

Distribution and chemical speciation of arsenic and heavy metals in highly contaminated waters used for health care purposes (Srebrenica, Bosnia and Herzegovina)

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Distribution and chemical speciation of arsenic and heavy metals in highly contaminated waters used for health care purposes (Srebrenica, Bosnia and Herzegovina)

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HIGHLIGHTS

- Acid mine drainage type waters used for decades for healthcare purposes were analysed.
- Extremely high contents of As (up to 6.6 mg/L) and other heavy metals were registered.
- Acidic springs decreased pH of the river from 7.3 to 3.4 in only 1.5 km distance.
- Geochemical modelling revealed dominance of oxidized forms of all elements.

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ABSTRACT

Determination of distribution and chemical speciation of arsenic and heavy metals in five acidic springs and in the receiving river near Srebrenica (Bosnia and Herzegovina) was carried out. These waters were used for centuries, and continue to be used, for health-care purposes. The composition and properties of all springs and the river water (after all inputs) resembled that of an acid mine drainage. Very low pH (<3.3), high sulphate concentration and extremely high contents of most of the measured elements (25) are found in all springs (e.g. arsenic and iron maximal concentration of 6.6 and 500 mg L^{-1}, respectively). Although of small discharge, spring waters caused the decrease of the receiving river pH (from 7.3 to 3.4) and the considerable increase of the concentrations of elements. The enrichment factor for the studied elements ranged from 1.2 for Sr up to 425 for As. In acidic spring waters, all elements were predominantly present in dissolved form. Elements associated to freshly-formed hydrous ferric oxide were prevailing in particulate forms only at the two most upstream sites in the river with pH>7. Geochemical speciation modelling (PHREEQC and WHAM-VI) revealed that As was mainly present as As(V), and Fe as Fe(III). Complexation of dissolved metals by organic matter was predicted to be significant only for the two river sites with neutral pH.

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1. Introduction

Arsenic (As) is an element of environmental concern worldwide because of its potential toxicity to humans. Exposure to drinking waters with high arsenic levels (World Health Organization limit>10 ppb; WHO Guidelines for Drinking-water Quality, 2011) have been associated with adverse health effects (Kaltreider and Hamilton, 2001; Nguyen et al., 2011). There is also scientific interest dedicated to the consequences of chronic ingestion (Kapaj et al., 2006; Liang et al., 2011; Mazumder and Dasgupta, 2011). Among the potential sources of arsenic in ecosystems, volcanism and related hydrothermal systems are of great importance (Nriagu, 1989). Ballantyne and Moore's (1988) study on arsenic aquatic geochemistry in hydrothermal stems showed the positive dependence of arsenic concentrations with reservoir temperature; a similar relation between arsenic and discharge temperatures has been reported in hotsprings (e.g., Aiuppa et al., 2003; Webster, 2003). Arsenic can also be associated with geothermal waters and has been reported in several regions, such as Iran, Greece or Italy (Aiuppa et al., 2006; Angelidis et al., 2007; Haeri et al., 2011). Geothermal waters are therefore known to be arsenic rich, but studies dedicated solely to arsenic, its concentration and its relationship to other metals in cold mineral waters are scarce.

The chemistry of As in aquatic systems is quite complicated and significantly differs from that of trace metals. In such environments, the arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and arsenite (H_3AsO_3) species are usually predominant (Chakravarty et al., 2002). These species have different mobility and toxicity to humans (Lenoble et al., 2002; Dixit and Hering, 2003). Their proportion is closely linked to the redox potential of the ecosystem (Masscheleyn et al., 1991; Katsoyiannis et

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al., 2007; Garnier et al., 2010; Weigand et al., 2010). The governing mechanisms concerning As in environment submitted to significant E_h gradient (e.g. at the water/sediment interface, AMD, …) depend mainly on the geochemistry of the considered ecosystem. The most significant are i) release into the water through the dissolution of arsenic-bearing phases, ii) or retention onto oxides (Wang and Mulligan, 2006; Amstaetter et al., 2010).

Central Europe is one of the many parts of the world facing natural water arsenic contamination (Krüger et al., 2005; Dangić, 2007; Kristoforović-Ilić et al., 2009; Ravenscroft et al., 2009; Ujević et al., 2010). Srebrenica area (eastern Bosnia and Herzegovina) is well known for its long mining history, as well as for its mineral waters of specific composition (Dangić and Dangić, 2007). Recent sediment analysis from one of these water springs, Ljepotica (Dangić and Dangić, 2001), showed that they are very rich in arsenic, lead and iron. These mineral springs have a very low pH, caused by the oxidation of sulphides to sulphate. Such low pH leads to the dissolution of minerals, which then enriches the water with different elements and can lead to excessive concentrations (Casiot et al., 2009). This is the common scenario in active or abandoned mines with acid mine drainage waters (AMD), which are considered to have such harmful effects on aquatic life that only adapted microorganisms can be encountered (Bruneel et al., 2006). However, unlike AMD, Srebrenica waters were used for decades, and continue to be used, for health-care purposes despite evidence of high arsenic and iron(II) content (Dangić, 2007). Still, no studies have surveyed the co-existing elements and their relationship to such extreme physical chemical parameters.

The extreme chemical changes apparent in this study are also of interest as the element composition varies from "normal" river water composition to an abnormal environment (similar to AMD), within a very short distance (1.5 km). Thus, the aims of this study were to provide i) a detailed chemical composition (especially of arsenic and other metals) of the river and its associated springs ii) to assess chemical speciation, as well as the dynamic behaviour of elements using PHREEQC (Parkhurst and Appelo, 1999) and WHAM-VI (Tipping, 1998) speciation codes.

