Environ Geochem Health (2007) 29:69–79
DOI 10.1007/s10653-006-9077-6

ORIGINAL PAPER

Multidisciplinary work on barium contamination of the karstic upper Kupa River drainage basin (Croatia and Slovenia); calling for watershed management

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Received: 10 May 2006 / Accepted: 21 November 2006 / Published online: 4 January 2007

Abstract The present work was designed as an extension of a previous study of a barium anomaly observed in stream sediments of the Kupa River. In its upper part the Kupa River drains a region underlain by a trans-boundary aquifer. The river is a significant water resource in a region of tourism, sport, and fishing in both Croatia and Slovenia. The contamination source is situated in Homer (Lokve), Croatia, where barite was mined until 10 years ago. The barium processing waste material (<3-mm fraction) was carelessly deposited in gardens, forests, and into a sinkhole, which has an underground link with the Kupica River, a tributary of the Kupa River. Barium waste and stream sediments were analyzed using comparative techniques: X-ray diffraction (XRD), X-ray fluorescence (XRF), Mössbauer spectroscopy, and grain size analysis. XRD of the waste material identified the major minerals quartz, barite, and dolomite and the Fe-containing minor minerals muscovite and goethite. Barite was identified as a minor or trace mineral in the Kupica River sediments. XRF analysis of the waste material has shown Ba and Fe to be the predominant elements, Ca and K to be minor elements, and Mn, Zn, Sr, Pb, Co, Cu, As, Zr, Rb, Y, and Mo to be trace elements. Mössbauer spectroscopy performed at room temperature (RT) was used to study iron minerals, particularly to obtain information on the valence status of Fe ions. Grain size analysis of the waste material (<63-μm fraction) has shown that it contains 23.5% clay-size material in comparison with 7–8% clay-size material in stream sediments. It is our aim to combine geochemical and medical methods to investigate the possible impact of waste disposal on human health in Lokve. At this stage of the work, concentrations of Ba and other toxic elements in the water compartment of the Kupica River (a source of drinking water) have not been monitored by Croatian Waters (name of the Croatian water authorities). The necessity of such measurements in future studies has been highlighted. A preliminary study of diseases diagnosed in Lokve shows that about 18% of the total inhabitants have serious medical problems. Diseases of the circulatory system,

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endocrine, nutritional, and metabolic diseases, neoplasms, and respiratory diseases predominate. This paper calls for further multidisciplinary research on the health effects of barium and trace elements, as well as for bioremediation of contaminated gardens and for watershed management of vulnerable karstic aquifers.

Keywords Barium contamination · Barite waste characterization · Karstic aquifers · Health problems · Gorski Kotar · Croatia · Slovenia

Introduction

A barium anomaly was recently observed by Frančišković-Bilinski (2005, 2006) for about 120 km along the Kupa River downstream from the Kupica River inflow. The anomaly in stream sediments originates from careless waste disposal into a sinkhole after barite extraction from ores mined in Homer (Lokve) situated at 729 m above sea level. The barium-contaminated part of the drainage basin is a significant water resource for Croatia and part of Slovenia, and it is a region of tourism, sport, and fishing. The upper part of the Kupa River drains a region underlain by a transboundary aquifer. According to the Water Framework Directive of the European Parliament and of the Council of Europe, establishing community action in the field of water policy, it is necessary to protect such important water resources. The karst hydrogeology of Gorski Kotar has been intensively studied by Biondić, Biondić, and Kapelj (2003, 2006) and by Biondić (2005). For the first time in the protection of karstic aquifers, Biondić (2005) has developed and applied a multi-layer analysis of the karstic region by GIS technology. The new method is applied to study the source of the Kupica and the Zeleni Vir, which are characterized by complex hydrogeological properties. The health effects on people who either worked in barite mines or are living near waste sites were not studied (by local health authorities) in connection with possible barium poisoning, although it is known (ATSDR, 2005) that those barium compounds, which dissolve well in water, may cause harmful health effects in people. Inspired by ideas of Selinus (2002), we aimed to perform a preliminary multidisciplinary study, working toward understanding a potential link between the geochemistry of the region and the health status of inhabitants exposed to barium. We suggest the location Lokve (Croatia) as a suitable site for studying the impact of barite mining on human health, and these results can be applied elsewhere in the world where similar problems exist.

