



Influence of oxic and anoxic groundwater conditions on occurrence of selected agrochemicals

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ABSTRACT

The occurrence and mitigation of selected pesticides and nitrates in surface and groundwater samples from two alluvions in the Republic of Serbia are investigated in this study. The influence of aquifer conditions on the degradation processes of pesticides and nitrates is considered as a potential removal mechanism of compound residues in alluvial groundwater. Nitrate concentration was analyzed in 144 groundwater samples in the Kovin-Dubovac drainage system and 63 samples at the Ključ groundwater source. The occurrence of 15 pesticides was monitored in groundwater in a total of 34 samples in the Kovin-Dubovac area and 14 samples at the Ključ groundwater source. Concentrations of selected pesticides and nitrates were monitored in eight samples from the Danube in the Kovin-Dubovac area and 15 samples from Velika Morava at the Ključ groundwater source. Both selected locations are agricultural areas. Results show that concentrations of nitrates (NO_3^-) are much higher in oxic groundwater conditions compared with concentrations in typical anoxic conditions. The opposite is the case for the concentration of pesticides that occurred in surface and groundwater samples. These results are very important for a better understanding of the self-purification potential of alluvial aquifers and assessment of aquifer condition influence, especially oxic or anoxic conditions, on the occurrence and mitigation of selected agrochemical residues in groundwaters.

Key words | anoxic conditions, groundwater quality, nitrates, oxic conditions, pesticides

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INTRODUCTION

According to the European Environmental Agency (European Environmental Agency 2018) the main sources of contamination that have an impact on groundwater chemical status are diffuse sources, from which the main pressure from the diffuse sources is agricultural. Modern agriculture is highly dependent on the use of agrochemicals for fertilization of crops and control of weeds and pests, due to their improvement of crop yields. Therefore, it is one of the main non-point pollutants of groundwater in irrigated areas (Jurado *et al.* 2012).

The use of fertilizers in the world has been declared as one of the main factors responsible for the occurrence of elevated nitrate (NO_3^-) concentrations in waters around

the world. Nitrates are very mobile in groundwater: they act like inert anions, very soluble, not binding to soils and their retardation in groundwater has not been identified (Rivett *et al.* 2008; Andrade & Stigter 2009). Nitrate contamination of groundwater sources is not solely from application of nitrogen-based fertilizers to land, but also from septic tanks or leaking sewers, spreading of sewage sludge to land and atmospheric deposition (Rivett *et al.* 2008). Nitrate concentrations in groundwaters higher than 3 mg N L^{-1} indicate anthropogenic influence (Babiker *et al.* 2004). If groundwater conditions are oxic, nitrates that have leached to groundwater do not express a decreasing trend. However, if groundwater conditions favor reduction processes, in

anoxic environments, then quantity reduction processes, such as volatilization to gaseous nitrogen or nitrogen(I)-oxide, or conservation, with reduction to NH_4^+ , occurs (Perović *et al.* 2017). According to the research by Andrade & Stigter (2009), contamination of groundwater with nitrates is controlled not only by redox state and dissolved oxygen concentrations, but also land use and lithology of the area, because the aerobic environment contributes to rapid nitrification of other forms of nitrogen.

Pesticides enter groundwater by leaching from agricultural fields through the soil profile, from surface water through river bank filtration or through accidental spills directly into wells. Pesticides are a wide group of chemical compounds, and their fate and behavior in groundwater depends greatly on their physicochemical properties (Arias-Estévez *et al.* 2008). The most important processes that influence pesticide behavior in groundwater are sorption, degradation, transport and bioaccumulation. Degradation has the greatest impact on pesticide elimination in groundwater, while sorption is less important due to the reversibility of the process and since it only delays transport of the contaminant (Greskowiak *et al.* 2017). What type of degradation process will occur depends on the structural affinity of a pesticide to a specified transformation process and conditions of the environment (Fenner *et al.* 2013). The presence of nitrate as an alternative electron acceptor can accelerate degradation of a pesticide, such as atrazine, in low-oxygen conditions (Papiernik & Spalding 1998).

