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Molybdenum, lead and zinc mobility potential in agricultural environments: a case study of the Kočani field, North Macedonia

Mobilnost molibdena, svinca in cinka v kmetijskih okoljih, primer Kočanskega polja (Severna Makedonija)

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Abstract

The research focuses on the assessment of potential toxic elements (PTEs) contamination of the soils of the Kočani field (North Macedonia) due to the surrounding past and current polymetallic mining activities. The Zletovska River drains the untreated wastewater from the Pb-Zn mine in the Zletovo-Kratovo region and is unfortunately used to irrigate the surrounding rice fields. Elevated levels of molybdenum (Mo) and especially lead (Pb) and zinc (Zn) were found in the soil samples from the rice fields near the Zletovska River (in the western part of the Kočani field), which are well above the limit and critical emission values for PTEs content in soils. In addition, Mo was consistently bound to water soluble, exchangeable and oxidizable fractions in all samples, while reducible and residual fractions were predominated by Pb and Zn. According to the sum of the water-soluble and exchangeable fractions, the mobility and environmental bioavailability potential of the investigated PTEs in the soil-plant system decreased in the following order: Mo > Pb > Zn. It is therefore very important to emphasize that when assessing the environmental impact of PTEs on the respective surroundings, not only the commonly considered trace and minor PTEs (such as Pb and Zn) that occur in geological materials should be taken into account, but also in lower contents (such as Mo). The translocation of PTEs within the ecosystem does not depend on their total content in the primary geological materials, but on their individual mobility and binding capacity.

Izvleček

Raziskava se osredotoča na onesnaženost tal s potencialno toksičnimi elementi (PTE) na območju Kočanskega polja (Severna Makedonija), ki se nahaja v bližini dveh še vedno aktivnih rudnikov, Sase-Toranice in Zletova-Kratova. V vzorcih tal riževih polj ob reki Zletovski smo odkrili povečane vsebnosti molibdena (Mo) in predvsem kritične vsebnosti svinca (Pb) ter cinka (Zn). Reka Zletovska odvaja neprečiščeno odpadno vodo iz rudnika Pb-Zn Zletovo-Kratovo, na območju Kočanskega polja pa se rečna voda uporablja za intenzivno namakanje riževih polj. S pomočjo rezultatov zaporedne ekstrakcijske analize smo ugotovili, da so deleži Mo večinoma topni v talni raztopini, izmenljivo vezani in vezani na organsko snov, medtem ko so deleži Pb in Zn večinoma vezani na Fe in Mn okside/hidrokside ter v preostanku. Nadalje smo določili mobilnostni potencial in biodostopnost preiskovanih PTE, ki se zmanjšujeta v naslednjem vrstnem redu: Mo > Pb > Zn. Posledično je pomembno poudariti, da pri ocenjevanju okoljskega vpliva PTE ne upoštevamo le splošno obravnavane PTE (kot sta Pb in Zn), temveč tudi tiste, ki se pojavljajo v kamninah, mineralih in tleh v manjših vsebnostih (kot je Mo). Premeščanje PTE v ekosistemu ni odvisna od njihovih celokupnih vsebnosti v primarnih geoloških materialih, ampak od njihovih individualnih lastnosti mobilnosti in vezave.

Introduction

Soil has always been important for people and their existence, especially as a resource that can be used for shelter and food production (Abrahams, 2002; Brevik et al., 2019). Agricultural land today accounts 45 % (48 million km^2) of the world's habitable land (Ritchie & Roser, 2019), and large parts of agricultural land are located near active mines (Wang et al., 2023a). Soil pollution with PTEs has therefore become a widespread global problem over the last four decades, posing a long-term threat to the health and quality of ecosystems (Matong et al., 2016; Wang et al., 2018; Wang et al., 2023a; Yin et al., 2020). The excessive accumulation of PTEs in agricultural soils is of great concern because soil, which contains various essential elements, is a primary nutrient carrier for plants. Food crops grown on contaminated agricultural soils can an accumulate elevated level of PTEs, indicating a potential health risk to the local population and to others if the crops are exported (Adriano, 2001; Pruvot et al., 2006; Wang et al., 2023a; Zhang et al., 2018a; Zhang et al., 2018b; Wang et al., 2023b). Consequently, numerous scientific studies around the world report serious health risks to humans from soils and plants contaminated with PTEs, including Mo (Frascoli & Hudson-Edwards, 2018; Han et al., 2019; Wang et al., 2018; Yin et al., 2020), Pb and Zn (Arenas-Lago et al., 2014; Li et al., 2014; Liu et al., 2022; Zhang et al., 2018a; Wang et al., 2023a).

Environmental risk assessment therefore requires the measurement of the total amount of PTEs in soils and the total amount of PTEs detected in the available/bioavailable fractions (Dean, 2007; Zhang et al., 2014; Kim et al., 2015). A widely used modified method for determining and evaluating the availability or binding forms of PTEs in soils is the sequential extraction method proposed by Tessier et al. (1979), in which the water-soluble and exchangeable fractions represent the most mobile fraction of the individual PTEs (Kabata-Pendias & Pendias, 2001; Dean, 2007).

