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A simulation experiment as a method for the investigation of the mobility of heavy metals from inundated land

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Abstract: A simulation experiment was used to study the interaction of river water with different soils (arable land, orchards, meadows, pastures and forestland). The results obtained by sequential extraction before and after the simulation experiment were compared in order to determine the substrates of the heavy metals in inundated land and to evaluate their mobility. Samples of various soils were collected from the region of the future accumulation Lake Bogovina (Serbia) and analysed for ten elements using AAS, GFAAS and ICP. Investigation of the nature of the association of heavy metals and the identification of their substrates were provided by a five-step sequential extraction. Correlation analysis was used as a method for the determination of the substrates for heavy metals. The good correlation among the microelements and certain macroelements indicated the substrates of the microelements. Manganese and iron had a good correlation with most of the microelements. Calcium had only a few correlations with some microelements. Some elements, such as nickel and cadmium, had one substrate before and another after the simulation experiment.

Keywords: zinc; heavy metals; accumulation lake; sequential extraction; inundated soil.

INTRODUCTION

Geochemistry of heavy metals is very important for the prediction of their behaviour in ecosystems, especially for their mobility and sorption processes.^{1–5} The mobility of microelements may be affected by different factors, such as: changes in pH and ionic strength.^{6–9} The action of microorganisms could contribute to a change in the environment and to an increased accessibility of metal ions.

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The aim of this work was to define the mechanisms that control the geochemical and ecochemical behaviour of heavy metals in the future accumulation Lake Bogovina (Serbia). The future accumulation Bogovina is near RTB (Mining and Melting Corporation – Bor) which discharged large amounts of heavy metals and, therefore, it is important to study the distribution of heavy metals and other parameters in the inundated land that could be important for the quality of water. An investigation of the nature of the associations of heavy metals and the identification of their substrates could contribute to an evaluation of possible mobilizations^{10,11} of heavy metals from future inundated land. The combination of a simulation experiment with sequential extraction was used in order to determine the substrates of heavy metals and evaluate their mobility. The method is new and was recently used in a study of the accumulation Lake Rovni.¹² Special attention was given to zinc, which was relatively abundant and significant amounts were found in various phases of the applied sequential extraction.¹²

Water circulates through different type of soils such as sediments, water deposits, arable lands, forestlands, meadows, *etc.* In such environments, microelements could be attached in several ways: non-specific (adsorbed), attached to carbonates by co-precipitation and sorbed on iron and manganese oxides.¹³ Microelements could be incorporated in the silica matrix, bonded to clay or bonded to organics (especially in arable land).^{14,15}

Substrates could be sources of microelements (heavy metals) and therefore contribute to environmental pollution. They could associate and release microelements depending of the conditions. Microelements can change or degrade substrates, which can result in the release of microelements in inundate water. The mobility of microelements is influenced by different factors, such as change of pH, redox potential and the effect of microorganisms that can change the environment and the mobility of elements.⁶⁻⁹

At the end of 80's, many authors used a combination of different extraction media to study soil samples. Very soon thereafter, they adopted a division of phases connected with the applied extraction means using extractants with suitable chemical properties that fulfilled the criteria of efficiency and selectivity.^{16,17} Since then, the method was adopted and changed by different authors.¹⁸⁻²³

Sequential extraction was chosen as a suitable method. By successive extraction of soil samples with different mediums, the extraction of a specific fraction of heavy metals was possible. Special attention was dedicated to mobile fractions of heavy metals, as they were the most interesting and the most important from ecochemical aspects.

One of the most common divisions of phases for sequential extraction is the following:

Sorptive (adsorptive and ion exchange) phase. This phase is used in order to estimate the maximal quantity of sorbed ions that a geological material can re-

lease without the visible decomposition of any mineral phase. Neutral solutions of salts (NH_4OAc , MgCl_2 , CaCl_2 , BaCl_2 , KNO_3 , *etc.*) are usually used for this extraction phase. Their concentrations (and ionic strengths) must be sufficiently high to initiate complete ion exchange and desorption from all substrates.

“Easily reducible” phase. Weak reduction means, for example, hydroxylamine is used for the selective reduction (solvent) of manganese oxy-hydrates and the most mobile fraction of amorphous iron oxides. All the microelements co-precipitated with these oxides will be detected in the solution.

“Moderate reducible” phase. For amorphous iron oxides, some stronger reduction agents are used, *i.e.*, oxalic acid, sodium dithionite and similar.

Organic-sulphide phase. The distinguishing of the organic and sulphide metal fraction in a geological material is one of the disadvantages of sequential extraction. This problem is still not resolved. Pure nitric acid, or its combination with other acids, is a very effective means but it leads to a noticeable decomposition of silicate material. The usage of the hydrogen peroxide is acceptable at higher temperatures and low pH (about 2).

Residual phase. This is the least interesting phase from the ecochemical viewpoint as it includes silicate and oxide materials as well as incorporated metal ions, *i.e.*, in natural conditions, this fraction cannot be mobilized from the geological material. Concentrated mineral acids and their mixtures are usually used for the decomposition of this crystal matrix.

EXPERIMENTAL

Soil samples

The future accumulation Bogovina will inundate 5.32 km^2 of land and the volume of the lake will be 77 millions m^3 ; the River Crni Timok will fill the accumulation. The sampling locations are shown in Fig. 1.