The adverse effect of nitrates in groundwater used for drinking water on human health which has been discussed the most is the hematological disorder methemoglobinemia (blue baby syndrome). In previous studies, there has been evidence that chronic ingestion of water with elevated nitrate content might cause teratogenicity, mutagenicity, and increase cancer potential (Camargo & Alonso 2006; IARC 2010). By International Agency for Research on Cancer (IARC) classification, nitrates are classified as probably carcinogenic to humans. This category is used when there is limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals.

The human population is exposed to pesticide residues not only through environmental mediums (e.g. air, water), but also through food. Elevated pesticide residues in drinking water can have adverse effects on human health,

ranging from short-term to chronic effects. Due to various factors included, such as level of exposure and type of pesticide, the risk associated with pesticides concentrations is complex to determine (Kim *et al.* 2017).

In order to assess groundwater source contamination risk with selected agrochemical residues in Serbia, surface and groundwater sampling campaigns were conducted by Jaroslav Černi Institute for Water Resources during the years 2009–2015. Concentrations of nitrogen in the forms of nitrates and ammonium and selected pesticides were monitored in four rivers in Serbia (Sava, Tisa, Danube and Velika Morava) and in the corresponding groundwaters. In this paper, the focus of the research is on two locations: the alluvial aquifer of the Danube River at the Kovin-Dubovac drainage system and the alluvial aquifer of Velika Morava at the Ključ groundwater source. These distinct locations were selected according to their different oxidic conditions.

During sampling campaigns, 15 pesticides were selected for observation in surface and groundwater sources, which were chosen according to their frequency of use and affiliation to priority or emerging lists of substances. These pesticides include: monocrotophos, carbendazim, imidacloprid, acetamiprid, dimethoate, monuron, simazine, carbofuran, carbaryl, atrazine, diuron, propazine, linuron, malathion and tebufenozide. Most frequently detected pesticides in both surface and groundwater samples were atrazine and carbendazim and they were selected in this paper for further research on degradation in different groundwater conditions. Atrazine, even though its use is banned, is frequently detected in groundwater and surface water samples (Fingler *et al.* 2017; Guillon *et al.* 2018).

The aim of the paper is to provide new information on the influence of oxidic or anoxic conditions in groundwaters for the mitigation of selected agrochemical residues. Results of the research could be used as an important tool in making decisions in choosing new locations of groundwater sources for drinking water supply.

DESCRIPTION OF STUDY AREAS AND PREVIOUS INVESTIGATIONS

According to the previously conducted thorough research on chemical properties of groundwater conditions, the Danube

River alluvion at the Kovin-Dubovac drainage system has typical anoxic groundwater conditions, while the Velika Morava alluvion at the Ključ groundwater source has typical oxidic groundwater conditions (Dimkić & Pušić 2014; Kovačević et al. 2017). These distinct locations were used as being representative for observation of the influence of oxidic and anoxic conditions on the degradation of selected agrochemical residues (Figure 1). Redox conditions in an aquifer are extremely important due to the influence on potential microbial degradation and abiotic processes for removal of pesticides.

The alluvial plane of the river Danube in the Kovin-Dubovac drainage system area is a typical three-layer setting composed of top, aquifer and bottom, with relatively homogeneous hydraulic conductivity throughout the area. Relevant properties for this study of the Kovin-Dubovac drainage system area are presented in Table 1.

The wells used for the observation of selected pesticide occurrence are self-discharging wells Bp-12 and Bp-19 in the first drainage line (Figure 1), with a distance of about 300 m from the river Danube. The travel time of water from the river to the wells according to the fact that the aquifer

is relatively homogeneous, with only a few possible preferential flow layers, was estimated to be around 35 days (Kovačević et al. 2017). Water is mostly infiltrated from the river to the wells, with almost no dilution from the hinterland (Dimkić & Pušić 2014).

Hydrogeological parameters of the extended area of the Ključ groundwater source are relatively uniform. Relevant properties of the Ključ groundwater source are presented in Table 1. With the observed wells for selected pesticide occurrence VB2, VB6 and VB7 (Figure 1) being located about 40 m from the river and according to the hydraulic conductivity of the aquifer, travel time is estimated to be around two days (Kovačević et al. 2017).

