable increase: > 30% improvement of fluoride adsorption capacity under batch conditions and generally > 50% improvement under the continuous flow conditions, based on the assessed performance indicators. This therefore suggests the concept and regeneration procedure explored in this study was effective and useful. The improved fluoride adsorption capacity of RAOCP is likely due to the creation of larger number of active sites in the regeneration process, which may be explained from the hard soft acid base (HSAB) concept . According to the concept, due to their inherent characteristics, hard acids prefer binding to hard bases while soft acids prefer binding to soft bases (Pearson, 1988). With a hardness (η) value of 7.0 ev, fluoride is ranked as the hardest base and would therefore posses a high affinity for Al, which is one of the hardest acids (η= 45.77). With the applied regeneration procedure, the adsorbed fluoride ions were therefore not stripped from the surfaces of the fluoride-saturated (exhausted) AOCP prior to the re-coating process, which consequently made it a better base material due to the presence of fluoride, for an enhanced binding of Al, in accordance to the HSAB concept. This most probably resulted in the creation of more hard Al active sites on RAOCP surfaces for fluoride adsorption compared to fresh AOCP which was synthesized by Al coating using virgin pumice as the base material. Further surface characterization and quantification of adsorption sites of AOCP before and after regeneration is, however, required to further help in explaining the increase of fluoride removal performance of RAOCP. Moreover multiple regeneration cycles are required to further investigate the trend of fluoride removal performance of RAOCP.

CONCLUSIONS

Aluminum hydr(oxide) coated pumice was found capable of reducing fluoride concentration of 5 ± 0.2 mg/L in model water to ≤1.5 mg/L (WHO standard, 2008) under continues flow conditions in laboratory- scale column experiments. An empty bed contact time (EBCT) of 24 min was found a suitable guide for design of full-scale water treatment systems that would allow an optimal use of the AOCP fluoride adsorption capacity. The fluoride adsorption capacity of exhausted AOCP, after the first cycle of regeneration was not only fully (100%) restored but increased by more than 30% under batch conditions, and more than 50% under continuous flow conditions, suggesting the effectiveness of the applied simple regeneration approach. This may presumably contribute to the economic viability of AOCP as a water defluoridation adsorbent. Extent of the fluoride adsorption capacity recovery after multiple r regeneration cycles, however, still will have to be verified.

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DEGRADATION OF 1,2,3-TRICHLOROBENZENE IN SYNTHETIC AND NATURAL WATER USING LP-UV/H_2O_2 ADVANCED OXIDATION PROCESS

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Abstract: This study investigates the efficiency of a UV/H_2O_2 advanced oxidation process using a low pressure (LP) mercury lamp for the degradation of 1,2,3-trichlorobenzene (TCB) in different water matrices. TCB was used as a model compound for chlorinated benzenes identified as priority pollutants by the European Water Framework Directive. The LP-UV/H_2O_2 advanced oxidation process, with a UV fluence of 600 mJ/cm^2 and 1 mg H_2O_2/L, was found to be very effective for TCB degradation (about 99%) in synthetic ultrapure water. The presence of humic acids and carbonate reduced TCB degradation efficiency, with high levels of TCB degradation (up to 80%) requiring application of a greater UV fluence of 4200 mJ/cm^2. The constituents of natural groundwater had the greatest influence on TCB degradation, where a maximum degradation of 62% was achieved. These results are supported by the TCB degradation kinetics. Based on the fluence-based rate constants, the presence of carbonate, humic acids and other water parameters significantly reduces the TCB degradation by advanced oxidation.

Keywords: 1,2,3-trichlorobenzene, LP-UV/H_2O_2, photolysis, humic acids, natural organic matter, carbonate

INTRODUCTION

There is growing interest about the occurrence of organic micro pollutants in water bodies, especially those used as potential drinking water sources. Some of these substances were classified as emerging water contaminants by the Environmental Protection Agency and the European Union, including pharmaceuticals, personal care products, pesticides, endocrine disruptors, surfactants, fire retardants and fuel additives, and they are continuously discharged into the environment as a result of their use in industry, medical care, agriculture etc. (Wols and Hofman-Caris, 2012). Different pollutants have been detected in aquatic ecosystems at ng/L – µg/L levels (Shu et al., 2013; Ribeiro et al., 2015).

Chemical pollution of surface waters can cause negative effects on the environment, aquatic organisms and human health. In early 2000, Directive 2000/60/EC therefore defined priority substances which pose a high risk to aquatic ecosystems. In 2008, a list of 33 priority substances or groups of substances was set at Union level by Directive 2008/105/EC, and Directive 2013/39/EU recently updated the water framework policy to include 45 substances or groups of substances and certain other pollutants which must be considered when defining environmental quality standards. Directive 2013/39/EU also stimulates the development of innovative, more cost effective technologies in water treatment.

Chlorinated benzenes, including trichlorobenzenes, pentachlorobenzene and hexachlorobenzenes, are listed as priority substances by Directive 2013/39/EU, due to their persistence, bioaccumulativity and toxicity. This group of pollutants is also regulated by national regulation (Official Gazette RS 24/2014) and the national drinking water standards (Official Gazette 42/98-4). Chlorobenzenes are widely used for industrial and domestic purposes such as solvents, degreasers, pesticides, herbicides, dyes, pharmaceuticals, disinfectants, rubbers, plastics and electrical goods, as well as intermediates in the production of other chemicals, and they have become ubiquitous pollutants (Li et al., 2014). Among them, trichlorobenzenes occur in three different isomeric forms: 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene. In the environment, they are detected in water, soil, and sediment, and are also bioaccumulated in fish, animals, and food crops, where they cause concern for human health (Ramasahayam, 2014).

Conventional water and wastewater treatments using physicochemical and biological processes are often unsuitable for removal of these pollutants from the environment, so in recent years, great attention has been paid to improving water treatment (Ribeiro et al., 2015). Advanced oxidation processes (AOPs) are considered efficient and environmentally friendly techniques which can be used for decomposition of various micro-pollutants in different water samples into less complex and less harmful by-products. Among the photochemical AOPs, the combination of UV light and H_2O_2 (UV/H_2O_2 process) is simple and efficient technique which includes photonic (direct UV photolysis) and hydroxyl radicals for oxidative degradation (Liao et al., 2016). To date, several studies have dealt with the degradation of chlorinated benzenes using advanced oxidation (Dilmeghani and Zahir, 2001; Real et al., 2007; Lin and Lin, 2007; Wang et al., 2015). However, there is a lack of data regarding the influence of different water constituents such as humic and fulvic acids and carbonates on the mechanisms and efficacy of trichlorobenzene degradation.

In order to address this, the main goal of this study was to investigate and compare the effect of LP-UV/H_2O_2 advanced oxidation on the removal of 1,2,3-trichlorobenzene, as a model substance of chlorinated benzenes in different water matrices. The influence of other water constituents such as humic substances, which are part of natural organic matter, anions and other water quality parameters on the degradation kinetics was also examined.

EXPERIMENTAL AND METHODS

Materials

Pestanal® 1,2,3-trichlorobenzene (TCB) was purchased from Sigma-Aldrich, and the internal standard pentachloronitrobenzene from Supelco. Humic acid (HA) was purchased from Fluka. Solvents methanol and hexane were obtained from J.T. Baker and were of organic residue analysis grade; 30% w/w reagent grade H_2O_2 was purchased from POCH S.A. All other chemicals were analytical grade and were used without further purification. Natural groundwater was sampled from Vojvodina, Serbia. Laboratory ultrapure deionised water was produced by *LABCONCO, WaterPro Ro/Ps Station.*

Photolysis and LP-UV/H_2O_2 process

The LP-UV/H_2O_2 experiments were carried out using a photochemical reactor with a quartz reaction vessel equipped with a 253.7 nm UV low pressure (LP) mercury lamp (Philips TUV 16W). The design of the reactor is presented elsewhere (Molnar et al., 2015). The applied H_2O_2 dose was 1 mg/L with an applied UV fluence in the range 100-6000 mJ/cm^2.

Experiments were carried out in synthetic water samples (ultrapure deionised water) spiked with an aqueous TCB solution to achieve an initial concentration of about 100 µg/L. The influence of the presence of humic matter (5 mg C/L) and carbonate anions (500 mg CO_3^{2-}/L) on TCB degradation efficacy was also investigated. Groundwater spiked with TCB was used as a comparable natural sample.

Analytical methods

Water samples were analyzed for total organic carbon (TOC) content by Elementar LiquiTOCII, with oxidation by platinum catalysed combustion at 850 °C.

TCB in water samples was analysed after liquid-liquid extraction with hexane using gas chromatography with electron capture detection (Agilent Technologies 6890 with ^{63}Ni ECD) with a DB-XLB column (J&W Scientific). A detailed procedure was given in Kragulj et al. (2013). TCB was quantified according to internal standard calibration using pentachloronitrobenzene as the internal standard. Method detection limit was 10 ng/l.

The pH was measured by portable instrument (WTW InoLab pH). UV_{254} absorbance measurements were performed in accordance with Standard Methods (APHA, 2012) on a CINTRA 1010, GBC Scientific Equipment spectrophotometer at a wavelength of 254 nm, with a 1 cm quartz cell, and the SUVA (Lmg^{-1}m^{-1}) was calculated.

RESULTS AND DISCUSSION

Degradation of 1,2,3-trichlorobenzene in synthetic water

Direct photolysis of TCB was conducted in synthetic natural waters in order to evaluate the contribution of photolysis and compare it with advanced oxidation which included UV light and H_2O_2. With UV photolysis alone, degradation of TCB was in the range 10-40%, with the maximum efficacy achieved by a high UV fluence

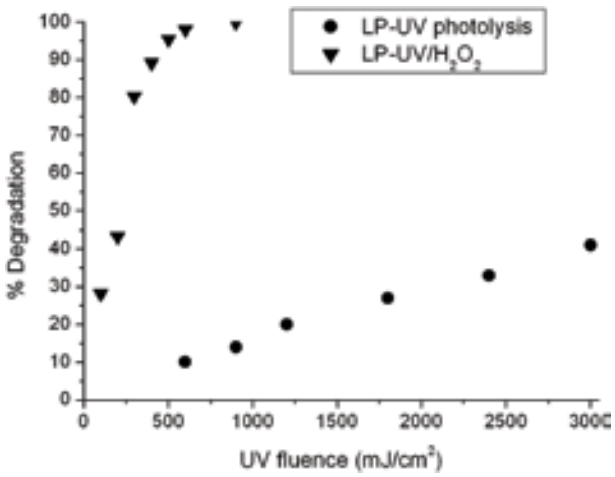

Figure 1: Degradation of TCB in synthetic water using LP-UV photolysis alone and LP-UV/H_2O_2 advanced oxidation

of 3000 mJ/cm^2. A significantly better TCB degradation efficacy of 28.1-99.9% was achieved using LP-UV/H_2O_2 advanced oxidation. The best efficacy of the LP-UV/H_2O_2 process was achieved using 5 times less UV fluence than in photolysis alone (figure 1).

Under these conditions using UV photolysis alone, degradation of TCB was only 10%, suggesting that the almost complete degradation of TCB during the UV/H_2O_2 process is mostly a result of attack by hydroxyl radicals formed during photolysis of the oxidant. Similary, Masten et al. (1997) suggested that for the degradation of 1,3,5-trichlorobenzene, ozone based AOPs can be efficiently applied.

Effects of humic acid and carbonate on the degradation of 1,2,3-trichlorobenzene in synthetic matrices

Humic acids (as a part of natural organic matter) and carbonates are naturally present in all water sources. In order to simulate natural conditions, synthetic water was prepared with the addition of carbonate and humic acid, in concentrations close to a number of groundwater sources found in Vojvodina, Serbia. Taking into account that UV photolysis did not significantly degrade TCB compared to advanced oxidation, additional experiments in synthetic water was carried out using only the LP-UV/H_2O_2 process (figure 2).

It is evident that the presence of humic acid, carbonate and their combination, considerably reduces the efficacy of TCB degradation compared to the results achieved in synthetic water without interfering constituents. At the UV fluence which achieved the best reduction of TCB (99%), the presence of carbonate dropped the efficacy to 48%, and the presence of humic acid dropped the efficacy even further to 28%. The simultaneous presence of carbonate and humic acids resulted in 44% TCB degradation, similar to carbonates alone, indicating that in presence of carbonate, HA has no further influence on reducing the efficacy of degradation.