Materials and methods

Study area and sampling locations

A map of the study area, together with numbers of seven sampling locations, is presented in Fig. 1. The area is located in the western part of the Kupa River drainage basin, which was described in detail by Frančišković-Bilinski, Bilinski, and Širac (2005), by Frančišković-Bilinski, Bilinski, Tibljaš, and Rantitsch (2005), and by Frančišković-Bilinski (2005, 2006). In Table 1 details about the sampling locations are given, including the exact locality, the name of the river or stream, the name of the recipient river, and the geographic coordinates. Mine waste was collected in Lokve.

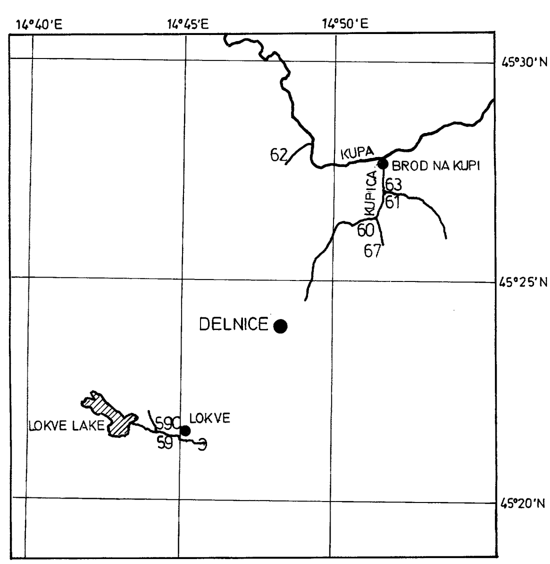

Fig. 1 Sketch map of study area with numbers of sampling stations. Barium-processing waste material is at location 59C

Table 1 Description of sampling locations of interest for the barium anomaly

Sample number	Type of sample	Locality	River	Flows into river	Coordinates	Meters above sea level
59C	Mine waste <3 mm	Homer	–	–	45°21′22.3 N 14°43′57.4 E	729
59	Sediment	Homer	Križ + Lokvarka	Sinking	45°21′25.0 N 14°44′07.0 E	720
60	Sediment	Mala Lešnica	Delnički potok	Kupica	45°26′23.5 N 14°51′00.8 E	210
61	Sediment	Iševnica	Curak	Kupica	45°27′01.5 N 14°51′14.5 E	208
62	Sediment	Grbajel	Bjelica	Kupa	45°27′59.3 N 14°48′40.6 E	203
63	Sediment	Iševnica	Kupica	Kupa	45°27′01.9 N 14°51′02.4 E	200
67	Sediment	Kupica source	Kupica	Kupa	45°25′48.9 N 14°51′32.3 E	280

Stream sediments were collected further away from Lokve in the deep karst region, with high-risk karst aquifers. The river, which had a direct underground connection with the pollution source, has to be precisely identified.

Analysis

Sampling and sample preparation

Sampling was performed between 26 and 30 July 2004. Samples of solid waste (59C) were taken near the sinkhole in the vicinity of the barite ore-processing site in Homer (Lokve). Stream sediments were taken in the streambed away from the riverbank to avoid contamination from soil. Samples were dried in the shade for several days. Dry sieving was performed using three standard sieves (Fritsch, Idar-Oberstein, Germany) with diameters of 2,000, 500, and 63 μm. The silt + clay fraction (<63 μm) was further analyzed.

X-ray diffraction

Mineralogical composition was determined by X-ray diffractometer (X-Pert MPD; Philips; start position: 82Q: 4.01; end position: 82Q: 62.99; generator settings: 40 kV, 40 mA). Crystalline phases were identified using the Powder Diffraction File (International Center for Diffraction Data 1997) and a computer program (X'Pert High Score 2002; Philips). Semi-quantitative mineralogical composition was determined as described in Boldrin, Juračić, Menegazzo Vitturi, Rabitti, and Rampazzo (1992).

X-ray fluorescence spectrometry

The experimental set-up, calibration, and quantitative analysis were described by Kump, Nečemer, Smodiš, and Jačimović (1996) and the reader is referred to this article for details.

The X-ray fluorescence (XRF) analysis system consisted of the X-ray spectrometer, a set of annular radioisotopic excitation sources, and spectrum analysis and quantification software. An X-ray spectrometer with a Si (Li) detector, an integrated signal processor (M1510; Canberra, Meriden, CT, USA), and a PC-based MCA card (S-100; Canberra) was utilized. A spectrometer resolution of about 175 eV at 5.9 keV was achieved. For excitation, the annular radioisotopic sources, Cd-109 (8 mCi), Fe-55 (10 mCi), and Am-241 (25 mCi; Isotopes Products Laboratories, Valencia, CA, USA) were utilized. The spectrum acquisition time was 10,000 s (Cd-109), and 5,000 s (Am-241 and Fe-55). Measurements of samples using Cd-109 and Am-241 were performed in air. Samples analyzed by the radioisotopic source Fe-55 were carried out in a vacuum.