Previously, research on removal of pharmaceutical compounds using riverbank filtration was conducted (Kovačević et al. 2017) at the Ključ groundwater source. The most frequently detected pharmaceuticals were the carbamazepine and metamizole metabolites 4-FAA and 4-AAA. In the previous paper by Mitrinović et al. (2016), it was established that the contribution of surface water in the wells at the Ključ groundwater source was around 30% (Figure 2). A detailed

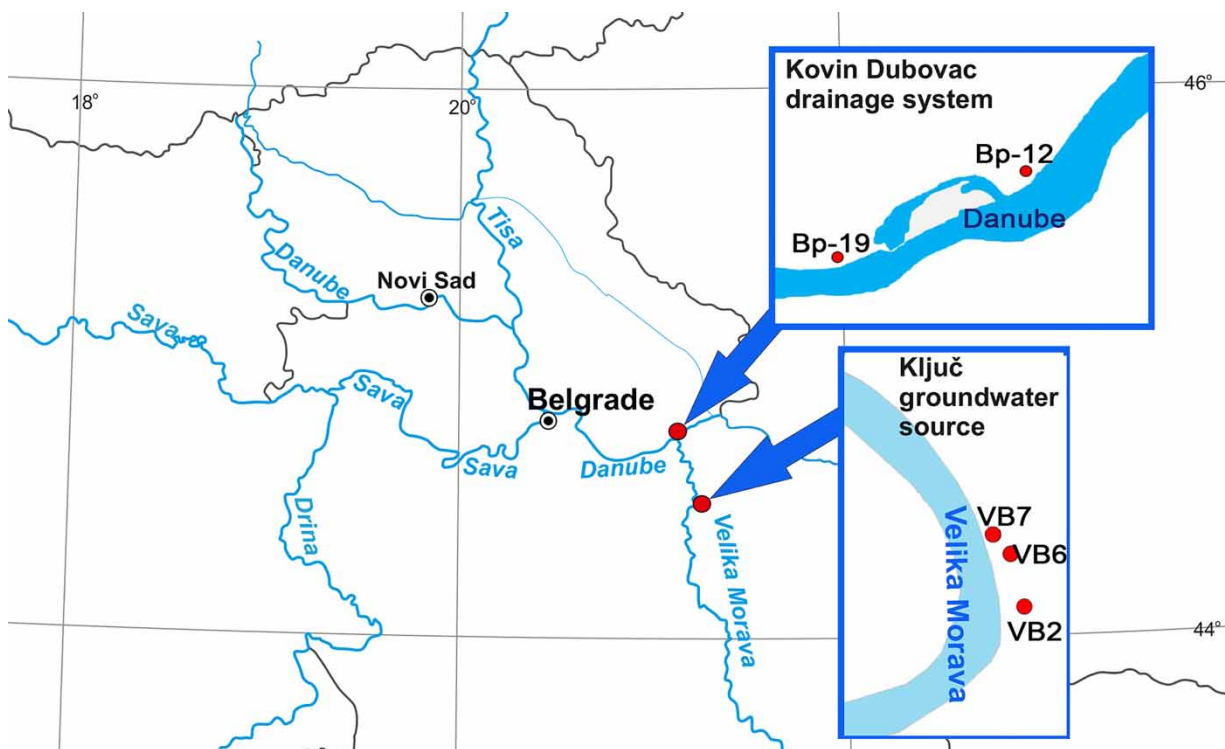
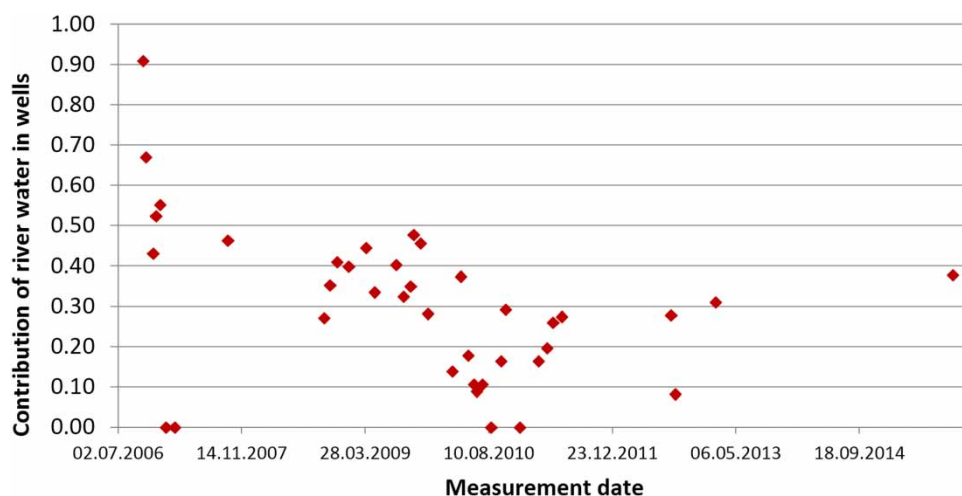