Compared to the Earth's crust, the PTEs abundance (e.g. Pb and Zn) in various polymetallic ore deposits are generally very high. These naturally occurring elevated PTEs contents are transferred to the immediate surroundings of the ore deposits, where they influence the chemistry of waters, sediments, soils, plants, etc. Primarily through the weathering of the geological background and secondarily through mining and extraction (Bradl et al., 2005; Liu et al., 2013; Zhang et al., 2018a; Wang et al., 2023a). The agricultural area of the Kočani field in North Macedonia, for example, is exposed to the environmental impact of two large mines nearby, Zletovo-Kratovo and Sasa-Toranica, where Pb and Zn have been continuously mined for over 45 years (Balabanova et al., 2014; Rogan Šmuc et al., 2009; Rogan Šmuc et al., 2010; Vrhovnik et al., 2013). Since the ore-mineral association in both mines is very diverse (Rogan Šmuc, 2010) it is necessary to investigate also the presence of other PTEs (for example Mo) and not only Pb and Zn.

In this context, the spatial distribution and possible translocation of Mo in comparison to Pb and Zn in the soils of the Kočani field are investigated. The main objectives of the present study are the following: (1) to estimate the distribution patterns of Mo, Pb and Zn in the soils of the Kočani field and (2) to assess the mobility and environmental bioavailability signature of Mo, Pb and Zn in soil samples.

Materials and methods

Study area

The Kočani field is located in eastern Macedonia, about 32 km from the city of Štip and 115 km from the capital Skopje. With an average length of 35 km and a width of 5 km, the Kočani field is located in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (Fig. 1).

The wider region is known as an agricultural and mining province (Zletovo Kratovo Pb-Zn and Sasa Toranica Pb-Zn mine). The main agricultural products of the region are rice, corn, tomatoes, cucumbers, peppers and other vegetables.

The Bregalnica River, together with its tributaries, represents the most important drainage system in the study area and is an important water supply for the irrigation of the surrounding rice fields. The main tributaries of the Bregalnica are the Kamenica River in the northeastern part of the study area and the Zletovska River in the west of the Kočani field (Fig. 1). The Kamenica drains the northeastern part of the Bregalnica catchment and flows directly into the artificial Kalimanci Lake, which was constructed to irrigate the rice fields during the dry season. It also drains the untreated mine wastewater from the Sasa Pb-Zn polymetallic ore deposit. The Zletovska River originally drained the central part of the Zletovo-Kratovo volcanic complex as well as the untreated mine wastewater from the Zletovo Pb-Zn mine and its ore processing facilities. The local farmers use both rivers to irrigate the nearby rice fields.

It was assumed that the soil mineral component of the Kočani field originated from a composite material of sediments from igneous, metamorphic and sedimentary rocks in the Kočani region (Dolenec et al., 2007; Aleksandrov et al., 1995). The sedimentary material was transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (Dolenec et al., 2007). The exposed lithologies of the Kočani field consist mainly of acidic to intermediate igneous rocks and to a lesser extent of metamorphic and sedimentary rocks, while the igneous basic lithologies (gabbros and basalts) were found only sporadically (Dolenec et al., 2007; Aleksandrov et al., 1995).

The mineral components of the Kočani soil are closely related to the acidic and intermediate rocks of the Kočani region and consist mainly of