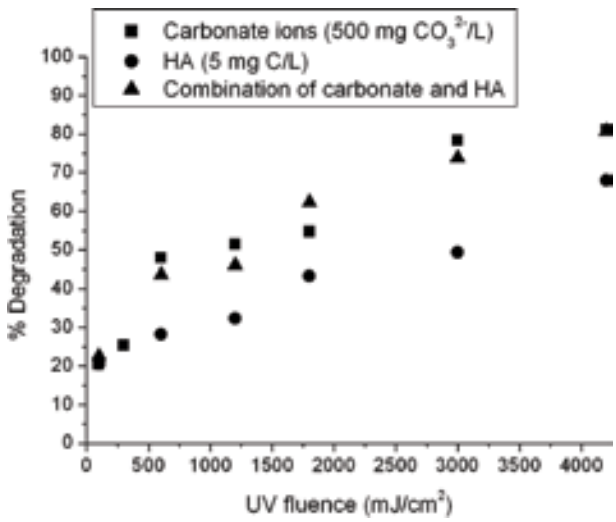

Figure 2: Effects of humic acids, carbonate and their combination on the degradation of TCB in synthetic water using UV/H_2O_2 advanced oxidation

TCB degradation was more effective when higher UV fluences were applied in the LP-UV/H_2O_2 process. Increasing UV fluence to 4200 mJ/cm^2 increased degradation efficacy up to 68% for the matrix containing HA, and up to 81% for matrices containing carbonate and their combination with HA. These results indicate that in the presence of interfering water constituents, it is necessary to apply about 14 times greater UV fluence to achieve the same efficacy as in the water without those additional constituents. These results suggest that in the presence of carbonate ions, some of the hydroxyl radicals react to form carbonate ion radicals, which are more selective in reactions with organic compounds than those of hydroxyl radicals with lower rate constants (Tuhkanen, 2004). It is also known that humic acids can either promote reactions with pollutants by forming photo oxidants or act as inhibitors of the UV/H_2O_2 process by scavenging OH radicals or adsorbing photons (Liao et al., 2016). In our study, humic acids were found to have a greater influence on TCB degradation than the carbonate.

Effects of natural water matrix on degradation of 1,2,3-trichlorobenzene in synthetic water

The natural water used in this study is rich in natural organic matter (NOM), indicated by a TOC value of 5.60 mg C/L. The specific UV absorbance (4.05 Lmg^{-1}m^{-1}), which can serve as a surrogate measure of aromatic carbon in the structure of NOM, indicates the particular role of hydrophobic organic matter in the water. NOM

characterisation showed that the main fraction of NOM in this type of water is the fulvic acid fraction, accounting for 45% of the total NOM, while the humic acid fraction was not detected. The results of applying LP-UV photolysis and the LP-UV/H_2O_2 process to this type of water are presented in figure 3.

Using LP-UV photolysis, a TCB degradation of 33-53% was achieved, and the LP-UV/H_2O_2 process was slightly at 37-62%. The small difference between photolysis and advanced oxidation could be explained by the presence of natural organic matter which can also compete in the oxidation reaction with OH radicals. In addition, as noted the carbonates present (420 mgCO_3^{2-}/L) act as scavengers of free radical species reducing the degradation process. In natural water, degradation of TCB was lower compared to the previously presented water types, indicating that some other water constituents (e.g. bromide, chloride) have an impact on the process efficacy, as well as the presence of fulvic acid and hydrophilic NOM in the natural water.

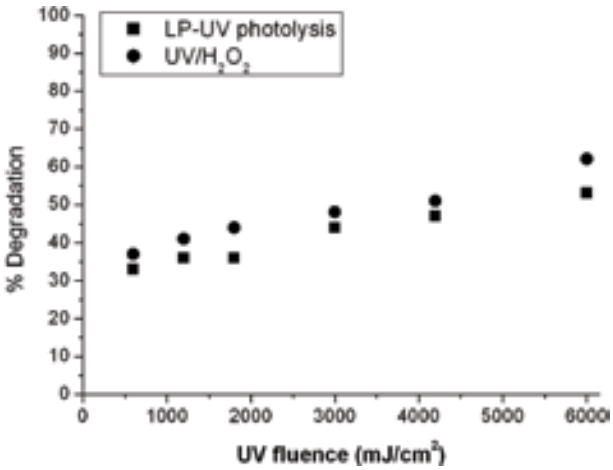

Figure 3: Influence of a water matrix rich in NOM on the degradation of TCB in natural groundwater using LP-UV photolysis alone and UV/H_2O_2 advanced oxidation

TCB decomposition kinetics

To better understand the effects of different water constituents, the kinetics of TCB decomposition were also considered. The degradation kinetics of micropollutants by LP-UV photolysis are presented by the following equation (Sharpless and Linden, 2003; Shu et al., 2013):

$$\frac{-d[P]}{dt} = k_d[P] \quad (1)$$

k_d (min^{-1}) is the time-based pseudo first-order rate constant for direct photolysis. If ln([P0]/[P]) is plotted versus the UV dose (mJ/cm^2), the corresponding direct photolysis fluence-based rate constant k'_d is obtained (Bolton and Stefan, 2002). Micropollutant degradation during LP-UV/H_2O_2 involves both UV direct photolysis and UV/H_2O_2 oxidation (Sharpless and Linden, 2003; Shu et al., 2013):

$$\frac{-d[P]}{dt} = (k_d + k_i)[P] = k_t[P], \quad (2)$$

where k_i is the pseudo first-order rate constant for UV/H_2O_2 oxidation and is a function of the second-order reaction rate constant for OH radical attack and the steady-state concentration of OH radicals. k_t can be determined from the slope of a plot of ln([P_0]/[P]) vs. reaction time. K'_t can be obtained from a plot of ln([P_0]/[P]) versus the UV dose (mJ/cm^2). The pseudo first-order rate constants for TCB in the presence of different water constituents with correlation coefficients are presented in table 1.

Based on these results, the degradation efficiency of TCB was improved 45 times in the presence of 1 mg H_2O_2/l, compared to photolysis alone (calculated k'_d was 0.172 x 10^{-3} cm^{2}mJ^{-1}). On the other hand, k'_t for the natural water sample was only 1.3 times higher than k'_d for photolysis alone (k'_d was 0.0665 x 10^{-3} cm^{2}mJ^{-1}), indicating the formed radicals are consumed in side reactions with natural organic matter (TOC was reduced by 6% by the process) and other ions such as carbonate, thereby reducing the degradation efficiency of TCB.

The degradation efficiency of TCB in ultrapure water is 22-37 times higher than in the presence of HA and carbonate. The simultaneous presence of carbonate and humic acids had no further impact on the rate constant.

Characteristics of water	k'_t / 10^{-3} cm^{2}mJ^{-1}	R^2
Ultrapure water	8.04	0.9936
Effects of carbonate	0.359	0.9468
Effects of HA	0.208	0.9514
Effects of carbonate and HA	0.334	0.9788
Effects of natural water matrix	0.0859	0.9545

Table 1. Pseudo first-order rate constants (fluence-based) by LP-UV/H_2O_2 process achieved in the presence of different water constituents

CONCLUSION

The LP-UV/H_2O_2 advanced oxidation process proved to be a promising technique for 1,2,3-trichlorobenzene degradation in water. In ultrapure synthetic water, TCB degradation occurred mostly due to oxidation by radicals forming by photolysis of H_2O_2, while the contribution of photolysis alone was minor. Humic acids and carbonate reduce TCB degradation efficacy. This is supported by fluence-based rate constants which are 22-37 times higher in ultrapure water than in the presence of HA and carbonates. In addition, greater scavenging effects were observed in the presence of humic acid alone than with carbonate alone or both. In the natural water sample, fulvic acids, carbonate and other water constituents reduced the TCB degradation efficacy. The similar fluence-based rate constants for photolysis and the UV/H_2O_2 process in natural water indicate that a large amount of hydroxyl radicals scavenging occurred. Such water types require a higher UV fluence and/or H_2O_2 dose to be applied in order to achieve efficient degradation of target compounds.

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LABORATORY INVESTIGATION OF HYDRAULIC CHARACTERISTICS OF FLY ASH AS A FILL MATERIAL FROM THE ASPECTS OF POLLUTANT TRANSPORT

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Abstract: Coal is a dominant commercial fuel around the world, and its increased used over the decades caused massive occupations of rich agricultural lands by fly ash landfills. In addition, the toxicity of fly ash motivates researchers to search for alternative uses. Different uses of fly ash include concrete and cement production, use as filler in asphalt concrete, construction of embankments, as filler instead of natural materials, etc. Depending on the use of fly ash, it is necessary to determine environmental parameters, such as the potential for pollutant transport/leaching after fly ash built-in. This study presents a methodology for determination of transport parameters (filtration coefficient, effective porosity, and longitudinal dispersivity) from experimental data collected from column experiments with conservative tracer on different mixtures of fly ash with stabilizers (4.8% lime and 5% cement). The transport parameters are determined using (1) numerical model results and (2) a novel-adapted analytical solution results against measured outflow tracer concentrations. The study shows that the addition of stabilizers decreases the filtration coefficient by an order of magnitude and the effective porosity by a half. The longitudinal dispersivity is not influenced by the addition of lime to the mixture, and is increased by 40% by the addition of cement. The novel adaptation of the analytical solution agrees well with both the numerical solution and the experimental results, and it is anticipated to be of high value for determination of transport parameters for practitioners who are not familiar with numerical methods.

Keywords: Fly ash, conservative tracer test, transport parameters

INTRODUCTION

Coal is a dominant commercial fuel in Serbia, as it is in many parts of the world. It is estimated that around 70% of all electricity in Serbia is produced by means of coal burning (EPS, 2014). This is why an increasing amount of valuable land (mostly rich agricultural) needs to be dedicated for the deposition of coal burning byproducts, mainly the fly ash. In addition, the toxicity of fly ash (Borm, 1997) and the environmental concern it presents, particularly due to possible leaching of hazardous materials (Izquierdo and Querol, 2012), inspire efforts to find alternative ways for fly-ash utilization. The good pozzolanic properties of fly ash make it usable for concrete production, as a retardant additive and a raw material in cement production (Ahmaruzzaman, 2010). Additionally, the fly ash is used as a replacement for stone filler for asphalt road surface. The fly ash is used for the construction of embankments or as filler instead of natural materials, since its properties correspond to properties of well compacted soil (Santos et al., 2011). It is also proved to be a good material for stabilization of soils with low mechanical characteristics, and it is used with or without activators– cement or lime.

The characteristic of fly ash is its local variety of physical and chemical properties, depending mainly on the coal composition. However, in order to use the fly ash it is necessary to determine its geotechnical and environmental parameters. Depending on the purpose for which the fly ash is used, the environmental parameters may include the potential for leaching of toxic materials, but also the potential for transport of pollutants, particularly when the intention is to use the fly ash for embankments, landfill liners, and road bases. These particular uses require the definition of pollutant transport properties of the fly ash, due to the contact of these structures with water (rivers, urban runoff, stormwater, etc.).

The aim of this study was to develop a methodology for determination of the transport characteristics of multiple fly ash samples using the experimental data. Through a series of experiments, fly ash and different

mixtures of fly ash with stabilization ingredients, such as lime or cement, were analyzed from the aspects of potential pollutant transport/leaching after its built-in.The main parameters of interest were the filtration coefficient, the effective porosity and the longitudinal dispersivity of the fly ash mixtures. The parameters of interest were determined through calibration of a mathematical model against experimental data. In addition to the numerical model, a novel adaptation of the analytical solution of Ogata and Banks (1961) is presented, that can help practitioners not familiar with numerical methods to determine model parameters.

MATERIALS AND METHODS

Experimental Setup

The experimental setup consisted of up-flow columns for the determination of pollutant transport characteristics of samples made of fly ash and fly ash – soil mixtures. The system was equipped with an upstream reservoir with a constant level controlled by a valve. The transport experiments consisted of dosing a specific concentration of conservative tracer (NaCl) at the upstream reservoir, and measuring concentration breakthrough at the columns' outlet pipe (detection reservoir, Figure 1).

The columns used for samples were identical and had a diameter (D) of 110 mm and a length (height) (L) of 105 mm (Figure 1). A total of three types of samples was used for the experiment, and their description is given in Table 1. The first sample consisted of pure fly ash, which was taken from the TPP Kostolac. The second and the third sample had a small percentage of lime or cement as additives (stabilizers) to the TPP Kostolac fly ash that improved both mechanical and hydraulical properties of the mixture. The particle size distribution of the analyzed fly ash was similar to silt, with 60-71% grains smaller than 0.075mm. The specific gravity of fly ash was 2.22. This is considered a class "F" fly ash according to ASTM C618 (2008) with SiO_2+Al_2O_3+Fe_2O_3 content above 70% and SO_3 less than 1%.

All samples were compacted to the same rate in order to simulate in situ conditions as realistic as possible (a standard compaction energy of 600 kN/m^2 was used). The percentage of stabilizers was adopted based on previous geotechnical and mechanical experiments that resulted in selection of optimal characteristics of such mixtures (UBFCE, 2015)

At the beginning of the experiment, all samples were saturated with clean water. Once the samples were saturated, the valve that controls the flow from the upstream reservoir was opened and salted water was introduced into the columns. The concentration of NaCl tracer was monitored frequently at the outflow, and this was done until the outflow NaCl concentration was equal with the inflow NaCl concentration (measured at the upstream reservoir). In the second part of the experiment, once the two concentrations were equalized, the clean water was introduced in the columns. This so-called fresh water forced the "contamination" a.k.a. salty solution to filtrate towards the outflow end. The tracer concentration was measured frequently at inflow and outflow reservoirs (Figure 1).

