Redox conditions and groundwater quality issues of selected alluvial aquifers in Serbia

B. Majkić-Dursun, J. Tončić, A. Petković and J. Ćolić

ABSTRACT

Redox conditions are an important regulator of aqueous biogeochemistry and knowledge about them is crucial for an understanding of the fate and occurrence of nitrates, emerging substances, and organic compounds in shallow groundwater. The aim of this paper is to determine redox categories, along with prevailing redox processes, and the differences in groundwater quality between shallow alluvial aquifers of Serbia’s major rivers. The research was conducted on public water-supply wells in the alluvial plain of the Velika Morava River, the Danube River, the Tisa River and the alluvial aquifer of the Sava River. The study period is 2010–2014 and the number of collected and analysed samples 243. The redox categories and processes are characterised by concentrations of aqueous redox species (dissolved oxygen, nitrate, dissolved iron, manganese, and sulphate and sulphide concentrations). Parameters such as Eh, total organic carbon, HCO₃⁻/CO₂, pH, total iron concentrations, temperature and specific conductivity were also analysed. Different geological and hydrogeological settings, groundwater abstraction, distances between the wells and the river, well depths, and anthropogenic impacts result in diverse redox conditions. Groundwater in selected alluvial aquifers is mostly defined as anoxic, with one predominant process, or mixed anoxic, with various redox processes occurring simultaneously.

Key words | alluvial groundwater, groundwater quality, redox categories, redox processes

INTRODUCTION

Groundwater resources are important for water supply and irrigation. As it moves through alluvial sediments, groundwater dissolves and precipitates different minerals and changes its own chemical composition. Redox processes affect groundwater quality (Stumm & Morgan 1996; McMahon & Chapelle 2008; Dimkić et al. 2011a). Redox conditions and the identification of predominant redox processes are important in the evaluation of increased natural and anthropogenic contaminants, including NO₃ and volatile organic compounds (McMahon & Chapelle 2008). These conditions also cause well-clogging and corrosion processes (Dimkić et al. 2011b, 2012; Majkić-Dursun et al. 2012; Majkić 2013). Redox processes are important in the regulation of aqueous biogeochemistry because the oxidation state of elements affects toxicity, adsorption, solubility and distribution between solid, aqueous and gas phases (Ryu et al. 2004). The classification of redox categories and predominant redox processes has been addressed by numerous authors and different divisions exist depending on the approach to the problems and the specificities of individual areas. Stuyfzand (1995) introduced the redox-index concept and classified redox environments. The distribution of redox zones based on the redox potential and hydrogen concentrations in contaminated areas is discussed by Chapelle et al. (1996). McMahon & Chapelle (2008) set the framework for the assessment of predominant redox processes and provide threshold concentrations for the determination of these processes in the regional aquifer systems in the USA. Their research was supplemented by Jurgens et al. (2009), who developed redox characterisation software.
The purpose of the present study is to offer one way of determining redox status, which can be used as a basis for understanding the biogeochemical processes that occur in the alluvial aquifers of large rivers in Serbia.

MATERIAL AND METHODS

*In situ* groundwater analyses included the determination of physicochemical parameters: redox potential Eh (mV), groundwater temperature T (°C), dissolved oxygen (DO) concentration (mg/L), electrical conductivity (µS/cm), and pH level. The measurements were conducted using a multi-parameter probe (SEBA multi-parameter Dipper KLL-Q, SEBA Hydrometrie, Germany). Concentrations of total iron and manganese were determined using an inductively coupled plasma instrument (ICP Spectro Genesis EOP II, Spectro Analytical Instruments, Germany) (SMEWW 2005, 21st edn, method 3120 B). Concentrations of Fe\(^{2+}\) were analysed by spectrophotometry, using samples filtered in the field (through 0.45 µm filters) and acidified with HCl (SMEWW 2005, 21st edn, method 3500-Fe B). Nitrate concentrations were analysed by spectrophotometry (SMEWW 1975, 14th edn, method 419 D). Sulphate concentrations were determined by applying the turbidimetry method (SMEWW 2005, 21st edn, method 4500-SO\(_4^{2-}\) E). H\(_2\)S concentrations were analysed by a volumetric method (ISO 10530:1992 method). Total organic carbon (TOC) concentrations were determined by using a Thermo Scientific carbon analyser (SMEWW 2005, 21st edn, method 5310 C), while HCO\(_3^-\) concentrations were analysed by a volumetric method (SMEWW 2005, 21st edn, method 2320 B).

