Determination of heavy metals in paddy soils (Kočani Field, Macedonia) by a sequential extraction procedure

Določitev težkih kovin v tleh riževih polj (Kočansko polje, Makedonija) z uporabo postopka zaporednega izluževanja

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Abstract: In this study we examine the distribution of heavy metals (As, Cd, Cu, Pb and Zn) in paddy soil samples from Kočani Field (Macedonia) by ICP-EAS and sequential extraction procedure. Very high concentrations of As (42 mg/kg), Cd (5.6 mg/kg), Cu (99 mg/kg), Pb (892 mg/kg) and Zn (1134 mg/kg) were found in the paddy soil sample from location VII-2 in the western part of Kočani Field, close to the Zletovska River, which drains the untreated effluents of the Pb-Zn mine in Zletovo and is used for the irrigation of the Kočani paddy fields. The mobility potential of heavy metals in the investigated paddy soil samples increases from As–Pb–Zn–Cu–Cd. We concluded that the paddy soil sample from location VII-2 had highly elevated heavy metal concentrations and revealed that the extraction characteristics of heavy metals represents a serious environmental potential risk for the surrounding ecosystems.

Izvleček: V študiji smo raziskovali razporeditev težkih kovin **(**As, Cd, Cu, Pb in Zn) v vzorcih tal riževih polj (Kočansko polje, Makedonija) z uporabo ICP-EAS in postopka zaporednega izluževanja. V vzorcu iz lokacije VII-2, ki se nahaja blizu reke Zletovske v zahodnem delu Kočanskega polja, smo našli zelo visoke koncentracije As (42 mg/kg), Cd (5,6 mg/kg), Cu (99 mg/kg), Pb (892 mg/kg) in Zn (1134 mg/kg). Visoke koncentracije težkih kovin so bile v vzorcu VII-2 zato, ker reka Zletovska odvaja neprečiščene odplake in odpadke z območja rudnika Pb-Zn Zletovo, kmetje pa jo uporabljajo za namakanje okolišnih riževih polj. V raziskovanih vzorcih narašča potencial mobilnosti v naslednjem zaporedju: As–Pb–Zn–Cu–Cd. Na podlagi zelo visokih koncentracij in izluževalnih lastnosti težkih kovin, prisotnih v vzorcu VII-2, smo ugotovili, da pomeni območje okoli imenovanega vzorca resno ekološko grožnjo bližnjim ekosistemom.

Original scientific paper

Key words: heavy metal contamination, paddy soil, sequential extraction procedure, Kočani Field, Macedonia
Ključne besede: težke kovine, tla, postopek zaporednega izluževanja, Kočansko polje, Makedonija

Introduction

Environmental pollution by heavy metals from base-metal mining operations and from abandoned mines can become a very important source of contamination of soils and poses a long-term risk to ecosystem health (Adriano, 1986). Elevated concentrations of heavy metals can be found in and around abandoned and active mines due to the discharge and dispersion of the untreated mines waste materials into nearby agricultural soils, food crops, riverine water and stream sediments (Jung, 2001; Korre et al., 2002; Lee et al., 2001; Liu et al., 2005; Lu & Zhang, 2005; Simmons et al., 2005).

The chemical behaviour of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g., fertilizer, sludge, amelter dust, slag), cation exchange and specific adsorption onto the surfaces of minerals and soil organic matter, and precipitation of secondary minerals (Manceau et al., 2000; McBride et al., 1997; McBride, 1999; Morin et al., 1999). Only soluble, exchangeable and chelated metal species in the soils are the labile fractions available for plants (Kabata-Pendias, 1993). For this reason, the measurements of the total amount of heavy metals in soils should be complemented with the measurements of the available fraction. A method widely used to assess the lability of heavy metals in soils and to provide detailed information on the heavy metal binding forms is the leaching of soils by means of chemical extractants. During recent decades, several leaching/extraction tests have been developed and modified for these purposes in the fields of geochemistry, marine chemistry and agricultural sciences (Tack & Verloo, 1995). Among the various sequential procedures presented, the most widely applied is that proposed by Tessier et al. (1979).