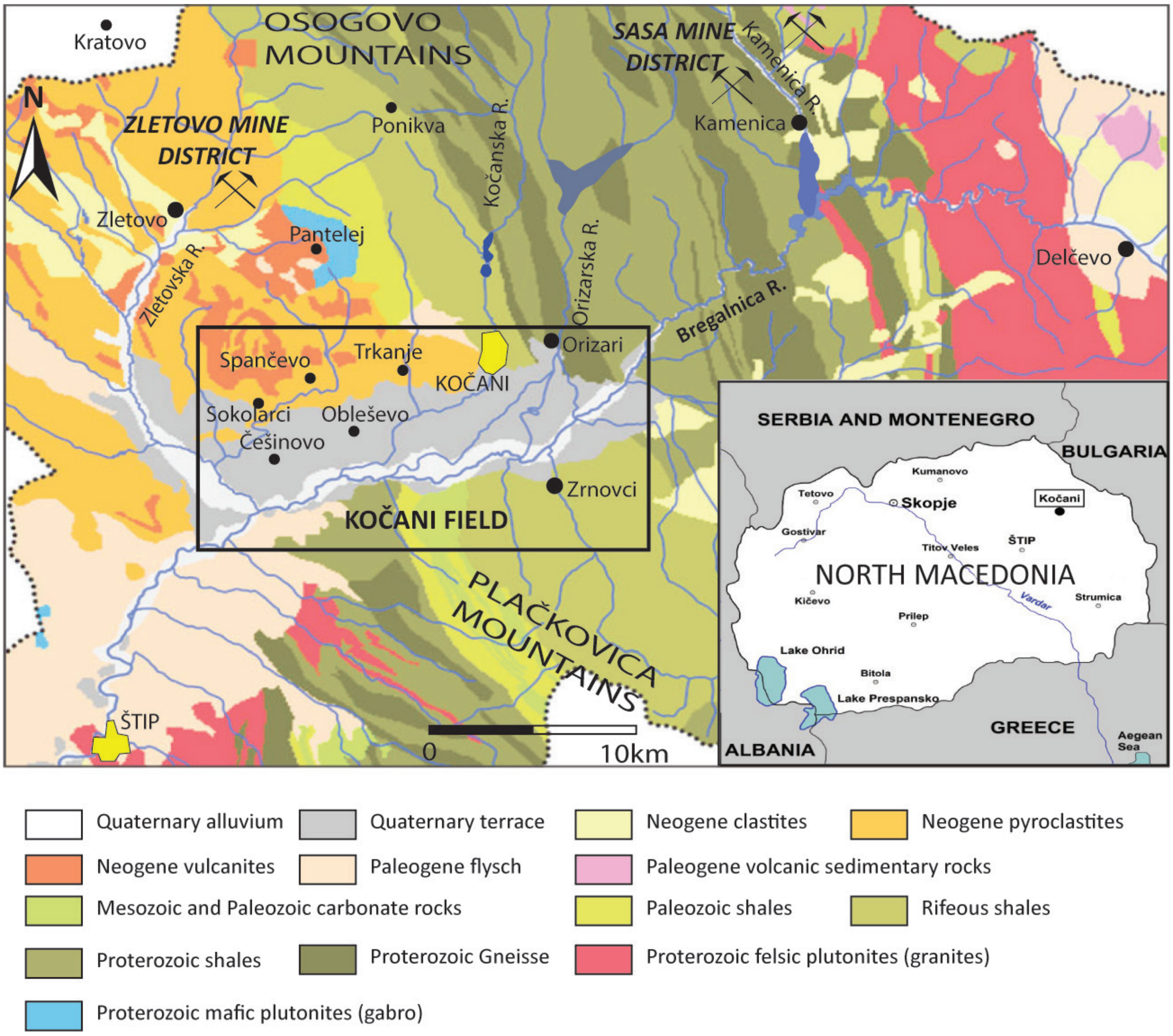

Fig. 1. Study area, Kočani field, North Macedonia. Geological map simplified after Balabanova et al., 2016.

the following minerals: quartz, plagioclase, muscovite-illite, orthoclase and chlorite together with small amounts of amphibole and kaolinite, while traces of calcite and dolomite were found only sporadically (Dolenec et al., 2007). No significant changes in the main soil mineral composition were found throughout the area studied. In addition, a number of secondary products of the soil were detected that originate from the surface-related chemical degradation of the parent material and/or the remobilization of anthropogenic PTEs. These secondary minerals are bixbyite, anglesite, lanarkite, ferrihydrite, clinoclase and chrysocolla (Dolenec et al., 2007; Rogan Šmuc, 2010).

Zletovo-Kratovo ore district

The Zletovo-Kratovo Pb-Zn ore district is located 5 km northwest of the village of Zletovo and about 7 km from the town of Probistip (Fig. 1). It is located in the central part of the Zletovo-Kratovo volcanic complex. The Pb and Zn mineralization occurs in dacitic ignimbrites, the most common volcanic rocks in the area. Ore mineral association includes galena (main ore mineral) and sphalerite, with subordinate pyrite, minor amounts of siderite and chalcopyrite, and occasional pyrrhotite, marcasite and magnetite. Minor occurrences of U-mineralization have also been discovered (pitchblende).

The Zletovo mine has an annual capacity of 400,000 tons of ore, with an average content of 8 % Pb + Zn within the ore (Tasev et al., 2019), and yields significant amounts of Ag, Bi, Cd and Cu (Tasev et al., 2019). The ore is concentrated during the flotation process in Probistip, and the tailings are stored in two tailings ponds in the adjacent valleys (Alderton et al., 2005; Rogan Šmuc, 2010).

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 (Fig. 1). It is established as one of the largest ore districts within the Besna Kobila-Osogovo Tassos metallogenic zone and occupies an area of about 200 km^2. The important Pb and Zn ore bodies are usually found in quartz/muscovite/graphitic schists, green schists and marbles. The ore mineral association consists of sphalerite, galena, pyrrhotite, pyrite, chalcopyrite, molybdenite, bornite, stibnite and locally cassiterite, accompanied by a series of bismuth and silver minerals as well as non-ore minerals such as skarn minerals, calcites, Mn-calcites and quartz.

The Sasa mine has been in production for over 45 years, yielding 90,000 tons of high quality Pb-Zn concentrate annually and 10 million tons of tailings material (Šajn et al., 2022). The flotation processes in the mine are used to concentrate the ore, and the tailings are stored in a dam in a narrow valley directly below the mine (Alderton et al., 2005; Vrhovnik et al., 2013).

Sampling

Soil samples were taken (year 2006) from 38 locations in seven profiles on the Kočani field (Fig. 2, sections I–VII). The profiles were organized according to the location of the rice fields, as we sampled not only the soil but also the rice. Since we sampled everything at the same time and the samples were agricultural soils, there were no general differences between them in terms of moisture content, soil properties, morphology... The near-surface paddy soils were taken from a depth of 0–20 cm. The soils were sampled with a plastic spade to avoid any metal contamination. Each soil sample consisted of five subsamples taken from an area of 1×1 m^2. The soil samples were air-dried at 25°C for one week and sieved through a 2 mm thick polyethylene sieve to remove plant debris, pebbles and stones. The samples were then ground to a fine powder in a mechanical agate mill.

Analyses

The **physical and chemical soil properties** (pH, CEC and total organic carbon) were determined at the Slovenian Agricultural Institute. The pH values were measured according to ISO 10390 and with a pH meter. CEC values were measured according to reference NF X31-108 and the Melich method modified according to Peechu et al. using flame atomic absorption spectroscopy (to determine exchangeable cations) and titration (to determine total exchangeable soil acidity). Total organic carbon values were measured using a UV/VIS spectrometer according to ISO 14235.