The redox classification was defined from geochemical redox indicators and is based on threshold concentrations of DO, nitrates (NO\(_3^-\)), iron (Fe\(^{2+}\)), manganese (Mn\(^{2+}\)), sulphate (SO\(_4^{2-}\)) and sulphide (H\(_2\)S).

The authors use an automated version of the redox classification scheme developed by Jurgens *et al.* (2009), in this paper, to define redox conditions and processes in shallow alluvial aquifers in Serbia. Primarily, redox software was used to classify groundwater redox conditions as oxic (DO ≥ 0.5 mg/L, and concentrations of Mn\(^{2+}\) and Fe\(^{2+}\) below threshold values), mixed, or anoxic. In the logical framework, if the criteria for more than one redox process are met, the general redox category is defined as mixed (oxic–anoxic or mixed anoxic). In order for mixed oxic–anoxic redox conditions to be met, the samples must contain DO ≥ 0.5 mg/L and the concentrations of some of the other chemical parameters need to be above threshold values (e.g. Mn\(^{2+}\) ≥ 0.05 mg/L, Fe\(^{2+}\) ≥ 0.1 mg/L). The threshold concentrations chosen to indicate an anoxic state are: Mn\(^{2+}\) ≥ 0.05 mg/L or Fe\(^{2+}\) ≥ 0.1 mg/L, with the concentration of DO below 0.5 mg/L. Nitrate reduction is defined by a nitrate concentration greater than or equal to 0.5 mg/L and DO < 0.5 mg/L. The threshold sulphate concentration is equal to or greater than 0.5 mg/L. In this framework, the Fe/sulphide ratio is used to distinguish between Fe(II)- and SO\(_4^{2-}\)-reduction. Groundwater samples with Fe/sulphide ratios less than 0.3 indicate that SO\(_4^{2-}\)-reduction is the predominant redox process, whereas a ratio greater than 10 indicates that Fe(III)-reduction is the predominant redox process. Samples with Fe/sulphide ratios between 0.3 and 10 signify that neither Fe(III)- nor SO\(_4^{2-}\)-reduction is predominant over the other, and are classified as mixed Fe(III)-SO\(_4^{2-}\). With regard to samples for which sulphide concentration data were not available, the redox process could not be defined more accurately than Fe(III)/SO\(_4^{2-}\)-reduction. The redox category was deemed undefined for samples that had less than five of the necessary input parameters or where DO data were not available.

The redox category of a groundwater sample is determined by the dominant type of redox process, called the predominant redox process. Other parameters described in this paper are used for groundwater quality definition.

GEOLOGICAL AND HYDROGEOLOGICAL CHARACTERISTICS OF SELECTED SHALLOW ALLUVIAL AQUIFERS

Kovin-Dubovac drainage system

The selected aquifer is located on the left bank of the Danube River in the South Banat Depression. The role of the protection system, comprised of nearly 300 drainage wells, dykes and drainage ditches, is to maintain groundwater levels at pre-defined depths and prevent spreading of the Iron Gate 1 HPP reservoir impact further inland. The
aquifer floor is made up of clays and clayey sands. The lower part of the aquifer is comprised of gravels and sandy gravels, whose grain sizes vary to a large extent. They are overlain by medium-size gravels, sandy gravels and gravelly sands. The thickness of this water-bearing layer is generally from 15 to 20 m, although in places it is as much as 30 m. This sequence of sediments ends with semi-permeable silty sands, silts and silty clays. Twenty-one drainage wells were selected to determine redox conditions.

Knićanin-Čenta drainage system

This drainage system is comprised of drainage ditches and self-discharging wells, built to protect riparian lands from elevated stages of the Danube River, resulting from the Iron Gate 1 HPP impoundment. The system is comprised of drainage channels, self-discharging wells (Danube bank) and wells equipped with submerged pumps (Knićanin). A specific feature of the drainage system is that it is formed in the alluvial sediments of three rivers, at the confluences of the Begej River and the Tisa River, and the Tisa River and the Danube. Medium-grain sands are dominant in the central and upper parts of the aquifer, whereas the lower part features sandy and fine-grain gravels. The aquifer floor is made up of clays and the roof sediments are semi-permeable silty clays. The aquifer thickness ranges from 15 to 28 m. Three wells along the Tisa in Knićanin and one well in the alluvial sediments of the Danube were selected to assess redox conditions.