Figure 1 | Locations of the observed wells for occurrence of pesticides at the Kovin-Dubovac drainage system and Ključ groundwater source.

Table 1 | Relevant properties of studied locations

Properties	Kovin-Dubovac drainage system	Ključ groundwater source
Aquifer composition	Sandy and sandy gravel soils	Sandy and gravelly soils
Aquifer hydraulic conductivity (m s^{-1})	$0.5\text{--}7 \times 10^{-3}$	7×10^{-5} (gravelly part) $10^{-5}\text{--}10^{-4}$ (sandy soils)
Aquifer thickness (m)	1.5–35 (with average value of 20)	Around 20
Overlying top layer hydraulic conductivity (m s^{-1})	10^{-5}	$10^{-8}\text{--}10^{-6}$
Overlying top layer thickness (m)	4 (first drainage line)	3–5
Redox potential (mV)	96	>350
Dissolved oxygen concentration (mg L^{-1})	0.06	5.77
Groundwater condition	Anoxic	Oxic

**Figure 2** | Contribution of surface water in observed wells in the Ključ groundwater source area; mean value 0.3.

description of the methodology for establishing the contribution of surface water in wells is presented in the paper by Mitrinović *et al.* (2016), and briefly, this methodology included measurement of nitrate concentrations in the river, nearest piezometer in the hinterland and well. Measured concentrations of nitrates in the piezometer and river were used in calculating the concentration of nitrates in the well, and the contribution of water from the river was established by changing the contribution of river water in the well until the minimal mean square error between the measured and calculated nitrate concentrations in the well was achieved. The equation for calculating nitrate concentrations in the well was $c(\text{NO}_3^-)_{\text{well}} = x \cdot c(\text{NO}_3^-)_{\text{river}} + (1 - x) \cdot c(\text{NO}_3^-)_{\text{piezometer}}$ where $c(\text{NO}_3^-)_{\text{well}}$ is the calculated concentration of nitrates in the well, x is the share of river water in the well, $c(\text{NO}_3^-)_{\text{river}}$

is the measured concentration of nitrates in the river, and $c(\text{NO}_3^-)_{\text{piezometer}}$ is the measured concentration of nitrates in the nearest piezometer in the hinterland. For these calculations, from the year 2006 to 2015, a total of 67 samples from the nearest piezometer in the hinterland, 180 samples from the well and 213 samples from the river were analyzed and used in the calculations.

During the transport period of water from the river to the wells, pharmaceuticals have time to degrade and sorb onto the aquifer material. Sorption is a reversible process and it has an effect on the transport time of compounds, but degradation affects the reduction of concentration (Greskowiak *et al.* 2017). In the paper by Kovačević *et al.* (2017) it was determined that with the hypothesis that there are no sources of pharmaceuticals in the

hinterland from which groundwater moves towards the river, the mean concentration of carbamazepine is constituted of around 35% of the mean concentration in Velika Morava river, while concentrations of metamizole metabolites are reduced to around 15% and approximately 4% for 4-FAA and 4-AAA, respectively, in groundwater compared with the concentration in surface water. Due to the fact that carbamazepine is a persistent substance in both oxic and anoxic conditions (Lekkerkerker-Teunissen *et al.* 2012; Hamann *et al.* 2016), it was concluded that the reduction of carbamazepine concentration was due to riverbank filtration. This information is significant, since it indicates that around 70% of infiltrated water at Ključ is from the hinterland. According to the research by Kovačević *et al.* (2017) at the Kovin-Dubovac drainage system, it was concluded that the concentration of persistent carbamazepine decreased from the river to the observed wells at the first drainage line by approximately 35%, which leads to the conclusion that over 60% of infiltrated water in the wells is from the river.