All soil samples were analysed for **Mo, Pb and Zn content** in a certified (ISO/IEC 17025) commercial Canadian laboratory (Bureau Veritas Mineral Laboratories, Vancouver, B.C., Canada) by one-hour extraction with 2-2-2-HCl-HNO_3-H_2O at 95 °C and ICP-MS. The accuracy and precision of the soil analysis was evaluated using international reference material such as Canadian Certified Reference Material Project (CCRMP) SO-1 (soil) and United

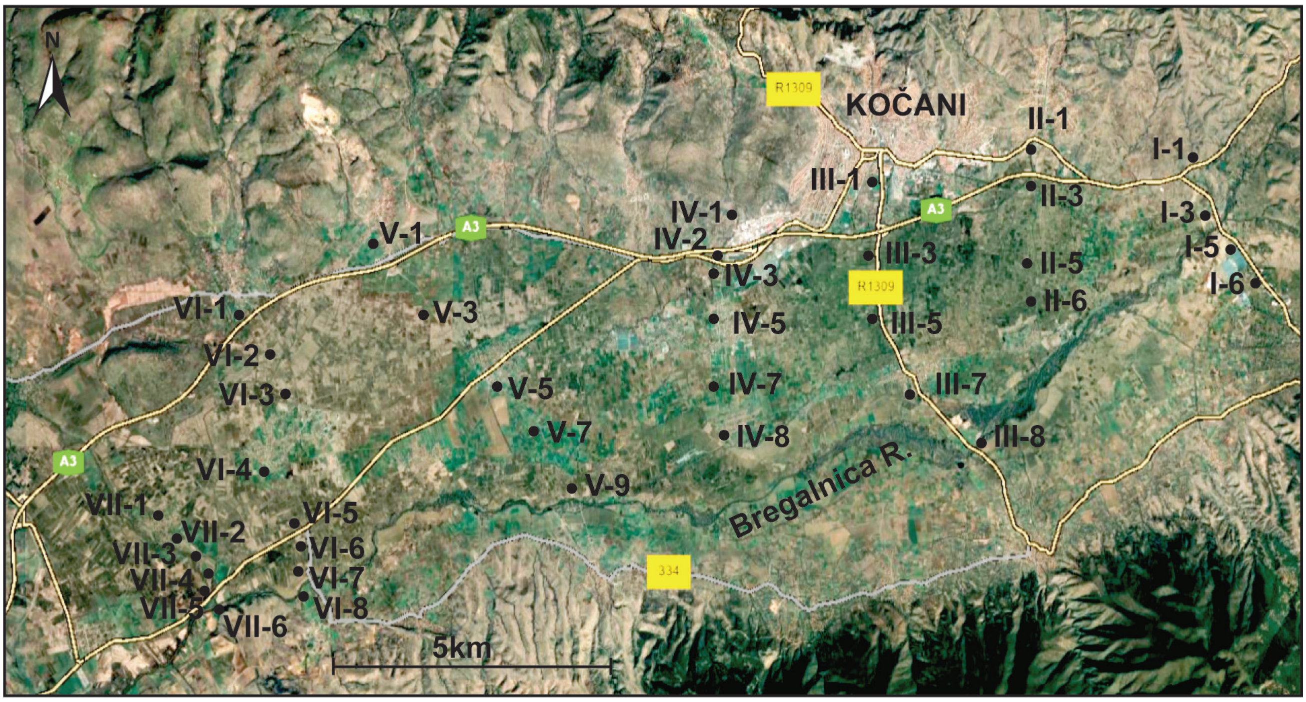

Fig. 2. Map of the locations of the soil samples.

States Geological Survey (USGS) G-1 (granite). The analytical precision and accuracy was better than ±5 % for the elements analysed (minor and trace elements), taking into account the results of duplicate measurements in 10 soil samples and duplicate measurements of the G-1 and SO-1 standards.

Five randomly selected soil samples (I-3, II-6, III-5, VI-4 and VII-2) were also analysed using a sequential extraction procedure to decipher the **Mo, Pb and Zn chemical bonding forms** (Li et al., 1995; Tessier et al., 1979). The 1 g of each soil sample was placed in screw-capped test tubes. A duplicate pulp split and a control sample of WSA (water leach), ESL (Na-acetate), OSL (Na-pyrophosphate), MSL (weak hydroxylamine), or FSL (strong hydroxylamine) monitored the precision and accuracy of each batch of 32 samples. To each sample, 10 ml of leaching solution was added; then the caps were screwed on and the tubes were subjected to an extraction procedure (Bureau Veritas Mineral Laboratories, Vancouver, B.C., Canada). The samples was leached, centrifuged, decanted and washed; the residue was then leached again in a five-step procedure from the weakest to the strongest solution: water → ammonium acetate → sodium pyrophosphate → cold hydroxylamine hydrochloride → hot hydroxylamine hydrochloride. A reagent blank was carried out in parallel with the leaching and analysis steps. The procedure and chemical fractions are listed in Table 1. After the sequential extraction procedure, the content of the analysed elements in the solution were measured using a Perkin Elan 6000 ICP-MS for the determination of over 60 elements (Bureau Veritas Mineral Laboratories, Vancouver, B.C., Canada). A QA/QC protocol included a sample duplicate to monitor analytical precision. A reagent blank was used to measure background and an aliquot of in-house reference material was used to monitor precision. A British Columbia Certified Assayer reviewed the raw and final data.

Tabela 1. Sequential extraction procedure with sequential fractions and chemical reagents.

Step	Fraction	Chemical reagents
1	Water soluble	Demineralized H_2O
2	Exchangeable	1 M sodium acetate
3	Oxidizable	0.1 M sodium pyrophosphate
4	Reducible	Cold 0.1 M hydroxylamine
5	Residual	Hot 0.25 M hydroxylamine

Basic statistical parameters for each element were calculated using Statistica VII. The Mo, Pb and Zn distribution maps were created with the Surfer 6 programme.

