Environ Geochem Health (2007) 29:21–32
DOI 10.1007/s10653-006-9057-x

ORIGINAL PAPER

Major and trace elements in paddy soil contaminated by Pb–Zn mining: a case study of Kočani Field, Macedonia

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Received: 27 November 2005 / Accepted: 19 July 2006 / Published online: 22 November 2006

Abstract The objective of this study was to assess the bulk chemical composition as well as the extent and severity of heavy metal contamination in the paddy soil of Kočani Field (eastern Macedonia). The results revealed that the paddy soil of the western part of Kočani Field is severely contaminated with Pb, Zn, As and Cd in the vicinity of the Zletovska River due to irrigation with riverine water that is severely affected by acid mine and tailing effluents from the Pb–Zn mine in Zletovo. The detected total concentrations of these metals are far above the threshold values considered to be phytotoxically excessive for surface soil. The paddy soil in the vicinity of the Zletovska River was also found to exhibit elevated levels of Ba, Th, U, V, W, Mo, Cu, Sb, Bi, Ag, Au, Hg and Tl, with concentrations above their generally accepted median concentration values obtained during this study. A correlation matrix revealed that the Mn and Fe oxides/hydroxides are the most important carrier phase for several trace elements, with the exception of rare earth elements (REEs). These also represent a major sink for the observed heavy metal pollution of thesoil. REEs are mostly associated with two phases: light (L)REEs are bound to K-Al, while heavy (H)REEs are bound to Mg-bearing minerals. Although there is no direct evidence of a health risk, the paddy soil in the vicinity of Zletovska River needs further investigation and an assessment should be made of its suitability for agricultural use, particularly in view of the highly elevated concentrations of Pb, Zn, As and Cd.

Key words Acid mine drainage · Heavy-metal contamination · Kočani Field · Macedonia · Paddy soil

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Introduction

Soil serves many vital functions, but its effect on food production is universal to all societies. It is thus of extreme importance to protect this resource and to ensure its sustainability (Wong, Li, Zhang, Qi, & Min, 2002). In this context special attention should be paid to the concentrations of trace elements in agricultural soils as these can be ingested by humans and animals through the food-chain structure as a result of their initial uptake by edible plants. A deficit or excess of these elements can cause serious problems in plant growth and animal and/or human health (Ferguson, 1990; Tiller, 1989). The total content of trace elements in soils depends mainly upon the bedrock type from which the soil parent material was derived but also on which pedogenic processes were carried out (Mitchell, 1974). Among the anthropogenic activities that can be considered to be important sources of trace element contamination of the surface environment are base-metal mining together with milling and grinding operations, the concentration of ore and the disposal of tailings along with the acid mine and waste water (Adriano, 1986). Elevated concentrations of heavy metals are generally found in and around abandoned and active mines due to the discharge and dispersion of the mines' waste materials, including tailings, into nearby agricultural soils, food crops and stream sediments (Hansman & Köppel, 2000; Jung, 2001; Korre, Durucan, & Koutroumani, 2002; Lee, Chon, & Jung, 2001; Li & Thorton, 2001; McKenzie & Pulford, 2002; Pestana, Formoso, & Teixera, 1997; Witte, Wanty, & Ridley, 2004; Wong et al., 2002). As a result, large areas of agricultural soil can also be contaminated. In addition, agricultural soils are also prone to pollution with toxic trace elements and other contaminants from fertilization processes, industrial and municipal waste discharges, transport activities and atmospheric deposition. Trace elements can also enter agricultural soils through irrigation (Chen, Zheng, Tu, & Zhu, 1999; Haygarth & Jones, 1992).

Although several studies have evaluated trace element concentrations in the soil and edible plants in various parts of the world (Kabata-Pendias & Pendias, 1992 and references therein), such studies are very scarce in Macedonia. As a result, very little is known about the distribution and concentration of trace elements in the soils and plants from different parts of Macedonia, which could have been affected by base-metal mining, milling and other industrial operations (both historical and recent). The aim of the investigation reported here was to obtain data that would contribute to a database on the distribution of major and trace elements as well as heavy metal contamination of the paddy soil from Kočani Field. In this paper, the term trace elements is used for elements other than the eight major abundant rock-forming elements such as O, Si, Al, Fe, Ca, Na, K and Mg, while the term heavy metals refers to trace metals and metaloids having densities greater than 5 g/cm^3 (Adriano, 1986). The soil of Kočani Field is likely to be polluted by heavy metals because of mining activities and acid mine drainage from the Zletovo-Kratovo and Sasa-Toranica ore districts.