MATERIALS AND METHODS

In the research period of the years 2006–2015, groundwater levels were monitored in 105 piezometers and wells at the Ključ groundwater source. Groundwater levels were monitored using water level meters and diver water level loggers. In the Kovin-Dubovac area, groundwater levels were monitored during the years 2010–2015 in 33 wells and piezometers. Groundwater levels at both locations during the mean river flow (data were measured in the period from 28th to 31st July 2012 for the Kovin-Dubovac area, and for Ključ groundwater source, data were measured from 8th to 10th February 2012) were used in order to obtain isolines of groundwater levels and assess the movement of groundwater in the research areas (Figures 3 and 4).

A total of 144 groundwater samples from the years 2010–2015 and in the year 2018 were analyzed for nitrate concentration in 14 wells and piezometers at the Ključ groundwater source. A total of 63 groundwater samples



Figure 3 | Kovin-Dubovac drainage system groundwater table levels, expressed in metres above sea level, with highlighted wells selected for pesticide concentration monitoring (Bp-12 and Bp-19); arrows indicate groundwater movement.



Figure 4 | Groundwater table levels at the Ključ groundwater source, expressed in metres above sea level; dots placed close to each other represent pumping wells with specifically highlighted wells selected for pesticide concentration monitoring (VB2, VB6 and VB7); dots with labels starting with 'Pb' represent observed piezometers; arrows indicate groundwater movement.

in the same research period were collected from the Kovin-Dubovac drainage system, from 28 wells and piezometers. Samples were collected in sterile containers and filled to the top, leaving no headspace under the screw cap. Samples were transported to the laboratory within four hours from the moment of sampling at a temperature of 4 °C. Standard Methods (APHA 2005) were used for analysis, with limits of quantification 0.05 mg N L⁻¹ for nitrates (NO₃⁻) and 0.02 mg N L⁻¹ for ammonium (NH₄⁺).

The total number of collected groundwater samples for detection of selected pesticides at the Kovin-Dubovac drainage system was 34, while eight samples were collected from the Danube River. At the Ključ groundwater source, 14 groundwater samples were collected, and 15 samples were collected from Velika Morava. Surface water samples were also analyzed for nitrate concentrations. Samples were collected mainly in spring and fall every year, due to seasonal variations of agricultural activities. Samples from both surface and groundwater were collected at the same

time. Groundwater samples were collected from the wells presented in Figure 1. Surface water samples were grabbed at a depth of around one m mid-stream. Samples were collected in one litre bottles and frozen within four hours from the sampling time until the analyses, which were performed within two weeks of receipt. Solid phase extraction (SPE) with the use of the Oasis hydrophilic-lipophilic balance cartridge (HLB, 200 mg/6 mL) from Waters (Milford, MA, USA) was chosen for preparation of both surface and groundwater samples for analysis of pesticide occurrence. Extracts were used for analysis by the liquid chromatography tandem mass spectrometry method (LC-MS/MS). The method was previously validated and detailed information about the recoveries, relative standard deviation, calibration curves, accuracy and precision, limits of detection (LOD) and quantification (LOQ) are available in previously published papers (Dujaković *et al.* 2010; Radović *et al.* 2015).

Briefly, it was determined that the optimal SPE of the analytes was achieved using 250 mL of the water sample with pH-value 6. The relative standard deviation was lower than 13%, which indicates good repeatability. High recoveries were obtained for all pesticides (>70%) in both surface and groundwater samples. Low limits of detection and limits of quantification were achieved for all the investigated compounds: in groundwater samples LOD was from 0.4 to 5.5 ng L⁻¹ and LOQ was from 1.1 to 18.2 ng L⁻¹; in surface water samples LOD was from 0.5 to 5 ng L⁻¹ and LOQ was from 1.3 to 16.5 ng L⁻¹ (Dujaković *et al.* 2010). The calibration curves exhibited good linearity. Matrix-matched standards were used to eliminate the matrix effect, with signal enhancement or suppression less than 20%.