2. Study area

2.1. Historical background of Srebrenica

"Srebro" means "silver". Since the fourth century AD, Romans called Srebrenica "Argentaria" after the silver ore. After the Romans, Turks and Austrians exploited the local mineral ores and left behind many mining trenches, which favoured the gradual formation of mineral springs. Evliya Çelebi, the famous Turkish traveller, was the first to publish information regarding mineral water from this area in the second half of the 17th century (Pašagić, 2008). The Austro-Hungarian physician Dr. Hans Duller drew attention to the healing characteristics of Guber waters at the beginning of the 19th century. "Guba" means "leprosy". The Guber water name dates from this period, after determining the effectiveness of these mineral resources in the treatment of skin diseases, especially leprosy. Ernst Ludwig, a Viennese chemist published the first chemical analysis of Srebrenica area mineral waters in 1890 in "Die Mineralquellen Bosniens — Die arsenhaltigen Eisenquellen von Srebrenica" ("Bosnian mineral sources — iron sources from Srebrenica containing arsenic") and suggested the exploitation and bottling of the waters. At that time, the experts noted 48 mineral springs of different discharges and chemical composition, five of them were chosen for their mineral composition (Pašagić, 2008). Bottling began in 1889 and ended with the beginning of the First World War. Commercial bottling and selling in pharmacies of the former Yugoslavia started again in 1956 as Guber waters were prescribed as medication for hypochromic anaemia by oral treatment or through baths. The public rehabilitation centre "Guber" and associated hotels were active until the beginning of the last war in Bosnia in 1995. There were many attempts for reactivation of the centre in the post-war period. Nowadays, there are some plans for the Guber site's re-activation and to restart the bottling of these mineral waters.

2.2. Sampling site

Water samples were taken along ca. 1.5 km long transect where the waters of main springs merge with the Bijela Rijeka River ("White River"), in an area situated in the mountain forest nearby Srebrenica (see Fig. 1 and Table 1 for more details). Sampling was carried out in July 2009 during the dry season. The Bijela Rijeka River was sampled at three stations: upstream of any visible spring water input (R1), after the confluence with the water from the first spring (R2), and then downstream after all spring water inputs (R3), where the river enters Srebrenica town (grey area on the map). Among the 48 previously reported springs, five were selected for sampling, from upstream to downstream (S1–S5). There probably exists other sources in winter (among the 48 reported), but at the time of sampling only main springs discharging the water were sampled. Underground and/or hidden sources probably contribute to the water supply, but they were not noticeable at the time of sampling. The exact river flow was not measured, but roughly estimated by visual inspection and comparison with some similar rivers, it ranges between 0.1 and 0.4 $m^3\ s^{-1}$, with a gradual downstream flow increase.

3. Experimental

Water samples were filtered on-site by 0.45 μm syringe filters (Sartorius), immediately acidified with HNO_3 to pH<2 and stored in precleaned (washed with 10% HNO_3 then thoroughly MilliQ water rinsed) HDPE bottles. Unfiltered samples were also acidified on-site and filtered through a 0.45 μm syringe filter just before measurement (ca. three months later) in order to remove potential small particles present in sample which are undesirable for ICP-MS measurement. Through acidification, elements associated to particles were leached to the dissolved phase. This fraction is considered to be the quasi-total concentration, and hereafter referred to as total element concentration. The samples dedicated to DOC and 3D UV–vis fluorescence measurements were preserved with NaN_3 (1 mM final concentration) and stored in precalcinated glass tubes.

Physico-chemical parameters (temperature, pH, dissolved oxygen, conductivity and redox potential) were measured in-situ (in the river main body and in each source) by Hydrolab MiniSonde 4a (OTT).

Dissolved organic carbon (DOC) concentrations were determined using a TOC-V analyser (Shimadzu), calibrated using sodium hydrogenophtalate standard solutions. The limit of detection is 0.1 $mg_C L^{-1}$ and the linearity ranged from 0.1 to 50 $mg_C\ L^{-1}$.

For each sample, the fluorescent properties of dissolved organic matter were studied by 3D UV–vis fluorescence spectroscopy (Hitachi F-4500), leading to organic matter characterization through the measurement of excitation–emission matrices (EEM) (Coble, 1996). An algorithm based on PARAFAC statistical methods (Stedmon et al., 2003; Luciani et al., 2008) was used to decompose all the EEMs, previously corrected from inner-effect (Luciani et al., 2009), in a set of identical fluorescent components providing information on the studied organic matter source. In this study, each fluorescence spectrum was successfully reconstructed by a linear combination of 4 components with 97% of recovery. The first component (labelled C1, see Table 1) was representative of biological activity as revealed by protein-like content (λ_{ex} 275 nm/λ_{em} 340 nm). The second component (labelled C2) was representative of recent type A humic substances (λ_{ex} 250 nm/λ_{em} 390 nm), whilst the third component (labelled C3, type C humic substances) (λ_{ex} 330 nm/λ_{em} 430 nm) was older with more complex structure. The fourth component (labelled C4) was specifically

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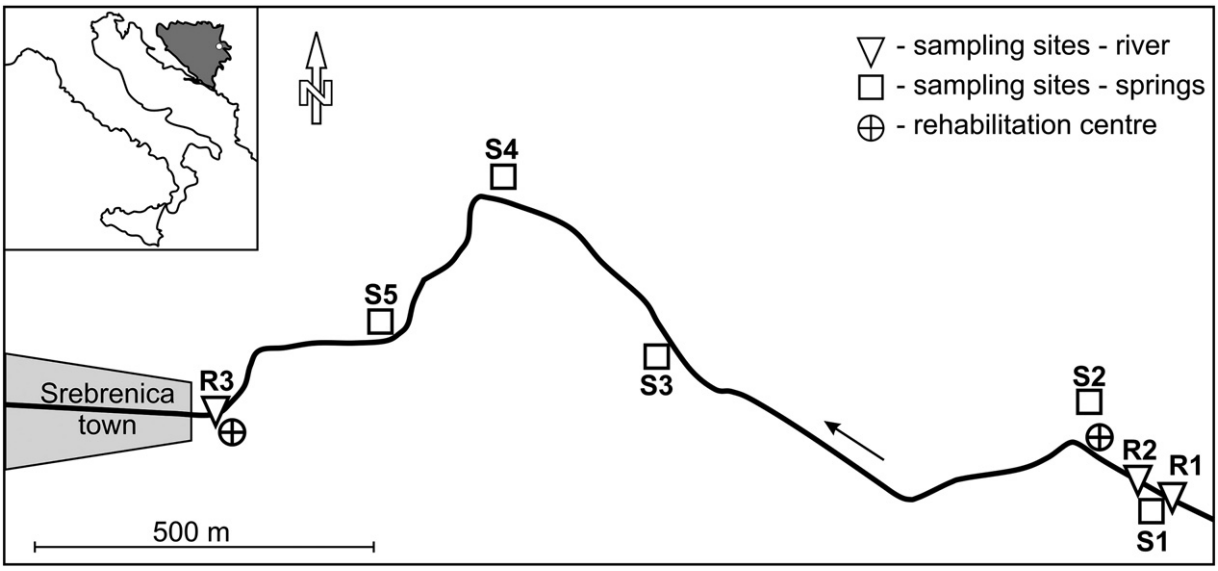


Fig. 1. Schematic representation of the sampling zone along the Bijela Rijeka River (Srebrenica area, Bosnia and Herzegovina).

attributed to soil humic acid fluorescence (λ_{ex} 380 nm/λ_{em} 465 nm) (Stedmon et al., 2003). Each component is presented in the Supporting information.