Study area

The study area of Kočani Field, with an average length of 35 km and an average width of 5 km, is located in the eastern part of Macedonia, about 32 km from the city of Štip. It is situated in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (Fig. 1). The paddy soil of Kočani Field has been estimated to originate from the composite material of the sediment derived from igneous, volcanic, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression, This depression was formed as a result of intense movements along the major border faults relative to the Plačkovica and the Osogovo blocks at the end of the Tertiary.

The city of Kočani, which is well known for its thermal waters,is located on the southern foothills of the Osogovo Mountains. The Bregalnica River, together with its tributaries, drains the igneous metamorphic and sedimentary rock ageing from Precambrian to Holocene as well as mine wastes and tailings from the abandoned and active Pb–Zn mines and polymetallic mineralization of the Serbo-Macedonian Massive. A broader region has a long history of mining, dating to the pre-Middle Ages, with the most recent phase of mining starting after the Second World War. There are several Pb–Zn ore deposits and Ag, As, Cu, Sb, Ba, Au and U mineralization related to the Tertiary acidic to intermediate volcanogeno-intrusive complexes of the Besna Kobila-Osogovo Tassos metalogenic zone in the east and Tertiary volcanogenic complexes of the Lece-Chalkidiki

Fig. 1 Map of the study area showing the drainage system of the Bregalnica River and its tributaries

metalogenic zone in the north of Kočani Field (Serafimovski & Aleksandrov, 1995).

The most severely polluted tributaries of the Bregalnica River are the Kamenica River in the NE part of the Bregalnica River drainage basin and the Zletovska River on the western side of Kočani Field. Both tributaries are severely impacted by acid mine drainage. The Kamenica River drains mine waste, including tailings, mill sewages and mine effluents of the Pb–Zn polymetallic ore deposit Sasa, directly into the artificial Kalimenci Lake constructed for the purposes of irrigating the paddy fields during the dry season. Upon mixing with the lake water, the concentrations of the pollutants decline. For this reason the Bregalnica River, when it leaves the Kalimednci Lake, is less polluted than the Kamenica River. The Zletovska River originally drains the central part of the Kratovo-Zletovo volcanic complex; it also drains the abandoned old mine sites and bare tailings as well as the effluents from the Pb–Zn Zletovo mine and its ore-processing facilities. Acid mine water and the effluents from tailings were discharged untreated into the riverine water that was used for the irrigation of the paddy fields of the western side of Kočani Field. The pollution of the Zletovska River by acid mine drainage is easily recognizable in the field. The bed sediments are coated with Fe and Mn oxides/hydroxides, which are the major sink for contamination with several trace elements. The Zletovska River, which is more polluted than the Bregalnica River, adds water to the Bregalnica River in the western edge of Kočani Field at Krupište.

Two small tributaries, the Orizarska and Kočanska Rivers, which drain the southern part of the Osogovo Mountains as well as the more or less untreated municipal wastes and domestic sewage of the cities of Kočani and Orizari were also used for irrigation of the paddy fields located in the NE part of Kočani Field (Fig. 1).

Materials and methods

Soil sampling

The objective of the field-sampling program was to characterize the concentrations of major, minor and trace elements in the paddy soil of Kočani Field, with the main emphasis being on the distribution and concentrations of the potentially toxic heavy metals, such as Pb, Zn, As, Cd, Sb, Bi, Ag, Cu, Au, Hg and Tl, which are predominantly related to the base-metal mining activities of this region. For this purpose paddy-soil samples were collected at 38 locations from seven profiles (sections I–VII) across Kočani Field, as shown in Fig. 2. Near-surface paddy soils (0–20 cm in depth) were sampled with a plastic spade to avoid heavy metal contamination. Near-surface soils were collected because in the agricultural soil it is not possible to distinguish the A, B and C horizon. Each soil sample comprised a composite of five sub-samples taken within a 1×1-m quadrate.

Mineralogical and geochemical analyses

The soil samples were air dried at room temperature (about 25°C) for 1 week and sieved through a 2-mm polyethylene sieve to remove plant debris, pebbles and stones. They were then ground in a mechanical agate grinder to a fine powder for subsequent X-ray diffraction (XRD) and geochemical analyses.