A Surveyor LC system (Thermo Fisher Scientific, Waltham, MA, USA) was used for the separation of analytes on a 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). The mobile phase was composed of methanol (A), deionized water (B), and 10% acetic acid (C). The mobile-phase gradient varied as follows: 0 min, A 33% B 66%, C 1%; 7.5 min, A 58% B 41%, C 1%; and 25 min, A 0% B 100%, C 0%. The initial conditions were then re-established and held for 15 min. The flow rate of the mobile phase was 0.5 mL min⁻¹. The injection volume was 10 μL.

Mass spectra were obtained using an LCQ Advantage quadrupole ion trap mass spectrometer (Thermo Fisher Scientific, USA). Electrospray ionization was applied to perform the mass spectrometric analyses, in positive ionization mode for all pesticides. The spray voltage was set to 4.5 kV and the sheath gas flow was optimized at 26 au (i.e., 26 arbitrary units) and auxiliary gas at 4 au. The capillary temperature was set to 290 °C.

RESULTS AND DISCUSSION

Groundwater table levels during mean river flow are presented in Figures 3 and 4 for the Kovin-Dubovac research area and Ključ groundwater source area, respectively. Groundwater table levels are presented as isolines with black arrows indicating the movement of groundwater at both locations.

In the Kovin-Dubovac area, groundwater moves from the river to the wells selected for monitoring of pesticide concentrations, Bp-12 and Bp-19 (Figure 3).

At the Ključ groundwater source, wells selected for monitoring of pesticide concentration are influenced by human activities, which can be concluded according to the movement of groundwater from the hinterland, composed of agricultural areas and settlements (Prugovo, Lučica, Ljubičevo, Požarevac), to wells VB2, VB6 and VB7 (Figure 4). These three wells selected for monitoring of pesticide concentration, with four other wells, represented in Figure 4, have a total abstraction rate of 167 L s⁻¹ (data from PUC Waterworks and Sewerage Požarevac) and groundwater movement direction is towards these pumping wells.

The mean values of nitrate concentration in surface water samples, during the research period, were 1.21 mg N L⁻¹ in the Danube River and 1.38 mg N L⁻¹ in Velika Morava. NO₃⁻ and NH₄⁺ concentrations, presented as mg nitrogen L⁻¹ in wells and piezometers at both locations are presented in Tables S1 and S2 in the Supplementary Material. The Kovin-Dubovac drainage system is a typical anoxic setting and the appearance of nitrogen compounds is mostly presented as NH₄⁺, while in typical oxidic groundwater conditions at the Ključ groundwater source nitrogen is mostly in the form of NO₃⁻. An overview of mean values for NH₄⁺ concentration in observed piezometers and wells