High resolution inductively coupled plasma mass spectrometer (HR ICP-MS, Element 2, Thermo Finnigan, Bremen, Germany) was used for the determination of dissolved and total element concentrations: Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Ti, Tl, U, V, and Zn. Quality control (QC) of HR ICP-MS measurements was checked by the determination of element concentration in "River Water Reference Material for Trace Metals" (SLRS-4, National Research Council Canada), as well as internal (in-lab) QC solutions. For most elements, a good agreement with the certified data was obtained (Table SI-1). The concentrations of elements in all samples were well above the instrumental and operational limit for the determination in freshwater samples.

Major ions were analysed by ionic chromatography (Dionex, DX-120): F^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. Anionic and cationic columns were loaded with quaternary ammonium (AS9-HC) or carboxylate-functionalized (CS12-A) groups, respectively. Anionic and cationic eluents were 9 mM Na_2CO_3 (Prolabo, Pro Analysis) and 20 mM CH_4SO_3 (Acros, Pro Analysis), respectively. In both cases the flow rate was 1 mL min^{-1}, and separated ions were quantified by

Table 1
Sites description, main physico-chemical properties of the sampled waters and contribution of different fluorescent components.

	Site ID	Site name	Traditional application	Distance from R1 (m)	GPS coordinates	pH[a]	E_h (mV)[a,c]	Cond. (μS cm^{-1})[a]	O_2 (%)[a]	T (°C)[a]	DIC[b] ($mg_C L^{-1}$)	DOC[b] (mg_C L^{-1})	Fluorescent contribution (a.u.)[d]			
													C1	C2	C3	C4
River	R1	Bijela Rijeka 1 (White River 1)	–	0	44°6′4.35″N 19°19′12.27″E	7.26	493	85	98.3	13.4	2.09 ± 0.03	0.67 ± 0.01	27	325	852	216
	R1	Bijela Rijeka 2 (White River 2)	–	10	44°6′4.57″N 19°19′11.99″E	6.71	545	96	88.0	13.8	0.62 ± 0.01	0.36 ± 0.01	115	476	437	148
	R3	Bijela Rijeka 3 (White River 3)	Oral and external use in baths	1500	44°6′7.08″N 19°18′18.07″E	3.35	610	694	NM[e]	NM[e]	<D[f]	0.44 ± 0.01	337	1172	434	321
Springs	S1	Očna voda (Eye water)	Eye and head troubles	4	44°6′4.40″N 19°19′12.19″E	2.23	813	5061	72.5	11.8	<D[f]	1.51 ± 0.03	43	112	106	211
	S2	Veliki Guber (Big Guber)	Various oral and external applications	100	44°6′6.65″N 19°19′8.84″E	3.25	822	940	74.1	16.0	<D[f]	0.36 ± 0.01	74	1708	496	467
	S3	Ljepotica (Beauty)	External use (skin)	650	44°6′9.59″N 19°18′46.03″E	2.77	811	1027	15.3	11.5	<D[f]	0.49 ± 0.01	282	544	386	128
	S4	Mali Guber (Small Guber)	Various oral and external applications	1000	44°6′16.68″N 19°18′35.82″E	2.73	779	1970	37.1	15.5	0.30 ± 0.01	0.54 ± 0.01	330	1798	481	533
	S5	Kožna voda (Skin water)	External use (skin)	1200	44°6′10.68″N 19°18′28.30″E	6.00	265	870	NM[e]	NM[e]	0.24 ± 0.01	0.20 ± 0.01	6215	576	294	567

[a] Average measurement errors based on standard deviation obtained using at least triplicate readings (T/0.1; pH/0.01; E_h/1 mV; Cond./0.2%; O_2/2%).
[b] Dissolved inorganic and organic carbon; measurement error expressed as standard deviation of three replicate measurements of the same sample.
[c] Redox potential expressed versus standard hydrogen electrode (SHE).
[d] Determined according to an algorithm based on PARAFAC statistical methods, see Experimental for explanations.
[e] NM — not measured due to probe failure.
[f] DL — detection limit.

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conductometry. QC for ionic chromatography and DOC/DIC measurements was checked by the determination of elements concentration in "River Water Reference Material" (MISSIPPI-03, Environment Canada), which are in good agreement with the certified data (data not shown).

4. Results and discussion

4.1. Major components, physico-chemical parameters and fluorescence measurements

The concentration of some of the major cations and anions varied between different springs by almost one order of magnitude. Numerical data for all measurements are given in the Supporting information document (SI). The highest concentrations of SO_4^{2-} (2.5 g L^{-1}) and K (29 mg L^{-1}) were measured at spring S1, whilst Ca was highest at springs S4 and S5 (~120 mg L^{-1}). High sulphate concentration, originating from sulphide oxidation, results in the low pH of these spring waters (Rimstidt and Vaughan, 2003; Casiot et al., 2005). High correlation factor obtained by Spearman's rank correlation analysis ($p<0.01$ and R-critical = 0.881) between pH and sulphate (−0.881), pH and conductivity (−0.976) and sulphate and conductivity (0.929) confirm the strong chemical relationships between these parameters (Olias et al., 2004).

All springs except S5 ("Skin water") were of very acidic pH (around 3), leading to a huge decrease of pH, from 7.3 to 3.4, in the examined section of the main river. In-situ measured redox potential was used for speciation calculations of As and Fe redox states. The relatively low redox potential measured at spring S5 (265 mV) is different to other sites and this behaviour is analogous to its other parameters such as pH, content of major components and fluorescence measurements, giving this site a distinct characteristic. Inorganic carbon content (DIC) was below the detection limit (0.1 mg_C L^{-1}) or very low in the springs due to low pH. Inorganic carbon concentrations in the river were low, with a gradual decrease downstream as a consequence of river water acidity increase.