The mineralogy of the soil samples was determined at the Department of Geology, Ljubljana, Slovenia by X-ray powder diffractometry using a Philips PW 3710 diffractometer and Cu*Kα* radiation. The samples were scanned at a rate of 2°C per minute over the range 2–70°C (2*θ*). The results were stored on a personal computer (PC) and analyzed with PC-Automatic Powder Diffraction (PC-APD) Philips software(Philips, Eindhoven, 1996). The diffraction patterns were identified using the data from the Joint Committee on Powder Diffraction Standard (JPDS standard-1977).

All of the paddy soil samples were analyzed for their major and trace element concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories,Vancouver, B.C., Canada) using different analytical methods. According to the reports, SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3, Ni and Sc were measured after fusion with a mixture of lithium metaborate/tetraborate and dissolution in nitric acid by inductively coupled plasma emission spectroscopy (ICP-ES). The total carbon and sulfur levels were determined by LECO, while LOI was based on loss of ignition. Ba and trace elements such as Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, Y, and rare earth elements (REEs) were determinedby ICP-MS after fusion with a mixture of lithium/tetraborate and dissolution in nitric acid. The remaining trace elements (Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl and Se) were analyzed by ICP-MS after the extraction of sub-samples for 1 h with HCl-HNO_3-H_2O (2:2:2) at 95°C. The accuracy and precision of the multi-element soil analyses were assessed by using an international reference

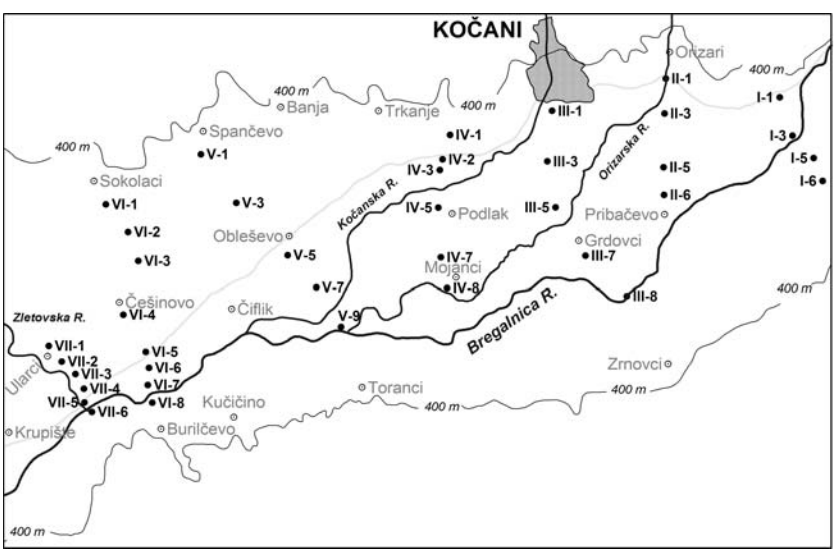

Fig. 2 Sampling location map of the study area

material such as USGS G-1 (granite) and CCRMP SO-1 (soil). The analytical precision and accuracy were better than ±4% for the major elements, ±6% for the REEs but between 4 and 7% for the minor and remaining trace elements based on the results of duplicate measurements on ten soil samples as well as duplicate measurements of the G-1 and SO-1 standards.

Statistical analyses

In order to investigate the elemental associations among the analyzed elements in the soil a Pearson *R* correlation analyses was applied to all 38 paddy-soil samples. Critical values of the correlation coefficients (r) were: 0.30 at $p \leq 0.05$; 0.40 at $p \leq 0.01$; 0.45 at $p \leq 0.005$; 0.50 at $p \leq 0.001$. Results that yield $p \leq 0.05$ were considered to be borderline statistically significant, while those that were significant at $p \leq 0.01$ were considered to be statistically significant. Results at $p \leq 0.005$ or $p \leq 0.001$ levels were assessed to be highly significant. The basic statistical parameters for each element and the statistical treatments mentioned above were performed using the original SPSS statistical software program (SPSS, Chicago, Ill.).

Results and discussion

The mean, median, range and standard deviation (SD) for the elemental concentrations in the paddy soil from Kočani Field are presented in Table 1. As the exposed lithologies in the surroundings of Kočani Field are predominantly composed of acidic to intermediate volcanic rocks (dacite ignimbrites, andesite ignimbrites, augite hornblende biotite andesite, andesitic tuffs and breccias) and, to a lesser extent, of metamorphic (amphybolites, gneisses, various shists, phylites and rare marbles) and sedimentary rocks (conglomerates, sandstones, claystones and limestones), while basic lithologies (gabbros and basalts) were found only sporadically, it is not surprising that the soil mineralogy and the elemental composition is closely related to those of the acidic and intermediate rocks of that region.