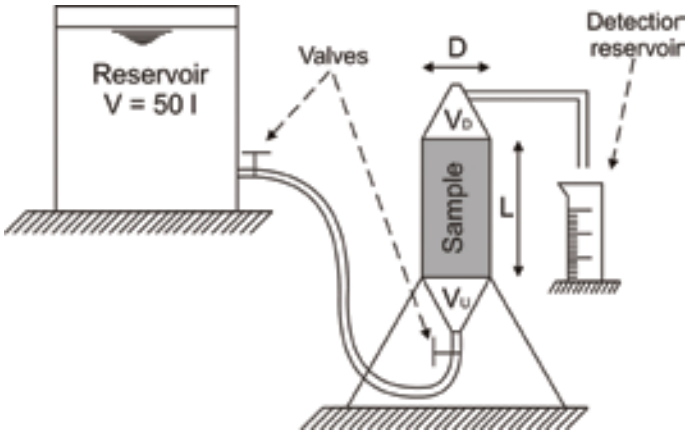

Figure 1: The experimental setup scheme

Fly Ash Source	Sample	Stabilizer	% of stabilizer in the mixture	Compaction Energy (kN/m^2)	porosity (-)	Compaction wettability (%)
TPP Kostolac	1	-	-	600	0.45	43.9
	2	Lime	4.8	600	0.42	41.8
	3	Cement	5.0	600	0.42	43.4

Table 1. Characteristics of material mixtures

During the conducted experiments, the inflow NaCl concentration was not constant in time, due to the existence of a small reservoir upstream from the sample (marked as V_u in Figure 1). The effect of this small upstream reservoir was that it diluted the introduced NaCl solution and therefore reduced the NaCl concentration at the upstream cross-section. Additionally, there was a small reservoir downstream from the sample (marked as V_D

in Figure 1) that also influenced the breakthrough curve. The effect of the downstream small reservoir included a time lag in the measured outflow NaCl concentration.

The aim of the experiments was to determine the flow properties of samples (the filtration coefficient and the effective porosity), as well as the pollutant transport properties (the advection and dispersion parameters). Since it was not possible to measure directly the effective porosity, nor the longitudinal dispersivity, it was necessary to develop a methodology for their estimation. The flow and transport parameters were determined using a mathematical model of transport of dissolved substance with the experimental data. The mathematical model was solved in two ways: (1) by adapting a form of the analytical solution, and (2) by a numerical method, as described in sections below.

Mathematical Model

One dimensional transport equation for substance, that is considered an ideal tracer, can be described as follows:

$$\frac{\partial C}{\partial t} = -v_{eff}\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

Where v_{eff} is the effective velocity of the stream (filtration flow), C is the concentration of the pollutant in water (NaCl in this case), D is the dispersion coefficient, t is the time and x is the space coordinate. The first part of the right side of the equation presents the advection term, while the second part presents the effect of the hydrodynamic dispersion. The dispersion coefficient can be presented using the longitudinal dispersivity, α_D, as $D = \alpha_D \cdot v_{eff}$.

Analytical Solution

The equation (1) can be rewritten to the form of the equation (3) by transforming the coordinate system into the one that moves with the same effective velocity as the filtration stream, presented by equation (2).

$$s = x - v_{eff}\, t \tag{2}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial s^2} \tag{3}$$

The equation (3) is a parabolic differential equation that has an analytical solution when the flow through a uniform and homogeneous sample is steady and the substance concentration at the upstream boundary (inflow) is constant (C_o). This analytical solution was developed by Ogata and Banks (1961), and is presented as equation (4) used for the calculation of the substance concentration at x = L, which is the cross section at the outflow i.e. the breakthrough curve.

$$C(x = L, t) = \frac{C_0}{2} erfc\left(\frac{L - v_{eff}t}{2\sqrt{Dt}}\right) \tag{4}$$

As previously stated, the NaCl concentration was not constant at the upstream boundary, due to the existence of a small reservoir, V_u. This effect required an adjustment of the constant-inflow-boundary analytical solution (Ogata and Banks, 1961). The modified analytical solution, developed to fit the boundary conditions of the conducted experiment, included a discretization of the upstream boundary concentration as depicted in Figure 2a. Once the varying upstream boundary concentration is presented as a sequence of multiple steps of constant concentrations, each increased by $\Delta C_{in,i}$, the solution is obtained by successive additions of separate analytical solutions valid for the constant inflow concentration, i.e. by the superposition of analytical solutions relevant to each time step Δt_i, as described by equations (5) and (6). The ti in equation (5) is the time when the inflow concentration increases for $\Delta C_{in,i}$. The effective velocity, v_{eff}, was calculated using the Darcy's law.

$$C(x = L, t) = \sum_i \frac{\Delta C_{in,i}}{2} erfc\left(\frac{L - v_{eff}(t - t_i)}{2\sqrt{D(t - t_i)}}\right) \tag{5}$$

$$\Delta C_{in,i} = C_{in,i+1} - C_{in,i} \tag{6}$$

Numerical Solution

A finite differences numerical method used for solving the 1D transport equation (1) is given in two different forms that depend on the Péclet number (equations (7) and (8)).

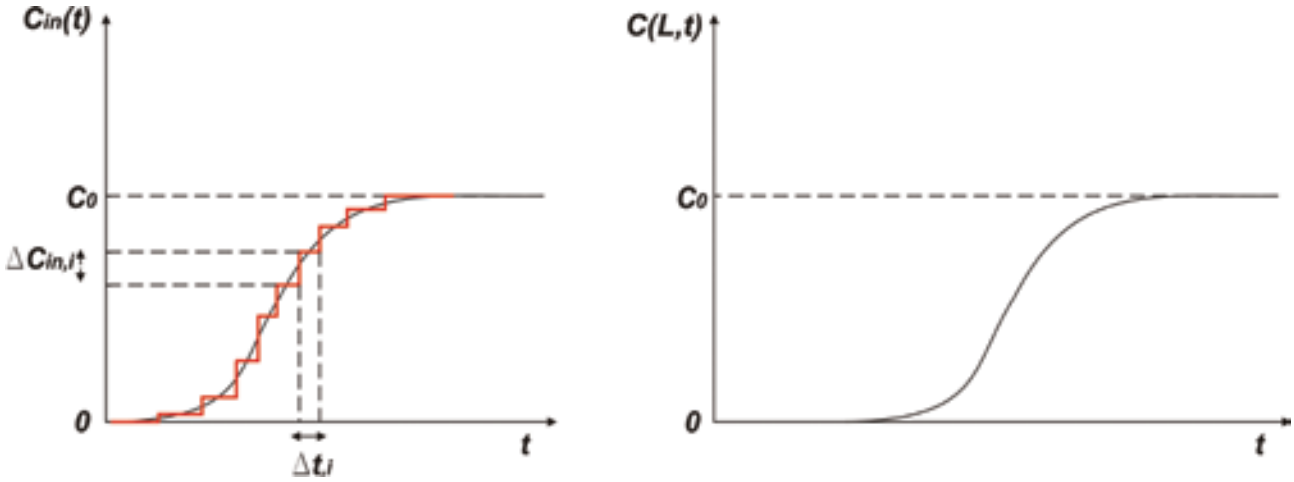

Figure 2: The discretization of the varying concentration at the upstream boundary: a) Diagram of the concentration at the upstream boundary, b) Calculated concentration at the downstream boundary as a result of the superposition of constant-inflow-boundary analytical solutions

$$C_i^{n+1} = C_i^n + \Delta t \left(-v_{eff} \frac{C_{i+1}^n - C_{i-1}^n}{2\Delta x} + D \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{\Delta x^2}\right) \quad \ldots (Pe < 2) \tag{7}$$

$$C_i^{n+1} = C_i^n + \Delta t \left(-v_{eff} \frac{C_i^n - C_{i-1}^n}{\Delta x} + D \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{\Delta x^2}\right) \quad \ldots (Pe > 2) \tag{8}$$

i and n in equations (7) and (8) are indices that describe the space and the time coordinates, respectively, while $Pe = \frac{\Delta x * v_{eff}}{D}$ is the Péclet number, which provides a ratio of advective to diffusive transport rates (Hyakorn and Pinder, 1983).

The numerical solution of the transport equation (7 and 8) complements a 1D numerical model for long term simulation of water filtration in the porous media, based on either the Richard's or the Darcy's equations (depending on the porous media saturation). Since the samples in the experiment were fully saturated, the effective velocity was calculated using the Darcy's law.

Boundary Conditions

Since the volumes of the two reservoirs at the upstream and the downstream side, V_u and V_D, affected the final concentration of the salt in both the inflow and the outflow, it was necessary to include them in the mass balance calculation. The inflow and the outflow salt concentrations were determined by equations (9) and (10) that describe the process of mixing of the salted and the fresh water during every time interval, Δt.

$$C_{in}^n = \left(C_0 - C_{in}^{n-1}\right) \frac{Q\Delta t}{V_u} + C_{in}^{n-1} \tag{9}$$

$$C_{out}^n = \left(C_{out-1}^n - C_{out}^{n-1}\right) \frac{Q\Delta t}{V_D} + C_{out}^{n-1} \tag{10}$$

C_{in} and C_{out} in equations (9) and (10) are concentrations of the pollutant in the inflow and the outflow (small upstream and downstream reservoirs), respectively, C_0 is the constant concentration in the large (main) upstream reservoir, Q is the flow through the sample, and V_u and V_D are the volumes of small reservoirs upstream and downstream from the sample.

Hydraulic and Transport Parameter Estimation

The filtration coefficient of the sample material, K, was determined using the least squares regression line on the Darcy's law i.e. by plotting the average velocity through the sample versus the hydraulic gradient. The effective porosity and the longitudinal dispersivity were determined by calibrating the modified analytical and the numerical solution against the measured outflow concentration. The coefficient of determination, R^2, was used as a measure of the agreement between the modeled and the measured outflow concentrations.

RESULTS AND DISCUSSION

Figure 3 presents the determination of the filtration coefficient, K, for the three samples, while numerical values can be found in Table 2. It can be seen that samples 2 and 3, which included a mixture of fly ash and stabilizers, had a lower filtration coefficient than the sample made of fly ash only. The addition of 4.8% of lime decreases the filtration coefficient by almost an order of magnitude, while addition of 5.0% of cement decreases filtration coefficient by an additional 35% when compared with the addition of lime.

The adapted analytical solution and numerical model results were compared with measured data on Figure 3, while the estimated values of the model parameters (effective porosity and longitudinal dispersivity) are shown in Table 2. The coefficient of determination, R^2, for each sample was higher than 0.98 (0.993, 0.978, 0.991 for samples 1, 2, 3, respectively), which can be considered an acceptable agreement level for the estimation of model parameters.

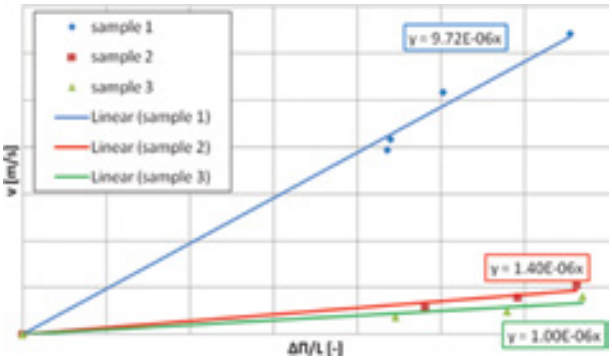

Figure 3: Determination of the filtration coefficient

The results in Table 2 indicate that the additives/activators significantly reduced the effective porosity of the fly ash. The effective porosity was found to be 0.30 for the "pure" fly ash, while the activators decreased the effective porosity to 0.13 (mixture with lime), and 0.18 (mixture with cement). It can be concluded that the addition of stabilizers (lime or cement) as 5% of mass decreases the effective porosity by a half. It is hypothesized that the decrease in the filtration coefficient is due to the conversion of lime and cement into pozzolanic compounds that block the pores of fly ash (Sivapullaiah and Baig, 2011). The estimated values of the longitudinal dispersivity (Table 2) indicate that the addition of lime does not influence, while the addition of cement increases the value of the longitudinal dispersivity by 40% when compared with the fly ash only sample. However, it should be noted that the value of longitudinal dispersivity for all three samples was found to be low. Since the longitudinal dispersivity value depends highly on the scale of the problem, the findings of the conducted experiment cannot be accepted as general values.

Fly Ash Source	Sample	Stabilizer	% of stabilizer in the mixture	porosity (-)	Filtr. coeff. (m/s)	eff. porosity (-)	long. dispersivity (m)
TPP Kostolac	1	-	-	0.45	9.7×10^{-6}	0.30	0.005
	2	Lime	4.8	0.42	1.4×10^{-6}	0.13	0.005
	3	Cement	5.0	0.42	1.0×10^{-6}	0.18	0.007

Table 2. Results of laboratory experiments: Hydraulic and transport parameters of fly ash with effects of stabilizers

The adapted analytical solution was found to agree quite well with the numerical model results (Figure 4), which enables it to be used as an alternative method for model parameter estimation. This is particularly of interest for practitioners who are not familiar with numerical methods, and need a quick solution.