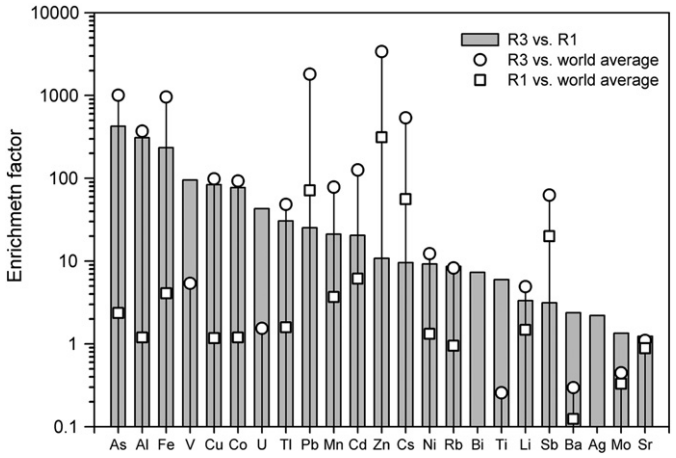


Fig. 3. Enrichment factors of dissolved concentration of elements in the Bijela Rijeka River (R3 vs. R1) and comparison of two river sites (R1 and R3) with world averages.

Dissolved organic carbon (DOC) content was generally low at all sites. Decrease of DOC at site R2 was probably due to the partial removal of organic matter by adsorption on newly formed ferrihydrite precipitate (Tipping, 1981; Gu et al., 1995; Eusterhues et al., 2011). Fluorescence decomposition (Table 1 and SI) showed that a protein-like fluorescent component (C1) dominates in spring S5 (characterized by a low amount of DOC and a neutral pH). This situation was not encountered at any other site. In S1, there was high DOC, but a low signal of fluorescence. This can be explained either by the presence of non-fluorescent organic matter, or by fulvic acids (humic acids are not expected at such acidic pH) fully complexed by trace/major metals (so not giving fluorescent signal due to quenching effect (e.g. Mounier et al., 2011)). The later is less probable due to the low pH and subsequent high H^+ competition toward the binding sites of the dissolved organic matter (e.g. Tipping, 1998; Garnier et al., 2004). So, in this spring, a

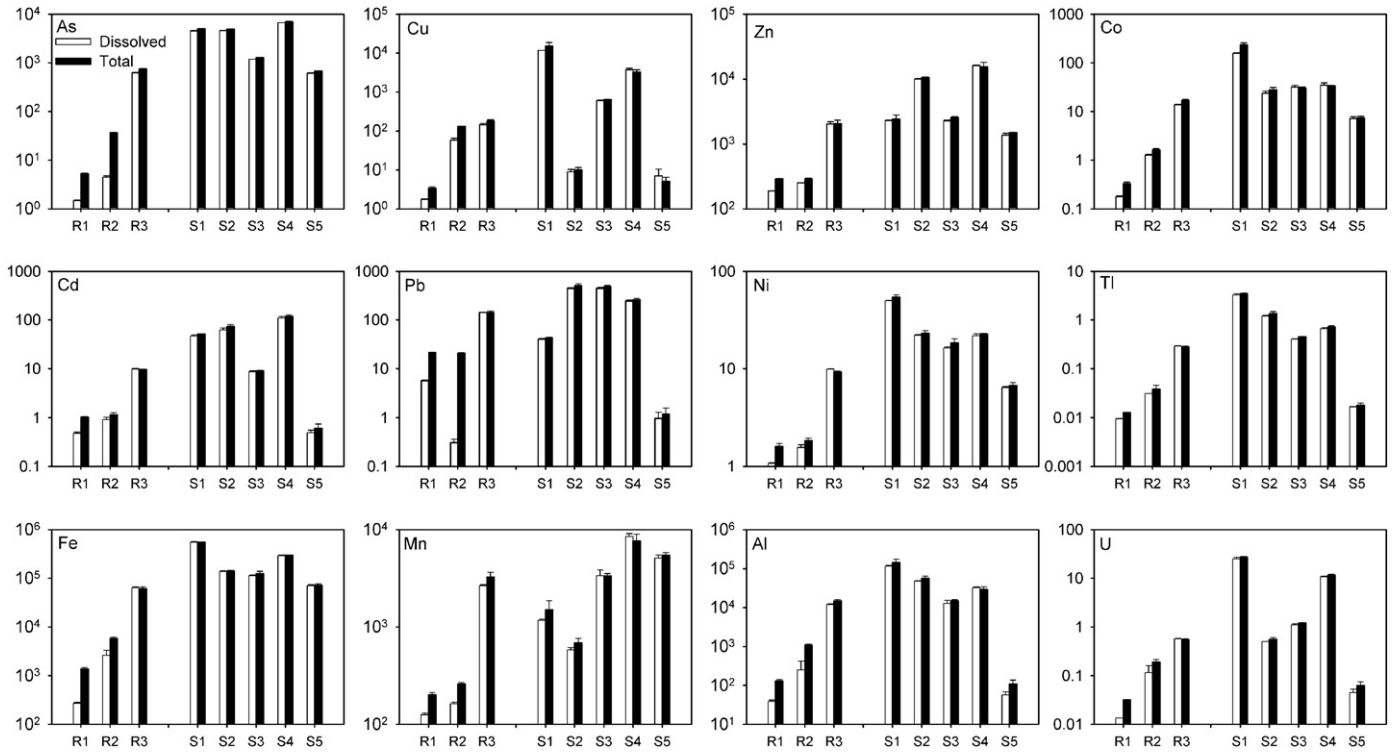


Fig. 2. Total and dissolved element concentrations in the Bijela Rijeka River from upstream to downstream (R1, R2 and R3) and accompanying springs (S1–S5). Concentrations are in μg L^{-1}. Note the concentration log scale.

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specific kind of organic matter is likely to be encountered. In all the other sampling waters, there was the co-existence of humic and fulvic acids (C2 and C3). Composition of humic substances is controlled by sorption on Fe precipitates and insolubility of humic acid at low pH, leading to the variations of C2 and C3 along the river (see Table 1).

4.2. Distribution of arsenic and metals

The distribution of dissolved and total concentrations of selected elements in water samples of the Bijela Rijeka River (R1, R2, R3) and in associated springs (S1–S5) are presented in Fig. 2. Concentrations on all plots are presented in logarithmic scale, because of considerable difference of element concentration ranges among sites. Due to very low pH and particulate content in spring waters and in river water at site R3, there were no substantial differences between total and dissolved concentrations of measured elements at these sites (Fig. 2 and Table SI-2). An extremely high concentration of Fe was measured in S1 (~0.5 g L^{-1}). Distribution of elements present a clear increase in concentrations as one moves downstream (R1 vs. R3) caused by the input of spring waters with their naturally elevated concentrations, the most enriched springs being S1 and S4.

