International Scientific Conference *People, Buildings and Environment 2016* (PBE2016)
29 September – 1 October, 2016, Luhacovice, Czech Republic, www.fce.vutbr.cz/ekr/PBE

EFFECT OF OXIC CONDITIONS ON BEHAVIOR OF POLLUTANTS IN GROUNDWATER

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Abstract

This work included presentation of micro and macro pollutants in groundwaters and detailed description of their transformation and transport process. These processes define basic quality and characteristics of aquifers depending on toxicity level. Research on wells of Belgrade's and Pozarevac's groundwater sources and rivers of Sava and Velika Morava nearby these sources provided data on concentrations of detected pollutants. Beside standard pollutants (dissolved oxygen, ammonium ion, nitrites, nitrates, sulphates, iron, manganese, total organic carbon) for underground waters, analysis of presence and behavior of pharmaceutical Carbamazepine at both mentioned sources. According to obtained results, changes in pollutants concentrations were analyzed regarding distance between observed wells and river. These changes depended on self-cleaning power of aquifers and toxic conditions explicitly defined in order to simplify comparison and provide understanding on pollutants action in different conditions.

Key words

macropollutants, micropollutants, oxicidy, self-purification.

To cite this paper: *Radakovic, B., Jeftenic, G., Kolakovic, S., Pesko, I., Mucenski, V., Kovacevic, S. (2016). Effect of Oxic Conditions on Behavior of Pollutants in Groundwater, In conference proceedings of People, Buildings and Environment 2016, an international scientific conference, vol. 4, Luhačovice, Czech Republic, pp. 243-251, ISSN: 1805-6784.*

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1 INTRODUCTION

Groundwater is the best source of drinking water supply because of its availability and self-purification power of aquifers that provide stabilization and improvement of water quality. During low water level periods groundwater play an important part in both improving the flow of watercourse as well as in creating and maintaining wetland habitats. According to estimated available water supply used for meeting the public and individual needs of rural areas citizens, approximately 500 m^3 of groundwater out of 678 million m^3 estimated capacity of Republic of Serbia is used. Maintaining the quality of groundwater by controlling and eliminating pollutants is of great importance and represents the basis for water management.

Pollutants are substances whose presence in the environment is of anthropogenic origin and depending on their nature, we can divide them into two categories: micro and macro pollutants [1]. Micro pollutants are compounds existing in environment in traces, usually synthetic compounds generated by human activities. Macro pollutants are compounds which include acids, salts, nutrients and organic matters [2]. Pollutants in groundwater represent a great problem of modern world, especially in cases when groundwater is being used as a source of water supply [3]. This problem has been separately analyzed for two water sources in our country: water source on the river Sava in Belgrade and water source Kljuc in Pozarevac on Velika Morava River.

2 METHODOLOGY

2.1 Sampling

For surface and groundwater sampling the following standards and methods were used:

- SRPS EN ISO 5667-1, Water Quality – Sampling, - Part 1: Guidelines for the design of sampling programs and sampling operations,
- JUS ISO 5667-6 1997, Water Quality – Sampling - Part 6: Guidance on sampling of rivers and streams,
- JUS ISO 5667-11 2005, Water Quality – Sampling – Part 11: Guidelines for groundwater sampling.

Surface water was sampled mid-stream, at a depth of about one meter. Groundwater samples were collected from wells in the immediate vicinity of the studied rivers. In the case 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. For pharmaceutical carbamazepine analysis all surface water and groundwater samples were collected using 1-liter amber glass bottles. The samples were stored unpreserved in refrigerators and were frozen (maximum 24 hours after sampling), up to the time of analysis (generally 2-3 days after sampling). Prior to analysis, the samples were passed through 1-µm glass fiber filters (Whatman GmbH, Dassel, Germany).

2.2 „In situ“ measurements

Water physicochemical parameter of the selected production and observation wells, such as dissolved oxygen was determined in-situ. A SEBA multiparametric MPS-D probe was used.

2.3 Analysis of chemical parameters

The tests related to the quality of surface water and groundwater have been conducted in accredited laboratories for physical and chemical water testing, the Institute for Water Resources "Jaroslav Cerni" in Belgrade. During the testing period water samples were taken for laboratory analysis of groundwater and river water chemical composition. Samples of surface and ground water are collected in the pre-prepared glass containers. After sampling in the field, the analysis of chemical parameters was carried out within a maximum of 24 hours from the time of sampling. Methods of physical and chemical tests are given in the following table 1.

