Mineralogical and heavy metal signature of acid mine drainage impacted paddy soil from the western part of the Kočani field (Macedonia)

Mineralna sestava in težke kovine v tleh riževih polj zahodnega obrobja Kočanskega Polja, onesnaženih s kislimi rudniškimi odplakami (Republika Makedonija)

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Abstract: The mineralogy and heavy metal contamination of the paddy soil from the western part of the Kočani field (Eastern Macedonia) due to irrigation of acid mine drainage affected riverine water from the river Zletovska were studied. Highly elevated concentrations of Pb, Zn, As and Cd and a pollution index (PI) in the range between 2 and 7 were found in all the investigated paddy soil samples in the vicinity of the river Zletovska. The main carrier phases of the several trace elements in the studied soil seem to be Fe and Mn oxides/hydroxides. Heavy metals such as Pb and/or Cu were also bound to secondary minerals like anglesite, lanarkite, clinoclase and chrysocolla. All these minerals were detected by XRD analysis. The measured total metal concentrations exceed various national and international thresholds, thus suggesting the need for further investigation and an assessment of the suitability of the paddy soil in the western part of the Kočani field for agricultural use.

Izvleček: Članek obravnava mineralno sestavo in vsebnost težkih kovin v tleh riževih polj na zahodnem delu Kočanskega polja v Makedoniji. Onesnaženje je posledica namakanja z vodo iz Zletovske reke, v katero se iztekajo s težkimi kovinami obogatene rudniške odplake iz Pb-Zn rudišča Zletovo. Z raziskavo smo ugotovili močno povečane koncentracije Pb, Zn, As in Cd v tleh riževih polj vzdolž Zletovske reke. Te znatno presegajo dovoljene vsebnosti za tla, ki se uporabljajo v poljedelske namene. Indeks onesnaženosti za Pb, Zn, As in Cd je med 2 in 7. Težke kovine so vezane za Fe in Mn okside ter hidrokside. Našli pa smo tudi sekundarne minerale, nosilce Pb (anglezit in lanarkit) ter bakra (klinoklaz in hrizokolo). Omenjene minerale smo določili z rentgensko difrakcijo.

Key words: heavy metals, paddy soil mineralogy, acid mine drainage, Kočani Field, Macedonia.

Ključne besede: težke kovine, mineralna sestava tal, kisle rudniške odplake, Kočansko polje, Makedonija.

Short scientific paper

INTRODUCTION

Coupled with the lack of pollution controls, mining activities together with increased industrial and municipal waste discharge and other pollutant emission in the broader region of Kočani have caused significant impacts on the agricultural soil. Mining is one of the most significant sources of heavy metals in the environment. Mining and milling operations together with grinding concentrating ores and the disposal of tailings, along with mill wastewater, and the mine provide obvious sources of contamination (ADRIANO, 1986). Elevated concentrations of heavy metals can be found in and around abandoned and active mines due to the discharge and dispersion of mine waste materials into nearby soils, food crops and stream sediments (LEE ET AL., 2000; JUNG, 2001; MCKENZIE AND PULFORD, 2002; WITTE ET AL., 2004). As a result, large areas of agricultural soil can also be seriously contaminated. Although all around the world several studies have evaluated the heavy metal concentrations in soils and edible plants (KABATA-PENDIAS AND PENDIAS, 1992), in Macedonia such studies are scarce. Therefore, very little is known about the distribution of heavy metals in agricultural soil from different parts of Macedonia, which could be affected as a result of historical and /or recent base-metal mining, milling and smelting activities.

This study was aimed at contributing to a database on the mineralogy and the heavy metal contamination of agricultural soil in Eastern Macedonia as a basis for a further study of the relationship between heavy metal soil geochemistry and the health of the ecosystem.

STUDY AREA

The study area represents the western part of the Kočani field, where the paddy fields are mostly irrigated with water from the river Zletovska (Fig. 1). The river Zletovska is among one of the most polluted tributaries of the river Bregalnica. It drains the central part of the Kratovo-Zletovo volcanic complex, the abandoned old mining sites and bare tailings as well as the effluents from the Pb-Zn mine Zletovo and its ore processing facilities. Acid mine water and effluents from tailing discharged untreated into the riverine waters which are used for the irrigation of the paddy fields of the western side of the Kočani field. The river Zletovska adit water to the river Bregalnica, which is far less impacted with acid mine drainage than the river Zletovska in the western edge of the Kočani field at Krupište.

