



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 hot springs (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 (H₂AsO₄⁻ and HAsO₄²⁻) and arsenite (H₃AsO₃) 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 (Casot 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 m³ 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 HNO₃ to pH < 2 and stored in pre-cleaned (washed with 10% HNO₃ 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 NaN₃ (1 mM final concentration) and stored in pre-calculated 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 hydrogencarbonate standard solutions. The limit of detection is 0.1 mg_CL⁻¹ and the linearity ranged from 0.1 to 50 mg_CL⁻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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