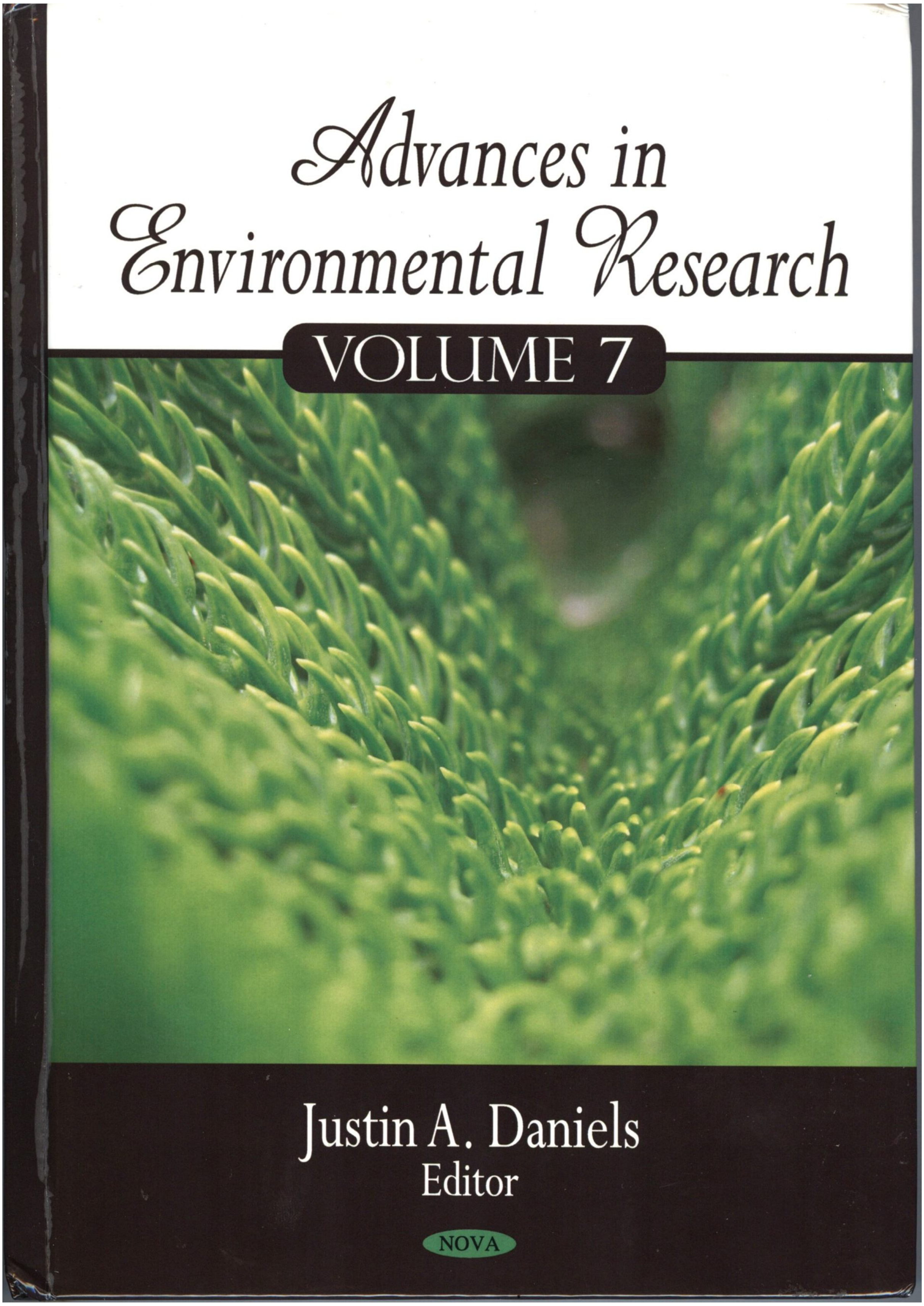

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JUSTIN A. DANIELS
EDITOR

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Chapter 2

GEOCHEMICAL CHARACTERISTICS AND ENVIRONMENTAL ASSESSMENT OF PADDY FIELDS: A CASE STUDY OF KOČANI FIELD (REPUBLIC OF MACEDONIA)

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ABSTRACT

Contamination of soils with heavy metals is widespread and induces a long-term risk to ecosystem health. This research focuses on the heavy metal contamination of the paddy soils from Kočani Field (Republic of Macedonia) originating from irrigation of the paddy fields by riverine water impacted by past and present base-metal mining activities and acid mine drainage.

The distribution and mobility characteristics of heavy metals (Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn) in Kočani paddy soil samples from Kočani Field were evaluated. Very high concentrations of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn were found in the paddy soils samples in the vicinity of the Zletovska River (western part of Kočani Field). The river drains the acid mine waters and tailing effluents from the Pb-Zn mine in Zletovo and it is used for irrigation of the surrounding paddy fields. The detected total concentrations of these metals are far above the threshold values considered to be phytotoxically excessive for the surface soil. Heavy metal contamination of Kočani paddy soils was also assessed using geoaccumulation index, contamination factor and contamination degree. The results of the applied indexs confirmed a very high contamination status for Kočani paddy soils. The mobility potential of the investigated heavy metals in paddy soil samples decreases in the following order: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag.

INTRODUCTION

Soil is a specific component of the biosphere because it is not only treated as geochemical sink for contaminants, but also as a natural buffer system controlling the transport of chemical elements and substances into the atmosphere, hydrosphere and biota. It has always been important to humans and their health, especially as a resource for shelter and food production. Unfortunately, the problem of heavy metals contaminating soils has become widespread globally over the past two decades and represents a long-term risk to ecosystem health and quality. Base-metal mining activities together with milling and grinding operations, concentrating ore and the disposal of tailings, acid mine and mill wastewater are all important sources of heavy metals entering into the environment (Adriano, 1986). Consequently, very high concentrations of heavy metals can be found in and around abandoned and active mines, and these can affect nearby agricultural soils, food crops, riverine water and stream sediments (Adriano, 1986; Bird et al., 2003; Jung, 2001; Jung & Thornton, 1997; Korre et al., 2002; Lee et al., 2001; Witte et al., 2004; Wong et al., 2002).

Accurate measurements of the heavy metal content of investigated soils are required to evaluate the potential risk of pollution. But only the soluble, exchangeable and chelated metal species in the soils are bioavailable in individual soil plant systems (Kabata-Pendias & Pendias, 2001). Therefore, the assessment of environmental risks requires measurements of the total amount of heavy metals in the soils and consequently, the amounts of the heavy metals present in the available fractions, too. A widely used modified method for the identification and evaluation of the availability or binding forms of heavy metals in soils is the sequential extraction procedure proposed by Tessier et al. (1979).

The excessive accumulation of heavy metals in agricultural soils around mining areas is a great concern because soil containing various elements is a primary nutrient medium for plants. Food crops grown in contaminated agricultural soils can accumulate elevated concentrations of heavy metals, presenting a potential health risk to local inhabitants (Adriano, 2001; McLaughlin et al., 1999; Pruvot et al., 2006; Zhuang et al., 2009). Several studies have reported that heavy metal pollution in mining areas has damaged the health of local inhabitants (Kachenko & Singh, 2006; Liu et al., 2005).

Numerous worldwide studies have investigated the heavy metal concentrations present in soils (Adriano, 1986; Jung, 2001; Jung & Thornton, 1997; Kabata-Pendias & Pendias, 2001; Korre et al., 2002; Lee et al., 2001; Liu et al., 2005; Lu & Zhang, 2005; Simmons et al., 2005; Witte et al., 2004, Wong et al., 2002; Yang et al., 2004). Although mining is one of the most important industries in the Republic of Macedonia, studies about heavy metal concentrations in soils descending from historical or current base-metal mining activities are scarce (Dolenec et al., 2007) and little is known about the distribution of heavy metals in soils in different parts of the Republic of Macedonia.

Kočani Field, located in eastern Macedonia, has a long history of base-metal mining (in the Pb-Zn Zletovo-Kratovo and Sasa-Toranica ore districts) and paddy rice (*Oryza sativa* L.) and maize (*Zea mays* L.) are the main agricultural products of the region. Previous investigations have shown that the riverine water from the Zletovska River and Bregalnica River, which are used to irrigate Kočani Field, is contaminated with heavy metals as a result of the inflow of acid mine water and untreated effluents from the ore processing facilities (Alderton et al., 2005). Metals usually enter into agricultural soils through irrigation processes

(Chen et al., 1997), and for this reason large areas of agricultural soil can become contaminated. Thus, the paddy soils in the Kočani Field area could also contain elevated levels of heavy metals, introducing risk to human and animal health.

The major aims of this study are:

- to investigate the mineralogy and the physicochemical characteristics of the paddy soils;
- to detect the total heavy metal concentrations and distribution in paddy soil samples and compare these results with permissible levels of heavy metals in arable soils;
- to apply the sequential extraction method (leaching procedure) to determine the bioavailability of heavy metals in the soil samples studied; and
- to assess the soil contamination by using various environmental indices, including the geoaccumulation index, contamination factor and degree of contamination.

GEOACCUMULATION INDEX (I_{GEO})

The geoaccumulation index was originally introduced by Müller (1969, 1979) to assess metal pollution by comparing the current and preindustrial metal concentrations within sediments. It can be also used to assess whether or not soils have been contaminated by heavy metals. I_{geo} is expressed by the following equation:

$$I_{geo} = \log_2 C_N / 1.5\, B_N,$$

where C_N is the measured concentration of the element in the pelitic sediment fraction (< 2 μm) and B_N is the content of the element in the fossil argillaceous sediment ("average shale") (Turekian & Wedepohl, 1961). The factor 1.5 is initiated to analyse the natural fluctuations of a given substance in the environment as well as small anthropogenic influences.

Table 1. Index of geoaccumulation (I_{geo}) and contamination level

I_{geo}	I_{geo} class	Contamination level
< 0	1	Uncontaminated
0–1	2	Uncontaminated to moderately contaminated
1–2	3	Moderately polluted
2–3	4	Moderately to highly polluted
3–4	5	Highly polluted
4–5	6	Highly to very highly polluted
> 5	7	Very seriously polluted

Hu et al., 2006.

In our study, we employed the modified calculation given by Loska et al. (2003), where C_N is the measured concentration of the examined metal N in the soils and B_N is the concentration of the studied metal N in the Earth's crust (Taylor & McLennan, 1995); because soil is a part of the layer of Earth's crust and its chemical composition is related to that of the crust.

I_{geo} values were classified into seven classes ranging from unpolluted to very seriously polluted (Table 1). Grade 6 indicated a 64-fold enrichment over the background values (Singh et al., 1997).

CONTAMINATION FACTOR (c^i_f) AND CONTAMINATION DEGREE (C_{DEG})

The contamination factor and contamination degree were defined by Hakanson (1980) to evaluate soil contamination by relating the concentrations in the surface layer of sediments to pre-industrial levels (average shale):

$$c^i_f = \frac{c^i_{0-1}}{c^i_n},$$

where c^i_{0-1} is the mean content of metals from at least five sampling locations and c^i_n is the pre-industrial value of each individual metal.

Instead of the pre-industrial values of individual metals, we used the concentrations of elements in the Earth's crust as a reference value, similar to the I_{geo} factor. This modification has been employed by Loska et al. (2003). The contamination factor was divided into four categories (Hakanson, 1980):

$c^i_f < 1$	Low contamination factor indicating low contamination
$1 \leq c^i_f < 3$	Moderate contamination factor
$3 \leq c^i_f < 6$	Considerable contamination factor
$6 \leq c^i_f$	Very high contamination factor

The contamination degree of the environment was represented as the sum of the contamination factors for all elements examined and was also divided into four classes (Hakanson, 1980):

$C_{deg} < 8$	Low degree of contamination
$8 \leq C_{deg} < 16$	Moderate degree of contamination
$16 \leq C_{deg} < 32$	Considerable degree of contamination
$32 \leq C_{deg}$	Very high degree of contamination

MATERIALS AND METHODS

Study Area

The Republic of Macedonia is located in southeastern Europe, in the heart of the Balkan Peninsula (Figure 1). It lies between 41°50′ latitude and 22°00′ longitude and has a surface of 25,713 km^2. The country borders Serbia in the north, Albania in the west, Greece in the south and Bulgaria in the east.