Mineralogy

On the basis of the XRD analyses, the paddy soil was found to consist mostly of quartz, plagioclase, muscovite-illite, ortoclase, and chlorite along with minor amphibole and kaolinite, while traces of calcite and dolomite were found only sporadically. There were no significant changes in the main mineral composition throughout the investigated area.

In addition to the natural minerals that were identified, a range of secondary products resulting from the surface-induced chemical degradation of the soil parent material and/or remobilization of the anthropogenically derived heavy metals was also detected. These included bixbyite (Mn_2O_3; JCPDS card no. 41-1442), anglesite ($PbSO_4$; JCPDS card no. 05-0577), lanarkite [$Pb_2(SO_4)O$; JCPDS card no. 33-1486], kremersite [$(NH_4K)_2FeCl_5 \times H_2O$; JCPDS card no. 28-0734], feroxihydrite (FeOOH; JCPDS card no. 22-0353), clinoclase [$Cu_3(AsO_4)(OH)_3$; JCPDS card no. 37-0447] and chrysocolla ($CuSiO_3 \times 2H_2O$; JCPDS card no. 03-0219). The secondary products, such as anglesite, lanarkite, clinoclase and chrysocolla, were detected in soil samples from Section VII, which is close to the Zletovska River. The presence of these diagenetic Pb and Cu minerals indicates that some of the heavy metal contamination is being remobilized.

Bulk soil geochemistry

The concentrations of the mean major elements (Si, Al, Fe, Mg, Ca, Na and K) of the paddy soil are close to or slightly lower than those of the mean upper crust reported by Wedepohl (1995) and Tylor and McLennan (1995). The trace elements analyzed during this study exhibit mean concentrations that are in general slightly above those which would be found in a profile of an average upper crust. The exceptions are Be, Nb, Sn, Ta, W, Mo and Th, which are depleted relative to mean concentrations in the average upper crust, and heavy metals such as Pb, Zn, As, Cd, Cu, Sb, Bi, Ag, Au and Hg, which in some soil samples exhibit considerably elevated concentrations that are several tenfold higher than those

Table 1 Descriptive basic statistics of the elemental contents in the paddy soil of Kočani Field

Elemental content	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	Na (%)	K (%)	Ti (%)	P (%)	Mn (%)	Cr (%)	Sc (μg g^{-1})	C_{TOT} (%)	S_{TOT} (%)	Ba (μg g^{-1})
Mean	28.41	7.98	4.26	0.93	1.90	1.68	2.14	0.54	0.11	0.13	0.006	16	1.59	0.06	762
Median	28.41	8.06	4.16	0.95	1.53	1.70	2.22	0.53	0.10	0.08	0.010	16	1.46	0.03	704
Minimum	25.14	6.45	2.70	0.59	0.67	1.11	1.14	0.37	0.06	0.03	0.000	12	0.70	0.01	297
Maximum	33.12	9.72	5.51	1.28	5.87	2.26	2.99	0.91	0.23	0.74	0.010	21	3.09	0.26	1631
SD	2.09	0.76	0.69	0.18	1.23	0.30	0.44	0.10	0.04	0.17	0.005	2	0.56	0.07	313

Elemental content	Be (μg g^{-1})	Co (μg g^{-1})	Cs (μg g^{-1})	Ga (μg g^{-1})	Hf (μg g^{-1})	Nb (μg g^{-1})	Rb (μg g^{-1})	Sn (μg g^{-1})	Sr (μg g^{-1})	Ta (μg g^{-1})	Th (μg g^{-1})	U (μg g^{-1})	V (μg g^{-1})	W (μg g^{-1})	Zr (μg g^{-1})
Mean	2.3	16.0	5.1	17.8	7.0	12.6	100	3.1	283	0.9	13.6	3.4	119	1.8	238
Median	2.0	16.4	4.4	17.4	6.9	12.2	104	3.0	194	0.9	12.7	3.0	112	1.8	229
Minimum	1.0	8.6	2.4	13.5	5.2	9.1	54	2.0	117	0.7	6.3	1.9	73	0.9	180
Maximum	4.0	21.3	11.1	23.2	10.6	16.3	150	5.0	694	1.3	25.9	5.6	182	3.3	366
SD	0.6	2.3	2.3	2.4	1.0	1.9	25	0.9	168	0.1	4.4	1.1	25	0.6	36