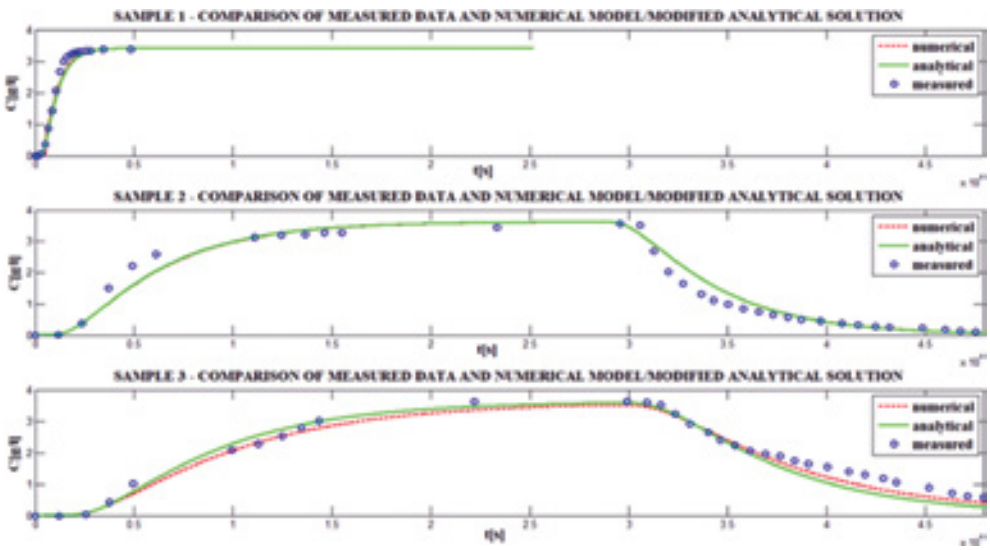

Figure 4: The comparison of measured data and numerical/modiffied analytical solution for each sample

CONCLUSIONS

This study included the analysis of the hydraulic/transport characteristics of fly ash and effects of stabilizers on its properties. The clean fly ash characteristics were compared with two mixtures: one with the lime mass content of 4.8%, and the other with 5.0% mass content of cement. These contents were previously determined as optimal by various geotechnical testings. The results indicate that both activators, lime and cement, reduced the filtration coefficient nearly by an order of magnitude, while the effective porosity was reduced by a half. The longitudinal dispersivity was found not to be influence by the addition of lime, while the addition of cement increased this parameter by 40%. These transport parameters are important and need to be taken into consideration in fly ash utilization, particularly in respect of its potential impact and interaction with the environment. Additionally, the study presented a novel adaptation of the analytical solution, which agrees well with both the numerical solution and the experimental results. This novel approach is anticipated to be of high value for practitioners who are not familiar with numerical methods that can be effectively used for determination of transport parameters.

ACKNOWLEDGEMENTS

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SEWER SYSTEM INSPECTION AND MAINTENANCE MODEL FOR GROUNDWATER PROTECTION

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Abstract: Groundwater protection is important for preserving drinking water. Karst aquifer is particularly sensitive to pollution from sewage. Sewer system inspection and maintenance model for groundwater protection consists of three objective functions: regular maintenance, extraordinary maintenance and investment maintenance. Regular maintenance includes the daily work of maintenance in terms of preventive action. Extraordinary maintenance includes a variety of activities to facilitate the operation of sewage with sudden disturbances of functioning sewage network. Investment maintenance deals with the replacement, renovation, restoration or repair of sewer pipes. The model includes the maintenance of the sewer, geodetic works, record the pipe from inside with TV camera external review of sewerage systems and hydrodynamic flushing pipe network. The model was calibrated and verified on a real project. Maintenance of sewage systems is a complex task from water-related activities that include a significant area: water protection within the protection of the environment. Significant branches mentioned water management is waste water drainage - channeling of settlements and industries.

Keywords: groundwater; maintenance; sewerage

INTRODUCTION

Maintenance of sewer systems is a complex tasks of water menagment that includs a significant area as water protection within the protection of the environment. One of the significant branches of mentioned water protection is waste water drainage, including channeling of settlements and industries.For the purpose of maintenance of sewer systems there were developed model that are based on the sewer inspection and consideration of the risk of falling functionality of sewer system (Savić 2009; Ward & Savić 2012; Ward et al., 2014). The wells are supplied with water from karstic aquifers. Sewage is right next to the well. Therefore, the rehabilitation of the sewage system is designed how to pollution from the wastewater can not get into the wells (Popovic et al., 2013). In this paper are described the performance indicators of sanitation, maintenance of sewer systems, external review of sewer systems, geodetic surveys, hydrodynamic flushing pipe network and CCTV as well as model for real sewer system mainteinance (Popović et al., 2013) using operational research methods, statistical methods and performance indicators.

METHODS

In developing the model there were used statistical methods of data collection, inspection of sewer systems (CCTV, phooto shootage surveying methods, etc…) and criteria optimization. Multifunctional optimization model of the sewer consists of three objective functions:1) Regular maintenance, 2) Extraordinary maintenance, 3) Investment maintenance. Regular maintenance involves the daily work on planned maintenance of functionality of facilities in terms of preventive actions for the all possible problems in the functioning of sewer system. Extraordinary maintenance includes activities to facilitate the functioning of sewer during sudden disturbances in some of the facilities of sewer network (Jevtić et al., 2011). Investment maintenance deals with the replacement, renewal, renovation or repair of the sewer. Objective function describes data and performance indicators that have been developed at the IWA - International Water Association (Matos et al., 2003; Anthony et al., 2003). Clearly objective functions are developed through significant optimization of all the data and indicators of performance. The model

was developed in two parts as shown in Figure 1. The first part of the model is the data processing which consists in part of geodetic data processing where the existing sewer system is recorded by geodetic methods and data were collected firstly of the sewers, pipe lengths and depths, as well as other geodetic data. During inspection of the sewer system were photographed roads and other facilities that are near sewer sections, as well as facilities that are located near sewer facilities and have an impact on the sewer system. Then we carried out the CCTV inside-recording of sewer pipes, manholes and other sewer facilities and assessed the state of the facilities using software WinCan V8 (WinCan8 2013). All collected data is then processed calculating the performance indicators (Matos et al., 2003) and then prepaed for the second part of the model, which defines criteria functions and alternatives.

The second part of the model is the optimization environment where multi-criteria optimization method VIKOR (Opricović 2009) is applied for the selection of the activities that are designed for different types of maintenance, especially for investment maintenance.

The required performance indicators are calculated using variables defined in the IWA (Matos et al., 2003). New variable wES (Eliminated sections) was included in model. These are the following variables:

1. wC1 Total length of sewer pipes (km)
2. wD1 Inspection of sewer pipes (km)
3. wD2 Cleaning of sewer pipes (km)
4. wD27 Replacement of sewer pipes (km)
5. wD38 Congestion sewer pipes (No)
6. wH1 Assessment period (d)
7. wES Eliminated sections (km)

The values of the input data for the operation of the model are given in Appendix.

Performance indicators describe maintenance of the sewer system and objective functions, as follows:

1. Regular maintenance of sewer
   - wOp1 - Sewer inspection (% / year)
   - wOp2 - Sewer cleaning (% / year)
2. Extraordinary maintenance of sewer
   - wD38 - Sewer blockages (No)
3. Investment maintenance of sewer
   - wOp23 Sewer replacement (% / year)
   - wDI Design Indicator (% / year)

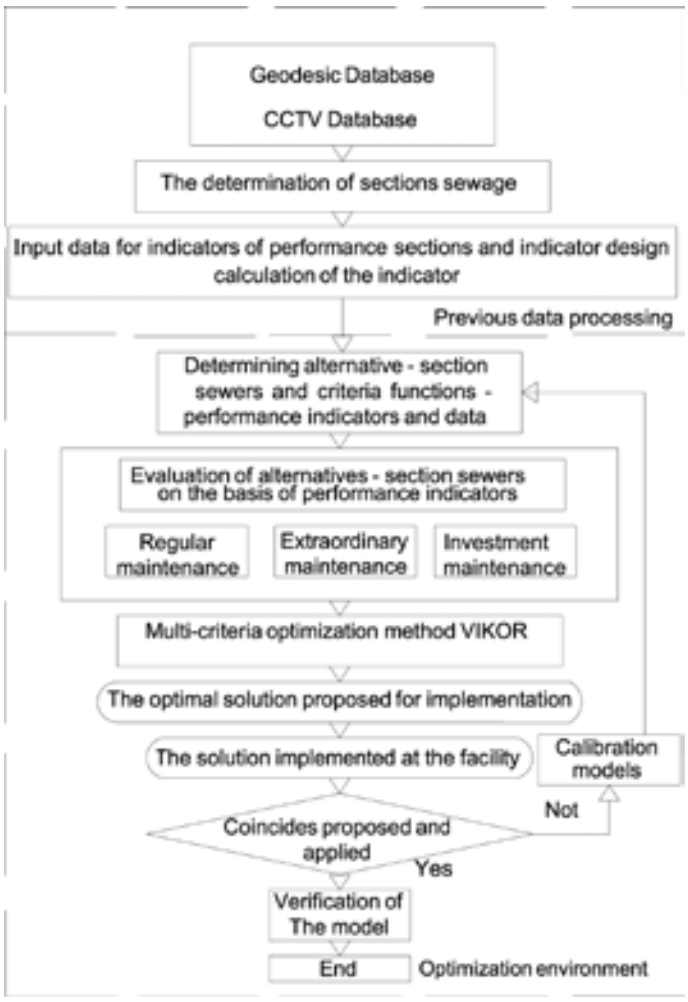

Figure 1: Data processing and multifunctional optimization

The Multifunctional optimisation model was developed in a large numbler of phase (Milojković et al., 2015a, b). The formulas listed below show the way in which the Multifunctional optimisation model calculates the selected performance indicators that are used to derive a compromised solution for sewer maintenance, for each sewer section separately.

wOp1 - Inspection of sewer pipes (% / year)

$$wOp1 = (wD1 \times 365 / wH1) / wC1 \times 100 \quad (1)$$

wOp2 - Cleaning of sewer pipes (% / year)

$$wOp2 = (wD2 \times 365 / wH1) / wC1 \times 100 \quad (2)$$

wOp23 - Replacement of sewer pipes (% / year)

$$wOp23 = (wD27 \times 365 / wH1) / wC1 \times 100 \quad (3)$$

wDI - Design Indicator (designed abolition of sewer section) (% / year)

$$wDI = (wES \times 365 / wH1) / wC1 \times 100 \quad (4)$$

In model is involved wD38 which is the result of the analysis of CCTV method. A method for multi-criteria optimization VIKOR, that is here used, has been developed to determine multicriteria optimal solution and it is very often used alone or together with other methods (Gwo-Hshiung et al., 2002; Opricović & Gwo-Hshiung 2004, 2007; Opricović 2009).

In the case of Multifunctional optimisation model the following Equation is used (6)

$$wOp = vko_{a\epsilon Ai}(f_1 (a), f_2 (a), \dots , f_n (a)) \quad (5)$$

Where is:

wOp - the operator for decision making based on the performance indicators of wastewater

A - the set of alternative sewer sections

$a = (x_1,x_2,....)$ - an alternative that has been obtained for certain values of the variables (x) system

f_i – i criteria function

vko - operator for multi-criteria optimal solution

In particular, for Multifunctional optimisation model, the Equation (7):

$$wOp = vko_{a\epsilon Ai}(f_1 (wOp1), f_2 (wOp2), f_3 (wD38), f_4 (wOp23), f_5 (wDI)) \quad (6)$$

Where is:

wOp1, wOp2, wD38, wOp23, wDI – performance indicators of wastewater and variables used and described in the following sections.

In this case, alternative solutions are different sections of the sewer. We are looking for the most problematic sections of the sewer system in terms of interventions on regular, emergency and investment maintenance, with priority given to investment maintenance as the most expensive for the investor.

Criteria function, as a representative of maintenance of sewer systems there were used different IWA performance indicators of sewer systems. We designed a new indicator wDI of investment maintenance and input data for the calculation of performance indicators based on the number of expected congestion os sewer pipes per year. Criteria functions are as follows:

wOp1- Sewer inspection (%/year)
wOp2- Sewer cleaning (%/year)
wD38- Sewer blockages (No)
wOp23- Sewer replacement (%/year)
wDI- Design Indicator (%/year)

Evaluation of alternatives is carried out according to the above criteria functions. Criteria functions can be expressed in the form of quantitative economic indicators, technical indicators, quantitative and qualitative indicators (scores or points). Values of parameters extremization of the criteria functions that determine the model:1 - maximum value of the function as the most suitable; 0 - minimum value of the function as the most favorable. In this model, the value for parameter extremisation for each criteria function is 1. The input for the other results, the optimization part of the model, after data processing in the first part of the model, is shown in Figure 2.

Figure 2: Results of the first part of the Multifunctional optimisation model

RESULTS AND DISCUSSION

After designing maintenance of sewer system, pipelines were obtained that are part of the investment maintenance. Results are completely new pipelines that have improved the functioning of the existing sewer system and belong to the investment maintenance, taking over the previuos function of the sewers. Derived sections that have been built in the first half of 2014 are entirely those of investment maintenance, as during this period are not constructed buildings that would have required new sections of the sewer system.