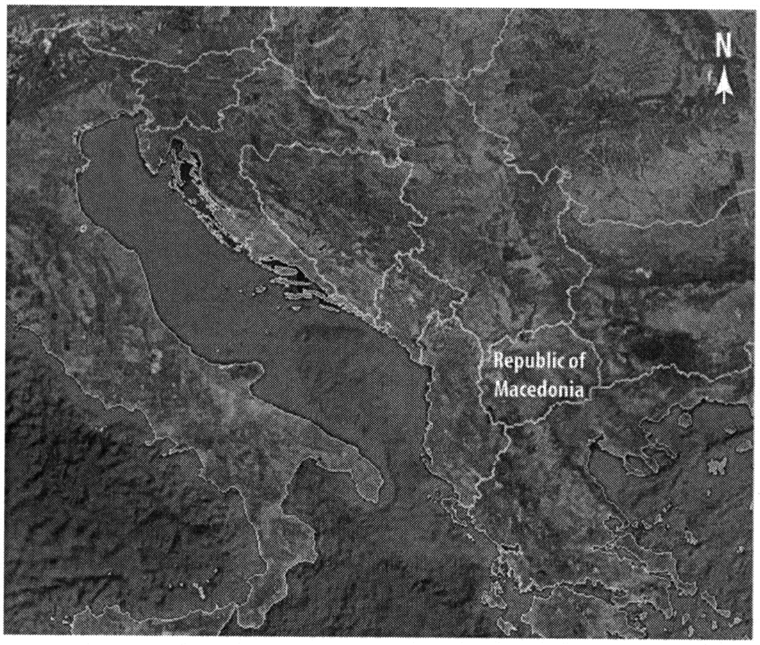


Figure 1. Geographical location of Republic of Macedonia.

Kočani Field is situated in eastern Macedonia, about 32 km from the city of Štip and 115 km from the capital city Skopje. With an average length of 35 km and width of 5 km, Kočani Field lies in the valley of the Bregalnica River between the Osogovo Mountains in the north and Plačkovica Mountains in the south (Figure 2).

The wider region is well known as an agricultural and mining province, with significant thermal activity. The most important agricultural products in the region are rice (*Oryza sativa* L.) and maize (*Zea mays* L.). The centre of the region, the city of Kočani (Figure 2), was founded on the southern foothills of the Osogovo Mountains. The municipality of Kočani area comprises 28 settlements with 38,092 inhabitants.

The Bregalnica River, together with its tributaries, represents the principal drainage system in the investigated area and is an important water supply for the irrigation of surrounding paddy fields.

The main tributaries of the Bregalnica River are the Kamenica River in the northeastern part of the study area and the Zletovska River to the west of Kočani Field (Figure 2). The Kamenica River drains the northeastern part of the Bregalnica River basin and flows directly into the artificial Lake Kalimanci, which was constructed for the irrigation of the paddy fields during the dry season. It also drains the untreated mine effluents from the Pb-Zn polymetallic ore deposit Sasa (Figure 2). The Zletovska River originally drained the central part of the Zletovo-Kratovo volcanic complex as well as the untreated mine effluents from the Pb-Zn Zletovo mine and its ore processing facilities. Both rivers are used by local farmers for the irrigation of the nearby paddy fields.

The Kočanska and Orizarska Rivers are two small tributaries of the Bregalnica River (Figure 2) that drain the southern part of the Osogovo Mountains, as well as the untreated municipal wastes and domestic sewage of the cities of Kočani and Orizari. The riverine water of the Kočanska and Orizarska Rivers is also used to irrigate the paddy fields located in the northeastern part of Kočani Field.

Figure 2. Study area, Kočani Field.

Repeated water sampling of the Zletovska River and its tributaries showed marked chemical variations of Ag (0.1–0.2 µg l^{-1}), As (1.9–173.3 µg l^{-1}), Cd (10–240 µg l^{-1}), Cu (10–1054.3 µg l^{-1}), Mo (0.3–0.9 µg l^{-1}), Ni (10–50 µg l^{-1}), Pb (50–80 µg l^{-1}), Sb (0.8–1.4 µg l^{-1}) and Zn (40–70070 µg l^{-1}) (Alderton et al., 2005), which can be explained by the water flow conditions, the varying degrees of mine edits and tailing dam leaching effluent inputs from the Pb-Zn Zletovo mine into the riverine waters. The host lithology is dominated by silicate minerals and thus there is little chemical buffering to counteract the high acidity in the waters.

The pollution of the Zletovska River is also easily recognisable from the field. The bed sediments are coated with Fe and Mn oxides/hydroxides, which are the major sink for contamination with several trace elements (Dolenec et al., 2007).

The detected concentrations of the heavy metals studied in the water samples from the Bregalnica River are lower than those in the water samples from the Zletovska River and its tributaries (mean values): Ag (0.1 $\mu g\ l^{-1}$), As (6.8 $\mu g\ l^{-1}$), Cd (3.3 $\mu g\ l^{-1}$), Cu (746.6 $\mu g\ l^{-1}$), Mo (0.9 $\mu g\ l^{-1}$), Ni (10 $\mu g\ l^{-1}$), Pb (20 $\mu g\ l^{-1}$), Sb (1.6 $\mu g\ l^{-1}$) and Zn (90 $\mu g\ l^{-1}$) (Alderton et al., 2005). The Kamenica, one of the most severely polluted tributaries of the Bregalnica, drains untreated mine effluents from the Pb-Zn polymetallic ore deposit at Sasa directly into the artificial Lake Kalimanci. Upon mixing with the lake water, the concentrations of the pollutants decline. For that reason, when the Bregalnica River flows out from the Kalimanci Lake, it is less polluted than the Kamenica and Zletovska Rivers (Alderton et al., 2005).

These investigations have confirmed that the water from the Zletovska and Bregalnica Rivers is contaminated with heavy metals as a result of the discharge of acid mine waters and untreated effluents from the ore processing facilities in the Zletovo-Kratovo and Sasa-Toranica districts (Alderton et al., 2005). The highly elevated concentrations of metals found in the water samples could also be related to the mineralogy of the individual deposits (Pb-Zn Zletovo-Kratovo and Sasa-Toranica ore deposits). The metallic sulphides were the primary source of heavy metals in the surrounding waters.

In addition, the abovementioned high concentrations of heavy metals in water samples from Kočani Field were comparable with the heavy metal concentrations in the waters from various mining regions around the world (Lee et al., 2001, Jung & Thornton 1997; Marqués et al., 2001; Moore et al., 1991; Yan Gao & Bradshaw, 1995).

SASA-TORANICA ORE DISTRICT

The Sasa-Toranica ore district lies in the Osogovo Mountains, 10 km from the city of Makedonska Kamenica and Lake Kalimanci (Figure 2). It is established as one of the largest ore districts within the Besna Kobila Osogovo Tassos metallogenetic zone, occupying an area of about 200 km^2. The important Pb and Zn ore bodies are usually found in quartz/muscovite/graphitic schists, greenschists and marbles. The mineral association consists of sphalerite, galena, pyrrhotine, pyrite, chalcopyrite, molybdenite, bornite, stibnite and local cassiterite, accompanied by a series of bismuth and silver minerals as well as non-ore minerals such as skarn minerals, calcites, manganese-calcites and quartz. The formation of the Sasa-Toranica deposit is related to the late Alpine tectonic, magmatic and mineralisation processes.

The main geological features of the area are three metamorphic complexes cross-cut by the Strumica diorite formation: leucocratic gneisses and Tertiary magmatites. The metamorphic complexes consist of Precambrian high crystalline metamorphic rocks, Pre-Silurian greenschists and Silurian-Devonian quartz/muscovite/graphitic schists, calc schists, marbles and phyllites (Serafimovski & Aleksandrov, 1995).

The Sasa mine has been in production for over 45 years, yielding 90,000 tons of high quality Pb-Zn concentrate annually and numerous tons of tailings material. Ore is concentrated by the flotation processes at the mine, and tailings material is accumulated in a dam in a narrow valley just below the mine (Alderton et al., 2005).

ZLETOVO-KRATOVO ORE DISTRICT

The Zletovo-Kratovo Pb-Zn ore district is situated 5 km northwest of the Zletovo village and about 7 km from the city of Probistip (Figure 2). It is located in the central part of the Zletovo-Kratovo volcanic complex. Pb and Zn mineralisation occurs in dacitic ignimbrites, the most common volcanic rocks of the area. The mineral association comprises galena (principal ore mineral) and sphalerite, with subordinate pyrite, lesser amounts of siderite and chalcopyrite and occasionally pyrrhotine, marcasite and magnetite. Minor occurrences of U-mineralisation have also been discovered (pitchblende).

The Zletovo-Kratovo district is also intimately associated with the Tertiary volcanism and hydrothermal activity. The major lithologies in the area are presented by andesites, dacites, dacitic ignimbrites and volcanic tuffs (Serafimovski, 1990; Serafimovski & Aleksandrov, 1995; Tasev, 2003).

The Zletovo mine has an annual capacity of 350,000 tons of Pb-Zn concentrate (8% Pb and Zn) and significant concentrations of Ag, Bi, Cd and Cu. Ore is concentrated by the flotation processes at Probistip, and tailings material is stored in two impoundments in the adjacent valleys (Alderton et al., 2005).

PADDY SOIL SAMPLING AND ANALYSIS

The sampling of the paddy soils was carried out in autumn 2005. The sampling locations are displayed in Figure 5. Paddy soil samples were assembled at 38 locations from seven profiles across the Kočani Field (Sections I–VII).

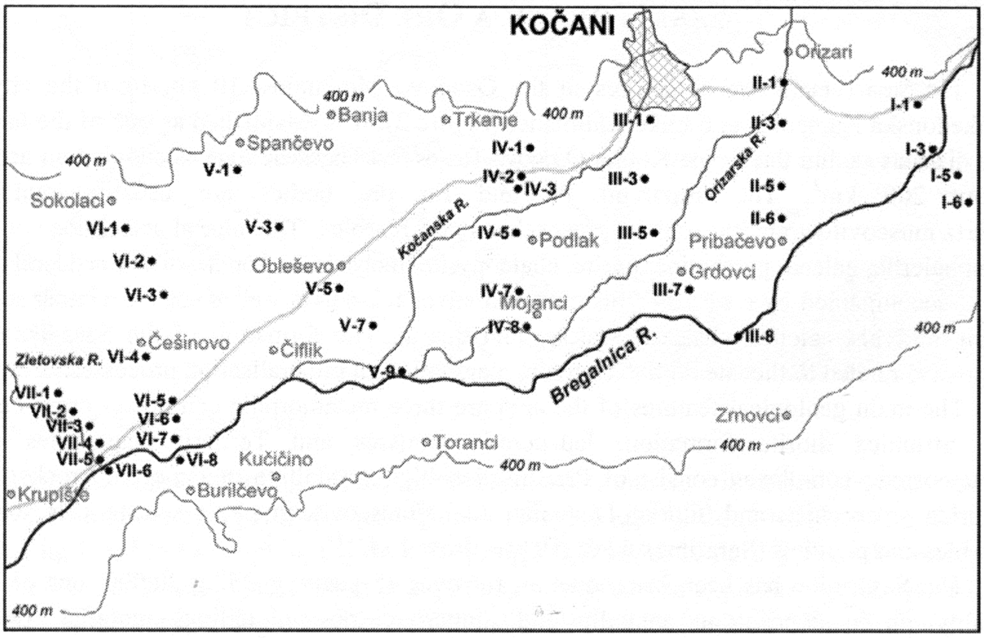


Figure 3. Paddy soil sampling locations (Kočani Field).