Studies about heavy metal concentrations in soil derived from the past and present mining activities in Macedonia are very rare (Dolenec et al., 2007). Consequently, very little is known about the distribution and concentrations of heavy metals in the soil from different parts of Macedonia, which could be affected due to historical and/or recent base-metal mining. Such an example is Kočani Field in eastern Macedonia, where the base-metal mining history of the region is very long and paddy rice (Oryza sativa L.) is one of the main agricultural products of the region. Previous investigations have shown that the riverine water from the Zletovska River and the Bregalnica River, used for the irrigation of the Kočani paddy fields, was contaminated with heavy metals as the result of acid mine water and the untreated effluents from the ore-processing facilities from the Zletovo-Kratovo and Sasa-Toranica ore district (Serafimovski et al., 2005). Therefore, it is very likely that the paddy soil in this area displays raised levels of heavy metals.

In this context, the present paper comprises the following:

(a) the determination of the total heavy metal concentrations in paddy soil samples from sampling points in Kočani Field;
(b) an application of the sequential extraction method (leaching procedure) for the definition of available fractions in soil samples from the Kočani Field;
(c) the estimation of the heavy metal distribution and mobility characteristics in the investigated soil samples and
(d) environmental risk assessment.

Materials and methods

Study area

Kočani Field, well known for its paddy fields and thermal waters, is located in the eastern part of Macedonia, about 115 km from the capital city, Skopje. With an average length of 35 km and width of 5 km, it is situated in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (Figure 1). The paddy soil of Kočani Field was estimated to originate from the composite material of the sediment derived from igneous, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (Dolenec et al., 2007).

The 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. The mining activities, the abandoned old mine sites and bare tailings, the large amounts of untreated waste material as well as the effluents from the Pb-Zn Zletovo and Sasa mines induced the expansion of heavy metal loads across the entire region. The acid mine waters and the untreated effluents from the ore-processing facilities and the tailings were discharged into the Zletovska and Bregalnica Rivers, which were used for the irrigation of paddy fields and therefore represented a further pollution source that could seriously affect the soil as well as the food and feed crops of Kočani Field.

Soil sampling and analysis

The sampling of the soil was carried out in autumn 2005 in order to investigate the distribution and concentrations of the potentially toxic heavy metals, including As, Cd, Cu, Pb and Zn, related to the base-metal mining activities of the region. The soil was sampled from 5 locations across the Kočani paddy fields. The sampling locations of the study area are shown in Figure 2. Near-surface soils were collected, because it is not possible to distinguish the A, B and C horizons in the agricultural soil. Each soil sample was made up of a composite of 5 sub-samples taken from within a 1 m × 1 m square. After air-drying at 25 °C for a week, the soil samples were disaggregated, sieved to 2 mm and then ground in a mechanical agate grinder to a fine powder (< 63 µm) for subsequent geochemical analysis.

All the paddy soil samples were analysed for their As, Cd, Cu, Pb and Zn concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd.) 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 soil analyses were assessed by using international reference material such as CCRMR SO-1 (soil) and USGS G-1 (granite). The analytical precision and the

Figure 1. Map of the study area, Kočani Field
Slika 1. Geografska karta Kočanskega polja

