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Barium anomaly in Kupa River drainage basin

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Abstract

The objective of this work is to present an example of environmental impact of barite waste management observed in stream sediments of the western part of the Kupa River drainage basin. It is a significant water resource for Croatia and a part of Slovenia. In addition, it is for both countries a region of tourism, sport and fishing. Sediments (fraction <63 μm) collected within the whole drainage basin have shown a significant barium anomaly in the western part. The highest concentration of total barium (5790 mg/kg) was determined in Kupica, a tributary of Kupa River. The barium anomaly was traced in Kupa River about 120 km downstream. Looking for the contamination source it was found that the anomaly originates from uncareful waste disposal into an abyss, after barite separation in Homer (Lokve), Gorski Kotar, Croatia. From there barite entered Kupica River subterraneous. Barite and albite were identified by XRD near the source of Kupica River as minor minerals, while quartz and dolomite ferroan were major minerals. This preliminary report does not give yet an answer about barium solubility in river water, about its bioavailability and consequently about barium pollution in the western part of the Kupa River drainage basin, however the possibility is highlighted and discussed.

Keywords: Barium anomaly; Stream sediments; Barite waste disposal; Contamination; Kupa River drainage basin

1. Introduction

Kupa River drainage basin, with a surface of 10,052 km^2 represents a significant water resource for Croatia, parts of Slovenia and Bosnia and Herzegovina. Some parts of the basin are national parks (N.P. Risnjak and N.P. Plitvice Lakes), situated in karstic regions. According to Biondić et al. (2003) karst aquifers in this region are of high risk. Middle and eastern parts were affected by the 1991–1995 war and parts are still under mines and difficult to sample. The study of organic pollutants in stream sediments by Frančišković-Bilinski et al. (2005) has shown that the western part of Kupa River drainage basin is more affected by organic pollutants (PCBs, total phenols and mineral oils) than the rest of the basin. Reported measurements from monitoring program of water quality (Public Health Institute of Karlovac County) show that upper flow of Kupa River belongs to water category II, although microbiological tests show water category IV. Barium was not monitored.

A detailed geochemical study of stream sediments (fraction <63 μm) by Frančišković-Bilinski (2005) has shown that concentrations of series of toxic elements (Sb, Cd, Cr, Co, Cu, Fe, Hg, Mo, Se and Ag) represent no danger for environment; that on very few locations slight toxic effects can be caused by Ni, Pb, Zn, Mn and P, while the highest contamination was observed for Ba. In the present work, barium anomaly and environmental impact of barite mine waste management in Homer, Lokve, Gorski Kotar will be presented. Possible barium pollution of Kupica and Kupa rivers will be highlighted and discussed.