The enrichment factor (EF) for dissolved elements in river (R3 vs. R1) ranged from 1.2 for Sr, up to 425 for As (1.47 to 624 μg As L^{-1}) (Fig. 3). The most enriched elements in their dissolved form were As, Al and Fe. This is a consequence of additional input of these elements by all acidic spring waters, as well as low pH at this point in the river, which maintains existing metals in a dissolved form. Nevertheless, when looking at their chemical composition, all spring waters and the river water downstream of the springs are similar to classical acid mine drainage waters (AMD). Concentrations of arsenic and metals in river water before the first spring confluent (R1) are comparable to world average (WA) values for river waters (Gaillardet et al., 2003), with the exception of Pb, Zn, Cs and Sb for which concentration in the river is increased by factor of at least 10 compared to WA values. Great differences in both element concentrations and main physico-chemical parameters between spring waters and the main river water causes dramatic changes of element behaviour and their chemical speciation. The most interesting sites in terms of element behaviour are the first two sites in the river (R1 and R2). As expected, at both sites the total metal concentrations were higher than dissolved ones, with particulate/dissolved ratio ranging up to 14.5 (for Ti). An iron partition ratio of 4.0 in R1 could suggest the existence of precipitates. Taking into account chemical composition at site R1, ferrihydrite is the most likely iron species to precipitate. Chemical speciation calculations show that in this case, the dissolved Fe concentration should be around 2.3 μg L^{-1}. However, a higher concentration of dissolved iron (and probably other iron-associated elements) of 270 μg L^{-1} was measured. This is probably because rather than occurring as a precipitate the ferrihydrite occurs in a colloidal form which is small enough to pass through 0.45 μm filter cut-off. Consequently, partition ratios of iron-associated elements (Pb, V, As) is operationally defined, and does not reflect real partitioning of metal forms. It has already been shown that Pb and As are preferably associated to the Al and/or Fe oxyhydroxides (Gault et al., 2003; Casiot et al., 2005, 2009; Butler et al., 2009) in AMD waters even at much lower pH than measured on site R1. High association of As and Pb to particulate Fe is evident on site R2. Although the S1 input is ca. 160 times smaller than that of the main river, a large fraction of Fe (and probably Al) ions from S1's discharge water precipitates directly upon mixing with the main water body. Formation of ferrihydrite is strongly evidenced by reddish-orange coatings after the confluent point, and afterwards along the river bed. Removal of trace metals and metalloids by sorption and/or co-precipitation are generally reported in such cases (Benjamin and Leckie, 1981; Herbert, 1996; Casiot et al., 2005, 2009). In our system at point R2, only the dissolved Pb concentration decreased, whilst

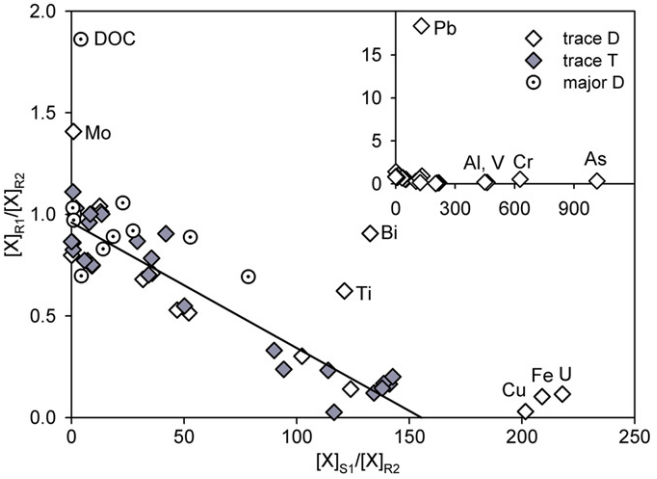


Fig. 4. Conservative or non-conservative behaviour of total (T) and dissolved (D) major and trace elements in the Bijela Rijeka River (R1 and R2) as a function of Očna Voda source (S1) dilution. The line was obtained by considering regression on the total trace elements data. Inset: plot of dissolved forms with extended axes.

for all other elements an increase is observed due to the additional input by S1 water. Adsorption on newly formed precipitates causes a relative increase of the particulate Pb and As fractions, leading to partition coefficients of 67 and 7.1, respectively. It should be noted that due to relatively low quantity of S1 water with low pH 2.2, mixing with river water produced only a slight decrease of pH (0.6 unit) at R2.

All spring waters had high to very high arsenic concentrations: around 600 μg L^{-1} (at S5) to almost 7000 μg L^{-1} (at S4). Though high, the arsenic level in S5 ("Skin water") was considerably below that of the other springs, confirming the specificity of this spring. Arsenic concentration in the studied area is not linked to geothermal activity (D'Alessandro et al., 2008; Birkle et al., 2010), dissolution of arsenic sulphide mineral being the most probable source of this element. According to Dangić and Dangić (2001), the central parts of the Srebrenica eruptive and ore-bearing area are mainly composed of dacite, pyritized dacite and contact-metamorphic rocks containing Sb, Pb, Zn, as well as other associated metals.

4.3. Dynamics of elements in the mixing zone of river and spring S1

A graphical method was used to study behaviour of elements during the mixing of river and S1 source water (Očna voda) (Potot et al., 2010). In this method, concentration and discharge of the two-components' mixing are related by the following equation:

$$Q_{R1} \times [X]_{R1} + Q_{S1} \times [X]_{S1} = Q_{R2} \times [X]_{R2} \quad (1)$$

where R1 and S1 are upstream of Bijela Rijeka River and Očna Voda respectively, and R2 is the resulting water in the Bijela Rijeka River after confluence with this spring (see Fig. 1), whilst Q is the waters' discharge (m^3 s^{-1}) and [X] is the concentration of an element X (μg L^{-1}).

From Eq. (1), the following relationship is derived relating the concentration ratios of $[X]_{R1}/[X]_{R2}$ and $[X]_{S1}/[X]_{R2}$:

$$[X]_{R1}/[X]_{R2} = -(Q_{S1}/Q_{R1}) \times ([X]_{S1}/[X]_{R2}) + (Q_{R2}/Q_{R1}). \quad (2)$$

According to Eq. (2), for conservative elements, the plot of $[X]_{R1}/[X]_{R2}$ vs $[X]_{S1}/[X]_{R2}$ should give a linear relationship, the intercept at Y-axis and the slope give discharge ratios Q_{R2}/Q_{R1} and Q_{S1}/Q_{R1}, respectively. Such a plot using the dissolved and total concentrations of the studied elements is shown. The solid line in Fig. 4, representing conservative behaviour calculated from total concentrations (closed symbol), showed that the discharge of source S1 was near 160-times smaller

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Table 2
PHREEQC calculations of Fe and Al speciation, solubility products, "truly dissolved" and colloidal Fe(III) and Al concentrations (see the text for details).