MATERIALS AND METHODS

For the purpose of this study paddy soil samples were collected at six locations along the river Zletovska (Fig. 1). Near surface paddy soil (0-20 cm in depth) were sampled because in the agricultural soil it is not possible to distinguish the A, B and C horizons. The soil samples were air dried at 20 °C for a week and sieved through a 2-mm polyethylene sieve to remove plant debris, pebbles and stones. They were then ground in a mechanical agate grinder to a fine powder for further mineralogical and geochemical analyses.

The mineralogy of the soil samples was determined at the Department of Geology, Ljubljana, Slovenia by X-ray powder

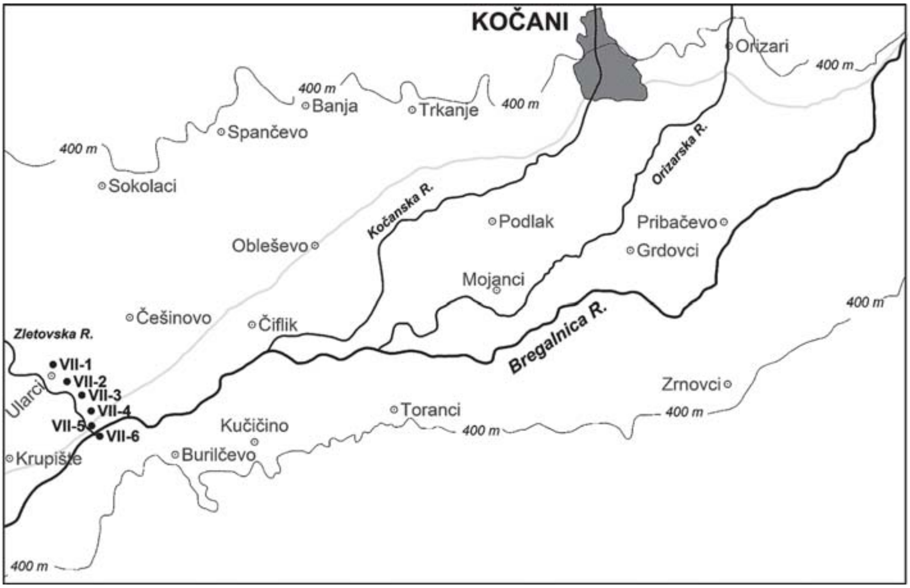

Figure 1. Sampling location map of the studied area.

diffractometry using a Philips PW 3710 diffractometer and CuKa radiation. The samples were scanned at a rate of 2° per minute, over the range of 2-70° (2Θ). The results were stored on a PC and analysed with PC-APD diffraction software. The diffraction patterns were identified using the data from the Powder Diffraction File (1977) - JPDS system.

The geochemical analyses were performed in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd.). According to the laboratory reports, 0.5 g of soil samples were extracted for 1h with 3 ml 2-2-2 HCl-HNO_3-H_20 at 95 °C and the extracts were analyzed for Pb, Zn, As and Cd content by ICP-MS. The accuracy and precision were better than ±5 %. This was indicated by the results of duplicate measurements of three paddy soil samples and duplicate measurements of a CCRMP SO-1 (soil) standard.

Results and Discussion

Mineralogy

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

In addition to the natural minerals identified a range of secondary products resulting from surface-induced chemical degradation of the soil parent material and/or remobilization of anthropogenically-derived heavy metals were also detected. These include bixbyite (Mn_2O_3 - JCPDS card number 41-1442), anglesite ($PbSO_4$ - JCPDS card number 05-0577), lanarkite ($Pb_2(SO_4)O$ - JCPDS card number 33-1486), kremersite ($(NH_4K)2FeCl_5.H_2O$ - JCPDS card number 28-0734), ferroxihydrite (FeOOH - JCPDS card number 22-0353), clinoclase ($(Cu_3(AsO_4)(OH)_3$ - JCPDS card number 37-0447) and chrysocolla ($CuSiO_3.2H_2O$ - JCPDS card number 03-0219). The secondary products such as anglesite, lanarkite, clinoclase and chrysocolla were detected in soil samples from section 7 close to the river Zletovska. These diagenetic Pb and Cu minerals indicate that some of the heavy metal contamination is being remobilised and reprecipitated.