In the phase of calibration in the model was added new criteria function, wDI-Design Indicator (designing abolition of sewer section), which enabled precise operation of the model. In model was entered variable wD38, since it is more convenient for working models. After much iteration of changes in the weight of criteria function, the calibrated model led to the weight presented in Table 1, ranking I, which enables accurate working model.

	Criterion function				
Ranking	wOp1	wOp2	wD38	wOp23	wDI
I	1	1	1	212	212

Table 1. Final weight value criteria for ranking different alternatives

In relation to investment maintenance of the sewer, after calibration the model acomplished complete accuracy. Model was verified in real sewer system (Table 2).

By applying this model of maintenance and design of sewer system which is a significant amount for the investor. This is accomplished primarily by inserting a new indicator wDI. The accuracy of the model is 100%.

The final result of the models of investment maintenance				Performed investment maintenance			
Code	Sewer section		L	Code	Sewer section		L
	From	to	(m)		From	to	(m)
A25	TF4-2	TF4-1	5.98	A1	TF1-4	TF1-3	8.42
A26	TF4-3	TF4-2	18.49	A2	TF1-3	TF1-2	10.69
A 9	TF2-4	TF2-3	14.21	A3	TF1-2	TF1-1	6.59
A11	TF2-2	TF2-1	73.82	A4	TF1-1	UF1	11.08
A12	TF2-1	UF2	11.57	A5	TF2-8	TF2-7	14.35
A20	TF3-3	TF3-3 pom	41.92	A6	TF2-7	TF2-4	12.71
A21	TF3-3 pom	TF3-2	29.98	A7	TF2-6	TF2-5	14.07
A22	TF3-2	TF3-2 pom	89.39	A8	TF2-5	TF2-4	10.59
A24	TF4-1	TF3-2 pom	19.43	A9	TF2-4	TF2-3	14.21
A38	TF5-2	TF5-1	20.69	A10	TF2-3	TF2-2	11.52
A39	TF5-1	UF5	17.14	A11	TF2-2	TF2-1	73.82
A 4	TF1-1	UF1	11.08	A12	TF2-1	UF2	11.57
A 7	TF2-6	TF2-5	14.07	A15	TF3-4C	TF3-4	75.87
A10	TF2-3	TF2-2	11.52	A17	TF3-4B	TF3-4C	12.19
A 1	TF1-4	TF1-3	8.42	A18	TF3-4A	TF3-4B	22.10
A 2	TF1-3	TF1-2	10.69	A19	TF3-6	TA1-27	9.87
A 3	TF1-2	TF1-1	6.59	A20	TF3-3	TF3-3 pom	41.92
A 5	TF2-8	TF2-7	14.35	A21	TF3-3 pom	TF3-2	29.98
A 6	TF2-7	TF2-4	12.71	A22	TF3-2	TF3-2 pom	89.39
A 8	TF2-5	TF2-4	10.59	A24	TF4-1	TF3-2 pom	19.43
A15	TF3-4C	TF3-4	75.87	A25	TF4-2	TF4-1	5.98
A17	TF3-4B	TF3-4C	12.19	A26	TF4-3	TF4-2	18.49
A18	TF3-4A	TF3-4B	22.10	A30	TF4-7	TF4-6	16.45
A19	TF3-6	TA1-27	9.87	A31	TF4-6	TF4-5	7.93
A30	TF4-7	TF4-6	16.45	A32	TF4-5	TF4-4	8.48
A31	TF4-6	TF4-5	7.93	A33	TF4-4	TF4-3	6.35
A32	TF4-5	TF4-4	8.48	A38	TF5-2	TF5-1	20.69
A33	TF4-4	TF4-3	6.35	A39	TF5-1	UF5	17.14
		Total	601.88			Total	601.88

Table 2. Comparison of planned and executed state of investment maintenance after the final iteration of the model

CONCLUSION

Objective functions: regular, emergency and investment maintenance of the developed model are described. Everybody pays a lot of attention on the maintenance of the investment as it is very expensive for the investor. The developed model for inspection and maintenance of sewer systems provides opportunities for big savings, especially in investment maintenance. Instead of building a new sewage system, since the entire sewer network was in poor condition, was repaired only part of the existing sewer. Preparation of the data carried through performance indicators: wOp1-Sewer inspection; wOp2-Sewer cleaning; wD38-Sewer blockages; wOp23-Sewer replacement; wDI Design Indicator, along with multi-criteria optimization environment gives excellent results in savings for the investors. New indicator, wDI Design Indicator gives a completely different approach to investment maintenance and opens up new perspectives for

the sewer system. Performance Indicator wDI provides great opportunities to save on investment maintenance. In addition, the investment maintenance has a crucial influence on the regular and extraordinary maintenance. The costs of regular maintenance are significantly lowered to a minimum because the length of the investment maintenance section is reduced.

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Appendix: The values of the input data for the calculation of criteria functions for different alternatives

Code	Sewer section		wC1	wD1	wD2	wD38	wD27	wH1	wES
	From	to	km	km	km	No	km	d	km
A1	TF1-4	TF1-3	0.00842	0	0	0	0.00842	365	0
A2	TF1-3	TF1-2	0.01069	0	0	0	0.01069	365	0
A3	TF1-2	TF1-1	0.00659	0	0	0	0.00659	365	0
A4	TF1-1	UF1	0.01108	0	0.01108	1	0	365	0.01108
A5	TF2-8	TF2-7	0.01435	0	0	0	0.01435	365	0
A6	TF2-7	TF2-4	0.01271	0	0	0	0.01271	365	0
A7	TF2-6	TF2-5	0.01407	0	0.01407	0	0	365	0.01407
A8	TF2-5	TF2-4	0.01059	0	0	0	0.01059	365	0
A9	TF2-4	TF2-3	0.01421	0.01421	0.01421	0	0	365	0
A10	TF2-3	TF2-2	0.01152	0.01152	0	0	0.01152	365	0
A11	TF2-2	TF2-1	0.07382	0.07382	0.07382	0	0	365	0.07382
A12	TF2-1	UF2	0.01157	0.01157	0.01157	0	0	365	0.01157
A13	TF3-5	TF3-5 pom	0.00568	0.00568	0.00568	0	0	365	0
A14	TF3-4	TF3-3	0.01233	0.01233	0.01233	0	0	365	0
A15	TF3-4C	TF3-4	0.00759	0	0	0	0.00759	365	0.00759
A16	TF3-5 pom	TF3-4	0.00979	0.00979	0.00979	0	0	365	0
A17	TF3-4B	TF3-4C	0.01219	0	0	0	0.01219	365	0
A18	TF3-4A	TF3-4B	0.0221	0	0	0	0.0221	365	0
A19	TF3-6	TA1-27	0.00987	0	0	0	0.00987	365	0
A20	TF3-3	TF3-3 pom	0.04192	0.04192	0.04192	0	0	365	0.04192
A21	TF3-3 pom	TF3-2	0.02998	0.02998	0.02998	0	0	365	0.02998
A22	TF3-2	TF3-2 pom	0.08939	0.08939	0.08939	0	0	365	0.08939
A23	TF3-1	UF3	0.00975	0.00975	0.00975	0	0	365	0
A24	TF4-1	TF3-2 pom	0.01943	0.01943	0.01943	0	0	365	0.01943
A25	TF4-2	TF4-1	0.00598	0.00598	0.00598	2	0	365	0.00598
A26	TF4-3	TF4-2	0.01849	0.01849	0.01849	2	0	365	0.01849
A27	TF4-9A	TF4-9	0.02932	0.02932	0.02932	0	0	365	0
A28	TF4-9	TF4-8	0.00564	0.00564	0.00564	0	0	365	0
A29	TF4-8	TF4-3	0.00617	0.00617	0.00617	0	0	365	0
A30	TF4-7	TF4-6	0.01645	0	0	0	0.01645	365	0
A31	TF4-6	TF4-5	0.00793	0	0	0	0.00793	365	0
A32	TF4-5	TF4-4	0.00848	0	0	0	0.00848	365	0
A33	TF4-4	TF4-3	0.00635	0	0	0	0.00635	365	0
A34	TF4-12	TF4-11	0.01125	0.01125	0.01125	1	0	365	0
A35	TF4-11	TF4-10A	0.01125	0.01125	0.01125	1	0	365	0
A36	TF4-10A	TF4-10	0.025	0.025	0.025	2	0	365	0
A37	TF4-10	TF4-3	0.0176	0.0176	0.0176	3	0	365	0
A38	TF5-2	TF5-1	0.02069	0.02069	0.02069	0	0	365	0.02069
A39	TF5-1	UF5	0.01714	0.01714	0.01714	0	0	365	0.01714
A40	TF6-12	TF6-11	0.00914	0.00914	0.00914	0	0	365	0
A41	TF6-11	TF6-10	0.01664	0.01664	0.01664	0	0	365	0
A42	TF6-10	TF6-9	0.02703	0.02703	0.02703	0	0	365	0
A43	TF6-9	TF6-8	0.00991	0.00991	0.00991	0	0	365	0

Code	Sewer section		wC1	wD1	wD2	wD38	wD27	wH1	wES
	From	to	km	km	km	No	km	d	km
A44	TF6-8	TF6-7	0.01384	0.01384	0.01384	1	0	365	0
A45	TF6-7	TF6-6	0.014	0	0.014	0	0	365	0
A46	TF6-6	TF6-5	0.00308	0	0.00308	0	0	365	0
A47	TF6-5	TF6-4	0.00305	0	0.00305	0	0	365	0
A48	TF6-4	TF6-3	0.00524	0	0.00524	0	0	365	0
A49	TF6-3	TF6-2	0.03093	0.03093	0.03093	2	0	365	0
A50	TF6-2	TF6-1	0.01357	0.01357	0.01357	2	0	365	0
A51	TF6-1	tf3-2 pom	0.01763	0.01763	0.01763	2	0	365	0
A52	TF7-6	TF7-5	0.00636	0.00636	0.00636	0	0	365	0
A53	TF7-5	TF7-4	0.00961	0.00961	0.00961	0	0	365	0
A54	TF7-4	TF7-3	0.0218	0.0218	0.0218	0	0	365	0
A55	TF7-3	TF7-2	0.022	0.022	0.022	0	0	365	0
A56	TF7-2	TF7-1	0.0299	0.0299	0.0299	0	0	365	0
A57	TF7-1	TFCS1	0.02121	0.02121	0.02121	0	0	365	0
A58	TFCS1	SAB JAMA	0.00336	0.00336	0.00336	0	0	365	0
A59	TF8-11	TF8-10	0.01249	0.01249	0.01249	0	0	365	0
A60	TF8-10	TF8-9	0.02014	0.02014	0.02014	1	0	365	0
A61	TF8-9	TF8-8	0.00183	0.00183	0.00183	0	0	365	0
A62	TF8-8	TF8-7	0.01973	0.01973	0.01973	1	0	365	0
A63	TF8-7	TF8-6	0.0021	0.0021	0.0021	0	0	365	0
A64	TF8-6	TF8-5	0.01932	0.01932	0.01932	1	0	365	0
A65	TF8-5	TF8-4	0.00637	0.00637	0.00637	2	0	365	0
A66	TF8-4	TF8-3	0.01139	0.01139	0.01139	2	0	365	0
A67	TF8-3	TF8-2	0.0065	0.0065	0.0065	3	0	365	0
A68	TF8-2	TF8-1	0.02143	0.02143	0.02143	3	0	365	0
A69	TF8-1	Collecting tank	0.0085	0.0085	0.0085	3	0	365	0
A70	TF10-1	TFCS1	0.02909	0.02909	0.02909	0	0	365	0
A71	TF9-1	Oiled sewage	0.02022	0.02022	0.02022	0	0	365	0
A72	Oiled sewage	Collecting tank	0.02255	0.02255	0.02255	0	0	365	0
Total	1.15734	0.95251	0.99151	35	0.16583	365	0.36115		

NOTES

PROTECTING WATER RESOURCES BY IMPLEMENTATION WATER SAFETY PLANS

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Abstract: Drinking water supply system in catchment, treatment, transmission, storage, distribution and consumers are always in danger of pollution that can threat the health of consumers. In the existing system quality control of drinking water is base on end-point monitoring approach. This however can identify the contamination but can not prevent the occurrence of contamination. Water safety plan by applying risk management can lead to prevention of pollution in water resources and helping to ensure the quality of the water. Implementation of WSP will lead to change in the attitude of end-point monitoring approach to process control and quality assurance of drinking water. WSP in Tabriz in Iran under the guidance of the World Health Organization Regional Office has been implemented. WSP currently is running in 15 cities. Implementation of WSP all across the country is mandatory which is clearly announced in the national drinking water quality strategy that has been approved by the Cabinet as a rule.

Keywords: catchment to consumer, Iran, water safety plans, WSP implementation

INTRODUCTION

The quantity and quality of the surface water and groundwater resources are affected by rapid economic development and climate change. According to Iranian national water and wastewater engineering company around 80% of Iranians rely on groundwater for their drinking water supply. Besides, water pollutants from industrial, agriculture and civilization activities restrict the availability of sustainable water resources. Due to water shortage on the one hand and the threat of water resources on the other hand, implementing water safety plan was the most appropriate strategy to deal with this problem.