Ključ water supply source

The Ključ water supply source provides water supply to the City of Požarevac. It is located on the right bank of the Velika Morava River. The aquifer is comprised of polycyclic riverine/lacustrine and alluvial sediments, whose total thickness ranges from 15 to 20 m. The part of the aquifer from which groundwater is extracted is predominantly comprised of sandy gravels. The thickness of these gravels in the Ključ area is from 6 to 11 m. The gravel sequence is locally overlain by sands whose thickness is from 2 to 6 m. The sandy sequence is covered by semi-permeable sediments, generally loess and clay, whose thickness ranges from 3 to 5 m. Samples from six in-line wells near the river were analysed.

Brzan water supply source

The Brzan water supply source provides water supply to the City of Kragujevac. This water source is located on the left side of the Velika Morava River and consists of 14 radial wells. In the central section of the groundwater source, the lower part of the aquifer is made up of silty sands and clays of Neogene age, while the edge is comprised of Palaeozoic schists. The water-bearing layer is made up of gravel-sandy sediments with an average thickness of 6 m and good filtration characteristics. This layer is covered by semi-permeable sediments, generally mud, silty clays and fine-grain silty sands. Six radial wells were chosen for groundwater quality analyses.

Belgrade groundwater source

The Belgrade groundwater source is comprised of 99 radial wells and about 50 tube wells, located along the Sava’s bank upstream from its confluence with the Danube. The Sava River alluvion was developed through several sedimentation cycles and sequences: sandy gravel, sands of various grain sizes, and silty and clayey sediments. The thickness of the Quaternary strata is up to 25 m. Dimkić & Pušić (2014) distinguish two cross-sectional zones, with regard to the grain sizes of the sediments. According to these authors, the lower zone consists of coarse-grain sediments in which radial well laterals are installed. These sediments occasionally feature clay, sandy clay and silt interbeds and lenses. The upper zone consists of fine-grain sediments, with poorer filtration properties. In this paper, chemical analyses of samples from 16 radial wells are presented.

RESULTS AND DISCUSSION

During the period 2010–2014, 243 groundwater samples were collected and analysed. Groundwater chemistry varies over space and time. Depending on the aquifer recharge, precipitation totals, and anthropogenic impact on the shallow alluvial aquifers, redox conditions can change (Majkić 2015).

The redox chemistry of the groundwater samples is presented with concentrations of DO, NO₃, manganese,
dissolved iron and sulphate, as well as values of the redox potential Eh (Figure 1). Redox categories and predominant redox processes defined for selected alluvial aquifers are given in Table 1.

The percentages of the well samples characterised as oxic, anoxic, or mixed are illustrated spatially in Figure 2. The groundwater samples from the selected aquifers were mostly found to be anoxic (Figure 2).

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**Figure 1** | Redox chemistry (DO, NO\textsubscript{3}, Mn, Fe\textsuperscript{2+}, SO\textsubscript{4}, Eh) of groundwater samples collected at the five locations shown in Figure 2. The box whiskers show 10th and 90th percentile concentrations. The boxes show 25th, 50th and 75th percentile concentrations.
The samples collected from wells along the Velika Morava River at the Kljuc water supply source are mostly oxic (62% of all samples, Table 1), with the exception of one well and its nearby piezometer, where the predominant process was defined as O2-Mn(IV) reduction. At this micro-location fine-grain sediments were locally deposited during fluvial sedimentation. Elevated concentrations of nitrates in the Kljuc area are shown in Figure 1.

Groundwater from the Brzan water supply source is characterised by different redox reactions, depending on the location of the wells and the operating mode. On the other hand, due to the unsuitable pumping regime of two wells in the central part of the groundwater source, the groundwater, rich in manganese, is aerated and the predominant redox process was defined as O2-Mn(IV) reduction (33% samples). The anoxic category was defined by Mn(IV) reduction and iron reduction (Table 1). These distinct processes in a relatively small area of the water source require detailed analysis in the future, primarily with regard to recharge pathways and pumping regimes.

The selected aquifers formed in alluvial sediments of the Danube, Sava and Tisa rivers provided relatively large proportions of anoxic samples for which the process was defined as Fe(III)/SO4^2− (Figure 2). Fine-grain sediments deposited during several deposition cycles were found to be rich in organic matter and less stable minerals. The groundwater samples from these sediments were mostly anoxic and exhibited elevated concentrations of dissolved iron. The most complex system of redox processes was defined for the Knicanin-Chenta area (Table 1, Figure 2). The complex alluvial sediment composition and hydrogeologic conditions at the mouths of the three rivers, an inappropriate production regime and the absence of sewerage in Knicanin caused a large divergence of the defined redox processes (Table 1).