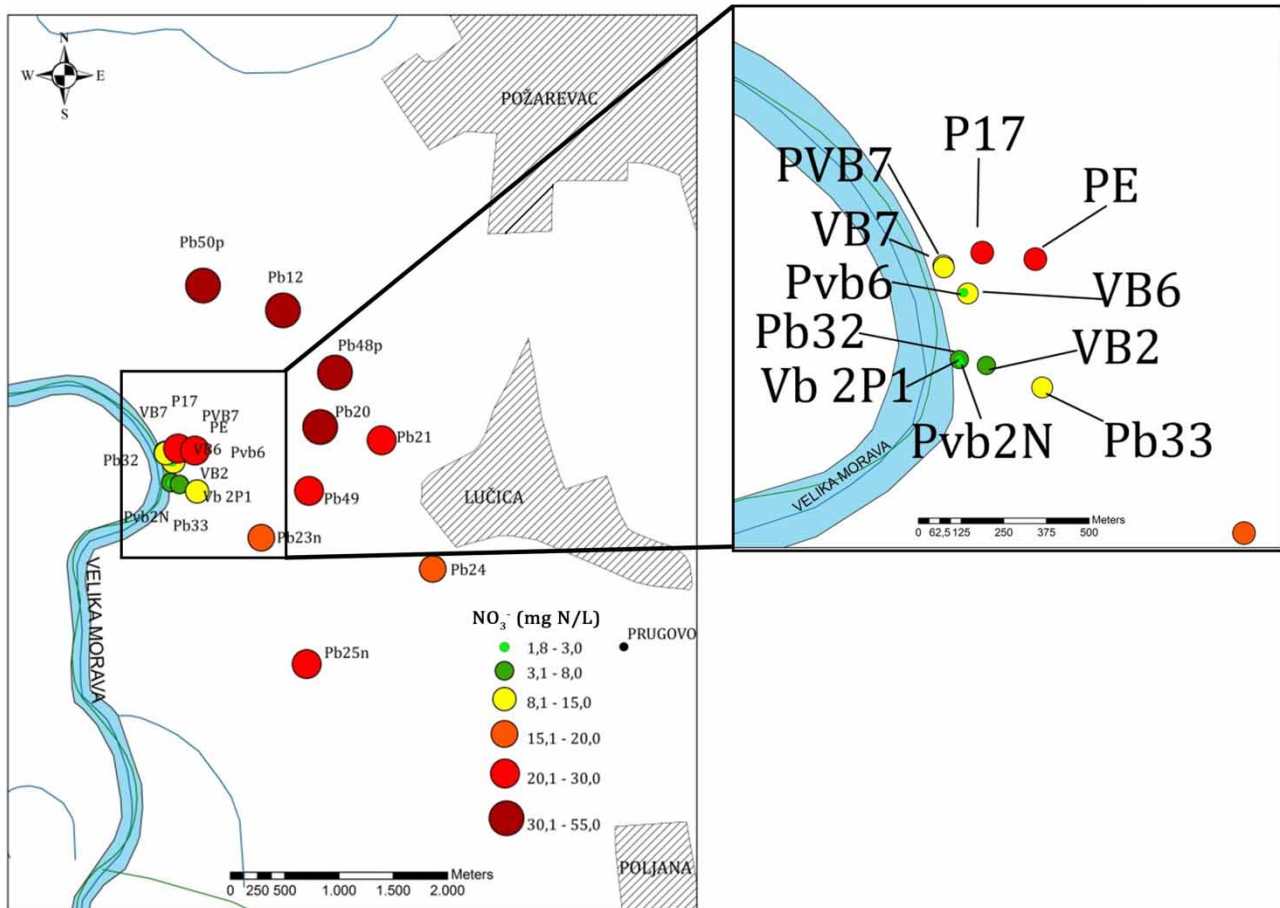


Figure 6 | NO_3^- concentration in observed piezometers and wells at the Ključ groundwater source.

concentration as well as groundwater movement towards well VB2 is a strong implication of this conclusion.

In the Kovin-Dubovac area, nitrate concentrations are lower due to anoxic conditions (Table S2 in the Supplementary Material), in which reduction processes occur, and nitrogen is transformed into forms other than nitrates. These results are in agreement with literature data stating that nitrate concentrations are much lower in anoxic groundwater conditions compared with oxic conditions (Landon *et al.* 2011).

Results of the monitoring of selected pesticide concentrations are presented in Table 2. Out of 15 targeted pesticides, only five of them were detected in the water samples. The most frequently detected pesticides at both locations in surface and groundwater samples were atrazine and carbendazim, which were chosen for further research. At the Ključ groundwater source, concentrations of pesticides

detected in both surface and groundwater samples, carbendazim and atrazine, are higher in surface water samples. Also, in the surface water samples, two more pesticides were detected, which were not detected in groundwater samples (i.e. concentrations were lower than LODs).

At Kovin-Dubovac, the number of detected pesticides is larger in groundwater samples compared with surface water samples. Atrazine, carbendazim and propazine are pesticides detected in both surface and groundwater samples, but propazine is not chosen for further discussion since it was detected in only one surface water sample. Atrazine and carbendazim concentrations are much higher in groundwater samples compared with surface water samples, even though most of the infiltrated water in the monitored wells is from the river Danube. The influence on greater pesticide concentration in the wells is from agricultural activities performed at the ground surface, which contribute

Table 2 | Detection of selected pesticides in surface and groundwater samples at the Ključ groundwater source and Kovin-Dubovac drainage system