Near surface paddy soils (0–20 cm in depth) were collected because it is impossible to distinguish the A, B and C horizon in the agricultural soil. The paddy soils were sampled using a plastic spade to avoid any heavy metal contamination. Each paddy soil sample comprised a composite of five sub-samples taken within a 1×1 m^2 square.

The paddy soil samples were air dried at 25°C for one week and sieved through a 2 mm polyethylene sieve to remove plant debris, pebbles and stones. Afterwards, they were ground in a mechanical agate grinder into a fine powder for subsequent X-ray diffraction (XRD), physicochemical parameters and geochemical analysis.

The mineralogy of the paddy soil samples was defined at the Department of Geology, (Ljubljana, Slovenia) by an X-ray powder diffractometry using a Philips PW 3710 diffractometer and Cu$K\alpha$ radiation. The samples were scanned at a rate of 2°C per minute over the range 2–70°C (2θ). The results were analysed 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).

The physical and chemical soil properties (pH, CEC, total organic C, conductivity and loss on ignition) were determined at the Agricultural Institute of Slovenia (Kmetijski Inštitut Slovenije), following established methods.

All paddy soil samples were analysed in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Vancouver, B.C., Canada). Heavy metals were detected after extraction for 1 h with 2-2-2-HCl-HNO_3-H_2O at 95°C by inductively coupled plasma mass spectrometry (ICP-MS).

The accuracy and precision of the heavy metal paddy soil analyses were assessed using an international reference material such as Canadian Certified Reference Material Project (CCRMP) SO-1 (soil) and United States Geological Survey (USGS) G-1 (granite). The analytical precision and accuracy were between 4 and 7% for the heavy elements. This was indicated by the results of the duplicate measurements in 10 soil samples as well as duplicate measurements of the G-1 and SO-1 standards.

SEQUENTIAL EXTRACTION PROCEDURE

Selected paddy soil samples (I-3, II-6, III-5, VI-4 and VII-2, Figure 4) were also analysed for the chemical partitioning (binding forms) of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn using a sequential extraction procedure (Li et al., 1995; Tessier et al., 1979). The paddy soil samples, weighing 1 g, were placed in screw-top test tubes. To each sample 10 ml of leaching solution was added. Afterwards, the caps were screwed on and the tubes were subjected to the appropriate extraction procedure depending on the stage of the leach. For the sequential leaching, the sample was leached, centrifuged, decanted and washed and then the residue was leached again in a five-step process from the weakest to strongest solution or chemical reagent. The procedure is presented in Table 2.

Table 2. Sequential extraction procedure (fractions and chemical reagents)

Step	Fraction	Chemical reagents
1	Water soluble	Distilled water
2	Exchangeable and carbonate bound	1 m ammonium acetate
3	Organic (oxidisable)	0.1 m sodium pyrophosphate
4	Reducible	Cold 0.1 m hydroxylamine hydrochloride
5	Reducible plus residual	Hot 0.25 m hydroxylamine hydrochloride

After the sequential extraction procedure, the concentration of the analysed elements in the solution was measured using a Perkin Elan 6000 ICP-MS for the determination of 60 or more elements. A QA/QC protocol incorporated a sample duplicate to monitor the analytical precision, a reagent blanks measured background and an aliquot of in-house reference material was used to monitor accuracy.

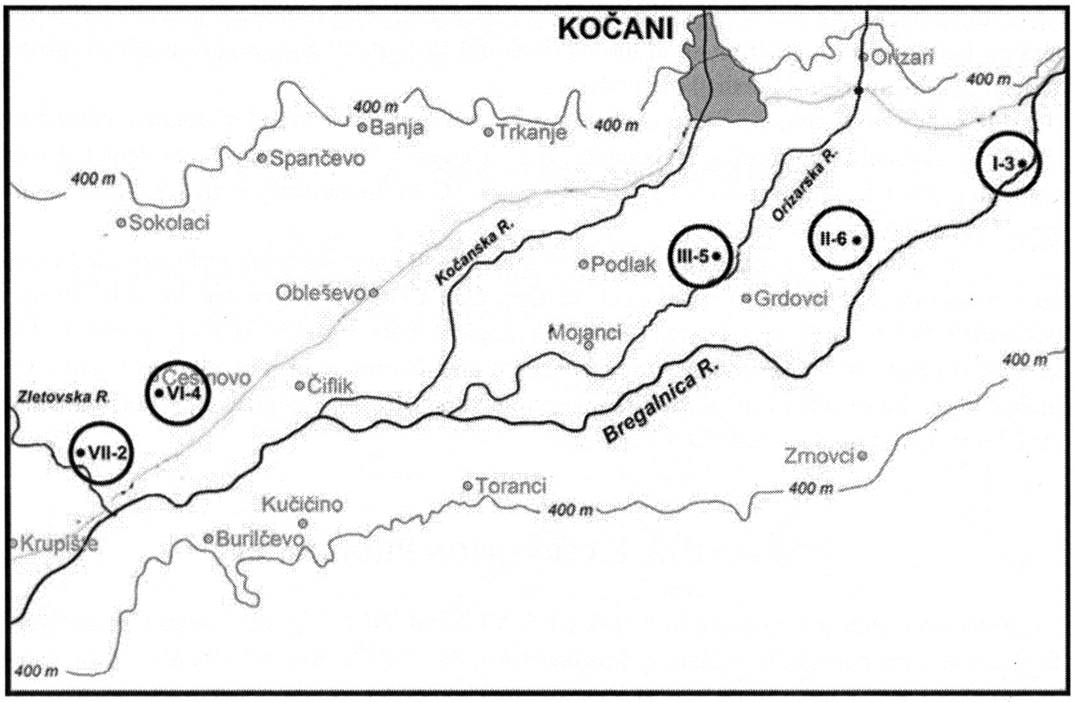


Figure 4. Paddy soil sampling locations for sequential extraction procedure.

STATISTICAL ANALYSIS

To investigate the elemental associations among the analysed elements in the soil we employed *t*-test analysis, which revealed significant differences at $\alpha \leq 0.05$ in paddy soil samples between the Sections I to VII for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn.

The basic statistical parameters for each element and the statistical calculations mentioned above were accomplished by the original statistical software program (Statistica VI).

RESULTS AND DISCUSSION

The paddy soil of Kočani Field was thought to originate from the composite material of the sediment derived from the igneous, metamorphic and sedimentary rocks located in the wider area of Kočani. The sediment material was transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (Dolenec et al., 2007).

Exposed lithologies in the area 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, metamorphic (amphibolites, gneisses, various schists, phyllites and rare marbles) and sedimentary rocks (conglomerates, sandstones, claystone and limestone), whereas basic lithologies (gabbros and basalts) were found only sporadically. Consequently, the soil mineralogy and elemental composition are closely related to the acidic and intermediate rocks of the Kočani region (Dolenec et al., 2007).

MINERALOGY OF THE PADDY SOIL

According to the XRD analyses, the paddy soil mostly consists of the following minerals: quartz, plagioclase, muscovite-illite, orthoclase and chlorite along with minor amounts of amphibole and kaolinite, meanwhile the traces of calcite and dolomite were found only sporadically. There were no significant changes in the main mineral composition identified throughout the investigated area. In addition, a range of secondary products resulting from the surface-induced chemical degradation of the soil parent material and/or remobilisation of the anthropogenically derived heavy metals was also detected. These secondary minerals were 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 $(NH_4K)_2FeCl_5 \cdot H_2O$; JCPDS card no. 28-0734), ferrihydrite ($FeOOH$; JCPDS card no. 22-0353), clinoclase ($Cu_3(AsO_4)(OH)_3$; JCPDS card no. 37-0447) and chrysocolla ($CuSiO_3 \cdot 2H_2O$; JCPDS card no. 03-0219). The secondary products, such as anglesite, lanarkite, clinoclase and chrysocolla, were mostly detected in soil samples from Section VII, which is located close to the Zletovska River. The presence of these diagenetic Pb and Cu minerals indicated that some anthropogenic heavy metals were being remobilised.

PHYSICOCHEMICAL CHARACTERISTICS OF THE PADDY SOIL

The physicochemical characteristics are given in Table 3. The overall area was characterised by weakly acidic pH (5.2–6). The conductivity was in the range of 6.61 to 51.09 mS/m. The cation exchange capacity values were relatively moderate, with an average value of 20.7 mmol/100 g. Total organic carbon ranged from 0.7–2.95% and LOI values were moderate (5.1–13.5%).

Table 3. Information about physical-chemical characteristics of the paddy soil samples from Kočani Field

	pH	**CEC (mmol/100g)**	**C organic (%)**	**Conductivity (mS/m)**	**Loss on ignition (%)**
range	5.2-6.0	11.4-38.6	0.70-2.95	6.6-51.1	5.1-13.5
mean	5.5	20.7	1.70	21.6	7.6

HEAVY METAL CONCENTRATIONS IN THE PADDY SOIL

Table 4 shows the concentrations of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn determined in the paddy soil samples from Kočani Field together with the assumed permissible level of heavy metals adopted by the National Environmental Protection Agency of Slovenia (Uradni list RS, 1996), typical heavy metal contents of comparable soils around the world (Bowen, 1979) and the maximum allowable concentrations (MAC) of heavy metals in agricultural soil proposed by the German Federal Ministry of Environment (1992). The permissible level of heavy metals and MAC of heavy metals signify the values above which toxicity is considered possible. Table 5 summarizes the descriptive statistical parameters (mean, median, range and standard deviation).

Heavy metal concentrations in the paddy soil samples are also presented in the Figure 5.

Antimony (Sb)

The average Sb value for soils of 1 μg g^{-1} was proposed by Kabata-Pendias & Pendias (2001). Increased amounts of Sb, ranging from 1.4 to 12.6 μg g^{-1}, were found in the household garden soils collected in the vicinity of the Dalsung Cu-W mine in Korea (Jung et al., 2002).

The Sb concentrations defined in the paddy soil samples from Kočani Field were 0.1–3 μg g^{-1}, with a mean value of 0.6 μg g^{-1} (Table 4, Table 5 and Figure 5). These concentrations correspond to the abovementioned Sb values for soils (Kabata-Pendias & Pendias, 2001).