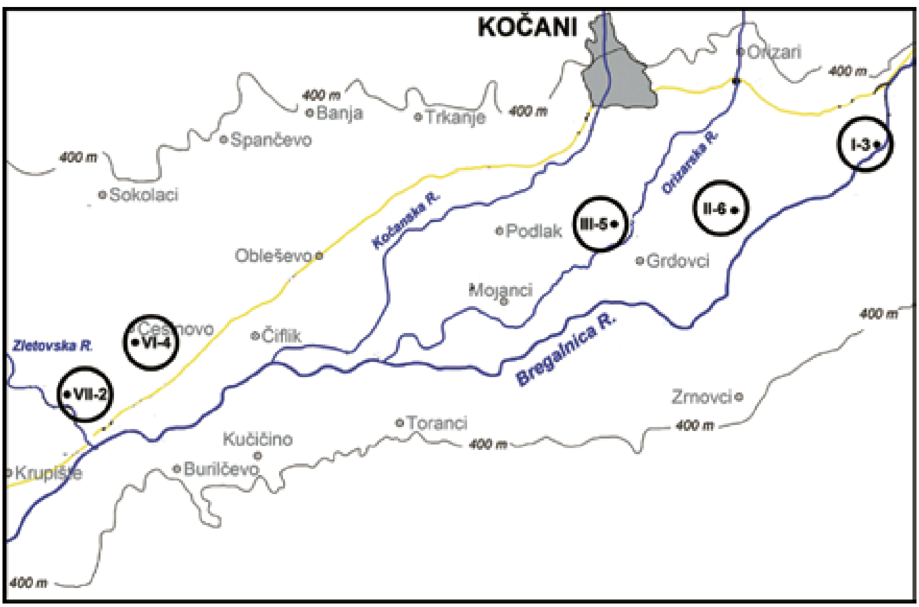

Figure 2. Sampling locations map of the study area
Slika 2. Geografski položaj vzorčnih točk

accuracy were better than ± 5 % for the analysed elements.

Sequential extraction procedure

Selected soil samples were also analysed for the chemical partitioning of As, Cd, Cu, Pb and Zn using a sequential chemical extraction method (LI et al., 1995; TESSIER et al., 1979). The soil samples weighing 1 g were placed in screw-top test tubes. To the sample was added 10 mL of leaching solution, the caps were screwed on and the tubes were subjected to the appropriate extraction procedure depending on the stage of the leach. For sequential leaching, the sample was leached, centrifuged, decanted, washed and then the residue was leached again, in a process of 5 steps from the weakest to the strongest solution. The sequential extraction procedure of heavy metals is precisely described in Table 1.

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

RESULTS AND DISCUSSION

Heavy metal concentration

The total concentrations of heavy metals (As, Cd, Cu, Pb and Zn) 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) and the maximum allowable concentrations (MAC) of trace elements in agricultural soil proposed by the German Federal Ministry of Environment (1992) as well as the critical soil total heavy metal concentration ranges given by KABATA-PENDIAS & PENDIAS (1984) are presented in Table 2. The critical total soil heavy metal concentration is defined as the range of values above which toxicity is considered to be possible.

The data clearly show that the paddy soil samples from locations I-3, II-6, III-5 and VI-4 contain slightly increased heavy metal concentrations but the paddy soil sample from section VII-2 in the vicinity of the Zletovska River is highly impacted with As, Cd, Cu, Pb and Zn. The concentration values in paddy soil sample VII-2 strongly exceeded the limit emission values reported by KABATA-PENDIAS AND PENDIAS (1984) and the national environmental protection agencies of Slovenia and Germany (Table 2).

Arsenic (As)

An elevated concentration of As (42.0 mg/kg) was detected in the paddy soil sample from section VII-2, which significantly exceeded the limit value of 20 mg/kg reported by the Environmental Protection Agency of Slovenia (Table 2).

Cadmium (Cd)

An increased Cd concentration (5.6 mg/kg) was determined in the paddy soil sample from location VII-2. The limit emission value for Cu concentrations in soils reported by the environmental protection agencies of Slovenia is 1 mg/kg and of Germany is 1.5 mg/kg (Table 2).