Location	Samples	Pesticide	Number of samples	Frequency of detection (%)	Min/max concentrations (ng L ⁻¹)
Ključ groundwater source	Groundwater	Carbendazim	14	21.43	1.8/3.0
		Atrazine	14	21.43	1.0/11.0
	Velika Morava	Carbendazim	15	33.33	3.1/269.0
		Atrazine	15	13.33	7.0/165.0
		Dimethoate	15	13.33	3.0/7.0
		Propazine	15	6.67	–/18.0
Kovin-Dubovac drainage system	Groundwater	Carbendazim	34	44.12	1.0/88.0
		Atrazine	34	38.24	2.0/64.0
		Carbofuran	34	2.94	–/6.0
		Dimethoate	34	5.88	1.2/9.0
		Propazine	34	5.88	–/1.0
	Danube	Carbendazim	8	50.00	1.5/10.0
		Atrazine	8	37.50	4.1/6.0
		Propazine	8	12.50	–/8.0

to higher concentrations by leaching of pesticides with irrigated water or atmospheric precipitation. The maximum concentration of carbendazim is almost nine times higher than the maximum concentration in surface water, and in the case of atrazine the ratio is ten times (Table 2). This is a strong indication of contamination from the surface.

The most frequently detected pesticides at both locations in surface and groundwater samples, atrazine and carbendazim, were chosen in this study for further research. According to the results, there is a strong indication of faster degradation of carbendazim and atrazine in oxic groundwater conditions compared with anoxic conditions. According to Mendizabal & Stuyfzand (2011) carbendazim has low mobility in anoxic and high mobility in oxic groundwater conditions, which could contribute to higher concentrations in anoxic conditions.

The presence of oxygen accelerates the degradation of atrazine (Ijpelaar *et al.* 2002) leading to atrazine degradation in oxic groundwater conditions by hydrolysis or oxidation processes (Fenner *et al.* 2013). The results of this study are in agreement with previously published research by Accinelli *et al.* (2001) where atrazine degradation was considerably slower in anaerobic conditions compared with aerobic conditions. In low-oxygen conditions, when nitrates are present, atrazine degradation can be accelerated (Papiernik & Spalding 1998), which leads to lower concentrations in anoxic conditions.

The hydrogeological conditions in Kovin-Dubovac and at the Ključ groundwater source area are similar concerning

hydraulic conductivity and composition of aquifer material and since both locations have agricultural fields at the surface and have a similar thickness of vadose zone, there is a strong indication of the crucial impact of oxic/anoxic conditions on the occurrence of the selected pesticides.

CONCLUSIONS

Groundwater conditions greatly influence the degradation processes of micropollutants. Agrochemicals, necessary in modern agriculture, enter environmental mediums after use. Concentrations of nitrates in groundwater at the Ključ groundwater source, their low concentrations in Velika Morava, and groundwater table levels indicate that groundwater contamination with nitrogen compounds is the result of anthropogenic activities in the surrounding settlements and agricultural activities. Movement of groundwater indicates that the source of nitrates in well VB2 is from agricultural activities, while concentrations of nitrates in wells located north of well VB2 (wells VB6, VB7) are under the influence of anthropogenic activities from the surrounding settlements. Nitrate concentrations are higher in wells VB6 and VB7, due to the symbiotic influence of agricultural activities and the presence of septic tanks in the settlements.

Concentrations of analyzed pesticides should be higher in groundwater samples at the Ključ groundwater source,

due to the previously mentioned influence of agricultural activities on the water quality. The indication is that pesticide concentrations are lower than expected, due to accelerated degradation in oxidic groundwater conditions.

In the Kovin-Dubovac drainage system, concentrations of pesticides are higher in groundwater samples compared with surface water. Contamination of groundwater source is the consequence of agricultural activities, but due to anoxic conditions, degradation of the observed pesticides is much lower than in oxidic conditions.

The results show that the removal rates of pesticides are higher in oxidic conditions, compared with anoxic, but also that they depend on the well distance from the surface water and the ratio of infiltrated water from the river. Groundwater with oxidic conditions is vulnerable to contamination by nitrates, but is favorable for the degradation of pesticides, while in anoxic conditions it is the opposite. When choosing groundwater sources for drinking water, these findings should be considered.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/ws.2019.178>.

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