Measurements					PHREEQC modelling						Calculations			
	Site ID	pH	$[Fe_{dissolved}]$ (M)	$[Al_{dissolved}]$ (M)	Fe(II) (%)	Fe(III) (%)	$a_{Fe(III)}$ (M)	a_{Al} (M)	$\log(a_{Fe(III)}/a_{H^+}{}^3)$	$\log(a_{Al}/a_{H^+}{}^3)$	$[Fe(III)_{truly\ dissolved}]$ (M)	$[Al_{truly\ dissolved}]$ (M)	$[FeOx_{colloidal}]$ (M)	$[AlOx_{colloidal}]$ (M)
River	R1	7.26	4.84×10^{-6}	1.42×10^{-6}	0.0	100.0	2.0×10^{-5}	5.2×10^{-3}	7.1	9.5	4.11×10^{-8}	1.44×10^{-7}	4.80×10^{-6}	1.28×10^{-6}
	R2	6.71	4.70×10^{-5}	9.27×10^{-6}	0.0	100.0	4.7×10^{-13}	4.4×10^{-10}	7.8	10.8	7.43×10^{-8}	4.95×10^{-8}	4.69×10^{-5}	9.22×10^{-6}
	R3	3.35	1.13×10^{-3}	4.39×10^{-4}	95.4	4.6	8.9×10^{-7}	3.6×10^{-5}	4.0	5.6	5.23×10^{-5}	4.39×10^{-4}	0	0
Springs	S1	2.23	9.87×10^{-3}	4.30×10^{-3}	1.0	99.0	1.3×10^{-4}	1.6×10^{-4}	2.8	2.9	9.77×10^{-3}	4.30×10^{-3}	0	0
	S2	3.25	2.47×10^{-3}	1.77×10^{-3}	0.6	99.4	4.2×10^{-5}	1.8×10^{-4}	5.4	6.0	1.03×10^{-3}	1.77×10^{-3}	1.43×10^{-3}	0
	S3	2.77	2.01×10^{-3}	4.73×10^{-4}	1.9	98.1	7.1×10^{-5}	4.5×10^{-5}	4.2	4.0	1.97×10^{-3}	4.73×10^{-4}	0	0
	S4	2.73	5.16×10^{-3}	1.18×10^{-3}	4.4	95.6	1.0×10^{-4}	7.0×10^{-5}	4.2	4.0	4.93×10^{-3}	1.18×10^{-3}	0	0
	S5	6.00	1.26×10^{-3}	2.09×10^{-6}	99.7	0.3	1.6×10^{-12}	2.1×10^{-11}	6.2	7.3	2.78×10^{-7}	2.09×10^{-6}	4.05×10^{-6}	0

(according to slope of the line) than the main river (R1). It appeared that most of the studied elements in dissolved form had conservative behaviour as well, with the exception of some outlying elements (Fig 4). Discrepancies from conservative behaviour exhibit two extreme cases:

1) DOC, Mo and Pb had smaller concentrations in the river after confluence with S1, which leads to $[X]_{R1}/[X]_{R2}$ ratios much above the other elements. In addition small $[X]_{S1}/[X]_{R2}$ ratio values for DOC, Mo and Pb reflect their similar concentration in S1 and R1.
2) For Al, As, Cu, Cr, Fe, U and V, $[X]_{R1}/[X]_{R2}$ ratios are low due to their considerable input from S1, which has very high concentrations of these elements (see Fig. 2 and SI). $[X]_{S1}/[X]_{R2}$ ratios are very high for these elements (200–950) compared to the conservative linearization of the majority of elements measured. There is evidence that their large, partial removal from the dissolved form at R2 is due to the formation of element precipitates and/or their adsorption on solid particles either newly formed (Fe and Al) or already present in river water.

In addition to these two extreme cases, Bi and Ti are found to be significant trace element outliers. This is likely due to a large input from S1 (Fig. 2 and Table SI-2), which is then less efficiently removed at the point of sampling, R2, compared to the other elements in case 2, such as Cu.

4.4. Modelling of chemical speciation of elements

Chemical speciation of studied elements was modelled in two successive steps, using PHREEQC (Parkhurst and Appelo, 1999) and WHAM-VI (Tipping, 1998) speciation codes. PHREEQC allows the calculation of inorganic element speciation, taking into account redox conditions and precipitation (saturation index with respect to mineral phases), but modelling of dissolved organic matter (DOM) is limited, whereas the WHAM-VI model includes different compositions of DOM.

4.4.1. Modelling with PHREEQC

During the first step, inorganic chemical speciation of elements was calculated by PHREEQC (MINTEQ default database) for all samples, using the measured physico-chemical parameters and the concentration of dissolved major and trace elements. Such calculation allows quantification of the proportions of the different forms for redox-sensitive elements such as As(III and V), Fe(II and III), S(−II and VI), and U(III, IV, V and VI). Results showed a predominance of the oxidized forms of As(V) and U(VI), as expected from positive measured values of E_h. So, even though As is present at high to very high concentrations in all of the springs, leading to a large increase of As at the sampling point R3, it is in its oxidised state, which is known to be less acutely toxic during human consumption. The partition of Fe between Fe(II) and Fe(III) forms, controlled by E_h and pH, varied along the river and most of the springs (Table 2). Fe is mainly present as Fe(III) in the river (R1–R2) and springs (S1–S4), and inversely as Fe(II) at R3 and S5, due to the lowest measured E_h. Additionally, PHREEQC calculations revealed that the saturation index (in log) of some mineral phases were positive (supersaturation, data not shown) for Al at R1 and R2, and for Fe(III) in all samples, which corroborates the observed reddish-orange coating of HFO on the river bed and at the output of all springs. Such precipitation of Al and Fe(III) hydroxides is responsible for the removal of some elements, observed along the river (Fig. 4). Presence of Al and Fe(III) hydroxides in colloidal form also controls speciation of dissolved trace elements by adsorption, which competes with the complexation reactions of DOM. Moreover, using the free activity of Al and Fe(III) determined by PHREEQC, it was possible to calculate the ion activity products (IAP: $\log(a_{Al}/a_{H^+}{}^3)$and $\log(a_{Fe(III)}/a_{H^+}{}^3)$). Values obtained for Al and Fe ranged from 2.9 to 10.8 and from 2.8 to 7.8, respectively. A solubility product ($\log K_{so}$) of 8.5 was adopted for the solubility control of Al $(OH)_3$, a value defined by Tipping et al. (2003). The value of $\log K_{so}$ for Fe $(OH)_3$ depends on ageing effects and could be as high as 5 for fresh precipitates or ~2.5 for aged precipitates (Tipping et al., 2003). In the studied site the precipitation of Fe(III) hydroxides is extremely rapid (as noticed on field right after R1–S1 mixing), therefore a solubility product ($\log K_{so}$) of 5 (corresponding to more soluble minerals) was adopted in our calculations for the solubility control of $Fe(OH)_3$. Under these conditions, Al and Fe(III) as hydroxide colloids can be expected in (R1, R2) and (R1, R2, S2 and S5), respectively (Table 2). In addition, it is possible to calculate the Al and Fe(III) limit concentrations (considered as "truly dissolved") then, by the difference to the Al and Fe(III) dissolved concentrations (respectively measured and calculated by PHREEQC), the colloidal AlOx and FeOx concentrations were obtained (Table 2).