Copper (Cu)

A high concentration of Cu (99 mg/kg) found in the paddy soil sample from sam-

Table 1. Sequential extraction of heavy metals
Tabela 1. Postopek zaporednega izluževanja težkih kovin

Step	Fraction	Chemical reagents
1	water soluble	distilled water
2	exchangeable and carbonate bound	1 M ammonium acetate
3	organic (oxidizable)	0.1 M sodium pyrophosphate
4	reducible	cold 0.1 M hydroxylamine hydrochloride
5	reducible plus residual	hot 0.25 M hydroxylamine hydrochloride

Table 2. Total elemental concentrations in the paddy soil samples of Kočani Field: **1**) critical soil total concentration ranges given by Kabata-Pendias & Pendias (1984); **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)
Tabela 2. Celotne koncentracije elementov v vzorcih tal riževih polj: **1**) kritične koncentracije težkih kovin v tleh, Kabata-Pendias & Pendias (1984); **2**) mejne vrednosti težkih kovin v tleh (Agencija za okolje in prostor, Slovenija (Uradni list RS 1996)); **3**) maksimalne dovoljene vrednosti slednih elementov v agrikulturnih tleh (Nemško zvezno ministrstvo za okolje, 1992)

Concentration	c(As)/(mg/kg)	c(Cd)/(mg/kg)	c(Cu)/(mg/kg)	c(Pb)/(mg/kg)	c(Zn)/(mg/kg)
Location					
I-3	18.7	0.5	40	81	162
II-6	11.8	0.3	26	32	100
III-5	8.3	0.2	33	24	102
VI-4	9.9	0.3	29	41	105
VII-2	42.0	5.6	99	892	1134
1	-	3-8	60–125	100–400	70–400
2	20	1	60	85	200
3	-	1.5	60	100	200

pling site VII-2 exceeded the limit emission value of 60 mg/kg, suggested by the environmental protection agencies of Slovenia and Germany (Table 2).

Lead (Pb)
The highest Pb concentration (892 mg/kg) was noticed in the paddy soil sample from section VII-2 and it is above the limits provided by the environmental protection agencies of Slovenia and Germany (85 mg/kg and 100 mg/kg) and the limit values by Kabata-Pendias & Pendias (1984), (100–400 mg/kg) (Table 2).

Zinc (Zn)
A very elevated concentration of Zn (1134 mg/kg) highly exceeding all the limit values (200 mg/kg and 70–400 mg/kg, Table 2) was found in the paddy soil sample from section VII-2.

All the studied heavy metals are important ore-forming elements and are paragenetically related to the Pb-Zn polymetalic mineralization of the Zletovo-Kratovo ore district (Zletovo mine) predominately drained by the Zletovska River (Dolenec et al., 2007). However, in the case of the paddy soil sample from sampling location VII-2 in the vicinity of the Zletovska River and Zletovo mine, it is clear that the continued mining activities producing enormous untreated mining wastes from Zletovo mine are the main source of As, Cd, Cu, Pb and Zn contamination.

Sequential extraction (heavy metal binding forms)

The highly stable forms contained in the residual are unlikely to be released under weathering conditions. On the other hand, soluble, exchangeable and chelated fractions are quite labile and hence more accessible to plants and the food chain (KABATA-PENDIAS, 1993). In the applied sequential extraction procedure, the labile/residual fractions considered were: water soluble (1), exchangeable and bound to carbonates fraction (2), bound to organic matter – oxidizable fraction (3), bound to amorphous Mn hydroxide – reducible fraction (4) and bound to amorphous Fe hydroxide and crystalline Mn hydroxide – reducible and residual fraction (5).

The water soluble fraction includes highly mobile and hence potentially available metal species. The exchangeable fraction contains weakly bound (electrostatically) heavy metal species, that can be released by ion-exchange with cations such as Ca^{2+}, Mg^{2+} or NH_4^+. Metals in the exchangeable fraction are also very available for plant uptake and therefore the most labile. The oxidizable fraction releases under oxidizing conditions metals linked to organic matter within the soil matrix into solution. The reducible fraction provides unstable metal forms connected with amorphous Mn hydroxides, which are easily discharged and approachable by the surrounding biota under reducing conditions. In the reducible plus residual fraction, the metals are bound to amorphous Fe hydroxides (reducible part) and under reducing conditions they are expected to be released into nature. The residual includes naturally occurring crystalline Mn hydroxide minerals, which may hold heavy metals within their cristalline matrix. Thus, heavy metals are not likely to be discharged under normal environmental conditions (DEAN, 2007; FILGUEIRAS et al., 2002; FUENTES et al., 2004; KAZI et al., 2002). Figure 3 displays the results of the sequential extraction procedure (heavy metal binding forms).