Ministry of Health, responsible for monitoring the drinking water quality in urban and rural area, is responsible for implementation of water safety plans (WSP). Iranian National Water and Wastewater Engineering Company (NWWEC) as a chief executive is responsible for supplying drinking water in cities and villages. This mission is carried out through 34 urban and 31 rural companies all across the country. For implementation of WSP Many measures have been carried out in Iran are as follows:

1. Formation of national WSP steering committee with representatives of the ministry of health, ministry of energy, interior ministry, ministry of agriculture, ministry of industry, ministry of petroleum and environmental protection agency that somehow have role in water resources pollution or have duties to protect water quality from catchment to consumer
2. The inclusion of WSP in the VII national drinking water quality strategy was adopted by the Council of Ministers and its implementation is mandatory (Ministry of health 2011).
3. Circulars mandatory of WSP implementation for at least one city or village.
4. Holding a number of workshops to explain the characteristics of the WSP for senior executives as prerequisite program.
5. Implementation of WSP in cooperation with the WHO's regional office in the city of Tabriz as a pilot.
6. Training Instructors for the WSP implementation in other cities and villages
7. Training auditors to assess WSP.

The objective of this article was to introduce the experiences of Iran in implementation and development of WSP as an effective measure for protecting water resources and quality assurance in water supply.

MATERIAL AND METHODS

The method is currently used to control water quality in Iran is based on the end-point monitoring approach. The major weaknesses of this method are including; (a) retrospective, (b) just identify the contamination not prevent, (c) just quality control not quality assurance, and (d) the volume of water that is tested rarely statistically representative the volume of water that is consumed. Bitter experiences such as viral infection in drinking water in a city with a large number of intestinal disease despite being negative coliform bacteria test results and appropriate concentration of chlorine residual in the distribution network or oil pollution incident at the entrance of water treatment plant with discharge of 10 m3/s because of ignoring the hazards in the system of water supply and many other accidents that cause pollution of water supplying, officials were forced to replace their existing system with another one with characteristics such as to avoid excessive reliance on end-point testing, focused on prevention and the focus on process control (NWWEC 2015).

EXECUTION PROCESS

Water Safety Plan implementation began in Iran from 2009 and as a first step national WSP steering committee with representatives of the ministry of health, ministry of energy, interior ministry, ministry of agriculture, ministry of industry, ministry of petroleum and environmental protection agency that somehow have role in water resources pollution, or have duties in water quality protection from catchment to consumer Established. Then, National Steering Committee (NSC) decided to have a city selected as pilot for the implementation of the water safety plan in collaboration with the WHO regional office consultants to gain experiences needed to implement WSP in other cities. With this intention, between some cities as a candidate at last Tabriz, because of the potential required for the project was chosen as a pilot. Tabriz city with a population of 1.7 million, more than 500 thousand water connection is the largest city in the north west of Iran (WHO 2009, 2011).

Tabriz selection criteria as pilot can be mentioned below:

1. Skilled and motivated human resources.
2. Advanced water laboratory with ability to test all kinds of parameters such as microbial, physicochemical, biological and micro pollutant such as heavy metals and DBPs.
3. The water supply system in Tabriz include various components such as river, dam reservoir, open canal of raw water, water treatment plant, transmission line, pumping stations, water storage tanks, water wells, disinfection systems and extensive distribution network and consumer that can be a good sample to exercise WSP steps .
4. Easy travelling of steering committee members and WHO's advisor between Tehran and Tabriz by Tabriz airport.

WSP implementation in Tabriz began in 2011 with the election of the members of the technical committee of Tabriz and holding a training course in cooperation with the WHO regional office and attended by members of the NSC. After one year, Tabriz WSP by the WHO assessor was evaluated and recommendations were made to fix defects. Also the results of Tabriz WSP were evaluated and criticized by members of the steering committee.

RESULTS OF TABRIZ WSP

In system description step of WSP in catchment, Technical committee of Tabriz WSP has not been able to gathering information from other organization, for example point pollution sources such as untreated industrial wastewater, geographical distribution of villages and effects of wastewater to environment and unsanitary disposal of solid waste in landfill sites wasn't considered. In identify hazards step of WSP implementation in catchment in comparison to other elements was not successful and wasn't lead to applied result that can prevent water resources pollution for example hazards like excessive usage of fertilizer and pesticides in agriculture division were not identified and there was no control measure to deal with them or hazards from unsanitary disposal of solid waste in landfill sites were neglected.

Despite the weaknesses in the implementation of WSP in catchment, applying WSP in water treatment plant transmission pipes, storage tank and distribution network was good experience for example isolation storage tank roof to prevent entering runoff or fencing around to prevent access irresponsible people shows an understanding of WSP. One of the most achievements of WSP in Tabriz is change attitude from treatment to prevention in authorities, it means instead of waiting until hazardous event occur and causing to crisis then try to deal with it, beforehand try to know it and somehow to control it.

SECOND PHASE OF WSP DEVELOPMENT:

In the second phase, the NSC in 2013 decided to extend the implementation of the WSP in three other cities including Isfahan, Ahwaz and Kashan. This time the selection criteria in addition to issues such as appropriate organizational structure and human resources, records of events that affected water quality and causes serious crisis was considered. This time, training for technical committees of mentioned cities was holding by iranian NSC and some members of the technical committee of Tabriz. According to the report presented by each technical committee of mentioned cities; steps of (a) description of the system (b) Identify hazards and hazardous events and risk assessment (c) determine and validate control measures, reassess and prioritize the risks and step (d) develop, implement and maintain an improvement is done and the rest of the steps gradually are running.

THIRD PHASE OF WSP DEVELOPMENT

After of presentation of WSP implementation process by the technical committees of cities in second phase and their results in the control of hazardous event and other positive aspects of WSP in national seminar, many cities declared their readiness to implement WSP voluntarily. So in 2013 the NSC selected 11 other cities to implementation WSP, including Zahedan, Mashhad, Tehran, Sari, Rasht, Gorgan, Kermanshah, Bandar Abbas, Shiraz, Karaj and Urmia (Figure 1). Then, subsequently technical committee for the implementation of WSP was established in the mentioned cities. Regional training courses for technical committee were held in 4 stages. According to NSC's evaluation plan, in the mentioned cities the steps of "the description of the system" and 'identify hazards and hazardous events and risk assessment" are completed. In order to monitor the progress of the WSP as well as fix problems in the WSP implementation, three auditing groups were formed by NSC and training course for them was hold in order to be familiar with auditing method of WSP and a checklist was prepare to be applied by these groups. The duty of these groups are attend in these cities and review the documentation of WSP implementation and providing guidance to correct mistakes and eventually reporting progress to NSC. NSC intends by continues auditing WSP, in case of successful WSP implementation, a certificate with a validity period of one year to be presented to the technical committee and with the results of the audit in the coming years, this certificate can be extended or cancelled.

Figure 1: The locations of the cities were selected for implementing WSP

DEVELOPMENT OF WSP IN RURAL AND URBAN WATER AND WASTEWATER COMPANIES

Urban and rural water and wastewater companies having water treatment plant, water transmission lines, storage tanks, distribution and consumer, so, they play a key role to WSP implementation in three parts of chain of water supply except catchment. The NWWEC in 2014 mandated the implementation of the WSP at least in a city and a rural complex in each company. This action will promote the process of WSP implementation. Representatives of the NSC in NWWEC have launched training operators of water and wastewater companies. Experiences gained from WSP implementation showed many of the measures that are currently doing in water and wastewater companies, especially in treatment plants and transmission pipeline, distribution and water storage tank are adaptable with WSP steps. And it is important to simplify the implementation of the WSP. For example, bacteriological, biological, physical and chemical tests of water quality in water treatment effluent, water storage tank or in water tap of consumer in compliance with national or international guidance by water and wastewater companies are adaptable with step 6 of WSP, operational monitoring, or physicochemical or microbiological tests carried out by the ministry of health or standard organization are adaptable with step 7 of WSP as validating WSP as a whole by external audit (WHO 2014).

However, some concepts, such as the identification of hazards and hazardous events, prioritize them by semi-quantitative risk matrix (WSP step3) or water supply system description (WSP step2) of issues that had not been done so far. WSP implementation for consumer issue that was not dealt with before and managers

believed water supply system is responsible for water quality before consumers' connection and the effects on health and quality of water by interior equipment consumers (like pump or storage tank) were ignored. In other words consumers weren't considered in chain of water supply. Therefore in WSP consumers' satisfaction is included as a major part of the plan.

CONCLUSION

With the implementation of WSP and learn more about different aspects of it, now there is no doubt about the necessity of this plan as a solution to prevent water resources' pollution and to ensure water quality. It is anticipated that with the full implementation of WSP in 15 towns, necessary experience achieved, especially on the steps of the program as well as to identify hazards, assess and validate the measures of control, prioritization of risks or determine the monitoring control measures, many of these experiences can be applied to other water supply systems. This will make the program more quickly done in other cities. WSP management model, in addition to his role in the issue of water quality and health can be considered a successful example of intersectional collaboration to resolve the similar issues.WSP implementation in the catchment is much more difficult and time consuming than other elements of water supply chain so it was decided WSP implementation in the treatment plant, transmission pipeline, water storage tank, distribution and consumer carry out by WSP group in water and wastewater co. And its findings will send to WSP technical team. So, technical committee will have more time to deal with catchment. On the other hand as a promotional tool in auditing plan for WSP implementation in the catchment is considered more points.

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DELINEATION OF THE MAIN CONDITIONS AFFECTING NITROGEN FORM IN SELECTED ANOXIC ALLUVIAL AQUIFERS IN SERBIA

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Abstract: Nitrogen complex chemistry is reflected in several oxidation states (from -3 to +5) in which nitrogen can persist depending on prevailing environmental biogeochemical conditions. The oxidation state of the elements in groundwater will preferably be determined by dissolved oxygen concentration and redox potential, followed by concentration and availability of present organic matter, nitrates, fero/manganese and sulfate ions, and dominant species of microorganisms. The aim of the paper is distinguishing which parameters are the main controllers of dominant reactions and final form of nitrogen present in anoxic alluvial aquifers, regardless of nitrogen origin. Research was conducted for selected drainage wells from Knićanin – Čenta (Danube and Tisa river), Kovin – Dubovac (Danube river) and selected wells from Belgrade groundwater source (Sava River). Parameters such as Eh, O_2, TOC, Fe^{2+}, H_2S concentrations and BART test results were all analyzed. The obtained results were used to define prevailing nitrogen form and dominant nitrogen transformation reactions, indicating different anoxic aquifers potential for nitrogen loss (N_2, N_2O) or conservation (NH^{4+}).The conclusion is that in anoxic alluvial groundwaters which were the subject of this research prevailing controlling factors are the concentration of total organic carbon (TOC), followed by presence of ferrous iron and sulfide, while C:N ratio would determine whether the nitrogen is subject of loss (N_2O, N_2) or conservation (NH^{4+}).

Keywords: nitrogen transformation, anoxic groundwater, BART test

INTRODUCTION

The amount of nitrogen present in soil, surface and groundwaters, is mainly affected by the lack of sewage systems, agricultural practice (fertilizer and manure application), increased cultivation of nitrogen fixing plants, and incorporation of residues. The main pathways of nitrogen enrichment of surface and groundwater are surface runoff, soil erosion and leaching. Coarse-textured soils and unconfined aquifers are usually at higher risk of NO_3^- leaching, although excessive rainfall or abundant watering can cause nitrates displacement beyond the root zone from any soil type. Nitrogen can be immobilized either by abiotic or biotic processes, where most of the immobilization to the soil organic matter is biotic (Bengtsson et al., 2003). Generally an accepted hypothesis is a positive relationship between the C:N ratio and rapid N immobilization and a negative relationship between the C:N ratio and N mineralization and nitrification. Bengtsson et al. (2003), suggest that soil C:N ratio may prove useful to predict site-to-site variations of the N transformations, while temporal variation of soil temperature and moisture will trigger dynamics of microbial biomass and activity that influence N transformations more than the spatial variation of the C:N ratio. The presence of sulfur as sulfate and thiosulfate has been shown to inhibit denitrification in soils, with the rate of denitrification negatively correlated to the sulfate (or thiosulfate) concentration (Kowalenko, 1979). In soil, sulfide has been shown to promote dissimilatory reduction of nitrate to ammonium (DNRA) rather than denitrification (Hiscock et al., 1991). Nitrate mobility in oxic environment is usually described almost as tracer's mobility, due to the stability in oxic environments and the inability of negatively charged ions to sorb to the sediment and soil particles. In anoxic, reducing conditions, nitrogen will be subject of reductive transformations: assimilation into biomass, respiratory denitrification, anaerobic ammonium oxidation (annamox), and dissimilatory nitrate reduction (DNR), usually associated with ammonium production (DNRA). Nitrate reduction processes as well as stoichiometry reactions in reductive groundwater are presented in Fig 1.