Heavy metals

The concentrations of Pb, Zn, As and Cd in the paddy soil in the vicinity of the river Zletovska together with the pollution index (PI) of the soils and the "assumed permissible level" of heavy metals adopted by the National Environmental Protection Agency of Slovenia (Ur. list RS 68/96) are presented in Table 1. In general, the PI can be computed by averaging the ratios of the metal concentrations in sampled soils to the assumed permissible level of metals (JUNG, 2001 and references therein). In this study the PI was calculated by the equation:

$$PI = \frac{\frac{Pb}{85} + \frac{Zn}{200} + \frac{As}{20} + \frac{Cd}{1}}{4} \quad (1)$$

From Table 1 it is clearly evident that the paddy soil is considerably impacted by the above-mentioned heavy metals. Their concentrations are far above the threshold values considered as phytotoxically excessive for surface soils, and the PI in all the samples exhibits values in the range between 2 and 7. The studied heavy metals are the most important ore forming elements and are paragenetically related to the Pb-Zn pollymetalic mineralization of the Kratovo-Zletovo ore district. They can form their own minerals (sulphides, sulpho-salts) or enter as trace elements into the structure of the other ore and gangue minerals (SERAFIMOVSKI, 1995). In paddy soil they are most probably

Table 1. Heavy metal concentrations in paddy soil from the western part of the Kočani field (* permissible level of heavy metal content - Ur. list RS 68/96; PI - pollution index).

Element		Pb	Zn	As	Cd	PI
Units		ppm	ppm	ppm	ppm	
Location	Sample No.					
VII-1	33	412	531	22	3	**3**
VII-2	34	892	1134	42	6	**6**
VII-3	35	727	893	35	5	**5**
VII-4	36	983	1245	48	6	**7**
VII-5	37	745	928	40	5	**5**
VII-6	38	296	384	21	2	**2**
	*	85	200	20	1	

bound to Mn and Fe oxides/hydroxides, also detected during this study by XRD analyses. It is well known that Mn and Fe oxides/hydroxides are very effective scavengers for heavy metals in oxic environments (Kabata-Pendias and Pendias, 1992; Wong et al., 2002; Aubert et al., 2004). Besides Mn and Fe oxides/hydroxides, anglesite and lanarkite as well as clinoclase and chrysocolla were also detected. The first two contain Pb, while the last ones are a carrier phase of Cu. All these minerals precipitated in soil as secondary minerals.

The total concentrations of heavy metals in soils can be derived from two sources: natural and anthropogenic. Therefore, it is not easy to decide a priori which of these two contributions will represent the main origin of heavy metal pollution. However, in the case of the paddy soil from the western part of the Kočani field it is undoubtedly clear that the anthropogenic impact due to acid mine drainage is the main source of the heavy metal contamination. The Zletovo Pb-Zn mine adit discharges an effluent of pH 3.4 with Pb concentrations of 60 mg l^{-1}, Zn at 39 mg l^{-1}, As at 1282 m l^{-1} and Cd at 176 mg l^{-1}. Due to this the river Zletovska is moderately to highly polluted, while the contamination of the bed sediments coated with Fe and Mn oxides/hydroxides, which are a major sink for metals, is significant. Due to irrigation the heavy metals are spread out and accumulated in paddy soil of the western part of the Kočani field. The observed excess contamination of the investigated paddy soil with Pb, Zn, As and Cd represents a serious problem because of their potential to be transfered to the food chain in the region. Paddy soil at the vicinity of the river Zletovska also exhibits elevated concentrations of Ba, Cs, Th, U, V, Mo, Cu, Sb, Bi, Ag, Au, Hg and Tl which are above the established median concentrations for these elements in the paddy soil of the Kočani field (Dolenec et al., 2005, in print).

Conclusions

Paddy soil in the western part of the Kočani field have considerably elevated concentrations of heavy metals such as Pb, Zn, As and Cd which could result in long term contamination due to irrigation with acid mine drainage impacted riverine water from the river Zletovska. The pollution index (PI) that is calculated for multi-element contamination is in the range between 2 and 7. The significant Pb, Zn, As and Cd concentrations, which are far above the critical values for these metals reported by various Environmental Protection Agencies, as well as the PI > 1 strongly suggest potentially negative effects of the investigated soil on the growth of the crops and/or on the human population due to the ingestion of contaminated crops. Fe and Mn oxides/hydroxides represent a major sink for soil heavy metal pollution. A source of Pb is also anglesite and lanarkite, while that of Cu are clinoclase and chrysocolla. These minerals are of secondary origin and were precipitated from paddy soil pore water. However, further studies are needed to clarify the heavy metal pollution of the agricultural soil from the whole Kočani field and the mechanisms governing bioavailability and heavy metal uptake by plants, since these are more dependent on the speciation of the metals than the total content.

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