Table 4. Total heavy metal concentrations in the paddy soil of Kočani Field

Element (µg/g)	Ag	As	Cd	Cu	Mo	Ni	Pb	Sb	Zn
Location									
I-1	0.7	3.4	0.1	14.9	0.5	15.6	19.1	0.2	53
I-3	0.2	18.7	0.5	40.3	1	31.1	81.3	0.6	162
I-5	0.1	5.6	0.2	32	0.5	29.7	18.8	0.2	85
I-6	0.7	5.1	0.1	25.9	0.5	25.7	13.1	0.2	70
II-1	0.1	6.1	0.2	26.7	0.5	29.4	26.6	0.2	93
II-3	0.1	5	0.1	29.1	0.4	28.2	21	0.2	81
II-5	0.1	5.3	0.2	24.9	0.5	22	20.8	0.3	80
II-6	0.1	11.8	0.3	25.7	0.6	20.8	32.1	0.8	100
III-1	0.1	6.1	0.2	27.2	0.6	27.5	18.1	0.2	89
III-3	0.1	3.1	0.4	32.6	0.3	25.4	20.4	0.2	95
III-5	0.1	8.3	0.2	32.7	0.5	36.8	23.9	0.2	102
III-7	0.7	8.2	0.2	16.8	0.3	13.9	22.1	0.4	64
III-8	0.7	4.2	0.1	21.8	0.5	20.8	10.5	0.1	64
IV-1	0.1	3.8	0.1	28.5	0.7	21.7	13.9	0.2	74
IV-2	0.7	3.5	0.2	17.1	0.6	17.3	17.9	0.2	68
IV-3	0.7	4.3	0.3	23.4	0.5	24.1	19.1	0.2	102
IV-5	0.1	6.3	0.2	25.7	0.6	25.5	15.4	0.2	94
IV-7	0.1	8.1	0.2	26.2	0.7	26.1	17	0.2	83
IV-8	0.1	5.9	0.2	28.9	0.6	28.6	18.1	0.2	96
V-1	0.1	10	0.2	19	0.7	9.1	30.8	0.3	85
V-3	0.1	7.8	0.2	20	0.6	9.5	26.9	0.2	73
V-5	0.1	6.5	0.2	25	0.6	22.8	22.1	0.2	98
V-7	0.1	6.4	0.2	22.8	0.4	17.2	17.8	0.3	67
V-9	0.1	4.5	0.2	20.8	0.3	16.7	19.2	0.3	69
VI-1	0.1	5	0.2	21.4	0.3	17.1	24.1	0.3	71
VI-2	0.1	6.8	0.3	24.5	0.6	9.9	39.4	0.2	76

Table 4 (Continued)

VI-3	0.1	10.1	0.3	34.1	0.6	22.3	35.4	0.3	86
VI-4	0.1	9.9	0.3	28.6	0.5	25.2	41.4	0.4	105
VI-5	0.1	10.5	0.3	25	0.5	21.7	39.6	0.4	94
VI-6	0.1	11.5	0.3	28.3	0.6	22	45.1	0.5	107
VI-7	0.7	7.7	0.1	19.3	0.5	16.4	20	0.4	66
VI-8	0.7	6.2	0.2	29.5	0.5	30.5	16.3	0.2	72
VII-1	0.9	22.2	2.7	48.8	1.3	10.9	411.9	1.8	531
VII-2	2	42	5.6	99.4	1.8	15.4	892.4	2.5	1134
VII-3	1.4	35.1	4.5	89.4	1.4	15.5	726.7	2	893
VII-4	2.1	47.6	6.4	80.1	1.8	11.9	983.1	3	1245
VII-5	1.6	39.6	5	68.3	1.6	14.1	745.1	2.2	928
VII-6	0.6	20.7	2	47.1	0.9	19.8	295.7	1	384
1	0.1-8	6	0.35	30	/	/	35	1	90
2	/	20	1	60	10	50	85	/	200
3	/	/	1.5	60	/	/	100	/	200

(1) typical contents of Ag, As, Cd, Cu, Mo, Ni, Sb, Pb and Zn in comparable soils around the world;
(2) limits for elemental concentrations in soil (Environmental Protection Agency of Slovenia (Uradni list RS 1996);
(3) maximum allowable concentrations (MAC) of trace elements in agricultural soils proposed by the German Federal Ministry of the Environment (1992).

Table 5. Descriptive basic statistic parameters for heavy metals in the paddy soils of Kočani Field

Elements (μg/g)	Ag	As	Cd	Cu	Mo	Ni	Sb	Pb	Zn
Mean	0.306	11.4	0.9	33	0.682	21.0	0.57	128	206
Median	0.100	6.7	0.2	26	0.600	21.7	0.25	22	88
Minimum	0.066	3.1	0.1	15	0.300	9.1	0.10	11	53
Maximum	2.100	47.6	6.4	99	1.800	36.8	3.00	983	1245
S.D.	0.541	11.3	1.7	20	0.389	6.8	0.72	260	310

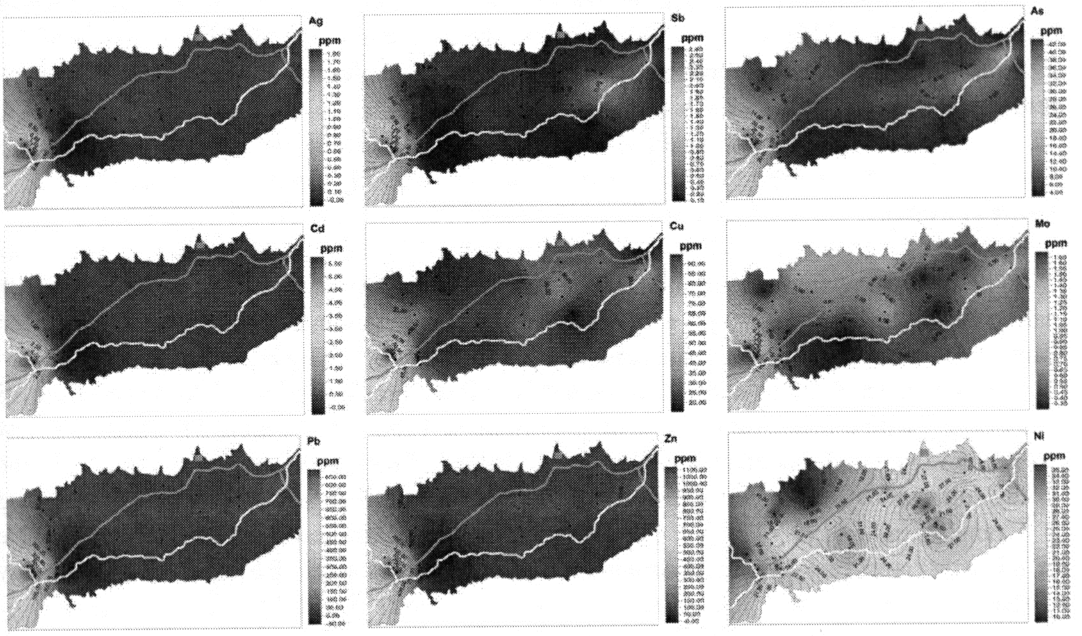


Figure 5. Heavy metal concentrations in the Kočani paddy soils.

Arsenic (As)

As values in uncontaminated, untreated soils rarely exceed 10 μg g^{-1} (Adriano, 1986). In agricultural soil impacted by past mining activities around the Songcheon Au-Ag mine (South Korea), the As concentrations were ranged from 53 to 490 μg g^{-1}, with a mean value of 230 μg g^{-1} (Lee et al., 2005).

The concentrations of As in the paddy soil samples from Kočani Field are much lower, ranging from 3.1 to 47.6 μg g^{-1} (mean 11.4 μg g^{-1}) (Table 4, Table 5 and Figure 5). However, very high concentrations of As in the range of 20.7 to 47.6 μg g^{-1} were found in the paddy soils samples from Section VII. The determined values significantly exceeded the typical As content within comparable soils around the world (6 μg g^{-1}) reported by Bowen (1979), as well as the limit of 20 μg g^{-1} reported by the Environmental Protection Agency of Slovenia (Table 4).

Cadmium (Cd)

In agricultural soil, the Cd background level is around 1 μg g^{-1} or lower (Whitby et al., 1978). According to Jung and Thornton (1996), the mean concentrations of Cd in soils around the area contaminated by past Pb-Zn mining in northwest Korea were 11.8 μg g^{-1} (0–15 cm depth).

In this study, the Cd concentrations in the paddy soil samples were in the range of 0.1 to 6.4 μg g^{-1}, with a mean value of 0.9 μg g^{-1} (Table 4, Table 5 and Figure 5), which is less than the global average Cd content in soil (0.35 μg g^{-1}) reported by Bowen (1979). Highly increased Cd concentrations (max. 6.4 μg g^{-1}) measured in the paddy soil samples from Section VII substantially exceeded the background Cd level of agricultural soil (1 μg g^{-1} or less) reported by Whitby et al. (1978) as well as the limit emission values of 1 μg g^{-1} and 1.5 μg g^{-1}, suggested by the environmental protection agencies of Slovenia and Germany, respectively (Table 4).

Copper (Cu)

The total Cu content determined in average world soil samples is around 30 μg g^{-1}, with values ranging from 2 to 250 μg g^{-1} (Bowen, 1979). In contaminated soils around the Pb-Zn Sambo mine in Korea, the Cu values ranged up to 1400 μg g^{-1} (Jung & Thornton, 1996).

The Cu concentrations defined in the paddy soil samples in Kočani Field ranged from 15 to 99 μg g^{-1} with a mean value of 33 μg g^{-1} (Table 4, Table 5 and Figure 5), which is below the average global Cu content in soils, i.e., 30 μg g^{-1} (Bowen, 1979). The Cu values in the paddy soil samples in Section VII were much higher than the calculated median value (26 μg g^{-1}), ranging from 47 to 99 μg g^{-1}. Consequently, these values exceed the limit emission value of 60 μg g^{-1} reported by the environmental protection agencies of Slovenia and Germany (Table 4).

Lead (Pb)

Agricultural soils around the world have a wide range of Pb content that depends on a number of factors, such as the parent material and anthropogenic input (Adriano, 1986). In China, Yang et al. (2004) found very high Pb concentrations (from 325 to 4317 μg g^{-1}) in paddy soils located near the Lechang Pb-Zn mine.

Pb concentrations ranging from 11 to 983 μg g^{-1} (mean 128 μg g^{-1}) (Table 4, Table 5 and Figure 5) were found in the paddy soil samples from the Kočani Field. The highest concentration values were, however, measured in the samples from Section VII, which exhibited Pb concentrations ranging from 296 to 983 μg g^{-1} (Table 4). This is above the median values of Pb content in contaminated agricultural soil reported by Lee et al. (2005) and Liu et al. (2005) and the limits proposed by the environmental protection agencies of Slovenia and Germany (Table 4).

Molybdenum (Mo)

The worldwide mean Mo value is 1.8 μg g^{-1}, as calculated by Kabata-Pendias & Pendias (2001). They also reported about Mo accumulation up to 38 μg g^{-1} (range 22.2 to 38.2 μg g^{-1}) in surface soils at an Mo processing plant in Chile.

The concentrations of Mo in the paddy soils from our study ranged from 0.3 to 1.8 μg g^{-1} (mean 0.68 μg g^{-1}) (Table 4, Table 5 and Figure 5), much lower than the limit value of 10 μg g^{-1} proposed by the Environmental Protection Agency of Slovenia (Table 4).

Nickel (Ni)

Soils across the world contain Ni within a broad range from 0.2 to 450 μg g^{-1} (Kabata-Pendias & Pendias, 2001). In Manali (southern India), an area affected by industrial activities, the Ni content in soils ranged from 11.8 to 78.8 μg g^{-1} (Krishna & Govil, 2008).

Ni concentrations ranging from 9 to 37 μg g^{-1}, with the mean value of 21 μg g^{-1} (Table 4, Table 5 and Figure 5), were measured in the paddy soil samples from the Kočani Field. The determined Ni values do not exceed the limit values for Ni in the soils (50 μg g^{-1}) reported by the Environmental Protection Agency of Slovenia (Table 4).

Silver (Ag)

The average Ag content for soils established by Bowen (1979) ranges from 0.01 to 8 μg g^{-1}. Kabata-Pendias & Pendias (2001) calculated that soils contaminated by past mining activities in Wales contain up to 9 μg g^{-1} of Ag.