Sample preparation The pulverized and homogenized samples were pressed into a pellet, using a pellet die and hydraulic press.

Calibration and quantitative analysis The X-ray spectra were analyzed by the AXIL spectrum analysis program, according to the method of van Espen and Jannssens (1993). The error evaluated from the AXIL program included the statistical errors of measured X-ray intensities, as well as errors in the mathematical procedure utilized in fitting the experimental spectral data. The overall uncertainty was in most cases better than 1%. The quantification and estimation of combined standard uncertainty (u) was carried out utilizing the QAES (quantitative analysis of environmental samples) software developed by Kump et al. (1996). It was used recently by Nečemer et al. (2003) and by Vogel-Mikuš et al. (2005). Sensitivities were determined from measurements on standard NIST-SRM-2704 River Sediment. The average values of concentrations for major and minor constituents were in most cases within 5% of the reference data. The accuracy of trace element determinations was worse (10% and more).

Mössbauer spectroscopy

Poorly crystalline iron phases were studied by Mössbauer spectroscopy at 300 K. For all experiments a ^{57}Co source with an activity of ~10 mCi in a Rh matrix was used. The velocity scale was calibrated with metallic Fe, which was also used as a reference for the isomer shift parameters. The speciation was computer-fitted by assuming Lorentzian or Voigt (mixture of Gaussian and Lorentzian) shapes for the resonance lines. The best least-squares fit parameters were used for characterization of Fe-containing phases.

Grain size analysis

The particle size distribution was determined in the <63-μm fraction, using an ''Analysette 22'' laser particle sizer (Fritsch) and a Mini Cell for particle sizes <100 μm. The instrument is composed of a measuring unit, a dispersing unit, a computer, and a printer. A helium-neon laser with a wavelength of 0.6328 μm is used. According to the operating principle, when a spherical particle is illuminated, a ''Frauenhofer diffraction pattern'' is produced. The diameter of the particle can be calculated and the surface of each particle determined. The specific surface area was automatically recorded.

Results

X-ray diffraction

The X-ray diffraction (XRD) method is used to characterize barium waste and to prove that there is a link between the waste generated in the barium mine and the stream sediments of the Kupica River.

Mineral compositions of samples (<63-μm fraction) were studied in detail with the aim of possibly identifying Ba- and Fe- containing minerals in waste material and in sediments. Jurković (1959) was the first in this region to report the ore paragenesis: barite, viterite, gel-pyrite, pyrite and markasite as hypogene minerals; goethite, lepidocrocite, hydrohematite, psilomelane, and calcedone as hypergene minerals. In the present work, quartz predominates as a major mineral in all samples (>30%). Among other major minerals, barite was found at location 59C (>30%), dolomite was found at location 59(>30%) and also at locations 59C, 61, 62, 63, and 67 (10–30%); calcite at locations 59 and 62 (>30%): albite at location 61 (>30%), and muscovite at location 60 (10–30%). Of the minor minerals (5–10%), goethite was found at location 59C; muscovite at locations 59C, 61, and 63; chlorite group minerals were found in samples 60, 61, and 63; albite at locations 63 and 67; sodium anorthite in sample 60; illite in sample 62, and barite in sample 67. The XRD pattern of barite in sample 67, at the source of the Kupica River, is the first and strongest evidence that there is a common characteristic between the barium waste and sediments in the Kupica River. Trace minerals (<5%) were near the detection limit of XRD. Therefore, they are probable, but not completely certain. Barite and muscovite were found in sample 59 and illite and biotite in sample 67. The program, X'Pert, gave the numbers of the JCPDF cards that have the best fit with experimental data. However, with the use of this program only the mineral group can be considered certain.

