Assessment of heavy metal contamination in paddy soils from Kočani Field (Republic of Macedonia): part II

Ocena onesnaženja s težkimi kovinami v tleh riževih polj iz Kočanskega polja (Republika Makedonija): 2. del

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Abstract: The identification of heavy metals (Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn) mobility and availability in Kočani paddy soils was evaluated by sequential extraction procedure. According to the sum of the water soluble and exchangeable fractions for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn measured in the paddy soils at Kočani Field, the mobility and bioavailability potential of the heavy metals studied declined in the following order: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag. Cd was consistently bound to bioavailable and leachable fractions, as were Mo and Sb, which were also significantly present in the oxidisable fraction. Cu and As were mostly linked to the oxidisable fraction, indicating relative mobility under oxidising conditions. The reducible and reducible / residual fractions prevailed for Zn, Pb, Ni, and Ag, signifying a relatively low mobility capacity.

Izvleček: Po postopku zaporednega izluževanja sem ocenila mobilnost in biodostopnost težkih kovin (Ag, As, Cd, Cu, Mo, Ni, Pb, Sb in Zn) v tleh riževih polj na Kočanskem polju. Glede na vrednosti težkih kovin v vodotopni in izmenljivi frakciji se le-te kot najbolj mobilne in biodostopne pojavljajo v naslednjem vrstnem redu: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag. Kadmij (Cd) je močno povezan z obema najbolj biodostopnima frakcijama, prav tako molibden (Mo) in antimon (Sb), ki v zmernih deležih nastopata tudi v oksidacijski

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frakciji. Cu in As sta najmočneje povezana z oksidacijsko frakcijo in tako relativno mobilna v oksidacijskih razmerah. V redukcijski in redukcijsko-finalni frakciji pa prevladujejo naslednje šibko mobilne težke kovine: cink (Zn), svinec (Pb), nikelj (Ni) in srebro (Ag).

Key words: assessment of contamination, heavy metals, paddy soil, sequential extraction procedure, Kočani Field, Republic of Macedonia

Ključne besede: ocena onesnaženja, težke kovine, tla riževih polj, postopek zaporednega izluževanja, Kočansko polje, Republika Makedonija

Introduction

Compared with other compartments of the biosphere, the persistence of contaminants in soil is very long and the contamination of soil, especially by heavy metals, seems to be virtually permanent. The excessive accumulation of heavy metals in agricultural soils around mining areas is a great concern affecting the following situations:

- entrance of metals into the food chain, presenting a potential health risk to local inhabitants;
- loss of vegetation cover induced through phytotoxicity; and
- cycling of metals to surface soil horizons by tolerant plants to induce toxic effects on flora and fauna (Adriano, 2001; Kachenko & Singh, 2006; Liu et al., 2005; McLaughlin et al., 1999; Pruvot et al., 2006; Zhuang et al., 2008).

To evaluate the true short- and long-term environmental impact of heavy metals in soils, the most crucial factors to consider are their mobility and bioavailability through soil-plant systems. But only the soluble, exchangeable and chelated metal species in the soils are bioavailable in individual soil plant system (Kabata-Pendias & Pendias, 2001). Therefore, assessing the environmental risks requires the measurement of the total amount of heavy metals in soils and the total amount of heavy metals detected in the available fractions, also. 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).

All previous investigations have shown and confirm the heavy metal contamination of paddy soils from Kočani Field (Republic of Macedonia) as a result of irrigation with riverine water which is affected by the inflow of acid mine and untreated effluents from the ore processing facilities (Zletovo-Kratovo and Sasa-Toranica ore district) (Dolenec et al., 2007; Rogan et al., 2009; Rogan Šmuc, 2010; Rogan Šmuc, 2010). Consequently, the objective of this study was to apply the sequential extraction method (leaching procedure) in order to determine the bioavailability of heavy metals in the soil samples studied and to evaluate the environmental risk in the Kočani soil system area.

Materials and methods

Sequential extraction procedure

Kočani paddy soil samples (I-3, II-6, III-5, VI-4 and VII-2, Figure 1) with the highest heavy metal concentrations (Rogan Šmuc, 2010) were selected for the chemical partitioning analysis (binding forms) of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb, and Zn by employing a sequential extraction procedure (Li et al., 1995; Tessier et al., 1979) in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Vancouver, B. C., Canada).