Results and discussion

The physico-chemical properties of the soil

The physico-chemical characteristics of the soil are listed in Table 2. All soil samples were characterised by a slightly acidic pH (5.2–6). CEC values were relatively moderate, with an average value of 20.7 mmol/100g. Total organic carbon was between 0.7 and 2.95 %.

Table 2. Information about physico-chemical characteristics of the soil samples from Kočani Field.
Number of measured samples (n) = 25.

	pH	**CEC** (mmol/g)	**TOC** (%)
Range	5.2-6.0	11.4-38.6	0.70-2.95
Mean	5.5	20.7	1.70

Mo, Pb and Zn content in the soil

As there are many samples, I have divided them into three groups according to their Mo, Pb and Zn content. The first group (1) comprises the samples with the lowest Mo, Pb and Zn contents, the second group (2) the samples with the medium Mo, Pb and Zn contents and the last, third group (3) the samples with the highest Mo, Pb and Zn contents.

Table 3 shows the contents of Mo, Pb and Zn determined in the soil samples from the Kočani field based on their descriptive statistical parameters (minimum, maximum, mean, median and standard deviation (SD)) together with the Decree on the limit, warning and critical levels of hazardous substances in soil (Ur. l. RS No. 68/96) and with the Dutch Target and Intervention Values, 2000 (the new Dutch list).

Table 3. Mo, Pb and Zn content (mg/kg) in the soil samples from the Kočani field together with their descriptive statistical parameters and with the proposed values for Mo, Pb and Zn in soil in the Decree on the limit, warning and critical levels of hazardous substances in soil (Ur. l. RS No. 68/96) and with the Dutch Target and Intervention Values, 2000 (the new Dutch list).

The Mo content in the soils was between 0.3 and 1.8 mg/kg (Table 3) and thus far below the limit of 10 mg/kg proposed in Ur. l. RS No. 68/96 and below the target (3 mg/kg) and intervention (200 mg/kg) values proposed in the Dutch Target and Intervention Values, 2000 (the new Dutch list). The Pb content in the soils was between 10.5 and 983 mg/kg, while the Zn content was significantly higher at 53 to 1245 mg/kg (Table 3). The highest Pb and Zn values were predominantly measured in the soil samples from section VII, which had a Pb

Table 3. Mo, Pb and Zn content (mg/kg) in the soil samples from the Kočani field together with their descriptive statistical parameters and with the proposed values for Mo, Pb and Zn in soil in the Decree on the limit, warning and critical levels of hazardous substances in soil (Ur. l. RS No. 68/96) and with the Dutch Target and Intervention Values, 2000 (the new Dutch list).

Statistical data	n	Min	Max	Mean	Median	Std. Dev.
Group/Element	**Mo**	**Mo**	**Mo**	**Mo**	**Mo**	**Mo**
1	12	0.3	0.7	0.48	0.5	0.13
2	20	0.3	1	0.57	0.6	0.14
3	6	0.9	1.8	1.47	1.5	0.34
All groups	38	0.3	1.8	0.68	0.6	0.39
	Pb	**Pb**	**Pb**	**Pb**	**Pb**	**Pb**
1	12	10.5	26.9	18.4	18.5	4.7
2	20	15.4	81.3	29.3	23	15.3
3	6	**295.7**	**983.1**	675.8	723.9	269.4
All groups	38	10.5	983.1	128	22.1	260.3
	Zn	**Zn**	**Zn**	**Zn**	**Zn**	**Zn**
1	12	53	74	67.6	68.5	5.6
2	20	76	162	95.7	94	17.9
3	6	**384**	**1245**	852.5	910.5	335.7
All groups	38	53	1245	206.3	87.5	309.8

Decree on the limit, warning and critical levels of hazardous substances in soil (Official Gazette of RS, No. 68/96)			
Element	**Limit levels (mg/kg)**	**Warning levels (mg/kg)**	**Critical levels (mg/kg)**
Mo	10	40	200
Pb	85	100	530
Zn	200	300	720

Target values and soil remediation intervention values soil/sediment for metals Dutch Target and Intervention Values, 2000 (the New Dutch List)			
Element	**National background concentration**	**Target values (mg/kg)**	**Intervention values (mg/kg)**
Mo	0.5	3	200
Pb	85	85	530
Zn	140	140	720

content of 295.7 to 983.1 mg/kg and a Zn content of 384 to 1245 mg/kg (Table 3). The Pb and Zn content of the soil in section VII exceeds all the levels specified in the Ur. l. RS No. 68/96 and the Dutch Target and Intervention Values, 2000 (the new Dutch list) (Fig. 3).

The Kočani field is also surrounded by two large polymetallic mineralized areas, e.g. the Pb-Zn ore districts of Zletovo-Kratovo and Sasa-Toranica. The soils in section VII, which is located near the Zletovska River and the Zletovo-Kratovo ore district, were exposed to a comparatively higher input of anthropogenic PTEs than other parts of the Kočani area. The polymineralic zone of Zletovo Kratovo consists of the main Pb and Zn minerals, galena and sphalerite, while no main Mo mineral is present. In addition to the main minerals mentioned, pyrite occurs in the Zletovo-Kratovo ore mineral association and, as reported by Hu et al. 2019 can also incorporate Mo into its crystal structure. Slightly elevated Mo levels were detected in the soil samples. The difference between the Mo, Pb and Zn contents in section VII and the other sections is shown in box and whisker plots (Fig. 4). The pollution in section VII is undoubtedly related to the irrigation of rice fields with water from the Zletovska River; previous studies have confirmed that the water of the Zletovska River was contaminated with PTEs from untreated mining wastewater (Alderton et. al, 2005; Dolenec et al., 2007; Rogan Šmuc, 2010). Repeated water samples from the Zletovska River showed marked fluctuations in Mo (0.3-0.9 µg/l), Pb (50-80 µg/l) and Zn (101-1250 µg/l) (Alderton et al., 2005; Dolenec et al., 2007; Rogan Šmuc, 2010). Elevated levels of Pb and Zn were also found in other soil sections, especially in sections V and VI. This increase is due to various sources, e.g. phosphate fertilisers (Zn) (Zhou et al., 2021; Alengebawy et al., 2021) and pesticides (Pb) in agriculture (Alengebawy et al.,