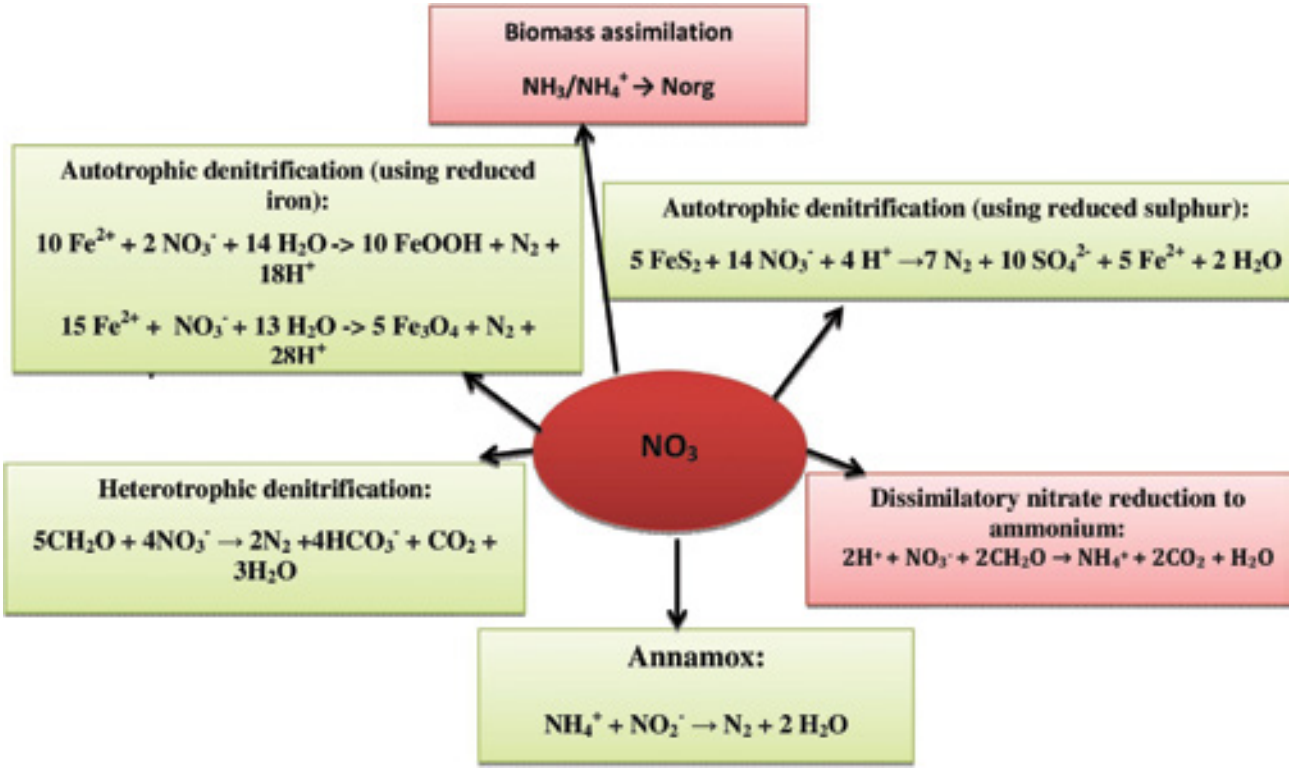

Figure 1: Illustration of possible nitrate transformation processes in reductive environment- red color denotes N conservation, while green color denotes nitrogen loss (N gasses production and loss to atmosphere)

MATERIALS AND METHOD

Drainage system Knićanin-Čenta

This drainage system is situated in the alluvial formation at the confluence of the Begej River into the Tisa River and Tisa River into the Danube. Medium-grain sands are dominant in the central and upper parts of the aquifer, while the lower part features sandy and fine-grain gravels (Majkić-Dursun et al., 2015). The base of the aquifer is made of clays while the top sediments are semi-permeable silty clays (Majkić-Dursun et al., 2015). For the definition of dominant nitrogen form, 4 facilities at the Tisa riverbank, and 3 facilities in Danube alluvial sediments were chosen. Lack of sewage network and intensive agricultural production are considered as the main sources of ammonium and nitrates in Knićanin-Čenta and Kovin-Dubovac alluvion.

Drainage system Kovin-Dubovac

Kovin-Dubovac is an alluvial plain of the left coast of Danube river between two settlements, Kovin and Dubovac, located in the southern part of the Banat depression. The deeper layers of the Danube's alluvial plain are composed of gravels and sandy gravels, with some cobbles even over 120 mm in diameter, with medium-grained sands, finely-grained silty sands, coal, alevrites and clay layers at their base. The upper part consists of semi-permeable sediments - silty sands, alevrites, silty clays and clay. In this paper, physicochemical and microbiological results are presented for 20 wells and piezometers situated at locations across the three drainage lines in Danube alluvial sediments.

Belgrade groundwater source

The Belgrade groundwater source is located along the Sava's river bank upstream from its confluence with the Danube. The Sava River alluvial formation was formed during several sedimentation cycles and sequences, and is comprised of: sandy gravels, sands of various grain sizes, and silty and clayey sediments (Majkić-Dursun et al., 2015). According to Dimkić and Pušić (2014) lower zone is consisting of coarse-grain sediments in which radial well laterals are installed. Occasionally clay, sandy clay and silt discontinuous beds and lenses may occur. The upper part consists of fine-grain less permeable sediments. In this paper, chemical and microbiological analyses from 12 piezometers and wells are presented. Nitrogen concentration is generally low for whole groundwater source which is in accordance with its use as a drinking water source.

Presented data are analyzed only for certain facilities, which were selected by simultaneous availability of chemical and microbiological data together. The data were collected with different frequency for the purposes of elaboration of different studies, under the Project No. TR37014 in the period 2010-2015 year.

In order to determine what are the relations existing among key factors affecting the final form of nitrogen in anoxic alluvial groundwater regardless of nitrogen origin, a comparative analysis of physicochemical and microbiological results for three alluvial aquifers with anoxic groundwater – Knićanin-Čenta, Kovin-Dubovac and Belgrade groundwater source, in R. Serbia, has been conducted. In-situ measurement of Dissolved Oxygen and Redox potential (Eh) were conducted using Multiparameter WTW 197i probes (Germany). Nitrate, nitrite and ammonium were analyzed using spectrophotometric methods, whereas volumetric method was used for sulfide. Detailed descriptions of the applied analytical methods are outlined in APHA (2005). TOC (total organic carbon) was quantified using Hiper TOC analyzer Thermo Scientific (United Kingdom). Performed BART tests (Hach Company, United States) have enabled detection of the following bacteria groups: Iron Related Bacteria (IRB-BART) with Winogradsky medium, Sulfate-reducing bacteria (SRB-BART) with Postgate C medium and Denitrifying bacteria (DN-BART) with nitrate-pepton medium. Defining present environmental groups of bacteria has enabled the estimation of current microbiological status of groundwater and potential transformation processes of nitrogen compounds. The correlation between the day, reaction type and the number of active cells in this study has been obtained by software QuicPop software 1.3 (Cullimor, 2010).

Location		Knicanin-Centa	Kovin	Belgrade water source
Sampling period (year)		2010-2012	2010-2015	2010-2015
Number of samples		22	125	61
Number of examined facilities		7	20	12
O_2 (mg/l)	min	<0.1	<0.1	<0.1
	max	1.6	2.35	2.17
	Avg.	0.2	0.15	0.3
Eh (mV)	min	23.5	20	48
	max	273	279	246.6
	Avg.	136.5	98.2	105.7
TOC (mgC/l)	min	1.2	1.1	1.1
	max	7.8	5.23	1.9
	Avg.	3.3	2.4	1.4
Fe^{2+} (mg/l)	min	0.18	<0.1	0.11
	max	3.7	5.41	4.13
	Avg.	1.1	1.82	1.4
H_2S (mg/l)	min	<0.02	<0.02	<0.02
	max	0.14	0.75	0.02
	Avg.	0.06	0.05	<0.02

Table 1. Average values of selected parameters for examined facilities affecting N-transformation

Information about the final compound of nitrogen resulting from transformation in water is important for two main reasons: 1) health and environmental hazard and 2) indication of aquifer potential for nitrogen conservation or loss. Acute or chronic ingestion of water with elevated nitrate concentration may exhibit various forms of harmful effects (Camargo and Alonso, 2006; Almasri and Kaluarachchi, 2004; Wolfe and Patz, 2002). Ingested nitrites and nitrates can induce methemoglobinemia in humans and have a potential role in developing cancers of the digestive tract through their contribution to the formation of nitrosamines (Wolfe and Patz, 2002). Some scientific evidences suggest that ingestion might result in mutagenicity, teratogenicity and birth defects, contribute to the risks of non-Hodgkin's lymphoma and bladder and ovarian cancers, etc. (Camargo and Alonso, 2006). Nitrate may indicate the presence of bacteria, viruses, and protozoa in groundwater if the source of nitrate is animal waste or effluent from septic systems (Almasri and Kaluarachchi, 2004).

RESULTS AND DISCUSSION

Rivett et al. (2008) suggested that after qualifying the environment (groundwater) based on redox value and oxygen concentration as reductive one, next influential factor in terms of nitrate transformation is the organic C concentration (in the paper TOC). In graphs (Fig.3, Fig.4, Fig. 5,) the parameters whose changes can be correlated to nitrogen transformation pathways are presented. In the case of high C content and sulfidic

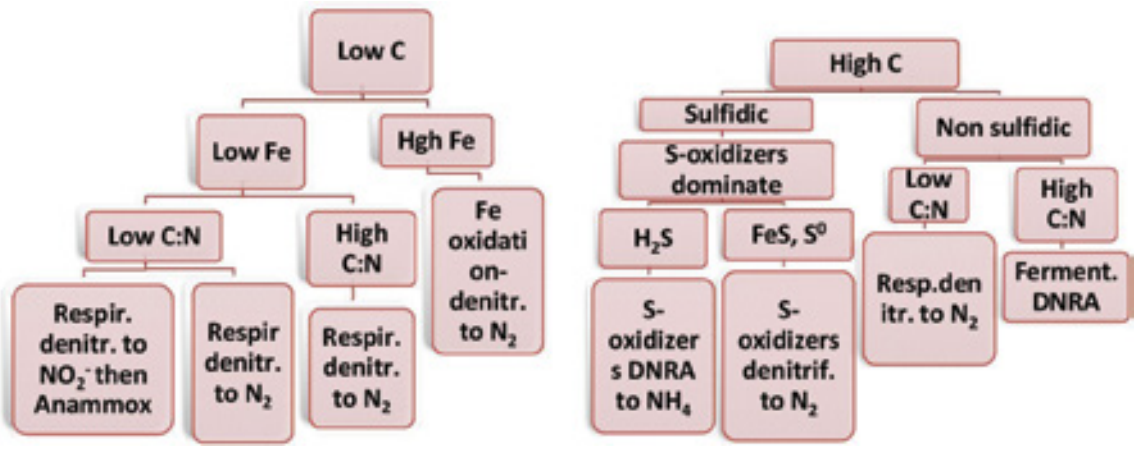

Figure 2: Illustration of the main pathway of nitrogen transformation and main conditions affecting dominant transformation. C:N ratios refer to the ratio of total organic carbon to nitrate (modified, Burgin and Hamilton, 2007)

waters (Knićanin-Čenta) correlation between parameters TOC, NH^{4+}, NO_3, Fe^{2+} and BART test results has been observed (Fig.3 and Table 2). In the case of variable high C / low C content, sporadicly sulfidic water (Kovin-Dubovac), correlation between parameters TOC, C:N, NH^{4+}, NO_3^-, Fe^{2+} and BART test results has been observed (Fig.4 and Table 2). For the third examined location (Belgrade groundwater source), carbon and nitrogen concentrations are low, with moderate activity of iron related and denitrificating microorganisms, indicating fulfillment of conditions for nitrogen loss (N_2, N_2O) by denitrification to N_2 (Fe oxidation) and respiratory denitrification to N_2O and anammox. This is the reason why correlation between TOC, NH^{4+}, NO_3^-, Fe^{2+} is presented (Fig.5).