Arsenic (As)

A significant fraction of As in the paddy soil samples from all five sampling locations was present in the reducible plus residual fraction (5) and the oxidizable fraction (3) (Figure 3A). The highest proportion of As in the reducible plus residual fraction was found in the paddy soil sample from location VII-2 (64 %) and the highest part of As in the oxidizable fraction was extracted from the paddy soil sample from sampling site III-5 (42.45 %).

Cadmium (Cd)

Figure 3B shows that Cd from all the paddy soil samples was strongly associated with the exchangeable phase (2), closely followed by the reduction phase (4). The highest share of Cd in the exchangeable phase was detected in paddy soil samples from sites I-3 (49.21 %) and VI-4 (47 %). The dominant part of Cd in the reduction phase was found in the paddy soil sample from section III-5 (68 %).

Copper (Cu)

Cu in all the paddy soil samples (Figure 3C) was almost entirely connected with

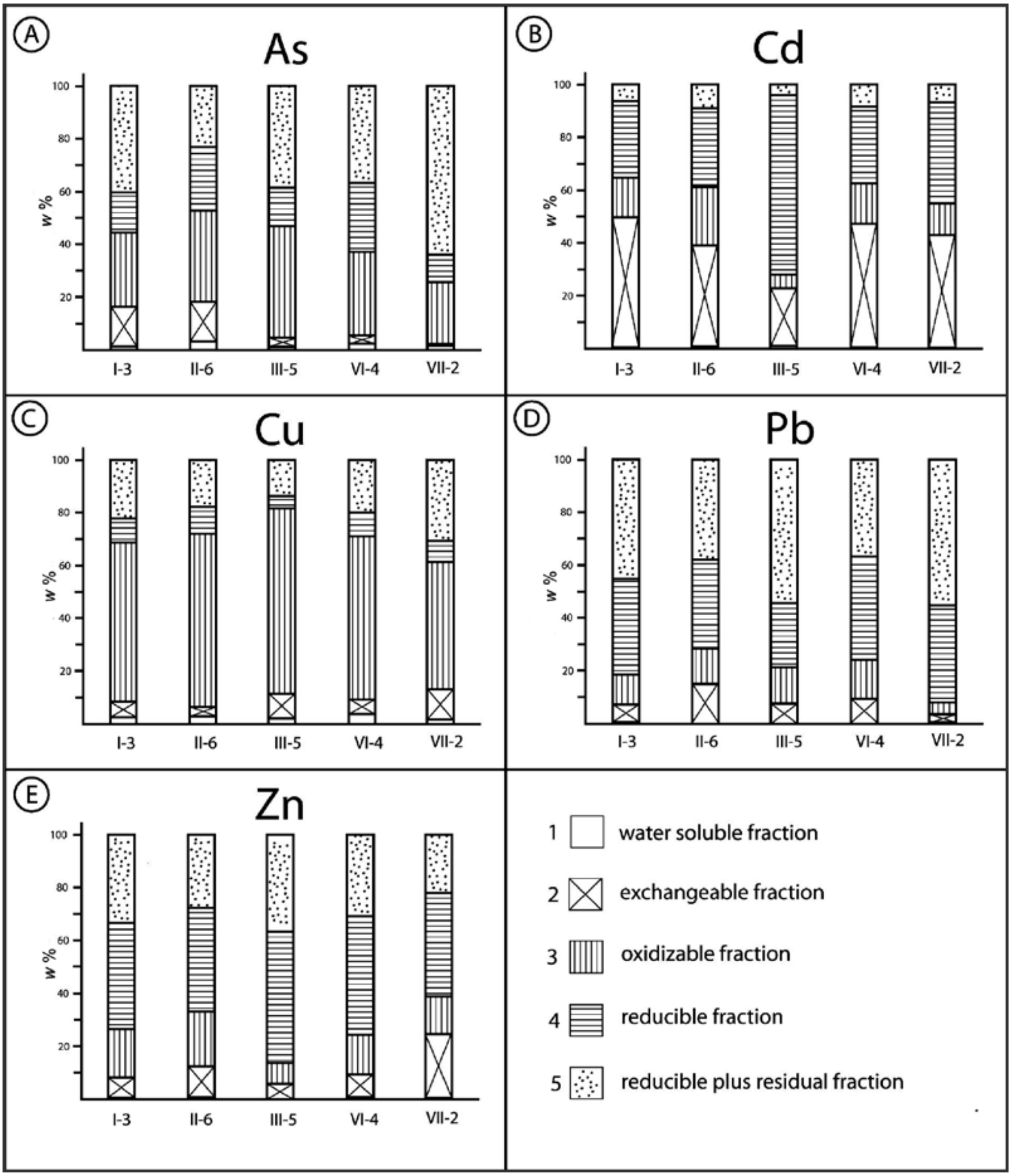

Figure 3. Heavy metal binding forms in paddy soil samples from different locations

Slika 3. Vezava težkih kovin v vzorcih tal riževih polj iz izbranih lokacij the oxidizable fraction (3). The highest part of Cu in the oxidizable fraction was extracted from the soil sample from section III-5 (70 %).

Lead (Pb)

In the paddy soil samples, a large part of Pb (Figure 3D) was bound to the reducible plus residual fraction (5) and the second most important fraction was the reducible phase (4). The highest amount of Pb in the reducible plus residual fraction was in the paddy soil sample from sampling site III-5 (54.46 %) and the highest share of Pb in the reducible phase was found in the paddy soil sample from section VI-4 (38.96 %).

Zinc (Zn)

The chemical partitioning of the Zn (Figure 3E) in the investigated paddy soil samples displayed that Zn was mainly associated with the reducible fraction (4) and weakly with the reducible plus residual fraction (5). The highest amount of Zn in phases (4) and (5) was determined in the soil sample from location III-5 (49.19 % and 36.9 %).