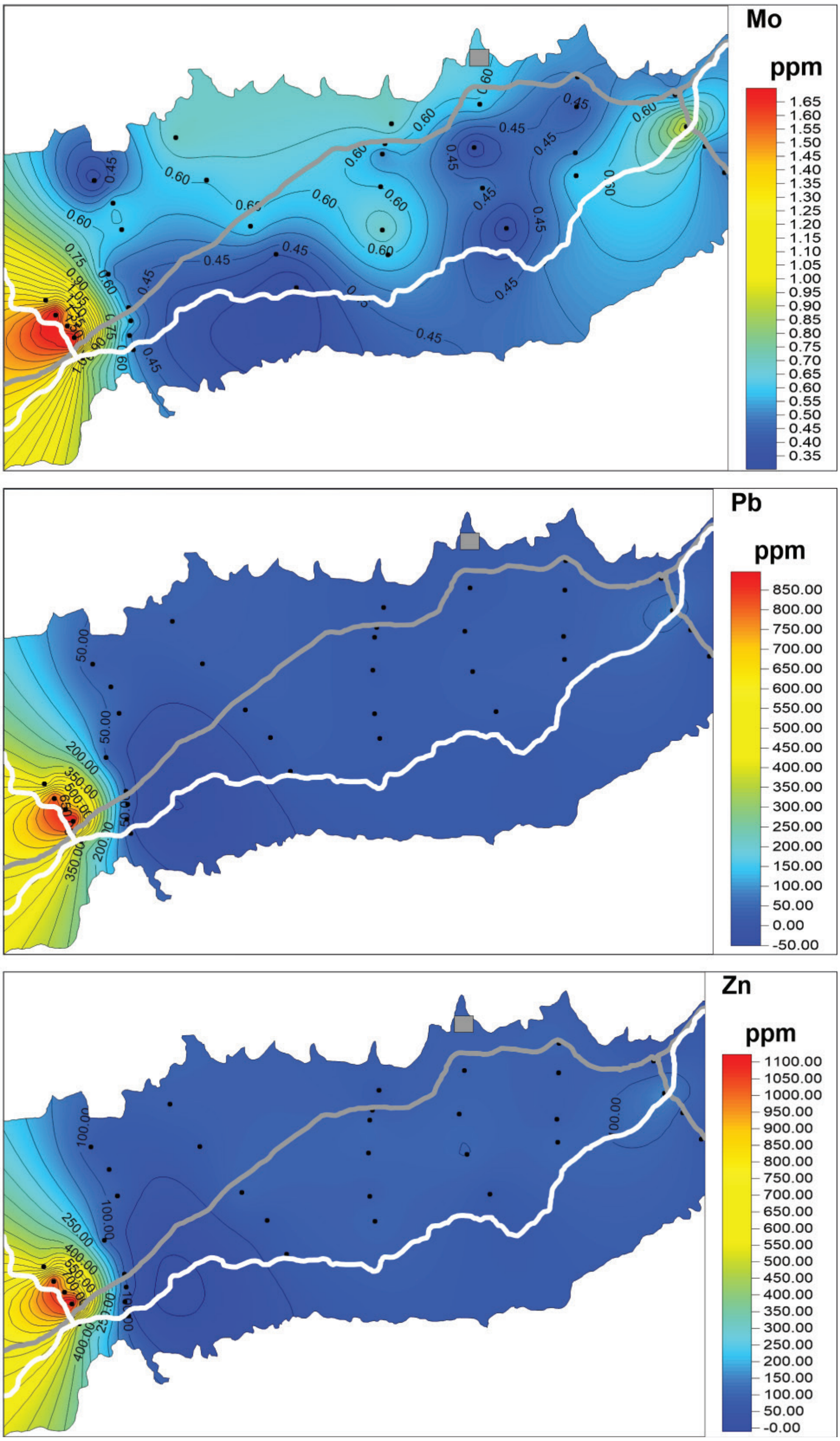

Fig. 3. The spatial distribution of Mo, Pb and Zn content, clearly denoting the enrichment with the investigated elements in the section VII.

2021; Bradl, 2005; Wang et al., 2023a) as well as urban and traffic-related sources (Pb, Zn) (Bradl, 2005; Wang et al., 2023a). It could also originate from the discharge of untreated municipal and domestic wastewater (Bradl, 2005) from the town of Kočani and the village of Orizari into the river systems of the Kočanska and Orizarska rivers, both of which are used for irrigation purposes.