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,

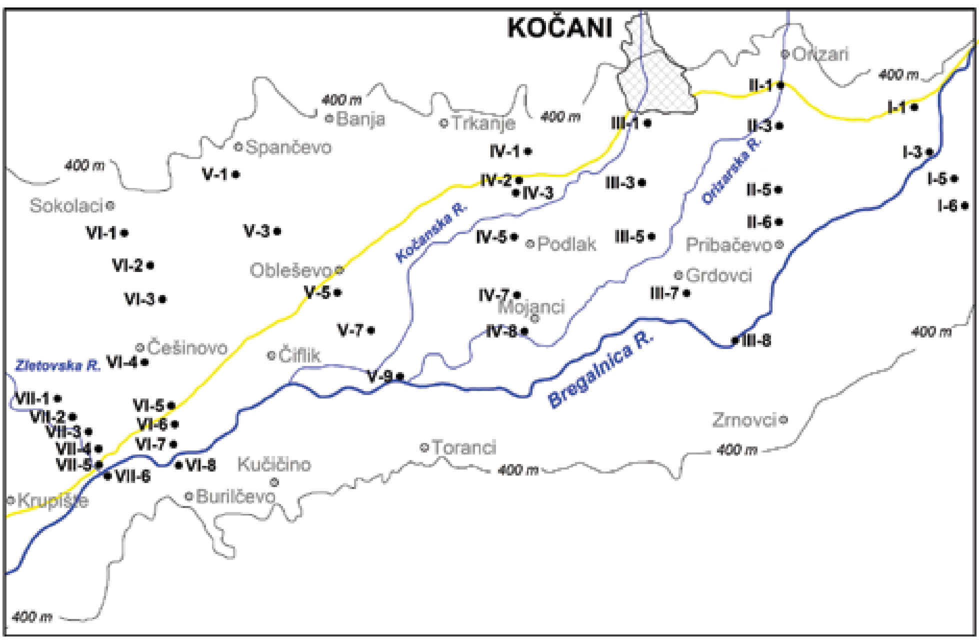

Figure 1. Paddy soil sample locations (sequential extraction procedure).

Table 1. 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

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 1.

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 appropriate accuracy.

Results

The mobility and bioavailability of heavy metals in paddy soils mostly depend on their types of binding forms. Figure 2 represents the results of the sequential extraction procedure (heavy metal binding forms).
The water soluble fraction (1) constitutes the most mobile and potentially the most available metal species easily released into the surrounding environment (Filgueiras et al., 2002).

The exchangeable fraction (2) includes metals weakly retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be coprecipitated with carbonates. Changes in ionic composition, which influence the adsorption/desorption reactions or lower the pH, can cause the remobilisation of metals from this fraction (Filgueiras et al., 2002). Exchangeable metal ions are treated as those that are released most readily into the environment (Filgueiras et al., 2002).

The oxidisable fraction (3) corresponds to elements occurring as oxidisable minerals and organically bound metals. They are assumed to remain in the soil for longer periods but can be mobilised by decomposition processes. The degradation of organic matter under oxidising conditions (Filgueiras et al., 2002) can lead to a release of soluble heavy metals bound to this component.

The reducible fraction (4) comprises unstable metal forms connected with amorphous Mn hydroxides. The metals strongly bound to these oxides are thermodynamically unstable under reducing conditions (Filgueiras et al., 2002).

In the reducible + residual fraction (5) the metals linked to amorphous Fe hydroxides (reducible part) under reducing conditions are expected to be released in nature. By contrast, the residual fraction contains naturally occurring crystalline Mn hydroxide minerals that can hold heavy metals within their crystalline matrix. Heavy metals in residual are not likely to be discharged under normal environmental conditions. Therefore, the metals associated with this fraction can only be mobilised as a result of chemical 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 2a). 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 2b). 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 2c). 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 2d). 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; Mbila 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 2e). 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 2f) 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). Results in this study are confirming 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 2g). Results given by Riffaldi et al. (1976) and 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 2h). 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 2i 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) and GONZALEZ et al. (1994). 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).

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 (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.