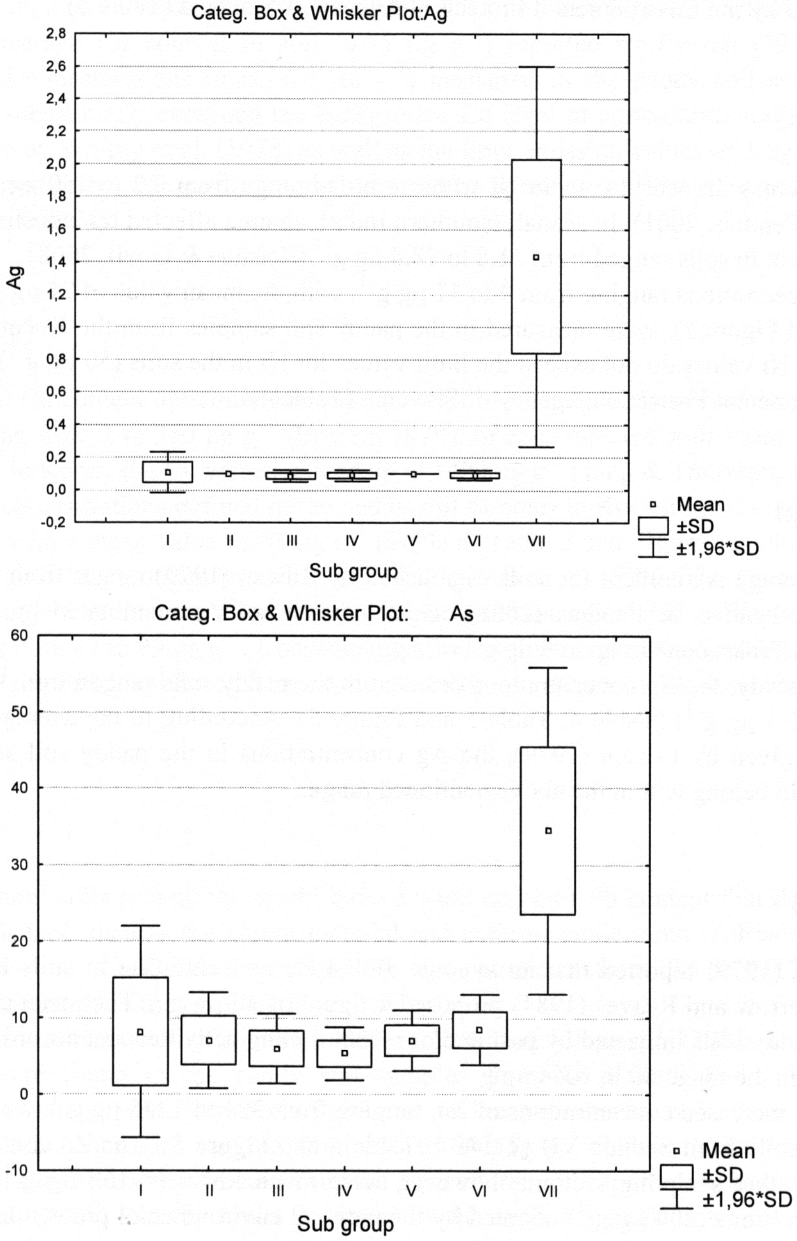
In our study, the Ag concentrations detected in the paddy soils ranged from 0.1 to 2.1 μg g^{-1} (mean 0.3 μg g^{-1}) (Table 4, Table 5 and Figure 5). According to the average worldwide Ag values given by Bowen (1979), the Ag concentrations in the paddy soil samples from Kočani Field belong within the abovementioned range.

Zinc (Zn)

Bowen (1979) reported that an average global Zn concentration in soils is 90 μg g^{-1}, whereas Berrow and Reaves (1984) proposed a figure of 40 μg g^{-1}. The mean concentration of Zn in paddy soils impacted by past and/or recent mining activities are, according to Lee et al. (2001), in the range 60 to 1064 μg g^{-1}.

Highly increased concentrations of Zn, ranging from 384 to 1245 μg g^{-1}, were defined in the paddy soils from Section VII (Table 4, Table 5 and Figure 5). The Zn content in paddy soils from other sampling sections, however, were much lower (< 162 μg g^{-1}). Compared with the Zn limits (200 μg g^{-1}) adopted by the national environmental protection agencies of Slovenia and Germany, Zn concentrations are predominantly raised only in the soil samples from Section VII (Table 4).

In order to compare the distribution of each heavy metal in the paddy soil samples between the Sections I–VII, whisker plots were employed (Figure 6). All soil samples in Sections I–VI had similar levels of median values, suggesting that their intersection differences were not substantial, while significant variations existed only between Section VII and the other sections. The only exception and consequently difference was is the distribution of the Ni values in the paddy soil samples.



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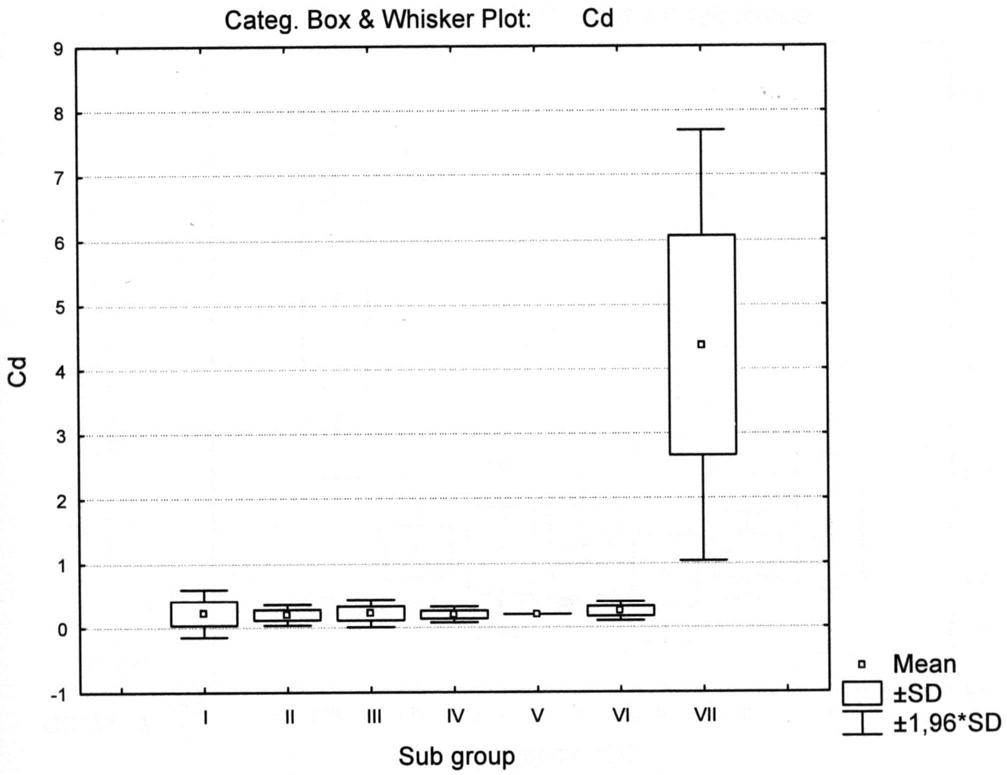

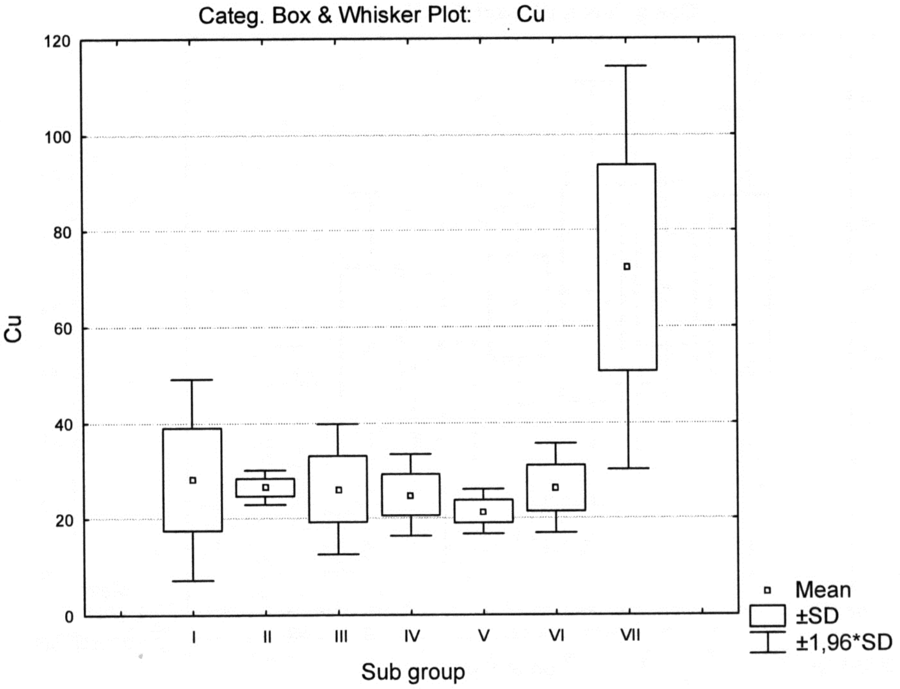

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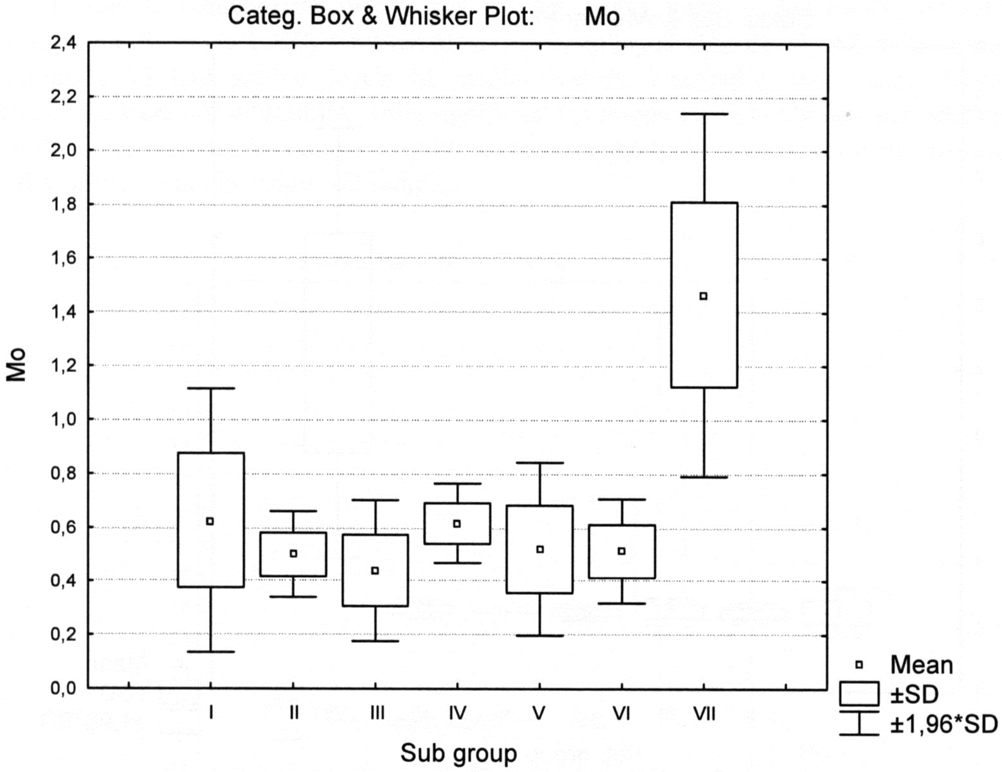