Tab. 1: Methods for chemical parameters analysis

Parameter	Method of analysis
Ammonium ion	[1]Guide, method P-V-2/B
Nitrites	[2]SMEWW 21st, method 4500-NO2--B
Nitrates	[1]Guide 1, method P-V-31/B
Sulfates	[2]SMEWW 21st, method 4500-SO42- E
Iron	[2]SMEWW 21st, method 3120B
Manganese	[2]SMEWW 21st, method 3120B
TOC	[2]SMEWW 21st, method 5310C

[1]Guide for drinking water, Standard Methods for The Examination of hygienic safety , Belgrade, 1990.
[2]SMEWW 21st, Standard Methods for The Examination of Water and Wastewater 21st Edition 2005, APHA, AWWA, WEF.

2.4 Analytical methods

Samples were analyzed with the slightly modified methods previously published [4] [5] in which 7 cardiovascular pharmaceuticals were added. The method was validated and the results are presented in previous work [6].

In brief, samples were preconcentrated using Oasis HLB (hydrophilic N-vinylpyrrolidine and lipophilic divinylbenzene), 200 mg/6 mL; from Waters, Milford, MA, USA) cartridges and 100 mL of water sample, with pH adjusted to 6. The cartridge packing was subsequently eluted with 15 mL of mixture methanol-dichloromethane (1:1). The extract was evaporated to dryness and reconstituted in 1 mL of methanol. Extract was vortexed and filtered through 0.45 µm polyvinylidene difluoride (PVDF) filter, acquired from Roth (Karlsruhe, Germany), into the autosampler vial and analyzed. The external calibration method with appropriate matrix-matched standards was used. Matrix-matched standards were prepared by adding 1 mL of the standard solution (at the concentration 100 µg/L for each analyte) to the blank extracts obtained following SPE procedure. Surveyor LC system (Thermo Fisher Scientific, Waltham, MA, USA) was used for the separation of the analytes on reverse-phase Zorbax Eclipse® XDB–C18 column, 75 mm×4.6 mm ID and 3.5 µm particle size (Agilent Technologies, Santa Clara, CA, USA). A precolumn, 12.5 mm×4.6 mm ID and 5-µm particle size (Agilent Technologies), was also used. For the LC–MSn analysis of pharmaceuticals in the positive ionization mode, the mobile phase was composed of methanol (A), deionized water (B), and 10 % acetic acid (C). Gradient changed as follows: 0 min B 30 % C 2 %; 30 min B 80 % C 2 %; 30.01 min B 98 % C 2 %; 33 min B 98 % C 2 %. The initial conditions were re-established and held for 5 min. The flow rate of the mobile phase was 0.3 ml/min. The injection volume was 10 µL. Mass spectra were obtained using the LTQ Fleet linear ion trap mass spectrometer (Thermo Fisher Scientific). Electrospray ionization was used to perform the mass spectrometric analysis. For the analysis of selected compounds, the spray voltage was set to 5 kV and the sheath gas flow was optimized at 35 au (i.e., 35 arbitrary units, from the scale of arbitrary units in the 0–100 range defined by the LTQ Fleet system). The capillary temperature was set to 350 °C. For each analyte, the selection of the precursor ion, the optimal collision energy, and the most abundant fragment ion was performed in the selected reaction monitoring (SRM) mode, for quantification purposes. The additional fragmentation reaction was selected for confirmation purposes. Specific operational conditions were optimized and can be found in [6].

3 RESULTS AND DISCUSSION

3.1 Characteristics of oxic groundwater sources based on source Kljuc on the river Velika Morava

Water source Kljuc is used for supplying Pozarevac town in nearby area with drinking water (fig. 1). The area represents alluvial plain of Velika Morava River and it's made of polycyclic river-lake and alluvial deposits.