XRF

Results obtained by the XRF method are presented in Table 2. The method is non-destructive and very suitable for fast determination of six major and 17 trace elements. The advantage of the method is that it is possible to determine concentrations of Si and Al relatively simply. It was found that Si predominates over Al, in agreement with the finding that quartz is

Table 2 Element analysis using the X-ray fluorescence (XRF) method in the <63-μm fraction of barium mine waste and of stream sediments (Al, Si, K, Ca, Ba, and Fe in percent, others in ppm)

Element	59C	59	60	61	62	63	67
Al	8.14	7.56	9.25	11.3	5.46	11.6	8.81
S	21.8	18.1	20.3	26.2	14.1	22.4	25.1
K	2.15	1.46	2.09	2.14	1.98	2.19	1.31
Ca	3.66	11.0	4.15	4.24	9.58	5.16	6.51
Fe	16.4	2.63	3.61	2.81	2.80	3.47	2.96
Ba	19.4	3.15	0.0352	0.0467	0.0358	0.6660	7.24
Mn	3,770	1,110	638	441	451	334	661
Co	750	–	–	–	–	–	–
Cu	128	72.4	70.8	43.6	52.3	60.5	59.0
Zn	1,720	129	114	70.8	79.0	77.4	89.1
As	176	97.2	60.0	48.4	51.7	36.9	49.4
Pb	718	176	191	119	145	193	91.3
Rb	36.7	61.3	104	89.7	87.9	97.7	56.70
Sr	2,220	413	85.5	76.7	95.5	146	65.0
Y	31.4	19.1	39.7	29.3	19.8	34.3	47.8
Zr	184	234	353	302	162	525	613
Mo	21.6	–	–	–	–	–	–
Ti	–	3,020	5,430	5,330	3,770	6,080	4,100
V	–	1,570	1,170	679	458	541	1,070
Cr	–	384	258	138	128	114	309
Ni	–	47.5	46.3	19.5	40.5	36.1	28.3
Br	–	6.71	28.0	2.73	33.4	15.4	18.1
Nb	–	5.90	10.1	9.56	7.84	9.97	6.70

the major mineral in all samples. The concentration of Ca is the highest in samples 59 and 62, in agreement with the finding of calcite as a major mineral in these two samples. The highest concentration of Fe is in Ba-mine waste (sample 59C), in which goethite was identified by XRD. Ba is present except in barium mine waste (sample 59C), also in the sediments of Lokvarka and Križ (sample 59), in the sediments of the Kupica River at its source (sample 67) and further downstream (sample 63). This is a second strong indication that there is a link between barium waste and stream sediments and that it was transported from Lokve by an underground connection to the Kupica River and with it to the Kupa River. Sample 59C, besides containing Ba and Fe, also contains elevated concentrations of several toxic elements: Mn, Co, Cu, Zn, As, and Pb. Multiple sediment screening values of toxic elements have been compiled by Buchman (1999). This spectrum ranges from presumably non-toxic levels to toxic levels. The values for Ba included in the list are not reported.

^{57}Fe Mössbauer spectroscopy

Mössbauer spectroscopy has proven to be a valuable complementary technique for the study of soils and sediments. It is useful for the characterization of poorly crystallized iron oxides and hydroxides. Selected spectra of samples 59C, 63, and 67, presented in Fig. 2, were fitted with two doublets. Hyperfine parameters, such as isomer shift (IS) and electric quadrupole splitting (QS), together with the relative resonance area (A, in percentage of total iron) are presented in Table 3. Mössbauer spectroscopy can provide quantitative information about the relative population of the iron species together with specific properties of the individual iron sites. The proportions of Fe(III) and Fe(II) were calculated and included in Table 3. The hyperfine parameters corresponding to the doublet sub-spectra indicate the presence of two Fe(III) environments (labeled du1 and du2) in sample 59C. The hyperfine parameters corresponding to the doublet sub-spectra in two sediment samples, 63 and 67, indicate the presence of one Fe(III) environment

Fig. 2 Mössbauer spectra of ^{57}Fe taken at room temperature with ^{57}Co source in a Rh matrix: <63-μm fraction of selected samples 59C (barium-processing waste material) and stream sediments of the Kupica River (63 and 67)