Elemental content	Y (μg g^{-1})	Mo (μg g^{-1})	Cu (μg g^{-1})	Pb (μg g^{-1})	Zn (μg g^{-1})	Ni (μg g^{-1})	As (μg g^{-1})	Cd (μg g^{-1})	Sb (μg g^{-1})	Bi (μg g^{-1})	Ag (μg g^{-1})	Au (μg kg^{-1})	Hg (μg g^{-1})	Tl (μg g^{-1})
Mean	33.6	0.68	33	128	206	21	11.4	0.9	0.6	0.4	0.3	17.8	0.08	0.38
Median	33.5	0.60	26	22	88	22	6.7	0.2	0.3	0.3	0.1	5.1	0.08	0.30
Minimum	24.1	0.30	15	11	53	9	3.1	0.1	0.1	0.1	0.1	0.2	0.02	0.10
Maximum	46.6	1.80	99	983	1,245	37	47.6	6.4	3.0	1.4	2.1	108.3	0.18	1.20
SD	5.9	0.39	20	260	310	7	11.3	1.7	0.7	0.3	0.5	24.6	0.04	0.28

Elemental content	La (μg g^{-1})	Ce (μg g^{-1})	Pr (μg g^{-1})	Nd (μg g^{-1})	Sm (μg g^{-1})	Eu (μg g^{-1})	Gd (μg g^{-1})	Tb (μg g^{-1})	Dy (μg g^{-1})	Ho (μg g^{-1})	Er (μg g^{-1})	Tm (μg g^{-1})	Yb (μg g^{-1})	Lu (μg g^{-1})
Mean	33	71	7.93	33.2	6.33	1.40	5.78	1.00	5.57	1.09	3.19	0.50	3.14	0.48
Median	32	68	7.71	33.5	6.25	1.38	5.59	0.98	5.55	1.11	3.26	0.51	3.20	0.49
Minimum	18	41	4.75	21.0	4.30	1.00	4.04	0.67	3.97	0.76	2.25	0.37	2.22	0.32
Maximum	50	103	11.50	45.9	8.70	1.91	7.84	1.47	7.86	1.52	4.30	0.69	4.20	0.65
SD	7	13	1.40	5.5	1.00	0.19	0.94	0.18	0.97	0.20	0.56	0.08	0.52	0.08

that would be found in an average profile of the upper crust.

Major elements

In terms of the major elements present in the paddy soil of Kočani Field, more than 75% of the macro-chemical components are accounted for by a Si-Al-Fe assemblage. This compositional relationship reflects a relatively high proportion of quartz, feldspars, muscovite-illite and chlorite in the soil samples, which is also suggested by the XRD analyses. These minerals are mostly derived from the acid to intermediate igneous rocks of the Osogovo and Plačkovica Mountains. The absence of carbonate minerals is reflected in the low Ca and Mg contents. However, the observed Ca and Mg concentrations could be related to the presence of feldspar and chlorite as well as to that of amphiboles and pyroxenes, which were also detected by XRD. The Na and K concentrations are partly related to the feldspar-muscovite-illite content and/or the presence of amphiboles. The major elemental composition of the paddy soil is close to that reported for acidic intermediate volcanites of the Zletovo-Kratovo and Sasa-Toranica ore districts by Stojanov, Serafimovski, Boev and Rakic (1995) and Aleksandrov, Serafimovski and Markov (1995), with the only exceptions being the lower content of K, Na and P. As these elements represent the major nutrients in agriculture (Jing, Wen, Guang, Qias, & Yan, 1990), their lower concentrations in paddy soil relative to the parent material could be attributed to crop removal as well to run-off and leaching (Yaron, Calvet, & Prost, 1996). Vegetation and conventional tillage may have an important influence on the chemical and biological processes in soil, such as accelerating the accumulation of organic matter and filtration rate, and increasing the surface acidity and extractable element concentrations (Karathansis & Wells, 1989).

Chemical partition of the major elements

The lack of a positive correlation of Si with most of the elements, with the exception of Na, Hf and Zr ($0.35 \le r \le 0.62$), suggests no preferred association of Si with the other elements. A zero to highly significant negative correlation ($0.0 \le r \le -0.78$) between Si and the other major elements (Al, Fe, Mg, Ca and K) as well as with the remaining trace elements, including REEs, indicates either that these elements have no affinity to Si and/or their removal from silicate phases during weathering and soil formation. A similar correlation pattern between Si and the other major elements was also found in the volcanic rocks of the Zletovo-Kratovo and Sasa-Toranica ore district (Stojanov et al., 1995; Aleksandrov et al. 1995, respectively). A significantly high correlation coefficient between Al and K ($r = 0.82$) suggests that these elements may have similar input sources and/or that they have a close association, predominantly in K-feldspars and muscovite-illite assemblages from the soil.