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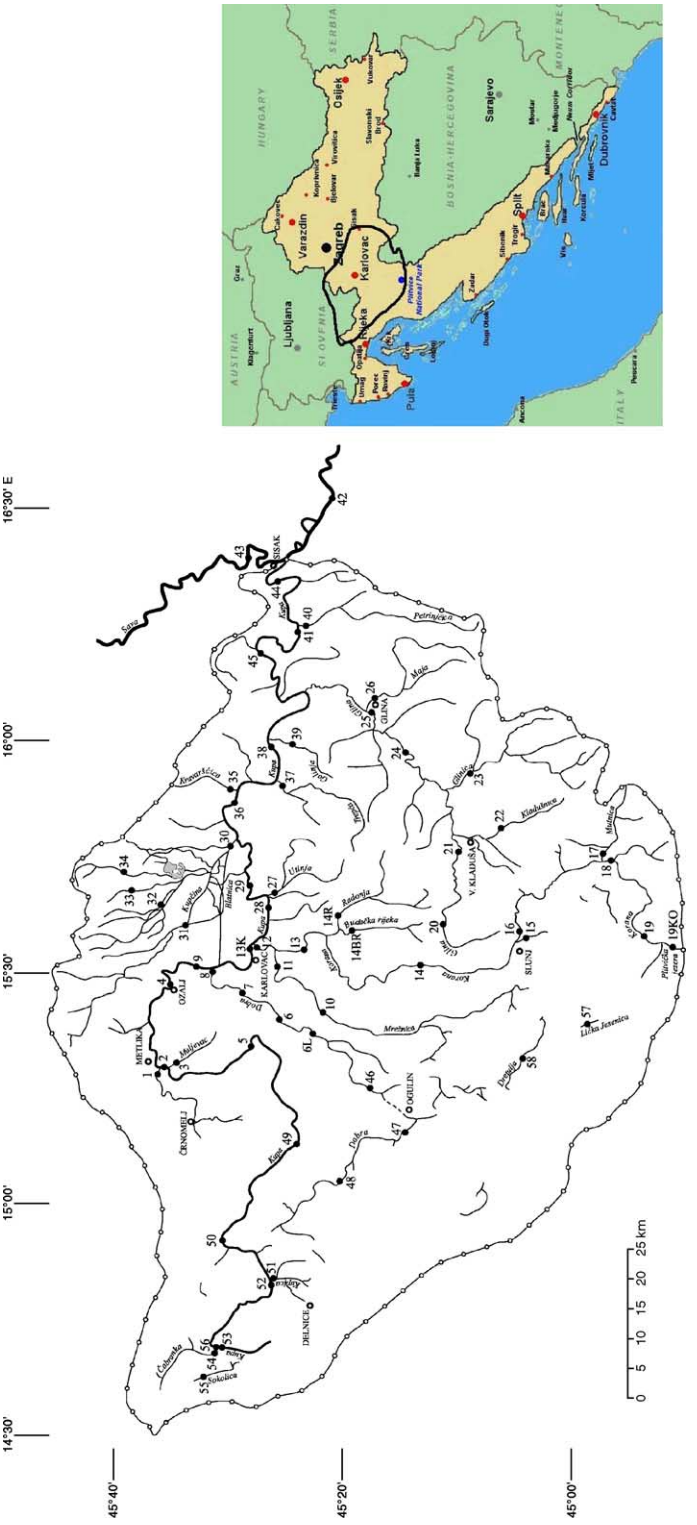

Fig. 1. Location of the Kupa River drainage basin (right) with sampling stations (left).

2. Materials and methods

The study area with 63 sampling locations is presented in Fig. 1, together with a location map for Slovenia, Croatia and Bosnia and Herzegovina. Sampling was performed during summer 2003 (June to August), when water levels were low. Stream sediments were collected and fraction <63 μm was prepared for mineralogical and chemical analysis by air drying at 30–35 °C and dry sieving, using three standard sieves of diameter 2000, 500 and 63 μm (Fritsch, Germany).

A diffractometer Philips 3040/60, X-pert MPD was used to identify mineralogical composition. Perkin Elmer SCIEX ELAN 6100 ICP-MS (ACTLABS, Canada) was used for elemental analysis, from which concentrations of barium will be presented in this work. Standard materials were from USGS: GXR-1, GXR-2, GXR-4 and GXR-6.

3. Results

Measurements of total barium in sediments, presented in Table 1, show an irregular distribution. Concentrations are in the range 12–5790 mg/kg. The geometric mean and median determined for the whole drainage basin are respectively 96 mg/kg and 85 mg/kg. Barium mineral could not be identified by XRD in these samples, due to the limitation of the method (minerals which are present <5% can not be identified with certainty).

To illustrate the different behavior of Ba in the Kupa and the two main tributaries, Dobra and Korana rivers, concentrations of total Ba are plotted vs. flow direction in Fig. 2. The highest concentration of barium was found in sample 51 in the Kupica River at the inflow to the Kupa River, suggesting that the pollution source is upstream of the Kupica River, which is a water source for the town of Delnice (5000 inhabitants). Additional sampling of stream sediment was performed near the source of Kupica River, in which barite and albite have been identified by XRD as minor minerals, while quartz and ferroan dolomite are major minerals.

Table 1
Concentrations of Ba (mg/kg) in sediments (fraction <63 μm) from the Kupa River drainage basin, including 2 stations from the Sava River (42 and 43)

Sample	Ba	Sample	Ba	Sample	Ba	Sample	Ba
1	52.9	14R	158	28	199	44	65.0
2	386	14BR	76.0	29	74.5	45	99.2
3	77.4	15	41.9	30	139	46	48.4
4	341	16	70.3	31	58.7	47	58.1
5	548	17	101	32	70.0	48	69.2
6	38.3	18	41.0	33	120	49	1060
6L	26.7	19	30.7	34	88.8	50	1070
7	46.8	19KO	12.3	35	61.5	51	5790
8	90.8	20	59.1	36	122	52	75.2
9	468	21	204	37	129	53	98.2
10	25.4	22	119	38	78.4	54	107
11	90.4	23	112	39	81.4	55	21.8
12	68.5	24	272	40	147	56	106
13	84.6	25	101	41	54.4	57	24.2
13K	262	26	105	42	169	58	20.9
14	37.7	27	51.8	43	140		