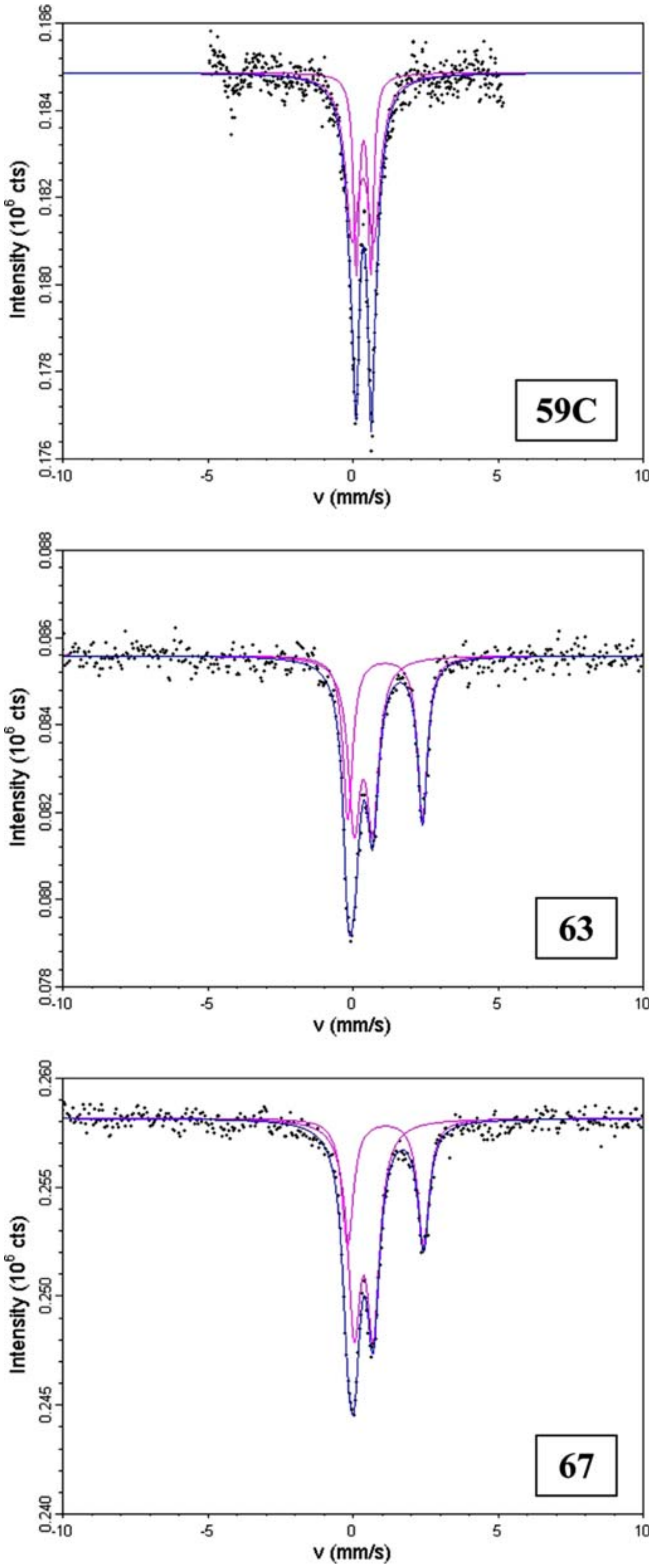

Table 3 Hyperfine parameters of Mössbauer spectra of selected samples (f<63 μm)

Number	Sub-spectra	IS mm/s	QS mm/s	Site	A%	Fe(III)/ Fe_{total}	Fe(III)/ Fe (II)
59C	du1/du2	0.368(86)/ 0.350(18)	0.502(27)/ 0.750(17)	Fe(III)/ Fe(III)	35(30)/65(32)	1	
63	du1/du2	1.112(13)/ 0.364(17)	2.574(27)/ 0.636(28)	Fe(II)/ Fe(III)	42.2(35)/ 54.8(31)	0.55	1.21
67	du1/du2	0.373(13)/ 1.126(17)	0.653(21)/ 2.615(33)	Fe(III)/ Fe(II)	63.4(25)/ 36.6(30)	0.63	1.73

and one Fe(II) environment in different proportions.

Grain size analysis

The particle size distribution and specific surface area described in the Materials and methods section were performed in the <63-μm fraction. The results for selected samples (59C, 63, and 67) are presented in Fig. 3. Sample 59C of waste material contains 23.5% of clay-size material (<4 μm) with a specific surface area of 1.6198 m^2/g. Sample 63 contains 7.08% of clay-size material with a specific surface area of 0.6161 m^2/g. Sample 67 contains 7.90% of clay-size material with a specific surface area of 0.6636 m^2/g. Specific surface areas determined in sediments are close to the value for calcite synthetic, reported by Franklin and Morse (1983). The complex mineral composition and the lack of solution data make it difficult to reach a conclusion about the trace element absorption capacity of sediments in the Kupica River.

Health problems in Lokve

A preliminary study was performed to make an overview of the health situation of inhabitants of Lokve, who have been exposed to barium for a long time.

Table 4 shows a summary of serious diseases and conditions diagnosed during 2005 in the general medical service, Lokve. The total number of inhabitants is 1,120. Diseases of the circulatory system predominate, consistent with the primary cause of death in the whole country. The second most common cause is endocrine, nutritional, and metabolic diseases. The third is neoplasms, and the fourth is respiratory diseases. The total number of people with serious diseases represents 18% of the total population of Lokve.