Measured and calculated heavy metal impact on the Kočani paddy soils revealed the following order of the heavy

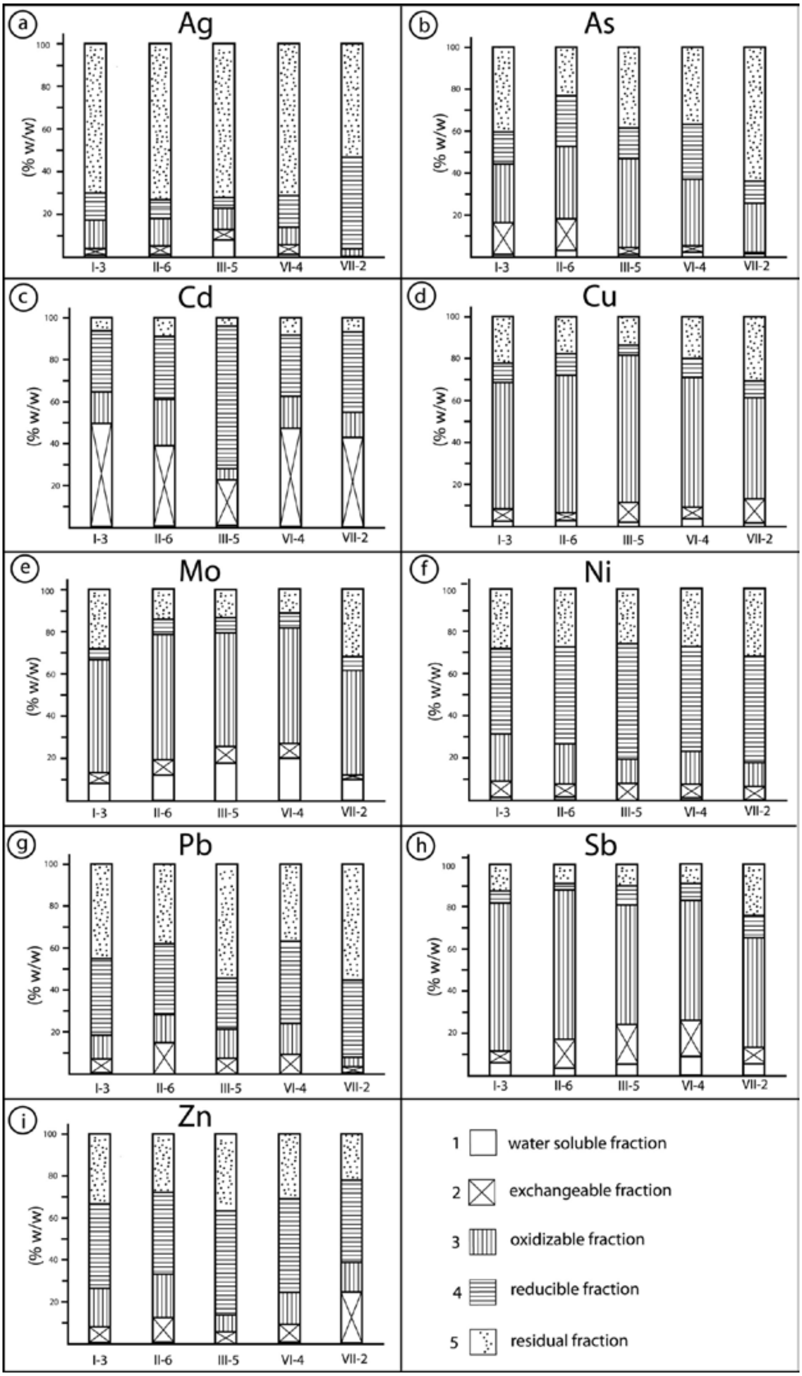

Figure 2. Heavy metal binding forms in paddy soil samples from sampling locations I-3, II-6, III-5, VI-4 and VII-2.

metals studied: Cd > As > Ag > Pb > Sb > Zn > Cu > Ni > Mo (Rogan Šmuc, 2010). However, the sequential extraction results are upgrading the previous mentioned study results (Rogan Šmuc, 2010), showing the mobility and bioavailability characteristics of heavy metals from soils to plants. According to the sequential leaching procedure results, Cd, Mo and Sb were consistently bound to bioavailable and leachable fractions and thus, they are treated as the most bioavailable to the surrounding ecosystems (plants). Therefore, a systematic study on heavy metal transfer from soils to crops and estimated daily intake for the local inhabitants of Kočani Field are essential.

Conclusions

Taking into account the sum of the water soluble (1) and exchangeable (2) fractions for Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn detected in the paddy soils at 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.

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.

Systematic study on heavy metal transfer from soils to crops, estimated daily intake for the local inhabitants of Kočani Field and project for diminishing heavy metal content in contaminated soils are essential.

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