The most exchangeable, highly mobile and readily available element to biota in the surrounding ecosystems in all the paddy soil samples is Cd, closely followed by Pb and Zn, mainly bound to amorphous Fe and Mn hydroxides in the reducible fraction. Pb and Zn are thus under reduction conditions thermodynamically very unstable and available to plants. Cu is dominantly linked to organic matter and under oxidizing conditions is potentially released into the environment. As is also weakly bound to organic matter. However, in larger proportions, As is connected to amorphous Fe hydroxides, which are to some extent leachable and thus potentially bioavailable and furthermore to potentially the least harmful, non-mobile residual fraction (crystalline Mn hydroxides). Consequently, the mobility characteristics and potential of heavy metals in the investigated paddy soil samples increases from As–Pb–Zn–Cu–Cd.

In general, a high proportion of heavy metals in the non-residual fractions of all the paddy soil samples may suggest a greater contribution of anthropogenic metals. From the environmental and utilization point of view, it is notable that the paddy soil sample from location VII-2 near the Zletovska River and Zletovo mine, which had highly elevated heavy metal concentrations exceeding the limits proposed by the environmental agencies and Kabata-Pendias & Pendias, (1984) and introduced heavy metal mobility characteristics, represents a serious potential risk for the surrounding ecosystems.

To assess the possible health risk, more detailed studies on heavy metal contamination in agricultural soils, irrigation and drinking water, rice and other edible crops as well as a dietary study of the local population are needed.

Conclusions

The present study examined the distribution of heavy metals (As, Cd, Cu, Pb and Zn) in paddy soil samples from Kočani Field, Macedonia. The heavy metal concentrations were determined by ICP-EAS analysis and heavy metal binding was defined with the sequential extraction procedure.