Discussion

After the separation of barite, the waste material (<3 mm) was spread into the environment in two ways. Partly, it was deposited into the sinkhole, ignoring the fact that karstic environments have vulnerable aquifers (Biondić et al., 2003, 2006). Ba contamination was spread by underground links to the Kupica River, a tributary of the Kupa River. The Kupica River serves as a drinking water supply for the town of Delnice. There are several processes that could release Ba, As, and other toxic metals into water. A study of the influence of pH and redox potential on the solubility of barite (Carbonell, Pulido, De Laune, & Patrick, 1999) has shown that about 4.4% of barite can be converted to a soluble form under acidic and anaerobic conditions, compared with approximately 0.3% under alkaline and either anaerobic or aerobic conditions. In the Kupica River, pH is 8.4, so alkaline conditions predominate. There is also a possibility that sulfate-reducing bacteria influence barite solubilization (Baldi et al., 1996).

The waste, sample 59C, was also deposited in the fields, forests, and gardens by people who were not aware of the Ba, Fe, and other trace element toxicity. People consumed vegetables grown on such deposits. Wild animals, such as bears, deer, rabbits, etc., consumed plants in this region. Brooks (1983) states that plants vary greatly in their ability to accumulate elements from the soil. The plants growing on barite

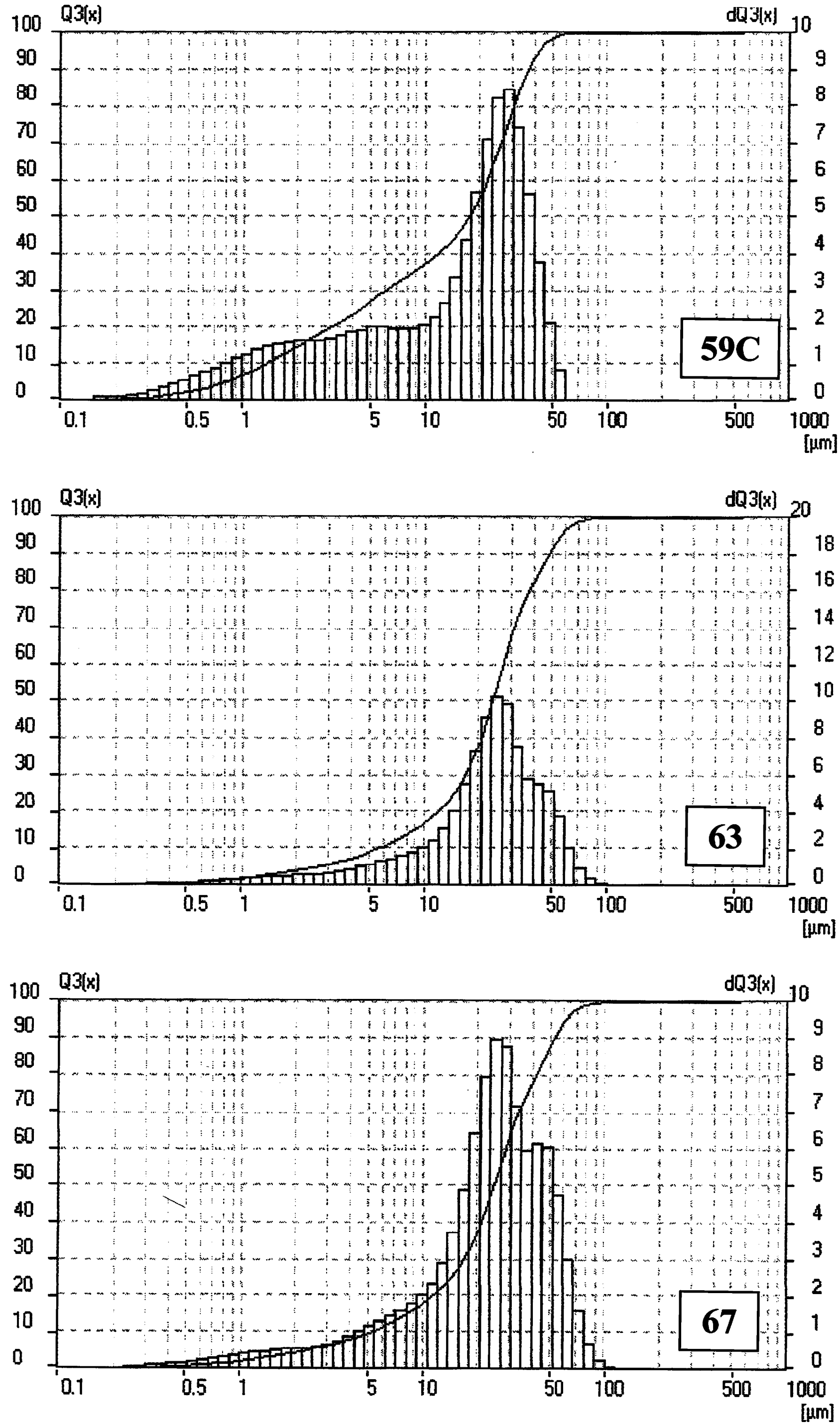

Fig. 3 Grain size analysis in <63-µm fraction of selected samples 59C (barium processing waste material) and stream sediments of the Kupica River (63 and 67) performed by the "Analysette 22" laser particle sizer and Mini Cell

waste disposed in Lokve have not yet been studied.

Until now, no attempt has been made to find accumulator plants that could grow in Lokve and that could be utilized to reclaim and re-vegetate adversely affected mining environments. Such plants are described for Ba (Raghu, 2001) and for As (Pratas, Prasad, Freitas, & Conde, 2005).

Table 4 Diseases and conditions diagnosed in the general medical service, Lokve (number of inhabitants 1,120)

Diseases	Cases	Male	Female