Other studied elements did not have positive saturation indexes, suggesting that dissolved/particulate partitioning was probably mainly controlled by adsorption processes on fresh FeOx and AlOx precipitates.

4.4.2. Modelling with WHAM-VI

The speciation of dissolved trace elements is known to determine their bioavailability and toxicity for biota. For some elements such as Cu or Pb, the dissolved concentration is mainly controlled by organic matter (such as humic substances) and/or inorganic colloids (such as Fe and Al hydroxides). Various models have been developed to describe the interactions of natural dissolved organic matter (DOM) with protons or metals, using discrete or continuous distribution of binding sites (e.g. Tipping, 1998; Kinniburgh et al., 1999; Lenoble et al., 2008). In this study, to calculate the speciation of dissolved fraction of an element, and particularly the interaction with DOM, the WHAM-VI model has been used, assuming a discrete distribution of binding sites which form mono- or bi-dentate complexes with proton and metal, as

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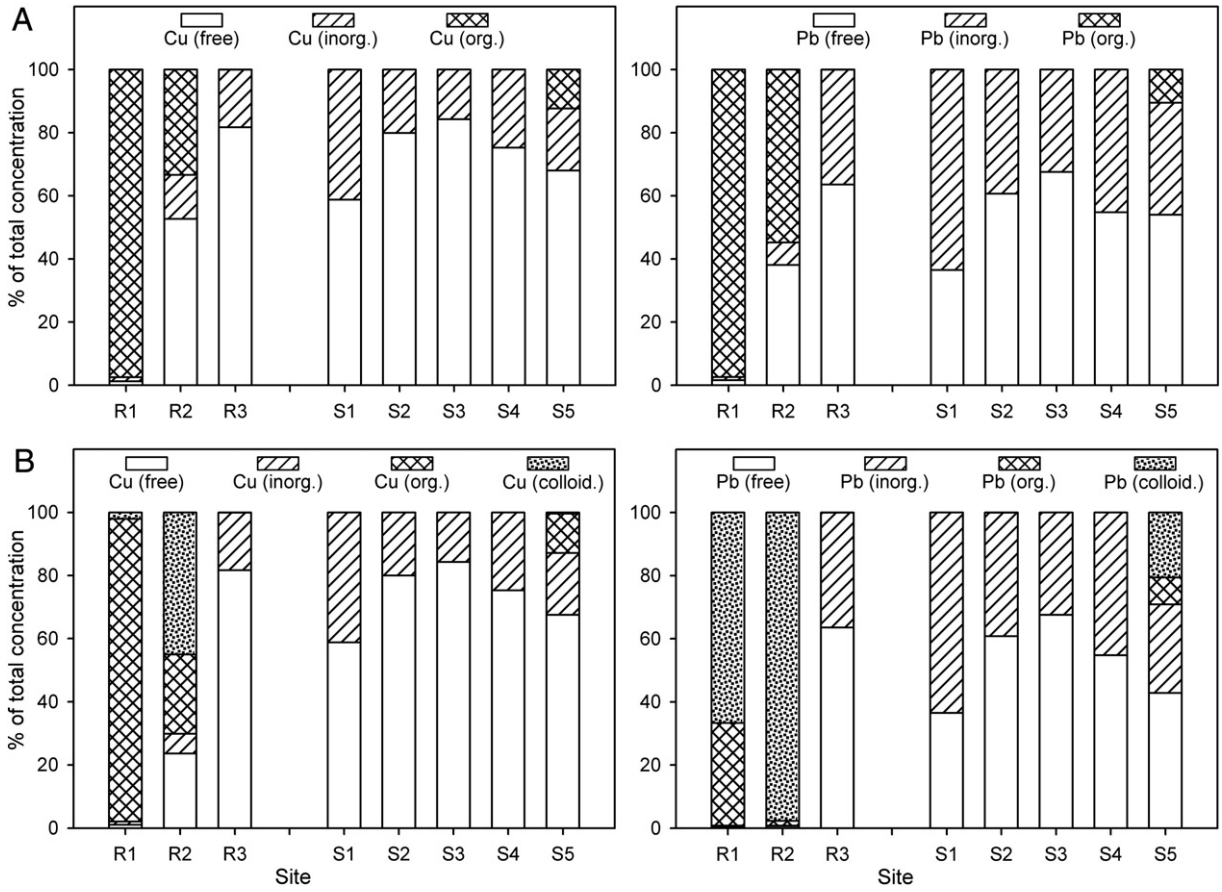


Fig. 5. Chemical speciation of Cu and Pb calculated by WHAM-VI: without (A) and with (B) colloidal form of AlOx and FeOx.