The results showed that the paddy soil sample (section VII-2) from the western part of Kočani Field in the vicinity of the Zletovska River exhibited very elevated concentrations of As, Cd, Cu, Pb and Zn, which significantly exceed the limits proposed by the Slovenian and German environmental agencies and critical soil total concentration ranges given by Kabata-Pendias & Pendias (1984). The elevated concentrations of As, Cd, Cu, Pb and Zn in paddy soil sample VII-2 undoubtedly indicate heavy metal contamination related to mining activities and acid mine drainage impacted on the riverine water, which is used by local farmers for irrigation purposes.

The most exchangeable, labile and available element for plant uptake and furthermore for the possible contamination of the surrounding ecosystem in all the paddy soil samples is Cd, closely followed by Pb and Zn. Elements Pb and Zn are mainly linked to amorphous Mn hydroxides and amorphous Fe hydroxides in the reducible fraction and thus under reduction conditions are very unstable and mobile. Cu is dominantly bound to organic matter and consequently released under oxidizing conditions into the environment. As is also weakly bound to organic matter. However, in larger proportions, As is connected to amorphous Fe hydroxides, which are usually released from the soil and more crystalline Mn hydroxides, which are not expected to escape under normal environmental conditions. The mobility potential of heavy metals in the investigated paddy soil samples increases from As–Pb–Zn–Cu–Cd.

It was found out that the paddy soil sample from location VII-2, with highly elevated heavy metal concentrations and the revealed mobility characteristics of heavy metals As, Cd, Cu, Pb and Zn, represents a serious environmental potential risk for the surrounding ecosystems.

To assess the possible health risk, more detailed studies on heavy metal contamination in the surrounding ecosystems as well as a dietary study of the local population are needed.

Povzetek

Izkoriščanje nahajališč kovinskih mineralnih surovin in predelava rude sta pomemben vir onesnaženja okolja s težkimi kovinami. Rudarjenje, drobljenje in mletje rude skupaj z odlagališči jalovine in odpadkov predelave je očiten vir onesnaženja. Povišane vsebnosti težkih kovin, ki izhajajo iz rudnikov kovin, so zabeležene na območju rudnikov in v njihovi širši okolici, v okolnih tleh, pridelkih, rečnih in podzemnih vodah ter rečnih sedimentih, kamor migrirajo zaradi dispergiranja in odlaganja rudniškega odpadnega materiala. Posledica tega onesnaženja so velike površine onesnažene pridelovalne površine. Posebno pozornost smo namenili predvsem koncentraciji težkih kovin v pridelovalnih tleh, saj preko užitnih rastlin in prehrambene verige lahko vstopajo v živalski in človeški organizem.

V študiji smo raziskovali razporeditev težkih kovin (As, Cd, Cu, Pb in Zn) v vzorcih tal riževih polj (Kočansko polje, Makedonija) z uporabo ICP-EAS in postopka zaporednega izluževanja. V vzorcu iz lokacije VII-2, ki se nahaja blizu reke Zletovske v zahodnem delu Kočanskega polja, smo našli zelo visoke koncentracije As (42 mg/kg), Cd (5,6 mg/kg), Cu (99 mg/kg), Pb (892 mg/kg) in Zn (1134 mg/kg).

Visoke koncentracije težkih kovin so bile v vzorcu VII-2 zato, ker reka Zletovska odvaja neprečiščene odplake in odpadke z območja rudnika Pb-Zn Zletovo, kmetje pa jo uporabljajo za namakanje okolišnih riževih polj. V raziskovanih vzorcih narašča potencial mobilnosti v naslednjem zaporedju: As–Pb–Zn–Cu–Cd. Na podlagi zelo visokih koncentracij in izluževalnih lastnosti težkih kovin, prisotnih v vzorcu VII-2, smo ugotovili, da pomeni območje okoli imenovanega vzorca resno ekološko grožnjo bližnjim ekosistemom.

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