Diseases of the circulatory system	Σ 126	Σ 45	Σ 81
I 10	92	26	66
I 20	1	–	1
I 21	18	13	5
I 25	1	1	-
I 34.0	1	–	1
I 40.4	1	–	1
I 42	8	3	5
I 64	4	2	2
Endocrine, nutritional, and metabolic diseases	Σ 25	Σ 8	Σ 17
E 03	4	–	4
E 05	1	–	1
E 11	19	7	12
E 78	1	1	-
Neoplasms	Σ 17	Σ 6	Σ 11
C 02	1	–	1
C 18	4	2	2
C 32	1	1	–
C 43.5	2	1	1
C 44	1	–	1
C 44.5	1	1	–
C 50	4	–	4
C 72	1	–	1
C 82	1	–	1
C 96.7	1	1	–
Mental and behavioral disorders	Σ 5	Σ 4	Σ 1
F 20	3	3	–
F 32	2	1	1
Diseases of the nervous system	Σ 4	Σ 0	Σ 4
G 20	1	–	1
G 35	1	–	1
G 40	1	–	1
G 91	1	–	1
Diseases of the eye and adnexa	Σ 1	Σ 1	Σ 0
H 40	1	1	–
Respiratory diseases	Σ 14	Σ 8	Σ 6
J 44	7	4	3
J 45	7	4	3
Diseases of the digestive system	Σ 1	Σ 1	Σ 0
K 50	1	1	–
Diseases of the skin and subcutaneous tissue	Σ 2	Σ 2	Σ 0
L 20	1	1	–
L 40	1	1	–
Diseases of the musculoskeletal system and connective tissue	Σ 5	Σ 2	Σ 3
M 05	2	1	1
M 07	1	–	1
M 10	1	1	–
M 81	1	–	1

Total number of diseased people is 200, which is 18% of the total population

As reported by Förstner and Heise (2006), assessment of sediment quality is still prone to a number of uncertainties with regard to regulation. In the investigated region studied in this work, in a sample of waste material (59C), there are a series of toxic elements that have concentrations far exceeding recommended values (not regulation) for sediment quality criteria (SMSP and FALCONBRIDGE NC SAS, 2005). In the following list, the first value in the parentheses represents the value found in sample 59C and the second represents the value causing severe toxic effects: Fe (16.4% vs. 4%), Mn (3,770 ppm vs. 1,110 ppm), Co (750 ppm vs. 50 ppm), Cu (128 ppm vs. 110 ppm), Zn (1,720 ppm vs. 820 ppm), As (176 ppm vs. 33 ppm), and Pb (718 ppm vs. 250 ppm). The values for Ba are significantly higher than the recommended value of <60 mg/kg. At the source of the Kupica River (sample 67), sediments contain As (49.4 ppm vs. 33 ppm) and Cr (309 ppm vs. 110 ppm) at concentrations that can have severe effects on aquatic life. Concentrations of Mn, Cu, Pb, and Ni are above the lowest effect level. Therefore, careless distribution of the waste into the environment might have serious consequences on local aquatic wildlife populations.