described in detail elsewhere (Tipping, 1998). In order to describe the metal–humic binding, the following parameters have to be defined: organic matter content (in g L^{-1}), percentage of reactive humic substances and its proportion as fulvic acid. It is generally assumed that organic matter is composed of 50% C. Default values for the other two parameters are both 100%. Two different calculations of the dissolved speciation using WHAM-VI were performed: case (A) took the calculated "truly dissolved" concentrations of Al and Fe(III), whilst case (B) used the same conditions, but with an addition of the calculated concentrations of colloidal AlOx and FeOx (Table 2) as reactive phases for trace elements. Results obtained (Fig. 5) showed that most of trace elements are mainly present as their free ions (e.g. Cd, Co, Ni, Zn) or inorganic complexes (e.g. As, U), i.e. their most bioavailable/potentially toxic forms, either in the river or in springs. Considering the extremely high concentrations recorded, this could have a significant effect on biota. On the contrary, Cu and Pb speciation can be more affected by the presence of DOM and colloidal AlOx and FeOx, depending on the site. In case (A) Cu and Pb are strongly complexed by organic matter at the R1 site (>97%) (Fig. 5). Downstream, increase in their total dissolved concentrations, inputs of competitive cations (Fe^{3+}, Al^{3+}, Ca^{2+}, …), decrease of DOC and acidification lead to a progressive decomplexation, ending at R3 as fully free and inorganic forms, so potentially more bioavailable and toxic. Addition of colloidal AlOx and FeOx significantly changed the behaviour of Pb (Fig. 5, case B), which was strongly adsorbed on such colloids at R1 and R2 sites (67 to 98%), and also less strongly complexed by DOM (33 to 2%). This explains Pb non-conservative behaviour in the river/spring S1 mixing (Fig. 4). Cu is also significantly associated to colloids in R2 (45%). At R3, due to acidification and the reduction of Fe(III) to Fe(II) (Table 2), both metals are fully present in their inorganic form. Concerning the springs, Cu and Pb organic complexation and/or sorption on AlOx/FeOx were observed only at S5, due to its less acidic pH.

5. Environmental and health considerations

The presence of high to very high levels of arsenic does not modify the taste, colour or odour of water. Consumption of high to extreme levels of As can lead to potential chronic or acute toxicity. Chronic toxicity is still not fully understood, and remains the focus of a great deal of research due to the global populations at risk (Mazumder and Dasgupta, 2011). The Bijela Rijeka River springs are mainly used by humans for external use (e.g. bathing), which is thought to be the least dangerous arsenic contamination pathway (Zartarian et al., 2006). However, changing agricultural practices in this area (e.g. irrigation) using this water could lead to arsenic entering the human food chain with possibly wider ranging consequences. Although arsenic compounds have been used for decades for health-care purposes, with its positive effects for treatment of some diseases recently "re-discovered" (Emadi and Gore, 2010), a comprehensive re-evaluation of the recommended doses and exposure pathways of application is strongly recommended, taking into account not only the arsenic content of this water, but also the content of some elements of concern to human health (e.g. U, Tl, Cd, Cr and Pb). It seems that such mineral waters were widely applied using "traditional" recipes (e.g. "The dose is 1–3 teaspoonfuls for children and 3 spoonfuls for adults 3 times a day.") as reviewed by Petraccia et al. (2006). Therefore, we hope that this work can lead to a more conscious management of Bijela Rijeka River waters and

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be the basis of further studies dedicated to the bottling and trading of 'safe' mineral waters.

Due to the acidic to moderately acidic pH measured in the spring waters and the main river after all spring water inputs (site R3), the chemistry of this system is not easily comparable to usual natural water bodies, but rather to effluents similar to acid mine drainage (Elbaz-Poulichet et al., 1999; Butler et al., 2008; Lambert et al., 2004). Such systems exhibit high temporal and spatial variability in chemistry and are generally considered as highly ecotoxic zones. The two most studied examples of European ecotoxic freshwaters are the Tinto and Odiel rivers, the most polluted fluvial-estuarine regions contaminated by thousands of years of mining (Davis et al., 2000; Sanchez-Rodas et al., 2005; Nieto et al., 2007; Sarmiento et al., 2012). The extreme environmental conditions, dramatically high metal concentrations and the specific microorganisms encountered in this environment mean that the Tinto and Odiel rivers are used as a model for astrobiology on Mars (Costas et al., 2007). In the present study, the same specificities are encountered, which makes the Bijela Rijeka River and its springs a scientific challenge.

6. Conclusions

Arsenic and heavy metal contents as well as their distributions and chemical speciation were studied in river waters and in five connected acidic spring waters near Srebrenica town (Bosnia and Herzegovina). These spring waters are known as arsenical-ferrous waters, having an acidic pH (down to 2.2). This natural water system is of research interest as it represents chemistry ranging from normal river water to an effluent similar to typical acid mine drainage waters. Furthermore, these highly contaminated waters have been used for decades and continue to be used for health-care purposes.

Chemical analysis showed that spring waters contain very high concentrations of elements, not only of arsenic and iron, but also of many other heavy metals and sulphate (causing low pH). Arsenic and iron content reached a maximum concentration of 6.6 mg L^{-1} and 0.5 g L^{-1} respectively. Before any spring water input, the river has element concentrations and physicochemical parameters in accordance with river world averages. However, input of acidic spring waters along a 1.5 km distance caused the pH to decrease from 7.3 to 3.4, whilst concentration of elements increased. The enrichment factor calculated for all the studied elements ranged from 1.2 for Sr up to 425 for As. High content of Fe caused formation of hydrous ferric oxide (HFO) on the river bed, which is observed as reddish coating.

Mathematical analysis of mixing zone between the river and the first spring showed that most of the dissolved elements follow conservative behaviour. However, discrepancy from the conservative line for some elements (Al, As, Bi, Cu, Cr, Fe, Mo, Pb, Ti, U, V) was found, either due to high input by S1 or their high affinity for particulates/colloids, and consequentially their relative removal from the dissolved form.

Speciation modelling by PHREEQC and WHAM-VI revealed that formation of colloidal forms of iron and alumina (operationally defined and measured as dissolved) should be taken into consideration, as these colloids act as competitive adsorptive sites for "truly dissolved" elements in competition with dissolved organic matter. Redox speciation modelling showed that arsenic is present in its oxidized form, As(V), whilst on two sites (with low pH and low redox potential) divalent iron is dominant.

The extremely dynamic behaviour of elements (many of which are associated with detrimental human health effects) with high spatial variability is exhibited by this study. The sites specific behaviour could mean that this area could be used as a microcosm to study natural geogenic As and metal contamination in Europe.

Bearing in mind that people still use these spring waters for "health-care purposes", that plans for re-establishing the medical centre and trading of bottled mineral water are under consideration, and given the presented findings, further evaluation of adequate dosage and exposure pathways should be reviewed.

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Appendix A. Supplementary data

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