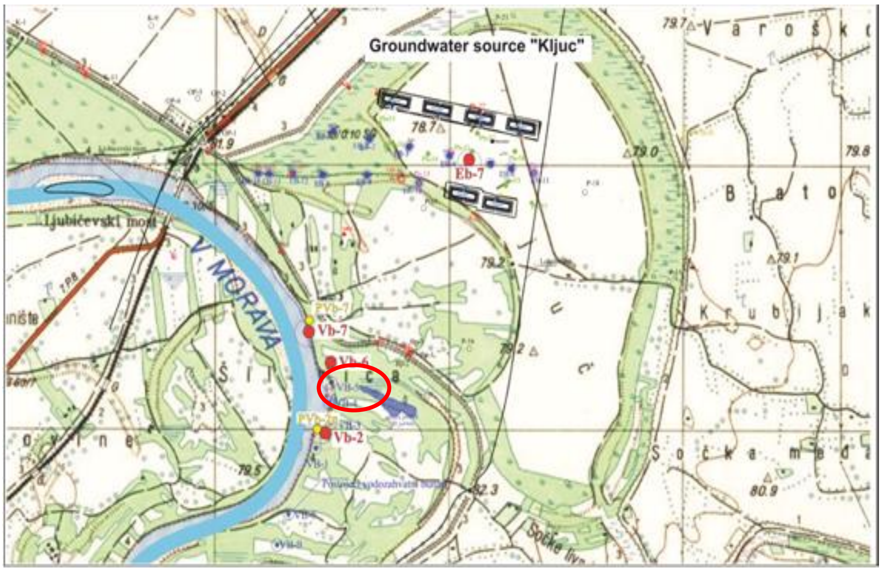

Fig.1: Location of source Kljuc on Velika Morava River [7]

Source Kljuc is characterized by oxic environmental conditions which imply conditions in which oxidation takes place with dissolved oxygen. Based on results of testing at source Kljuc, that includes determining the concentration of TOC (Total Organic Carbon), nitrate, nitrite, sulfate, and others, a conclusion that concentration of observed parameters change depending on distance between analyzed well and river can be derived (tab. 2).

Tab. 2: Preview of the concentration changes of the observed parameters in April 2013, with the distance from the river

Parameter	Unit of Measurement	Velika Morava	VB-2 Well
Dissolved oxygen	mgl^{-1}	10.5	5.22
Ammonium ion	mgl^{-1}	0.02	0.01
Nitrites	mgl^{-1}	0.034	<0.005
Nitrates	mgl^{-1}	1.20	4.89
Sulfates	mgl^{-1}	28	120.8
Iron	mgl^{-1}	2.192	0.0029
Manganese	mgl^{-1}	0.10	0.19
TOC	mgl^{-1}	3.3	2.36

By observing obtained results of analysis, significant concentration of oxygen in the groundwater can be noticed, which represents initial and the most important indicator of oxic environment. From the standpoint of oxygen balance, biochemical oxidation of organic matters and the oxidation of mineral substances of aquifer's skeleton, especially those containing ferrous iron, is of great importance. Various elements can be found in water in different oxidation conditions. Typical examples of different behavior in different oxidation conditions are:

- Iron – In highly oxic conditions of aquifers, dissolution of iron from sediments is unlikely. Iron in its bivalent form is much more soluble in water, as opposed to trivalent forms. After oxidation, when iron transform in trivalent form, its solubility is decreasing and it tends to accumulate. Behavior of manganese is very similar to the behavior of iron, and the results of the analysis show increase in concentration at the site of the well.
- Nitrogen - Nitrate nitrogen occurs in predominantly anaerobic environments, where its mobility in water is emphasized [8].

By observing the values of tested parameters, it is noticed that concentration of particular parameters in the well changes depending on the distance from the river. The concentration of majority of heavy metals, as well as iron and manganese metals, decreases during the groundwater flow due to sorption processes [9]. However, in the case of the study there is slight increase in manganese concentration in the groundwater for 0,09 mgl-1, which may be the result of dissolution of manganese from the sediments of aquifers.

The most common pollutant in groundwater is nitrogen in form of nitrate. In aerobic conditions, nitrates are very stable and appear as a stable form of nitrogen. For many years now the quality of water sources Kljuc has been compromised with contaminated groundwater from the hinterland, with a high concentration of nitrates which is increasing every day. The cause of this is fertilization of arable farmland and discharge of insufficiently purified sewage water into the environment. Based on the results increase in concentration of nitrate can be noticed in the area between river and well which is very important indicator of how far this problem has progressed.

Sulfur is usually found in groundwater in the form of sulfate and analysis shows much higher concentration of it in well compared to that of in river. If the sulfur appears in the form of hydrogen sulfide, even concentrations less than 10 mgl-1 can cause unpleasant characteristic odor, which is not the case for observed source of water because recorded hydrogen sulfide concentrations is less than 0.02 mgl-1.

Based on the results of research conducted during 2011 and 2013, which included the determination of the concentration of pharmaceuticals carbamazepine, obtained values are shown in tab. 3.

It can be concluded that a pharmaceutical carbamazepine occurs in a large number of samples in the concentration ranging from 2 to 40 ngl-1. Comparing the results of the analysis of carbamazepine in surface and underground water give us an insight into the change in concentration in groundwater due to the effects of the process of self-purification, sorption and other processes that occur in groundwater [10].