Trace elements

The most significant characteristics of the paddy soil from Kočani Field are highly elevated concentrations of Pb, Zn, As, Cd, Sb, Bi, Au, Hg, Tl, Cu and Mo in soil samples from Section VII in the vicinity of the Zletovska River (Fig. 2). On the basis of the Environmental Quality Standard for Soil (Natural Environmental Protection Agency of Slovenia; Rr. list RS 68/96) and the total concentrations of trace elements considered to be phytotoxically excessive levels in surface soils (Kabata-Pendias & Pendias, 1992), the measured concentrations of Pb, Zn, As and Cd are far above the threshold values. This strongly suggests potentially negative effects of the paddy soil in the vicinity of the Zletovska River on the growth of rice and other edible crops and/or on the human population due to the ingestion of food contaminated with heavy metals. Although the elevated concentrations of Ba, Sb, Bi, Au, Hg, Tl, Cu and Mo in the same soil samples were below the above-mentioned threshold values, their enrichment also suggests that the paddy soil close to the Zletovska River receives a comparatively high input of anthropogenically derived heavy metals. This heavy metal pollution is undoubtedly related to the irrigation of the paddy field with water from the Zletovska River, which in turn is considerably affected by the mining and milling operations and the weathering processes of tailing from the Pb–Zn Zletovo ore deposit. Many areas throughout the world have been shown to have heavy metal contamination in their soil, plants, waters and sediments as a result of metalliferous mining activities (see Adriano, 1986; Bird et al., 2003; Johansson, Xydas, Messios, Stoltz, & Greger, 2005; Jung, 2001; Korre et al., 2002; Lee et al., 2001; Li & Thorton, 1993, 2001; Ulrich, Ramsey, & Helios-Rybicka, 1999; Witte et al., 2004; Wong et al., 2002;). Metals associated with Pb–Zn polymetallic mineralization of the Zletovo-Kratovo ore district, which is drained predominantly by the Zletovska River and it tributaries, are Pb, Zn, As, Cd, Cu, Ag, Au and Ba and, to a lesser extent, W, Mo, U, Sb, Bi and Tl (Serafimovski & Aleksandrov, 1995). All of these metals are important ore-forming elements and are paragenetically related to the above-mentioned polymetallic mineralization. They can form their own minerals (sulfides, sulfosalts, sulfates, oxides) or enter as trace elements into the structure of the other ore and gangue minerals (Serafimovski & Aleksandrov, 1995).

Due to acid-mine drainage and the direct input of Zletovo Pb–Zn mine effluents of pH 3.4 with mean Pb concentrations of 66 mg l^{-1}, Zn at 39 mg l^{-1}, As at 128 mg l^{-1}, Cd at 176 mg l^{-1}, Cu at 677 mg l^{-1} and U at 396 mg l^{-1} (Serafimovski, Alderton, Mullen, & Fairall, 2004), the Zletovska River can be considered to be moderately to highly polluted relative to the Bregalnica River, which is used for the irrigation of the paddy soil of Kočani Field.

The highest concentrations of U and Th were found in the paddy soil between the villages of Sokolarci and Spančevo (samples V-1, V3 and VI-1, VI-2, VI-3; Fig. 2) and could be related to the U mineralization at Bajlovci and the U occurrences near the Sokolarci village. It is interesting to note that the paddy soils from Sections I, II, V and VII exhibit a very high content of (up to 108 mg g^{-1}) Au, which was attributed to the polymetallic epithermal mineralization of the Zletovo-Katovo ore district.

Elevated concentrations of some trace elements were also observed in the paddy soil of the central and eastern parts of Kočani Field (Fig. 1). These are related to the increased discharges of untreated municipal and domestic waste from the city of Kočani and the village of Orizari into the riverine system of the Kočanska and Orizarska Rivers, both of which are also used for the irrigation of paddy fields. The elevated concentrations of elements are above the median concentration values obtained for the Kočani paddy soil during this study (Table 1) and can be explained not only by irrigation with more or less polluted riverine water but also by an input of anthropogenically derived trace elements, possibly related to the use of various fertilizers and pesticides as well as through urban and traffic sources and atmospheric deposition. The use of commercial fertilizer and animal waste for manuring is indicated by the δ^{15}N values of the paddy soil and the rice which ranged from +2.0 to +12.5‰ (T. Dolenec et al., unpublished).