The redox conditions of a large number of samples, for which the redox process could not be defined more closely, were deemed complex (22% of the samples were undefined). The predominant redox process Fe(III)/SO4^2− was defined for 44% of the samples from the Kovin-Dubovac aquifer (Table 1). Fe(III) reduction was defined for 27% of the samples, whereas only 6% of the samples indicated parallel iron and sulphate reduction Fe(III)-SO4^2−. All samples that featured Fe(III)-SO4^2− reduction were collected in the summer period (during the 2011 drought). Mn(IV) reduction

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**Table 1 | Redox categories and predominant redox processes defined for selected alluvial aquifers**

<table>
<thead>
<tr>
<th>Selected aquifer</th>
<th>Kovin-Dubovac</th>
<th>Kničanin-Čenta</th>
<th>Ključ</th>
<th>Brzan</th>
<th>Belgrade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Redox category</td>
<td>2 Redox process</td>
<td>3 Samples (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxic</td>
<td>O2</td>
<td>–</td>
<td>–</td>
<td>62</td>
<td>17</td>
</tr>
<tr>
<td>Mixed (oxic–anoxic)</td>
<td>O2-Mn(IV)</td>
<td>2</td>
<td>6</td>
<td>23</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>O2-Fe(III)</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O2-Fe(III)/SO4^2−</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O2-Fe(III)-SO4^2−</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Anoxic</td>
<td>NO3</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>Mixed (anoxic)</td>
<td>NO3-Mn(IV)</td>
<td>2</td>
<td>6</td>
<td>9</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>NO3-Fe(III)</td>
<td>–</td>
<td>9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>NO3-Fe(III)/SO4^2−</td>
<td>3</td>
<td>9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>NO3-Fe(III)-SO4^2−</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Anoxic</td>
<td>Mn(IV)</td>
<td>14</td>
<td>6</td>
<td>–</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Fe(III)</td>
<td>27</td>
<td>9</td>
<td>–</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Fe(III)/SO4^2−</td>
<td>44</td>
<td>19</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mixed (anoxic)</td>
<td>Fe(III)-SO4^2−</td>
<td>6</td>
<td>6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Undefined</td>
<td>–</td>
<td>–</td>
<td>22</td>
<td>3</td>
<td>–</td>
</tr>
</tbody>
</table>

Fe(III)/SO4^2−: The process was defined as reduction of Fe(III) or SO4^2− if no sulphide concentration data were available. If the criteria for more than one redox process were met, the general redox category was defined as mixed (oxic–anoxic or anoxic) and the process separated by a dash (meaning ‘and’, e.g. the ‘NO3-Fe(III)’ redox process is a mixture of nitrate- and iron-reducing groundwater).
was defined for 14% of the samples (micro-location on the west side of the area). In a small percentage of the samples, there was parallel reduction of nitrate with manganese or iron, immediately following application of fertilisers on farmland (autumn period).

For groundwater samples from selected wells from the Belgrade groundwater source the redox category was defined as anoxic because in 66% of the samples the predominant redox process was Fe(III) or SO$_4^{2-}$ reduction. For those samples that registered sulphide in addition to the other
five constituents, the process was defined as iron reduction in 6% and parallel reduction of iron and sulphate in 2% of all samples. Mixed oxic–anoxic groundwater defined as \( \text{O}_2-\text{Fe(III)}-\text{SO}_4^{2-} \) was identified in 8% of the samples, probably as a consequence of an inadequate pumping mode. All samples that featured \( \text{NO}_3-\text{Fe(III)}-\text{SO}_4^{2-} \) reduction were collected in the October–November campaign.

Many of the important redox processes are microbially mediated near-neutral pH levels and in the low temperature range. Thus, the measured groundwater temperatures and pH levels indicated almost ideal conditions for bacterial activity. Groundwater temperature ranged from 12.8 to 15.2 °C, and the average pH values were from 7.1 to 7.4.