Tab. 3: The results of the analysis of pharmaceuticals carbamazepine in groundwater of source Kljuc on the Velika Morava River [6]

Registered substance	Total positive findings	Location of registration	Date and concentration	RANGE OF CONCENTRATION (ngL^{-1})
Carbamazepine	**5/6**	Vb-2/P1	30.6.2011. **(17 ngL^{-1})**	**2-40**
		Vb–2/P1	11.11.2011. **(23 ngL^{-1})**	
		Vb–2/P1	10.09.2013. **(40 ngL^{-1})**	
		Vb-2/P1	26.09.2013 **(2 ngL^{-1})**	
		Vb–2/P1	26.09.2013 **(27 ngL^{-1})**	

3.2 Characteristics of anoxic groundwater source based on the Belgrade source

Belgrade groundwater source represent a groundwater resource whose wells pumps groundwater of compact type aquifer. Exploited wells are located in the vicinity of the river Sava, at some points with the distance from the coast less than 10 m (fig. 2).

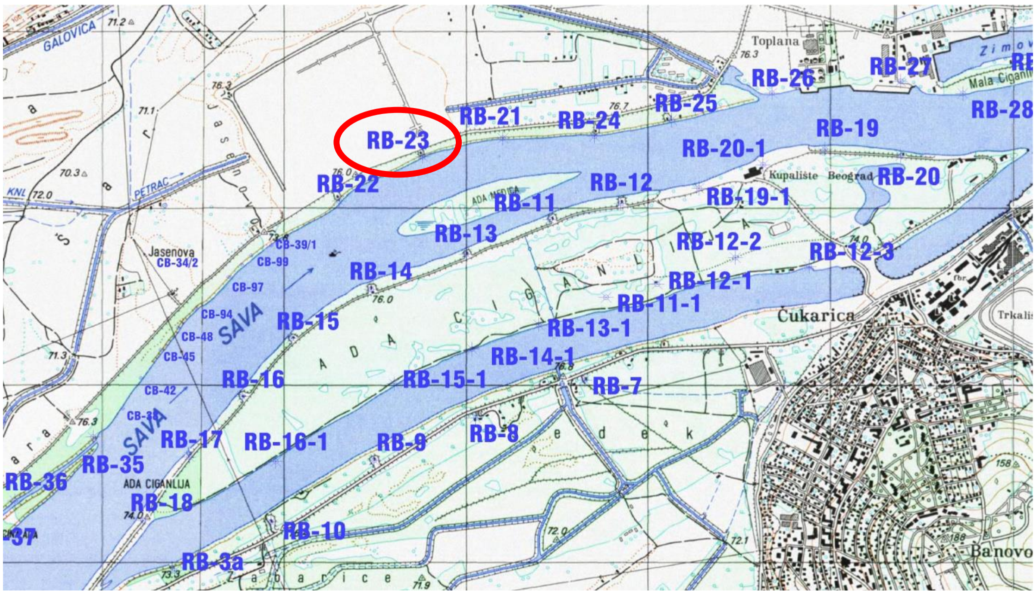

Fig. 2: Localities of sources in the city of Belgrade [7]

Belgrade water source falls into anoxic groundwater sources category. Anoxic sources are characterized by absence of oxygen where anaerobic bacteria prevail, whereby the biochemical oxidation is carried predominantly at the expense of nitrate, compounds of trivalent iron, four-coordinate manganese, and sulfate [8].

After the completion of the parameters analysis on the Sava River and the selected RB-23 well, obtained parameters results are shown in tab. 4.

Based on the results of the analyzed parameters a different concentration in the river Sava and in the groundwater can be noticed, which is the result of different oxic conditions, self-purifying potential, dissolution of sedimentary factors, or possible contamination that occurs in the observed area.

Tab. 4: Preview of the concentration changes of the observed parameters in April 2013, with the distance from the river

Parameter	Unit of Measurement	Sava	RB-23 Well
Dissolved oxygen	mgl^{-1}	10,17	0,76
Ammonium ion	mgl^{-1}	<0,02	0,43
Nitrites	mgl^{-1}	0,006	<0,005
Nitrates	mgl^{-1}	0,93	1,32
Sulfates	mgl^{-1}	42,3	30,4
Iron	mgl^{-1}	0,10	0,29
Manganese	mgl^{-1}	0,05	0,44
TOC	mgl^{-1}	2,38	1,25

The river is characterized by oxic conditions because of its openness to the atmosphere, while the Belgrade groundwater source is characterized by anoxic conditions, which can be determined by observing the results obtained by analyzing the concentration of dissolved oxygen, which is in deficit, amounting to only 0.76 mgl-1.