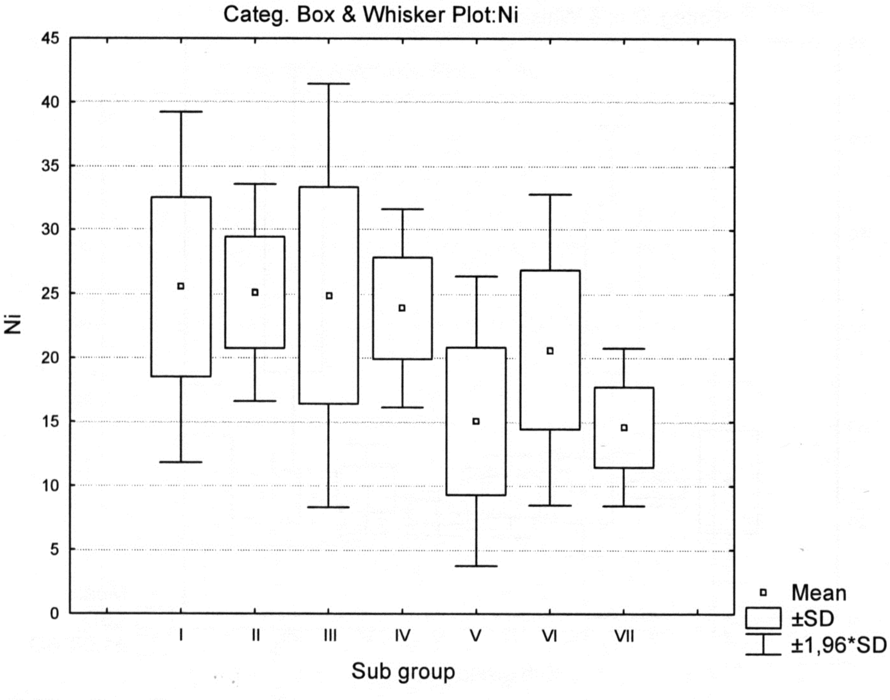

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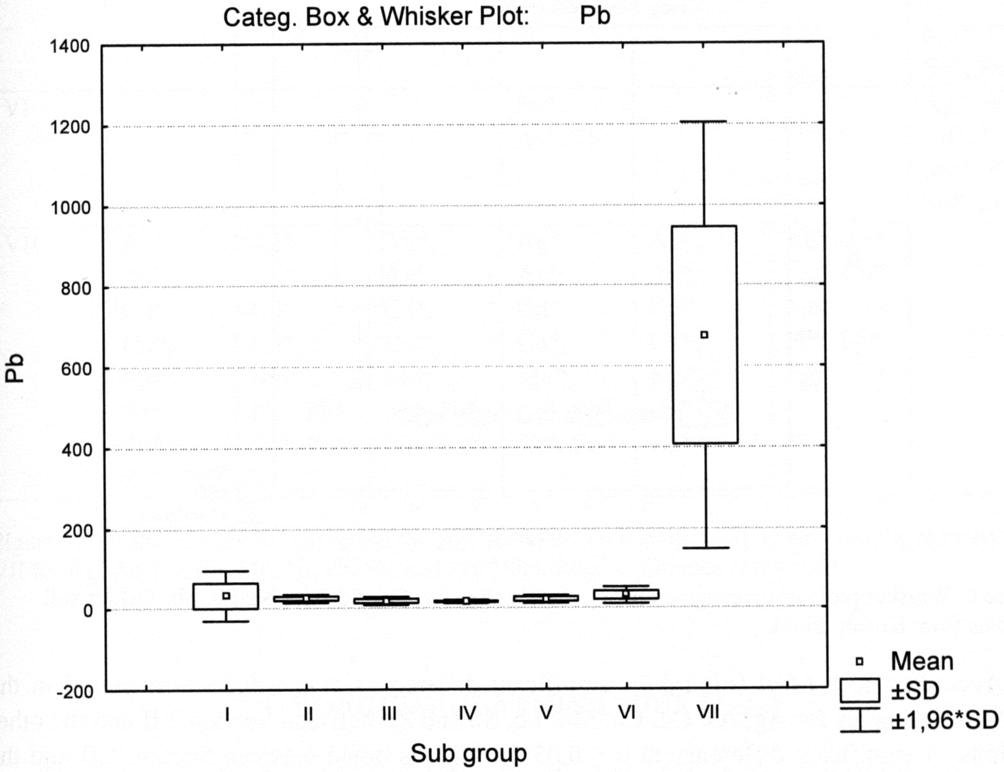

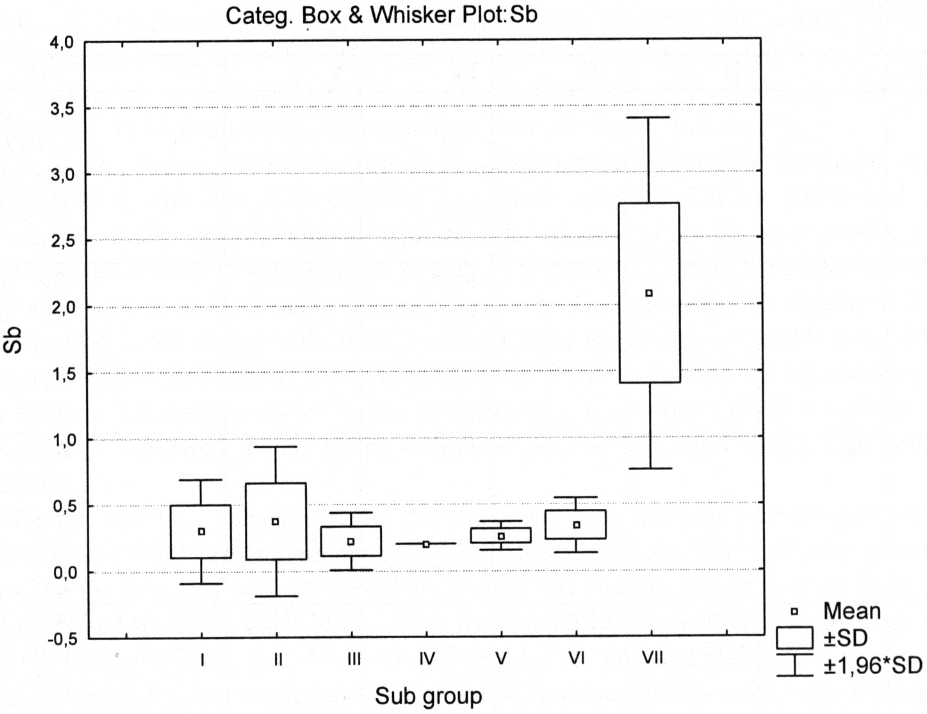

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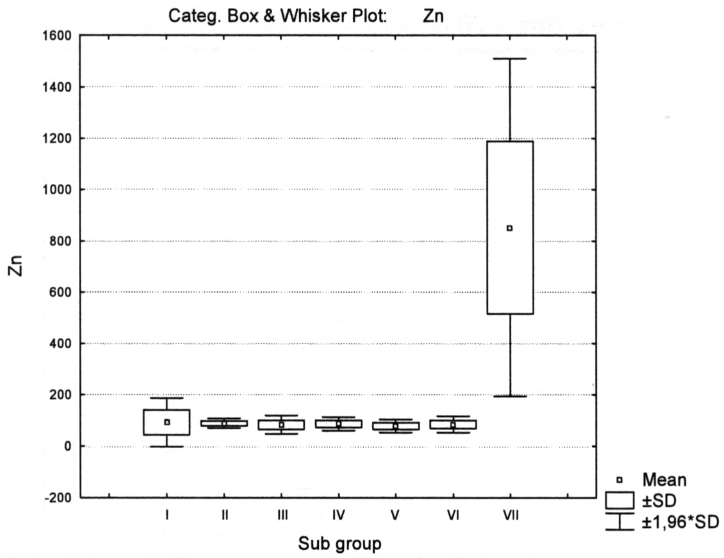

Figure 6. Whisker plots of investigated heavy metals (Ag, As, Cu, Cd, Mo, Ni, Pb, Sb, Zn) for soil samples from Kočani Field.

According to a *t*-test (Figure 7), significant differences at $\alpha \leq 0.05$ were found in the paddy soil samples for Ag, As, Cd, Cu, Mo, Pb, Sb and Zn between Section VII and the other sections. A significant difference at $p \leq 0.05$ for Ni was noted between Section VII and the other sections.

Section	I	II	III	IV	V	VI	VII
I					Ni*		Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*
II				Mo*, Pb*	Ni*, Cu*		Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*
III				Mo*		Pb*	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*
IV		Mo*, Pb*	Mo*		Pb*, Ni*, Sb*	Pb*, As*, Sb*	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*
V	Ni*	Ni*, Cu*	Pb*	Pb*, Ni*,			Ag*, As*,

				Sb*			Cd*, Cu*, Mo*, Pb*, Sb*, Zn*
VI				Pb*, As*, Sb*			Ag*, As*, Cd*, Cu*, Mo*, Pb*, Sb*, Zn*
VII	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*	Ag*, As*, Cd*, Cu*, Mo*, Ni*, Pb*, Sb*, Zn*	Ag*, As*, Cd*, Cu*, Mo*, Pb*, Sb*, Zn*	Ag*, As*, Cd*, Cu*, Mo*, Pb*, Sb*, Zn*	

Figure 7. Results of *t*-test, which reveal the significant differences at $\alpha \leq 0.05$ between the sections I to VII for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb, and Zn. *Significant difference at $\alpha \leq 0.05$.

GEOACCUMULATION INDEX (I_{GEO})

The I_{geo} values for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn in the studied soils are shown in Figure 8. Reference values (upper continental crust, Taylor & McLennan, 1995) for the investigated heavy metals were 0.05 μg g^{-1} for Ag, 1.5 μg g^{-1} for As, 0.098 μg g^{-1} for Cd, 25 μg g^{-1} for Cu, 1.5 μg g^{-1} for Mo, 20 μg g^{-1} for Ni, 20 μg g^{-1} for Pb, 0.2 μg g^{-1} for Sb and 71 μg g^{-1} for Zn. The calculated I_{geo} values ranged from –2.9 (Mo) to 5.4 (Cd).

The Mo I_{geo} values were the lowest of all metals studied. Therefore, the paddy soils were uncontaminated with Mo. The obtained I_{geo} values revealed that all paddy soil samples examined were also uncontaminated with Ni. The I_{geo} results for Cu were mostly negative, except the values from the paddy soils located in Section VII, which have been characterised as uncontaminated to moderately contaminated. The I_{geo} values for Sb displayed a distinct contamination level: paddy soils from Section I were moderately polluted, from Section II uncontaminated to moderately contaminated, from Sections III and VI uncontaminated and from Section VII moderately to highly polluted. The I_{geo} values for Zn were lower than 0 (Sections I–VI) and 3–4 for the paddy soils from Section VII, signifying a high pollution of these soils.

The calculated I_{geo} values revealed that the paddy soils from the central and eastern parts of the Kočani Field were moderately to highly polluted with As. The maximum values of I_{geo} determined in the paddy soil samples from Section VII classified these soils as highly to very highly polluted with As. The Ag I_{geo} values indicated uncontaminated to moderately polluted paddy soil samples from Sections I–VI and very highly polluted paddy soils in Section VII. The I_{geo} results denoted highly to very seriously polluted paddy soils with Cd and Pb in Section VII and uncontaminated to moderately contaminated paddy soils with Cd and Pb in Sections I–VI.

In general, the paddy soils from Kočani Field were characterised as highly to very seriously polluted with Cd, Pb, Ag and As, moderately to highly polluted with Zn and Sb, uncontaminated to moderately contaminated with Cu and uncontaminated with Ni and Mo.