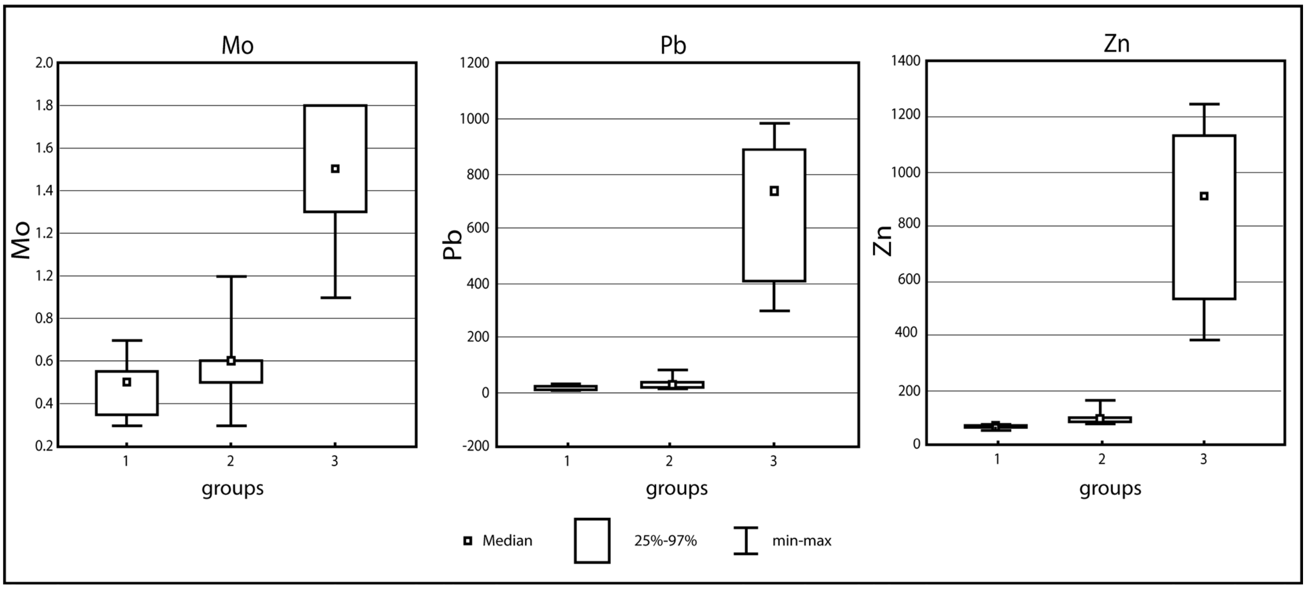

Fig. 4. Box and whisker plots of Mo, Pb and Zn for soil samples from the Kočani field.

Mobility potential and environmental bioavailability of Mo, Pb and Zn from soils

A sequential extraction method was used to assess the mobility potential and environmental bioavailability of Mo, Pb and Zn in the investigated environment. No significant differences were noted in the distribution/partitioning of the elements within the selected samples originating from different sites, but there is an obvious difference in the sequential fractions in which the elements are most abundant.

The most abundant fraction for Mo was the oxidizable fraction, and the other important fractions for Mo were the residual and the water-soluble fractions (Fig. 5). This is supported by the findings of Kabata-Pendias & Pendias (2001), Wichard et al. (2009), Xu et al. (2013), Marks et al. (2015), Matong et al., (2016) and Alvarez-Ayuso & Abad-Valle (2017) that Mo in soil is predominantly associated with organic matter (e.g. organometallic complexes).

Pb and Zn were mainly bound to the residual fraction and the reducible fraction (Fig. 5). The results of Riffaldi et al. (1976), Kabata-Pendias & Pendias (2001), Liu et al. (2013), Nemati et al. (2013), Arenas-Lago et al. (2014), Kennou et al. (2015), Matong et al. (2016) and Zhang et al. (2018) also indicate that Pb is mainly associated with the residual fraction and Mn oxides as well as Fe and Mn hydroxides. The association of Zn with Fe and Mn hydroxides in soils was similarly demonstrated by Kabata-Pendias & Pendias (2001), Arenas-Lago et al. (2014) and Alvarez-Ayuso & Abad-Valle (2017). Rice cultivation in the Kočani rice fields generally requires frequent flooding. Different flooding conditions have different effects on the mobility and environmental bioavailability of PTEs. Fe and Mn oxides are important adsorbents for PTEs in soils under oxidising conditions (Lee, 2006). Under reducing conditions (flooded fields), however, a relatively high proportion of PTEs is detected in the exchangeable fraction, as the PTEs adsorbed on the Fe and Mn oxides release (Charlatchka & Cambier, 2000; Lee, 2006). As the soil samples were taken under oxidising conditions (non-flooded fields), Pb and Zn are mainly associated within the reducible and residual fractions.

The mobility and environmental bioavailability of Mo, Pb and Zn in soils depends primarily on the nature of their binding forms in the soil. The water-soluble and exchangeable fractions are considered to be the most mobile and bioavailable fractions, in contrast to the residual fractions, where the PTEs are strongly bound to the crystalline structures of the minerals present in the soil matrix and are stable (Dean, 2007; Nemati et al., 2013). Mo was consistently bound to bioavailable and leachable fractions (Fig. 5) in all samples, while Pb and Zn predominated in reducible and residual fractions (Fig. 5), indicating a relatively low mobility potential. The sum of the water-soluble and exchangeable fractions for Mo, Pb and Zn detected in the soils of the Kočani field shows that the potential mobility and environmental bioavailability of these elements for plants in the studied area decreases in the following order: **Mo > Zn > Pb.** It is very important to point out that in polymetallic areas exposed to the anthropogenic influence of several PTEs, environmental pollution must be assessed not only for the PTEs that