On the observed water source a lower concentration of nitrogen in the form of nitrate can be noticed, which is of great importance for water quality. The concentration of nitrate in ground water increased to 0.39 mgl-1, which is 41.95% in relation to the surface water.

Tab. 5: The results of the analysis of pharmaceuticals carbamazepine in groundwater of Belgrade source [6]

<table>
<tr><th>Total number of analyzed samples</th><th>Registered substances</th><th>Total positive findings</th><th>Location of Registration</th><th>Date and concentration</th><th>RANGE OF CONCENTRATION (ngL^{-1})</th></tr>
<tr><td rowspan="7">TOTAL 29 samples
Rb –16 – 4 samples 2 MIB
Rb16-P2 -2 samples MIB
Rb16-P3 - 2 samples MIB
Rb – 20 - 2 samples
Rb 5 – 1 sample
Rb 37 – 1 sample
Rb -5m – 2 samples
Rb -8m – 2 samples MIB
Rb – 8m - P2 – 2 samples MIB
Rb 5-P1 – 1 sample
Rb – 21 – 3 samples
Rb-21-P2 – 2 samples
Rb -41 – 1 sample
Rb-41/P-2p – 1 sample
Rb-41/P-2d – 1 sample
Rb 3m – 1 sample
Rb-49 – 1 sample</td><td rowspan="7">Carbamazepine</td><td rowspan="7">7/29</td><td>Rb–16
11.09.2013.</td><td>(12 ngL^{-1})</td><td rowspan="7">5-14</td></tr>
<tr><td>Rb–8m-P2</td><td>(11 ngL^{-1})</td></tr>
<tr><td>Rb-8m
11.09.2013</td><td>(6.8 ngL^{-1})</td></tr>
<tr><td>Rb–8m/P–2
11.09.2013</td><td>(13.7 ngL^{-1})</td></tr>
<tr><td>Rb–16
11.09.2013</td><td>(8.1ngL^{-1})</td></tr>
<tr><td>Rb–16/P–2
11.09.2013</td><td>(5.7 ngL^{-1})</td></tr>
<tr><td>Rb–16/P–3
11.09.2013</td><td>(10.2 ngL^{-1})</td></tr>
</table>

Also, increase in ammonium ions can be noticed, which occurs predominantly in anaerobic conditions, as well as iron and manganese in groundwater.

In the oxidizing water, concentration of sulfate usually range between 5 to 30 mgl-1, however, by measuring the concentrations in the observed well, the average concentration reaches higher values as an indicator of reducing conditions prevailing in the area.

Measured values of manganese on the site of wells are higher than in surface water with measured value of 0.05 mgl-1 and reaching a value of 0.44 mgl-1 causing the increase of manganese bacteria and unpleasant odor of water. In addition to manganese, increase of iron concentration in the wells is noticed, which can be attributed to the dissolution of their shares from the aquifer sediments.

Apart from Kljuc source, Belgrade source is also a subject of analysis of pharmaceuticals carbamazepine concentrations which is shown in tab. 5. Carbamazepine is present in a relatively large number of samples (tab. 5).

4 CONCLUSION

In recent years, there was a dramatic increase in the number of contaminated sources of water supply due to the increased concentration of pollutants, primarily nitrates, for which regulation of border values for emission of pollutants in waters and time limits for their reach within Law on Waters sets a maximum permissible concentration.

For many years the quality of water source Kljuc has been compromised by groundwater from the hinterland, with a high content of nitrates which is increasing every day. By observing the results of the analyzed parameters, we conclude that the concentration of nitrate, sulfate and manganese in groundwater at the site of VB-2 well increased compared to the concentration registered in the Morava River. The concentrations of other monitored parameters (dissolved oxygen, ammonium ion, nitrites, iron and TOC) is significantly reducing due to self-purification potential for which oxic conditions are favorable.

Belgrade anoxic groundwater source is characterized by increase in the concentration of ammonium ions, nitrates, iron and manganese, while the concentration of other observed parameters decrease in the location of RB-23 well, compared to the Sava River. The percentage of reduction in the concentration of the parameters from the river to the well compared with oxic source Kljuc is smaller, which can be attributed to a deficit of oxygen and slow biodegradation processes.

ACKNOWLEDGEMENTS

The work reported in this paper is a part of the investigation within the research project TR 37003 "Development of hydro-information system for monitoring and early drought warning", supported by the Ministry for Science and Technology, Republic of Serbia. This support is gratefully acknowledged.

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