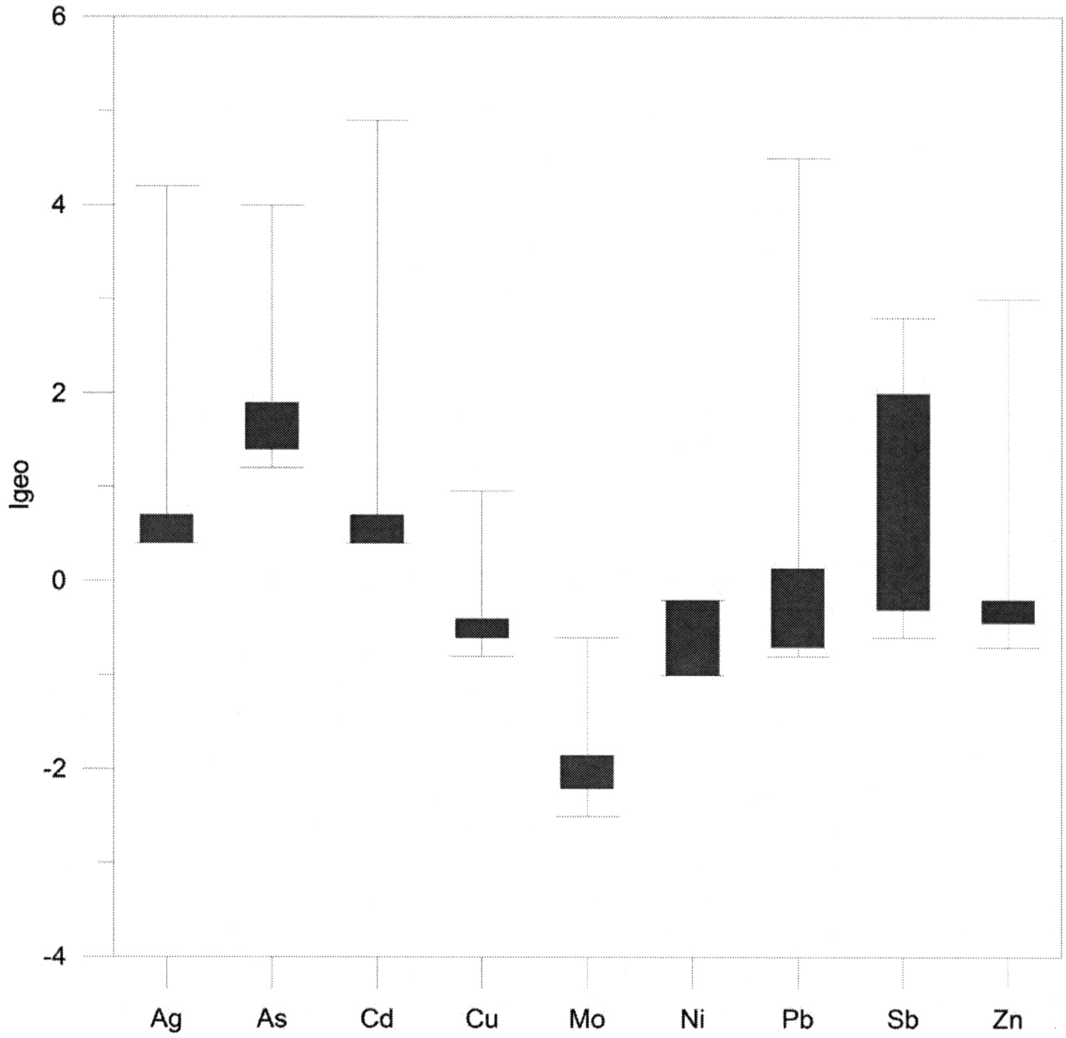

Figure 8. I_{geo} values for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn in the studied soils.

CONTAMINATION FACTOR (c^i_f) AND CONTAMINATION DEGREE (C_{DEG})

According to contamination factor (c^i_f) values (mean), the paddy soils from the Kočani Field were classified as slightly (low) contaminated with Mo, moderately contaminated with Cu and Ni, considerably contaminated with Ag, Pb, Sb and Zn and very highly contaminated with Cd and As (Figure 9). The highest Ag, As, Cd, Pb, Sb and Zn c_f^i values (very high contamination factor) and the highest Cu and Mo c_f^i values (moderate contamination factor) were defined in the paddy soil samples from Section VII. The highest Ni c_f^i values (moderate contamination factor) were determined in Section I. The calculated c_f^i values entirely confirmed the I_{geo} results.

The complete assessment of the paddy soil contamination was evaluated by degree of contamination (C_{deg}). The C_{deg} (mean) of the studied soils samples was 36.2 (Table 6), which signified very high contamination. Cd and As represented the largest contamination degree factors with 23% and 20%. Ag and Pb both contributed 16%, Sb 9% and Zn 8%. Cu, Ni and Mo negligibly influenced the soil contamination with 4%, 3% and 1%, respectively.

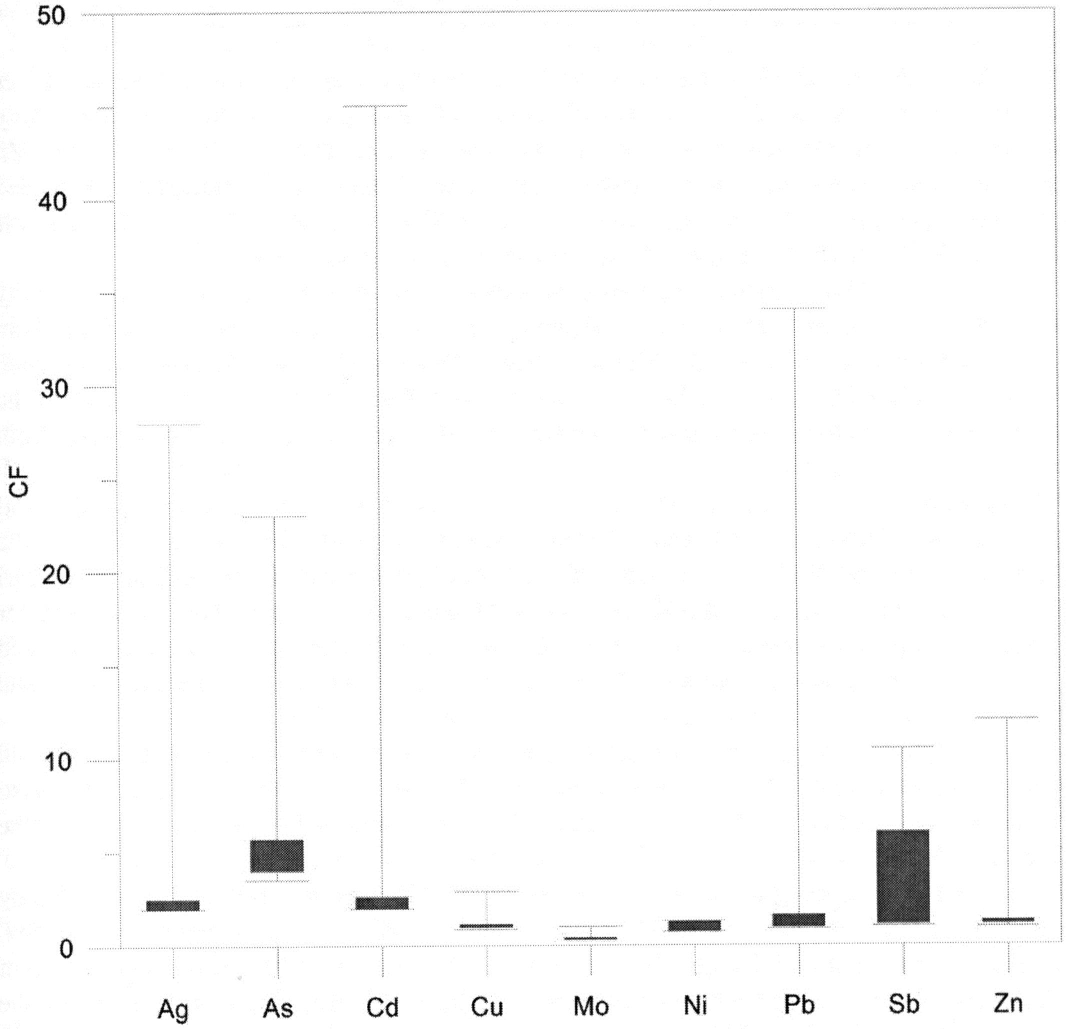

Figure 9. Contamination factor (c_f^i) values for the paddy soils from the Kočani Field.

Table 6. Contamination factors and degrees for heavy metals in the paddy soils from Kočani Field

Metal	Range	Average
Ag	2–28	5.8
As	3.5–23	7.3
Cd	2–45	8.3
Cu	0.9–2.9	1.3
Mo	0.3–1	0.4
Ni	0.7–1.3	1.1
Pb	0.9–34	5.9
Sb	1–10.5	3.4
Zn	0.9–12	2.7
Degree of contamination	12.2–157.7	36.2

The paddy soil samples from Section VII, located in the vicinity of the Zletovska River and Zletovo-Kratovo ore district, received a comparatively higher input of anthropogenically derived heavy metals than other parts of the Kočani area. The As, Cd, Cu, Pb and Zn concentrations determined in the paddy soils from Section VII significantly exceeded maximum permissible levels. The distinction between heavy metal contents in Section VII and the other sections was also confirmed by statistical analysis.

The studied heavy metals are important ore-forming elements and are paragenetically associated with the Pb-Zn polymetallic mineralisation in the Zletovo-Kratovo ore district, an area predominately drained by the Zletovska River (Dolenec et al., 2007). Thus, the pollution is undoubtedly related to the irrigation of the paddy fields with the riverine water from the Zletovska River, which drains acidic mine waters and untreated mining waste effluents from the Zletovo-Kratovo mine.

Elevated concentrations of As, Cd, Cu, Pb and Zn were observed in other paddy soil sections (especially Sections V and VI). This elevation originates from the discharges of the untreated municipal and domestic waste from the city of Kočani and the village of Orizari into the riverine systems of the Kočanska and Orizarska Rivers, which are both used for irrigation purposes (Dolenec et al., 2007). The increased concentrations of the investigated heavy metals could also be explained by the agricultural application of various fertilisers and pesticides, urban and traffic sources and atmospheric deposition.

Although the concentrations of Ag, Mo, Ni and Sb were below the mentioned threshold values, their enrichment in the paddy soil samples near the Zletovska River was also noticeable. This situation confirms the higher input of heavy metals in the area around the Zletovska River.

The high anthropogenic impact on the paddy soils in Section VII was demonstrated by the calculation of the following environmental indexes: geoaccumulation index, contamination factor and degree of contamination. The elevation of the heavy metals present in the paddy soil samples from the other parts of Kočani Field was similarly verified with the results of the environmental indexes. From an environmental point of view, it is evident that the paddy soil samples from Section VII represent a serious risk to the surrounding ecosystems.

SEQUENTIAL EXTRACTION PROCEDURE

Figure 10 represents the results of the sequential extraction procedure (heavy metal binding forms).

The mobility and bioavailability of heavy metals in paddy soils mostly depend on their types of binding forms. The water soluble fraction (1) includes easily soluble metal species which are highly mobile and potentially bioavailable in the environment. The leaching of metals in this fraction represents a major environmental concern (Filgueiras et al., 2002).

The exchangeable fraction (2) contains (electrostatically) weakly bound heavy metal species, which can be released through ion exchange processes, and metals that are precipitated with carbonates. Changes in ionic composition, influencing adsorption–desorption reactions or lowering the pH, could cause the remobilisation of metals from this fraction. Metals in the exchangeable fraction are the most readily available for plant uptake and thereby very labile (Filgueiras et al., 2002).

The oxidisable fraction (3) corresponds to elements occurring as oxidisable minerals and organically bound metals. Under oxidising conditions, this fraction releases metals linked to organic matter within the soil matrix into the solution (Filgueiras et al., 2002). The reducible fraction (4) comprises unstable metal forms connected to amorphous Mn hydroxides. The elements strongly bind to these hydroxides are thermodynamically very unstable under reducing conditions (Filgueiras et al., 2002).