The oxidation–reduction potential (Eh) ranged from 51 to 227 mV (samples from Belgrade groundwater source). This parameter differed to a large extent in the Knićanin area (23 to 274 mV), while field measurements at Brzan and Klijuč showed high positive values (221 to 370 mV). High positive values are associated with oxic groundwater, as opposed to low redox potential values measured in anoxic groundwater (Figure 1). The oxidation–reduction potential indicated a large variation in values of the well samples classified as mixed or anoxic and was limited in its utility to clearly defined redox processes.

Average TOC concentrations ranged from 7.3 mg/L (Knićanin-Čenta) to 1.1 mg/L (Belgrade; standard deviation \( \sigma = 0.25 \)). The average TOC concentration in the groundwater at Klijuč was 2.0 mg/L (\( \sigma = 0.38 \)) and similar values were obtained for Ković-Dubovac (2.3 mg/L, \( \sigma = 0.36 \)) and Brzan (2.1 mg/L, \( \sigma = 0.15 \)). The elevated TOC values of the Knićanin-Čenta alluvial aquifer may be a consequence of anthropogenic pollution and lack of a sewage system in that area. The average TOC concentrations, measured in Serbian shallow alluvial groundwater, are similar to those in tested European groundwaters (mean value 2.69 mg/L) (Gooddy & Hinsby 2008). Relatively uniform TOC values do not indicate differences, or lack thereof, between the analysed alluvial aquifers. This is consistent with the opinion of Gooddy & Hinsby (2008) that the amount of TOC/DOC itself does not provide information on how reactive or reducing the environment is.

The concentration of HCO$_3^-$ was the highest in the samples from Knićanin-Čenta (average 524 mg/L, maximum 1595 mg/L). The average concentration measured at the Belgrade groundwater source was lower (296 mg/L, \( \sigma = 42.9 \)). The study showed that NO$_3^-$ concentrations were lower in anoxic samples (Figure 1, Belgrade and Ković aquifers) than in oxic samples (Figure 1, Klijuč water supply source), which is consistent with NO$_3^-$ degradation by denitrifying bacteria under anoxic conditions.

The highest concentrations of total iron were measured at Knićanin-Čenta (average 4.1 mg/L) and Ković-Dubovac (average 2.8 mg/L). The concentrations of total iron and Fe$^{2+}$ were below the detection limit in the samples collected from the Klijuč water supply source (mostly oxic groundwater) and the radial wells at the Brzan source, where the redox categories were defined as oxic or mixed oxic-anoxic. The average concentration of total iron in groundwater from the radial wells in the Sava River’s alluvial sediments was 1.7 mg/L (maximum 4.8 mg/L and minimum 0.14 mg/L).

The concentration of sulphates decreased from oxic groundwater (Klijuč water supply source) to anoxic groundwater. Low concentrations were measured at Ković-Dubovac (Figure 1). Also, the presence of sulphide in the samples from Knićanin-Čenta and Ković-Dubovac indicated that the groundwater conditions at the time of sampling were anoxic. In future surveys, it will be necessary to increase the number of sulphide measurements and include this parameter in routine monitoring.

The conductivity was the highest at the Knićanin-Čenta aquifer (970 μS), followed by the Brzan (841 μS) and Belgrade groundwater sources (529 μS, the lowest). For the samples of oxic groundwater collected from the Klijuč water supply source, the calculated coefficient of correlation between the sulphate concentration and conductivity is higher (\( r = 0.84, n = 34 \)) than that of the anoxic and mixed anoxic groundwaters from Ković-Dubovac and Knićanin-Čenta (\( r = 0.61, n = 111 \)).

**CONCLUSION**

The results of this research can be used as one layer of understanding of groundwater quality issues. The oxidation–reduction potential (Eh), a commonly used field parameter to discern redox conditions, showed a large variation in values of the well samples classified as mixed or anoxic, and was limited in its utility to reliably indicate concrete redox processes. Generally, it can be used for a rough assessment of redox conditions.
Knowing the concentrations of redox species and the predominant redox process can be very useful, to provide information concerning the distribution of pollutants, the chemical species relevant for well-ageing assessments, the distribution of micro-elements, and the potential environmental impact of the redox status of shallow groundwater. Groundwater abstraction through pumping wells and boreholes results in a decline in the aquifer’s piezometric head in a certain area. It can cause mixing of different redox conditions, which accelerates clogging and corrosion processes and pollutant mobility. Furthermore, pumping wells, particularly high-capacity municipal and irrigation wells, can integrate multiple flow paths characterised by various redox processes.

The results of this study are potentially applicable to the redox chemistry of other alluvial aquifers in Serbia, which is an emerging area of interest.

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