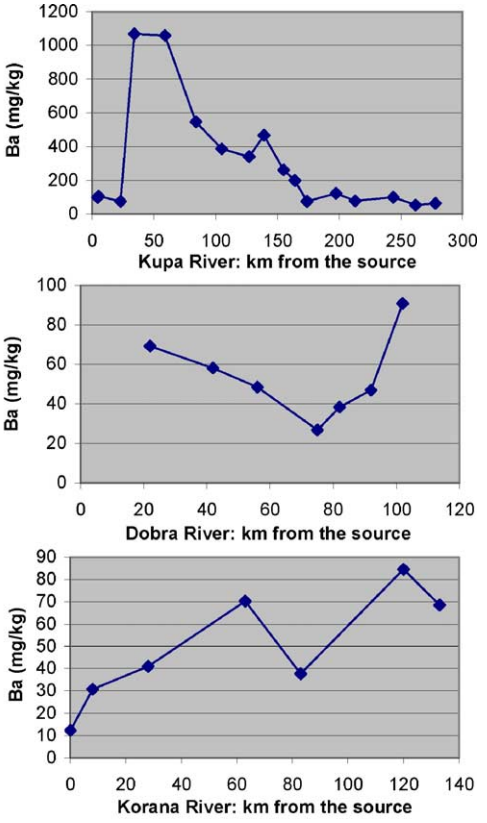

Fig. 2. Distribution (km from the source) of barium (mg/kg) in the Kupa River and in its tributaries, the Dobra and Korana rivers.

4. Discussion and conclusions

Pollution source was assumed to be the closed barite mine in Homer, Lokve. The mine is situated at 747 m above sea level, while the Kupica River source is at about 200 m above sea level. Although several authors (Jurković, 1961; Palinkaš et al., 1993) have studied genesis of barite in this region, environmental impact of barium has not been mentioned yet. During the production of barite ore at Homer, the coarse fraction was separated by sieving. The remaining fraction (<3 mm) was treated as non-toxic insoluble waste. It was disposed in the

nearby environment in fields and gardens, where vegetables are grown, and mostly in an abyss, which has an underground link with the Kupica River, as it is situated in deep karst. Although the barite mine was closed some years ago, the contamination problem remains. Barium availability and consequently barium pollution in western part of the Kupa River drainage basin is not yet proved, although sediments contain high concentrations of Ba. Contamination was traced in the Kupa River about 120 km downstream after the confluence with the Kupica River. Recommended values for barium in sediments are <60 mg/kg (US Federal Criteria). Some barium compounds dissolve easily in water and are found in lakes, rivers and streams. Fish and aquatic organisms accumulate barium, as reported by ATSDR (Agency for Toxic Substances and Disease Registry). Barium in sediments studied here could be a "chemical time bomb", because toxicity of barium is dependent on solubility of barite. Measurements of Ba in waters of Kupica and Kupa rivers, which are in contact with contaminated sediments, do not exist yet. According to Carbonell et al. (1999), Ba^{2+} can be transferred from alluvial sediments into aqueous phase. Solubility is higher at low pH and anaerobic conditions. In alkaline waters solubility is lower, but it exists under anaerobic and aerobic conditions. Kupica and Kupa rivers have a pH ~ 8.5, therefore lower solubility of barite is expected. Dalay et al. (2002) have determined Ba^{2+} both in waters and stream sediments in the Himalaya Region. Dissolved barium ranges from 17 to 871 nM. Baldi et al. (1996) have shown that bacteria *Desulfovibrio desulfuricans* can dissolve barite. Similar process could occur in soils, where barite waste was spread and in sediments of the present studied region. EPA (US Environmental Protection Agency) allows 2 mg/kg of Ba in drinking water. The consequence of ingesting low levels of Ba, over a long term is not yet known. Further multidisciplinary research of barite mine waste with comparative methods (XRD, XRF and Mössbauer spectroscopy), its solubility in the Kupica and Kupa rivers and its health effects on inhabitants, including different specialists from Croatia and Slovenia, is in progress.

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