In the reducible + residual fraction (5), the metals are linked to amorphous Fe hydroxides (reducible part) and under reducing conditions are expected to be released in nature. The residual fraction contains naturally occurring crystalline Mn hydroxide minerals, which could hold heavy metals within their crystalline matrix. Heavy metals in residuals are unlikely to be discharged under normal environmental conditions. Therefore, the metals associated with this fraction can only be mobilised as a result of weathering (Dean, 2007; Filgueiras et al., 2002; Fuentes et al., 2004; Kazi et al., 2002).

In all paddy soil samples, Ag was dominantly associated with the reducible + residual fraction (5) and then, in minority, with the reducible fraction (4) (Figure 10a). This agrees with Kabata-Pendias & Pendias (2001), who demonstrated that despite several mobile complexes Ag is immobile in soils if the pH is above 4. The percentage of Ag present in the fractions followed the order: water soluble fraction (1) < exchangeable fraction (2) < oxidisable fraction (3) < reducible fraction (4) < reducible + residual fraction (5).

The highly relevant fraction of As in the paddy soil samples was bound to the oxidisable (3) and reducible + residual fraction (5). The association of As with the reducible fraction (4) was also highly significant (Figure 10b). This is confirms the general finding that although As compounds are readily soluble, As migration is greatly limited due to the strong sorption by organic matter, hydroxides and clays (Kabata-Pendias & Pendias, 2001). The percentage of As in the sequential extraction fractions followed the order: water soluble fraction (1) < exchangeable fraction (2) < reducible fraction (4) < oxidisable fraction (3) < reducible + residual fraction (5).

The chemical partitioning of Cd in the investigated samples indicated that Cd was mainly linked to the exchangeable fraction (2) and reducible fraction (4) (Figure 10c). The association of Cd with the two most labile fractions, exchangeable and reducible, is in agreement that Cd is most mobile in acidic soils within the range pH 4.5–5.5 (Kabata-Pendias

& Pendias, 2001) (average pH in the paddy soils from Kočani Field: 5.5). The percentage of Cd in the determined fractions was in the order: water soluble fraction (1) < reducible + residual fraction (5) < oxidisable fraction (3) < reducible fraction (4) < exchangeable fraction (2).

The highest content of Cu was associated with the oxidisable fraction (3), followed by the reducible + residual fraction (5) (Figure 10d). Consequently, Cu forms highly stable complexes with the organic matter and its mobility and bioavailability can be controlled by binding with soluble organic matter (Adriano, 1986; Li et al., 2001). The percentage of Cu in extraction fractions was in the following order: water soluble fraction (1) < exchangeable fraction (2) < reducible fraction (4) < reducible + residual fraction (5) < oxidisable fraction (3).

The most abundant fraction for Mo was the oxidisable fraction (3). Other important fractions for Mo were residual and water-soluble fractions (Figure 10e). This is supported by findings of Kabata-Pendias & Pendias (2001), that a great proportion of soil Mo is associated with organic matter and Fe hydrous oxides. The percentage of Mo present in the fractions followed the order: exchangeable fraction (2) < reducible fraction (4) < water soluble fraction (1) < reducible + residual fraction (5) < oxidisable fraction (3).

The reducible fraction (4) was the highest for Ni (Figure 10f) and the percentage of Ni in the fractions increases in the order: water soluble fraction (1) < exchangeable fraction (2) < oxidisable fraction (3) < reducible + residual fraction (5) < reducible fraction (4). In soils, Ni is usually related to either organic matter or amorphous oxides, and at soil pH < 6 is easily available (Kabata-Pendias & Pendias, 2001). Our results confirm this statement.

In the paddy soil samples, a large proportion of Pb was bound to the reducible + residual fraction (5), and the second most important fraction was the reducible (4) (Figure 10g). Results given by Kabata-Pendias & Pendias (2001) also indicate that Pb is mainly associated with organic matter, Mn oxides and Fe and Al hydroxides. The percentage of Pb in the fractions followed the order: water soluble fraction (1) < exchangeable fraction (2) < oxidisable fraction (3) < reducible fraction (4) < reducible + residual fraction (5).

Sb was significantly connected with the oxidisable fraction (3) (Figure 10h). On the contrary, Kabata-Pendias & Pendias (2001) reported about strong association of Sb with Fe and Mn hydroxides. The percentage of Sb in other fractions was low and followed the order: water soluble fraction (1) < reducible fraction (4) < exchangeable fraction (2) < reducible + residual fraction (5) < oxidisable fraction (3).

Figure 10i shows that Zn in the paddy soils was dominantly associated with the reducible fraction (4) and the reducible + residual fraction (5). The association of Zn with Fe and Mn hydroxides in soils has been similarly widely recognised by Kuo et al. (1983). The less important associations of Zn with the water soluble and exchangeable fractions might indicate the influence of flooding in the paddy soils, because Zn migrates downwards readily in soil profiles (Kabata-Pendias & Pendias, 2001). The percentage of Zn determined in the fractions followed the order: water soluble fraction (1) < exchangeable fraction (2) < oxidisable fraction (3) < residual fraction (5) < reducible fraction (4).

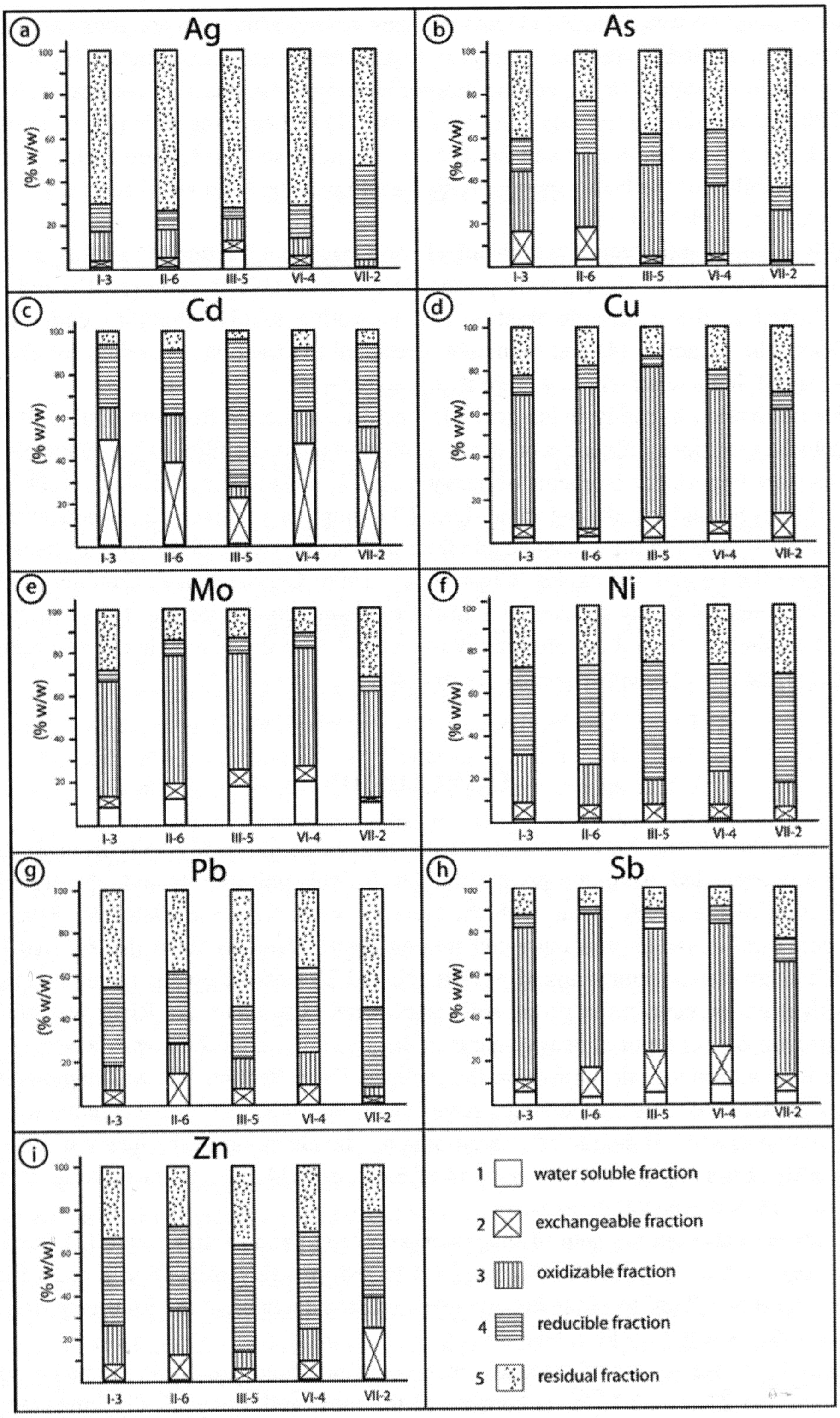

Figure 10. Heavy metal binding forms in paddy soil samples from sampling locations I-3, II-6, III-5, VI-4 and VII-2.

The amounts of water soluble (1) and exchangeable (2) fractions are considered the most mobile and bioavailable fractions. Very high proportions of heavy metals in bioavailable fractions could indicate a strong contribution of anthropogenic metals in studied soils (Wong et al., 2002). According to the sum of water soluble (1) and exchangeable (2) fractions for the Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn detected in paddy soils in Kočani Field, the mobility and bioavailability of the heavy metals studied decline in the following order: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag.

Cd was consistently bound to bioavailable and leachable fractions (1 and 2), as were Mo and Sb, which were also significantly present in the oxidisable fraction (3). Cu and As were mostly linked to the oxidisable fraction (3), indicating relative mobility under oxidising conditions. The reducible (4) and reducible + residual (5) fractions prevailed for Zn, Pb, Ni, and Ag, signifying a relatively low mobility capacity.

Rice cultivation in paddy fields generally requires moderate flooding. Different flooding conditions have various influences on the mobility and bioavailability of heavy metals. Fe and Mn oxides are important adsorbents of heavy metals in soils under oxidising conditions (Lee, 2006). However, under reducing conditions (flooding), a relatively high concentration of heavy metals is found in the exchangeable fraction because of the dissolution of heavy metals adsorbed on the Fe and Mn oxides (Chuan et al., 1996; Charlatchka & Cambier, 2000; Lee, 2006). We collected paddy soil samples in the oxidising conditions and from our study it is evident that Zn, Pb, Ni and Ag are mainly associated with the reducible (4) and reducible + residual (5) fractions and consequently less mobile.

CONCLUSION

As, Cd, Cu, Pb and Zn concentrations determined in the paddy soils from Section VII significantly exceeded maximum permissible levels. This pollution is undoubtedly related to the irrigation of the paddy fields with the riverine water from the Zletovska River, which drains acidic mine waters and untreated mining waste effluents from the Zletovo-Kratovo mine. Although the concentrations of Ag, Mo, Ni and Sb were below the mentioned threshold values, their enrichment in the paddy soil samples near the Zletovska River was noticeable, confirming the higher input of heavy metals in the area around the Zletovska River.

The high anthropogenic impact on the paddy soils in Section VII was demonstrated by the calculation of the following environmental indexes: geoaccumulation index, contamination factor and degree of contamination. The elevation of the heavy metals present in the paddy soil samples from other parts of Kočani Field was similarly verified with the results of the environmental indexes.

Taking into account the sum of the water soluble (1) and exchangeable (2) fractions for the Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn detected in paddy soils from Kočani Field, the mobility and bioavailability of the heavy metals studied declined in the following order: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag.

According to the results of the heavy metal concentrations present in the paddy soils, the area around the Zletovska River is considered the most anthropogenically impacted part of Kočani Field. The highly elevated concentrations of the analysed heavy metals are clearly related to the past and current mining activities, especially in the Zletovo-Kratovo ore district.

A project to diminish heavy metal content in contaminated soils by adding materials with a high capacity to bind metals in slightly mobile fractions (phosphorites, zeolites, montmorillonites and humic organic matter) is in preparation.

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