Knićanin-Čenta

The average values for the selected physicochemical and microbiological parameters for seven sampling sites at Knićanin-Čenta facilities have been analyzed and compared with the mutual dependence of observed changes. BART tests showed that facultative anaerobes with anaerobes are dominant microorganisms in this area. Moderate to high activity of iron reduction is observed. Very high activity of sulfate reducers and heterotrophic bacteria which indicate anaerobic mineralization of organic matter dominate in the whole area. Parralel nitrate and iron reduction is probably the consequence of constant nitrate inflow, probably as a result of the absence of sewage network and intensive agriculture. Burgin and Hamilton, (2007) and Oshiki et al., (2013) stated sulfate reducers and iron related bacteria could be responsible for NH^{4+} concentration increase in anoxic groundwaters. Many authors observed that nitrate reduction by iron oxidation results in NO_2^- product, which transforms into N_2 or NH^{4+} and Fe^{3+} (Korom 1992; Rivett et al, 2008; Oshiki et al., 2013). Low TOC concentration (to 3 mg/l) is accompanied by low ferrous concentration (<0.68 mgFe^{2+}/l) (Fig.3), which according to Fig. 2 leads to nitrogen loss, whether by denitrification or denitrification coupled to anammox. The NO_3^- decrease and NH^{4+} increase are followed by simultaneous TOC increase (Fig 3.). Increase in TOC concentration above 3 mg C/l is accompanied by ferrous concentration increase, where dominant form of

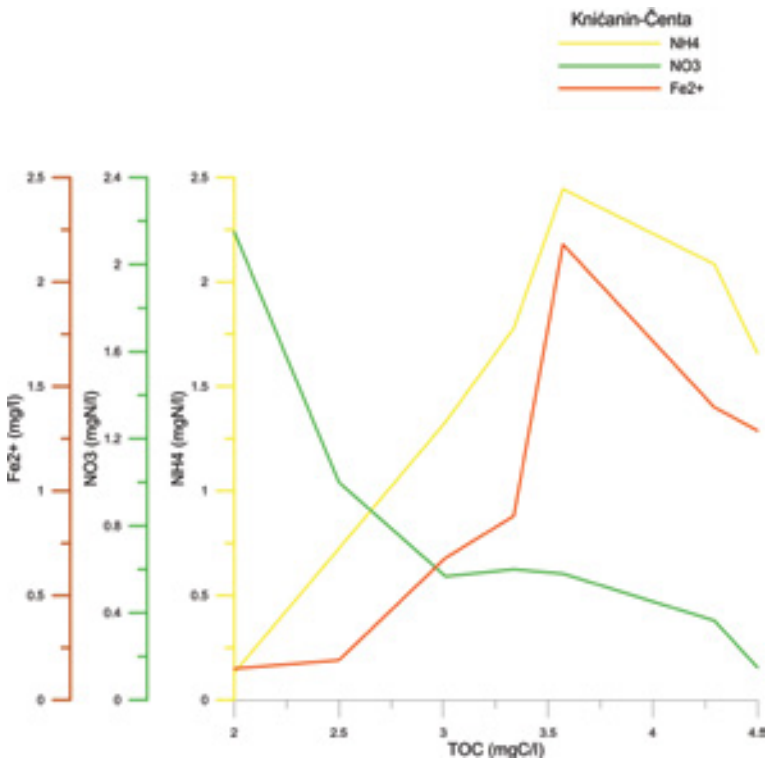

Figure 3: Comparative analysis of NH_4, NO_3 and Fe^{2+} concentration change with TOC increment in Knićanin-Čenta

nitrogen becomes NH^{4+}. NO_3 reduction to NH_4, might be attributed to secondary metabolism of sulfate reducers and DNRA process (avg. log SRB 3.41 p.a.c/ml) or even iron related bacteria (avg. log IRB 4.17 p.a.c/ml). If it is assumed that the first process might be nitrate reduction by iron oxidation (avg log IRB 4.17 p.a.c/ml), the resulting product is NO_2^-, which transforms into N_2 or NH^{4+} and Fe^{3+}. Fe^{3+} can be reduced back to Fe^{2+} in presence of organic matter. BART test results (Table 2.), and inverse dependency of NH^{4+} and NO_3 concentration might be related to TOC and Fe^{2+} increment and bacteria consortium observed in groundwater.

Location		Knicanin-Centa	Kovin	Belgrade water source
Sampling period (year)		2010-2012	2011-2012	2011-2012
Number of samples		21	27	24
Number of examined facilities		7	20	12
log p.a.c/ml IRB	min	0.30	0.90	2.14
	max	4.55	5.15	4.55
	Avg.	4.17	3.78	2.74
log p.a.c/ml SRB	min	0.90	0.90	1.0
	max	4.26	5.0	2.69
	Avg.	3.41	2.45	1.57
log p.a.c/ml DN	min	1.26	0.78	0.78
	max	4.24	4.24	4.24
	Avg.	2.92	2.38	2.20

Table 2. BART test results in log p.a.c/ml for selected facilities in Knićanin-Čenta, Kovin-Dubovac and Belgrade groundwater source

Kovin-Dubovac

For the Kovin-Dubovac area iron reduction, denitrification activity, and moderate to very high activity of sulfate reducers were observed. Examined area can be microbiologically characterized as reductive-anoxic with dominating reactions of Fe^{3+} reduction and dentrification, with observed sulfate-reduction which sporadically was very high. Based on high number of heterotrophic aerobic bacteria high concentration of organic matter is mineralized mostly under anaerobic conditions. Variably low C / high C concentrations indicate favorable conditions for both, N loss and conservation. Low C concentrations are accompanied by lower NH^{4+} concentrations. Low C concentration, according to Burgin and Hamilton (2007) might induce nitrogen loss. Sulfide concentrations are generally below detection limit (0,02 mg/l), with sporadic sulfide appearance. TOC concentration increase is followed by NH^{4+}, C:N ratio, and Fe^{2+} increase (Fig. 4). The assumption is that sporadic sulfide appearance and high C enables S-oxiders to perform their secondary metabolism of NO_3^- transformation to NH^{4+} - DNRA (max log p.a.c/ml SRB 5.0). High Fe^{2+} concentration is in accordance with intensive activity of iron reducing bacteria. When TOC is high and sulfides are absent, high C:N ratio indicates conditions for fermentative DNRA (Fig. 2.).

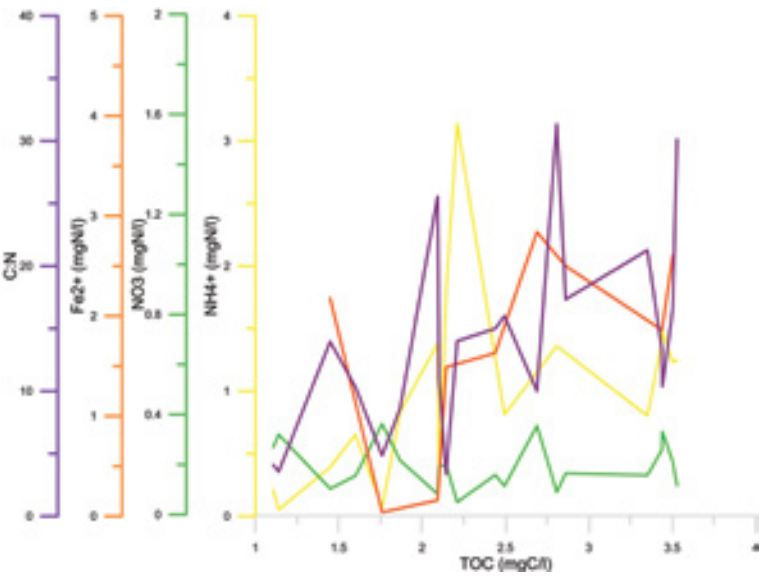

Figure 4: Comparative analysis of NH_4, NO_3, Fe^{2+} and C:N change with TOC increament in Kovin-Dubovac

Belgrade groundwater source

Generally nitrogen compounds concentrations are very low here, as well as TOC concentration. Mostly anoxic conditions, Fe^{2+} availability, low TOC concentration and mainly absence of nitrate indicate that any NO_3^- input

will probably result in N loss (N_2O, N_2), rather than conservation (NH^{4+}). Out of all three sites, recorded bacteria activity in Belgrade groundwater source is the lowest (Table 2). Low Fe^{2+} concentration is accompanied by low C:N ratio, indicating conditions for respiratory denitrification to N_2O and then anammox. Low C and sporadically high Fe^{2+} will probably lead to Fe^{2+} oxidation and denitrification to N_2.

CONCLUSION

Complex transformation and transport processes of nitrogen compounds through unsaturated and saturated environment depend on mutual and oftentimes simultaneous combining of physicochemical-biological transformations, controlled by prevailing, usually variable, conditions of environment. Based on reviewed literature, and results of the research presented in this paper, the conclusion is that precisely defining of the leading process of any transformation is very hard, because of variable chemistry, availability of multiple electron donors and existing of different redox zones in close proximity. Also, the main limitation of BART assays is the fact that in the real environment bacteria commonly operate in communities containing up to one hundred different types all living in harmony and attempts to culture "pure" cultures essentially means concentrating on only those that are able to be cultured. The comparative analysis for three different alluvial groundwater sources has been presented trying to clarify which parameters might be the most important in determining the nitrate fate. The conclusion is that C increase can be correlated to the ammonium increase. This ammonium increase can be attributed to sporadic sulfide appearance (S-oxiders DNRA to NH^{4+}), or high C:N ratio (fermentative DNRA). N loss (evaporation of N_2, N_2O) is probably related to low C content, where Fe^{2+} concentration will determine whether the nitrate will undergo reduction by Fe-oxidation (high Fe^{2+} content), or it will be subject to respiratory denitrification or respiratory denitrification with anammox (low Fe^{2+} concentration).

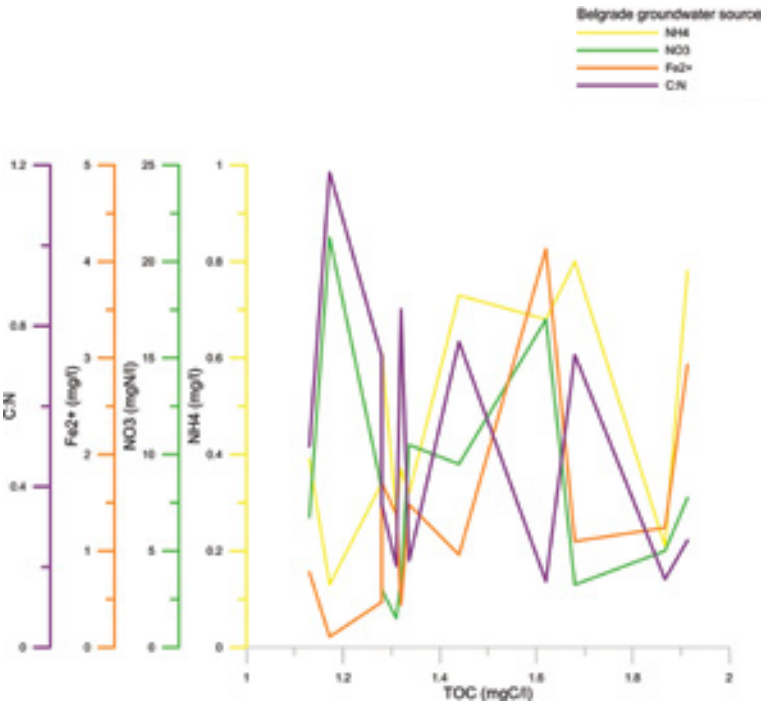

Figure 5: Comparative analysis of NH_4, NO_3, Fe^{2+} and C:N change with TOC increament in Belgrade groundwater source

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Preduzeće za specijalizovane usluge u hidrotehnici

***"BEOGEOAQUA"** d.o.o. je preduzeće koje vrši specijalizovane usluge u hidrogeologiji i hidrotehnici. Najvažnije aktivnosti preduzeća vezane su za poslove izvođenja, održavanja i regeneracije bunara. Pored toga, obavljamo poslove projektovanja, izrade Elaborata i Studija. Vršimo nadzor i kontrolu kompletnog procesa izrade bunara. Kod opremanja svih hidrotehničkih objekata nudimo kvalitetnu i raznovrsnu opremu.*

•Za sagledavanje stanja objekata preduzeće vrši ispitivanja:

- Prohodnosti konstrukcije;
- Kalibracije konstrukcije;
- Opit crpenja;
- Monitoring.

HEMIJSKO-HIDRAULIČKA REGENERACIJA BUNARA

Postupak hemijsko-hidrauličke regeneracije predstavlja kombinaciju hemijskih metoda regeneracije za razaranje produkata inkrustacije gvožđa i mangana, kao i hidrauličkih metoda, kojima se vrši opterećenje i rastresanje prifilterske zone.

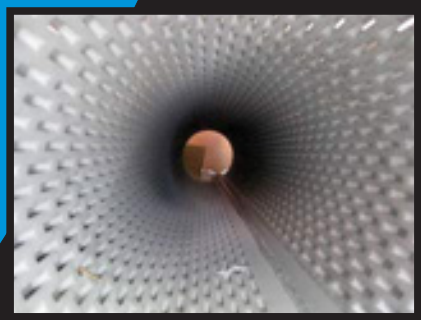
Preduzeće se specijalizovalo i steklo značajne reference na poslovima hemijsko-hidrauličke regeneracije vodozahvatnih objekata različitog tipa:

- **Kopanih bunara;**
- **Bušenih bunara**

PROJEKTOVANJE

Stručnjaci preduzeća uspešno obavljaju poslove projektovanja, analizu, izradu elaborata, studija.. . Posedujemo bogat fond tehničke dokumentacije sa izrađenom bazom podataka.

Preduzeće u saradnji sa firmom "PST Bohr" izvodi sanaciju bunara sa horizontalnim drenovima, utiskivanjem novih.



Preduzeće se bavi i snimanjem kako vertikalnih, tako i bunara sa horizontalnim drenovima, podvodnom kamerom u cliju utvrđivanja trenutnog stanja unutrašnjosti bunarske konstrukcije, odnosno drenova.

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