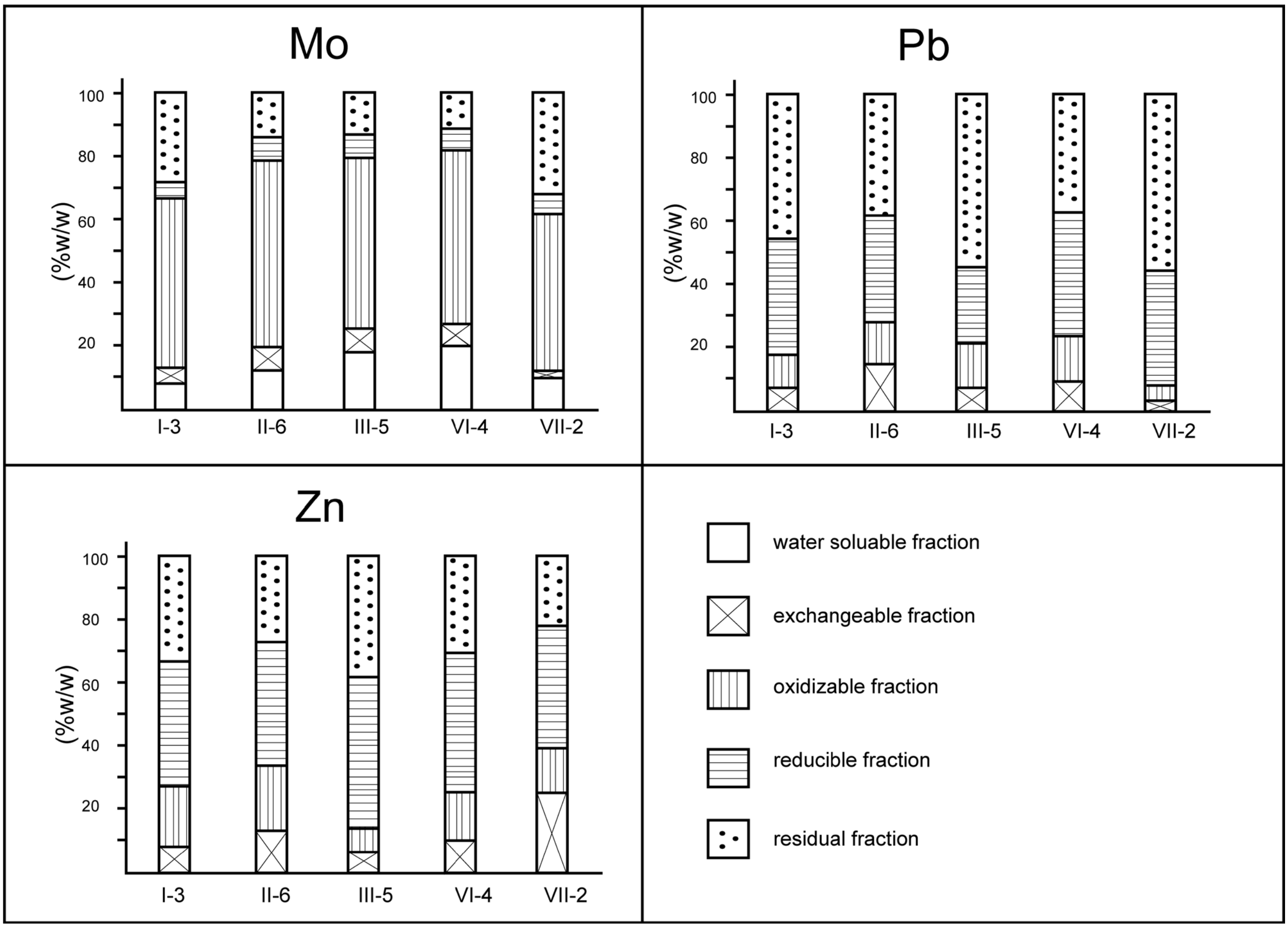

Fig. 5. Mo, Pb and Z binding forms in soil samples from sampling sites I-3, II-6, III-5, VI-4 and VII-2.

are present in high total content, but also for those whose contents are not so high (Kabata-Pendias & Pendias, 2001; Dean, 2007). The mobility potential and environmental bioavailability of PTEs do not depend on their content in the various minerals, ore mineral, rocks, sediments and soils, but on their individual nature and their ability to bind in the different minerals, amorphous materials and organic matter.

Conclusions

The Pb and Zn contents determined in the Kočani soils from section VII were well above the maximum permissible values for the PTEs content of soils (according to Slovenian legislation and new Dutch list). Although the Mo content was below the mentioned limits, its accumulation in the soil samples near the Zletovska River was conspicuous, which confirms the higher anthropogenic PTEs contamination in this area. The mine's wastewater is discharged uncontrolled into the Zletovska River, which therefore contains extremely high concentrations of PTEs (Alderton et al., 2005), and is used to irrigate the nearby rice fields. The Zletovska River is thus considered the most anthropogenically influenced part of the Kočani field. The very high contents of analysed PTEs in agricultural soils are most probably related to past and present mining activities, especially in the Zletovo-Kratovo ore district.

According to the sum of the water-soluble (1) and exchangeable (2) fractions of Mo, Pb and Zn detected in the soils of the Kočani field, the mobility potential and environmental bioavailability of the studied PTEs (from soils to plants) decreased in the following order: Mo > Zn > Pb. For this reason, it is very important to assess the potential mobility of all PTEs in areas exposed to multi-element contamination, as mobility usually depends not only on the amount of PTEs in the minerals, ore mineral, rocks, sediments and soils, but also on their individual nature, their preferential binding and their mobility potential.

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