From Mössbauer spectroscopy it can be suggested that the Fe-containing phase of barite waste is composed of α FeOOH and β FeOOH, based on the similarity of parameters obtained on an aged, high molecular weight hydrolyzed iron (III) fraction (Hanžel & Bilinski, 1984). It can be tentatively assumed that Fe(III) is present in phylosilicates in both sediment samples and that Fe(II) is present in chlorite in sample 63 and in dolomite in sample 67.

From the grain size analysis, intensive downstream transport of clay particles can be predicted. High specific surface area in sample 59C can explain the affinity of numerous trace elements with the waste material.

The town of Delnice and the settlement of Lokve, with its suburb Homer, belong to Primorsko-Goranska Županija County. From the available statistics from this county (available in Croatian at http://www.zzjzpgz.hr) and from the European Health for All database, HFA-DB (WHO, 2006), it is evident that a contrast exists regarding the health status of this county compared with the whole of Croatia and with the EU. Mortality, expressed as the age-specific mortality rate (ASMR), is increasing in Croatia and in Primorsko-Goranska Županija County, compared with the EU average. The main causes of mortality are diseases of the circulatory system and neoplasms. Mortality is caused to a lesser extent by respiratory diseases, by unknown diseases, and by poisoning. The standardized mortality from neoplasms in the EU average constantly decreases, while in Croatia and in Primorsko-Goranska Županija County, it increases. Women in Primorsko-Goranska Županija County show significantly higher mortality from breast cancer (C50) in comparison with the EU average and with the whole of Croatia. This seems to be a significant reason for looking for possible causes. In traditional medical practice, according to Moeller (1997), physicians deal with patients according to clinical interventional models. There is intervention, but not control over the disease and no elimination of its source. Such practice was also common in Lokve. Medical geology, which we aim to introduce in the future, is concerned with the materials affecting public health and processes. In the present paper, we suggest that Ba, Fe, and a series of trace elements (Mn, Co, Cu, Zn, As, and Pb), present above toxicity levels (SMSP and FALCONBRIDGE NC SAS, 2005), could have impact on human health. It is known (ATSDR, 2005) that high levels of barium can cause problems with the heart, stomach, liver, kidneys, and other organs. Such diseases predominate in Lokve. Barium has not yet been classified by the Environmental Protection Agency (EPA) with regard to its human carcinogenicity, because there are no available studies in people. Inhabitants of Lokve, particularly of Homer diagnosed with neoplasms, could be used to measure their exposure to barium and to other trace elements found in waste materials. Diseases diagnosed in inhabitants of Delnice could add to the understanding of the health effect of barium and other trace elements originating from drinking water.

Conclusions

This work has demonstrated the detailed characterization of barite waste material from a closed barite mine in Homer, Lokve, Croatia. The waste was spread into the environment. Barite waste is a serious pollution source, although, due to ignorance, it was previously treated as non-toxic insoluble waste and was spread into the karstic environment. The waste is composed of the major minerals quartz, barite, and dolomite and the minor minerals goethite and muscovite. The major elements are Si, Ba, Fe, and Al. The minor elements, which can in addition to Ba and Fe cause severe toxic effects, are Mn, Co, Cu, Zn, As, and Pb.

The waste, deposited into a sinkhole, entered the aquatic environment and contaminated the Kupica River, which is the source of drinking water for Delnice. A brief description of health problems of the local population in Lokve has shown that about 18% of the people have serious diagnoses and that new cases of neoplasms are occurring. A similar study of the health problems in the town of Delnice is suggested. The work presented here calls for monitoring by the Croatian water authorities of Ba and other toxic elements in the water of the Kupica and the Kupa rivers, for the continuation of multidisciplinary research into the toxicity of barium, particularly involving the local inhabitants exposed to it, for possible decontamination of gardens, and for possible watershed management. The work regarding an assessment of sediment quality studied here can be considered preliminary, until the European framework directive (WFD) comes up with environmental quality standards for sediments.

Acknowledgements This research was funded by the Ministry of Science, Education, and Sport of the Republic of Croatia, project 0098041 (principle investigator H. Bilinski). Additional support for sampling and Mössbauer analysis was obtained from the bilateral project Croatia-Slovenia (principal investigators H. Bilinski and D. Hanžel). The authors thank D. Tibljaš (Croatia), P. Kump (Slovenia), and K. Kovacs (Hungary) for allowing us to use their equipment and programs for XRD, XRF, and grain size analysis respectively. Special thanks go to Mrs Željka Turukalo, the inhabitant of Homer, who has kindly shown us the locations where barium waste was spread in gardens, forests, and the sinkhole.The paper has been edited by Professor George Helz, a native English speaker and geochemist. He is particularly acknowledged for his kind help.

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