Chemical partition of trace elements

A significant characteristic of the paddy soil from Kočani Field is the very close association of heavy metals, such as Pb, Zn, As, Cd, Ag, Bi, Mo, Ba, Tl and Hg, as indicated by a highly significant correlation ($0.63 \leq r \leq 1$) between each of these metals. This correlation suggests their close link with the previously mentioned polymetallic mineralization as well as their common geochemical characteristics.

On the other hand, the highly significant correlation between Pb, Zn, As, Cd, Ag, Bi, Cu, Mo, Ba and Tl with Mn ($0.74 \leq r \leq 0.99$) indicates that these elements are bound in soil to Mn oxides/hydroxides. Their significant to highly significant positive correlation ($0.42 \leq r \leq 0.59$) with Fe further indicates a possible association of the mentioned trace elements with Fe oxides/hydroxides. It is known that Mn and Fe oxides/hydroxides are very effective scavengers for heavy metals in oxic environments (Arakel & Hongjun, 1992; Aubert, Probst, & Sille, 2004; Kabata-Pendias & Pendias, 1992; Taylor, McKenzie, Fordham, & Gillman, 1983; Wong et al., 2002). Arsenic and base metals are retained in typical sediments and soils, primarily through sorption to fine-grained Fe and Mn oxyhydroxide minerals that occur as grain coatings, film and clay minerals (Rose, Hawkes, & Webb, 1978). As the Mn oxides and Fe hydroxides were detected by XRD analyses in practically all of the paddy soil samples analyzed, we suggest that these minerals represent a major sink for the heavy metal contamination of the agricultural soil from the studied area. However, the riverine sediments of the Zletovska River were also coated with Fe and Mn hydroxides and also exhibited highly elevated Pb, Zn, Ag, Cd, Cu and Ag concentrations due to their attraction to the Fe/Mn oxyhydroxide phase (Serafimovski et al., 2004).

A highly significant positive correlation of Cr and Ni with Mg and with each other ($0.58 \le r \le 0.90$) suggests the presence of the former two elements in the lattice of such Mg-bearing minerals as amphiboles and pyroxenes, as also detected by XRD in several soil samples. The mineralized mafic and ultramafic lithologies, as well as metamorphic rock, which could be the main sources of these minerals, are also exposed in the drainage area of the Bregalnica River. Consequently, in the paddy soil, the presence of Ni and Cr seems to be associated mostly with the detritial fraction.

Rare earth elements

The concentrations of REEs in the paddy soil from Kočani Field are presented in Table 1. The mean RE elemental levels in the paddy soil were slightly higher relative to those reported by Use and Bacon (1978) for the mean concentrations of the average upper crust and for the soils. The relatively high amounts of REEs can be attributed to the predominantly granitic lithologies that are exposed in the drainage area of the Bregalnica and Zletovska Rivers as well as in the surroundings of Kočani Field. It is well known that granitic rocks contain a larger amount of light rare earth elements (LREEs: La-Sm) than other igneous rocks, such as basalts and andesites (Herman, 1970; Reiman & Carital, 1998 and references therein). Among the essential minerals, salic minerals preferentially concentrate the LREEs, and the femic minerals concentrate the heavy rare earth elements (HREEs: Gd-Lu). The REEs in the paddy soil seem to be released mainly from parent material during weathering and soil formation. Due to their low solubility and relative immobility in the upper crust, the REEs are very useful for studying sedimentary environments because sediments inherit the source rocks' REE composition profile and, therefore, carry information on the origin of those rocks (Ross, Guevara, & Arriberé, 1995). Fractionation and mobilization of the REEs during weathering could be related to geochemical reactions that involve changes in the pH values in soil and waters (Duddy, 1980; Ross et al., 1995).

The elevated levels of HREE content can be explained by the contribution of the mafic and ultramafic lithologies to soil formation. The preferential decomposition of femic minerals and calcic plagioclases relative to the more resistant sodic and potassium feldspars during weathering of the exposed lithologies in the drainage area of the Bregalnica River and its tributaries seems to result in an enrichment of HREEs to the paddy soil. This may be related to the irrigation of paddy fields with water from the Bregalnica River. Another source of HREEs is the amphiboles and pyroxenes present in the paddy soil.

A study of lateritic soils has shown that there is a preferential retention of LREEs onto the solid phases and preferential transport of the HREEs in the solution phase (Sholkowitz, 1992). REEs can also be enriched during the soil-formation processes, even if the source material is not granitic rock (Yoshida, Muramatsu, Tagami, & Uchida, 1998). In addition, REEs are used as fertilizer additives for the stimulation of the growth of cereals, vegetables, fruits and tea (Brown, Rathjen, Graham, & Tribe, 1990; Yuan, Shan, Huai, Wen, & Zhu, 2001). Phosphatic fertilizer added to agricultural soils could thus be a source of REEs as well as of U and Th (Tsumura & Yamasaki, 1993; Yoshida et al., 1998). Although the data for REE concentrations in soils are limited compared with those in rocks and meteorites (Yoshida et al., 1998), we suggest that the observed concentrations of REEs in paddy soil are generally attributed to the concentrations of these elements in predominantly acidic and intermediate igneous rocks, which are the main source materials for the paddy soil of Kočani Field. The possible contribution of REEs due to the application of phosphate fertilizers seems to be negligible.

Chemical partition of REEs

The Pearson correlation indicates a different chemical combination of REEs. It is interesting that we did not obtain a statistically significant positive correlation between REEs and Fe and/or Mn, suggesting that in the paddy soil of Kočani Field Fe and Mn oxides/hydroxides are not important as the carrier phase, although several studies have shown that REEs in soils were bound to Fe and Mn oxides (Aubert et al., 2004; Land, Öhlander, Ingri, & Tunberg, 1999; Walter, Nahon, Flecoteaux, Girard, & Melfi, 1995). A highly significant correlation ($0.60 \le r \le 0.85$) of La, Ce, Pr and Nd with Al and indicates the importance of alumosilicate minerals as a carrier phase of most of the LREEs. On the other hand, a highly significant correlation ($0.61 \le r \le 0.81$) of La, Ce, Pr and Nd with Be, Rb, Nd and Ga as well as with Ta and Sn ($0.63 \le r \le 0.73$) suggests that these elements may also be concentrated in plagioclases, K feldspars and other minerals, such as zircon, rutile, ilmenite, as well as in other silicates related to granitic rocks and/or sulfidic mineralization.

Another characteristic is the highly significant correlation of Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu ($0.70 \le r \le 0.98$) with Y, and, to lesser extent, with Sc ($0.60 \le r \le 0.77$), as well as with Mg ($0.45 \le r \le 0.62$) and Cr ($0.61 \le r \le 0.69$). Such correlations indicate that HREEs are associated with some accessory minerals, such as monacite, xenotime, and garnets, as well as with amphiboles and pyroxenes derived from intermediate and/or basic lithologies.

Conclusions

The multi-elemental (Pb, Zn, As and Cd) contamination of the paddy soil from the western part of Kočani Field, indicated by concentrations far above the critical values of these elements reported by various environmental protection agency, reveals a long-term contamination due to irrigation with acid mine drainage into the Zletovska River. Paddy soil in the vicinity of the Zletovska River also exhibits elevated concentrations of Ba, Cs, Th, U, V, Mo, Cu, Sb, Bi, Ag, Au, Hg and Tl, which are above the established median concentrations for these elements in the soil samples of Kočani Field.

The anthropogenic input of heavy metals to the paddy soil from the central and eastern parts of Kočani Field can be attributed to irrigation with more or less contaminated water from the Kočanska and Orizarska Rivers, with the latter resulting from the input of municipal and domestic waste. However, a possible contamination from fertilization processes, transport activities and atmospheric deposition should also be taken into account.

The main carrier phase of several trace elements, with the exception of the REEs, in the studied soil are Fe and Mn oxides/hydroxides, which were also detected by XRD analyses. The distribution and enrichment of REEs in paddy soil is supposed to be controlled by the distribution of K and Al for LREEs and Mg for HREEs.

To clarify the heavy metal pollution of the agricultural soil from the whole Kočani Field and the mechanisms governing bio-availability and heavy metal uptake by plants, since these latter two processes are more dependent on the speciation of the metals than the total content, further studies are required.

Acknowledgements This research was financially supported by the Ministry of Higher Education, Science and Technology of the Republic of Slovenia (Bilateral Project between Republic of Macedonia and Slovenia for the years 2004–2005), and Geoexp, d.o.o., Tržič, Slovenia. Constructive comments by the editor and the reviewer helped improve the paper. Thanks to are extended to Dr. Paul McGuiness for the language corrections.

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