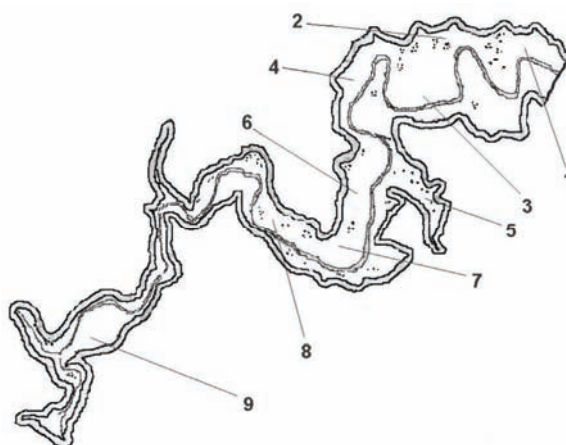


Fig. 1. Shape of the future Lake “Bogovina” with the sampling locations marked.

The soil of the future accumulation Bogovina differs considerably due to land exploitation¹² (Table I). During the sampling, special care was given to the percent distribution and additionally to the area pattern. Hence, the samples were taken from three locations of arable land, three locations of forestland and one location each of pastures, meadows and orchard. Furthermore, one sample was taken from suspended detritus.

TABLE I. The percent of different soils types of the future accumulation “Bogovina”

Land use	Percent	Number of samples	Label of samples
Arable land	30.1	3	1, 3, 8
Orchards	2.7	1	4
Meadows	16.8	1	7
Pastures	15.5	1	6
Forestland	24.6	3	2, 5, 9

Due to the dangerous atmospheric accumulation of heavy metals emitted by the large smelting corporation RTB Bor and their possible deposition on the land, it was decided to remove the surface layer of the basin (30 cm in depth). Therefore, samples were taken from the depths: 30–40, 40–50 and 50–60 cm. All samples were denoted by Arabic numbers from 1 to 9, while the samples from a depth of 30–40 cm were marked as A, from 40–50 cm as B and from 50–60 cm as C. Thus, the complete set of samples was: 1A, 1B, 1C, 2A, 2B,...,9A, 9B and 9C. The studied suspended detritus layer was denoted as M.

One portion of each soil sample was subjected to sequential extraction in five phases. Another portion of each sample was left in contact with river water (simulation experiment) and then another sequential extraction was performed.

Simulation experiment

The simulation experiment was realised according to a previously described procedure.¹² Each sample was transferred into a 10-L cylindrical plastic vessel and left in contact with 8 L of river water. The experiment was performed at 5–8 °C. The height of the soil was 10 cm and the height of the water column was 30 cm in all vessels. Small aliquots (100 cm³) were pipetted from the middle of water column each week. The experiment lasted eight weeks and the dependence of emission, pH, O₂, P, Mn, Ntotal, NH₄⁺, NO₂⁻ and NO₃⁻ on contact time were monitored.²⁴ For all experiments, the microelements were determined as well as their possible substrates.

Procedure for sequential extraction

The five-step procedure developed by Tessier¹⁷ and Polić¹⁶ was used to define the fractions of trace metals. Sequential extraction could provide information about the association of microelements with appropriate substrates. In addition, this analysis was complemented by experiments in which the processes at the bottom of the future lake were simulated. Furthermore, the sequential extraction performed after the simulation experiment could provide important data about the activity of microorganisms, re-absorption processes and co-precipitation of microelements on the available substrates. The solid/solution ratios were 1:45. The summarized procedure is shown in Table II.

Instrumental methods of analyses

All filtrates obtained in the simulation experiment and in the sequential extraction were analyzed by the appropriate technique. Flame AAS was used for the determination of Cu, Ni,

Fe, Pb, Mn, Co, Mg, Ca, K, Na, Cd and Cr (Perkin Elmer – A100). ICP was used for the determination Si and Al (ICP-ARL3410). Flow injection (cold vapour) was used for the determination of Hg (quartz tube, SnCl₂ as the reductant, Ar as carrier gas) (Perkin Elmer – FIMS100).

TABLE II. The sequential extraction procedure

No.	Phase	Reagents, conditions, time
1	Exchangeable	1M CH ₃ COONH ₄ , pH 7, 2 h
2	Bound to carbonates and easily reducible	0.6 M HCl, pH 4, 0.1 M NH ₂ OH and HCl, pH 2, 12 h
3	Moderately reducible	0.2 M (NH ₄) ₂ C ₂ O ₄ and 0.2 M H ₂ C ₂ O ₄ , pH 3, 7 h
4	Organic-sulphide	HNO ₃ , pH 2, 30 % H ₂ O ₂ , 85 °C, 3h, 3.2 M CH ₃ COONH ₄ , 30 min
5	Residual	6M HCl, 85 °C, 9 h

RESULTS AND DISCUSSION

The results obtained by the sequential extractions were grouped by phases for each element. The content of each element was determined before and after the simulation experiment and then the results were compared.

The most common elements are shown in Table III, and these elements represent substrates that associate many microelements.

TABLE III. The most common elements (in ppm)

Element	Phase				
	I	II	III	IV	V
Ca	500–1300	75–1400	–	–	–
Mg	5–20	4–14	–	2.4–30	15–150
Fe	–	15–45	110–340	1–6.1	25–330
Mn	–	5–15	–	4.2–20.6	–
Al	–	8–34	31–204	–	203–1830
Si	–	3–19	25–91	–	–
K	–	–	–	–	31–226

The results obtained in this study could be interpreted in two ways. The first is a comparison of the results before and after the simulation experiments and the other is to correlate the microelements with possible substrates or microelements with other microelements (Table III).

The changes of the concentrations of zinc before and after the simulation experiment are shown in Fig. 2.

Zinc was associated with manganese and iron oxy-hydroxides (high concentration of zinc in the third phase). The concentrations before and after the simulation experiment were similar. The only exception was in the fourth phase, where the amount of zinc after the simulation experiments was several times higher than before. Similar results were obtained by other authors.^{25,26}

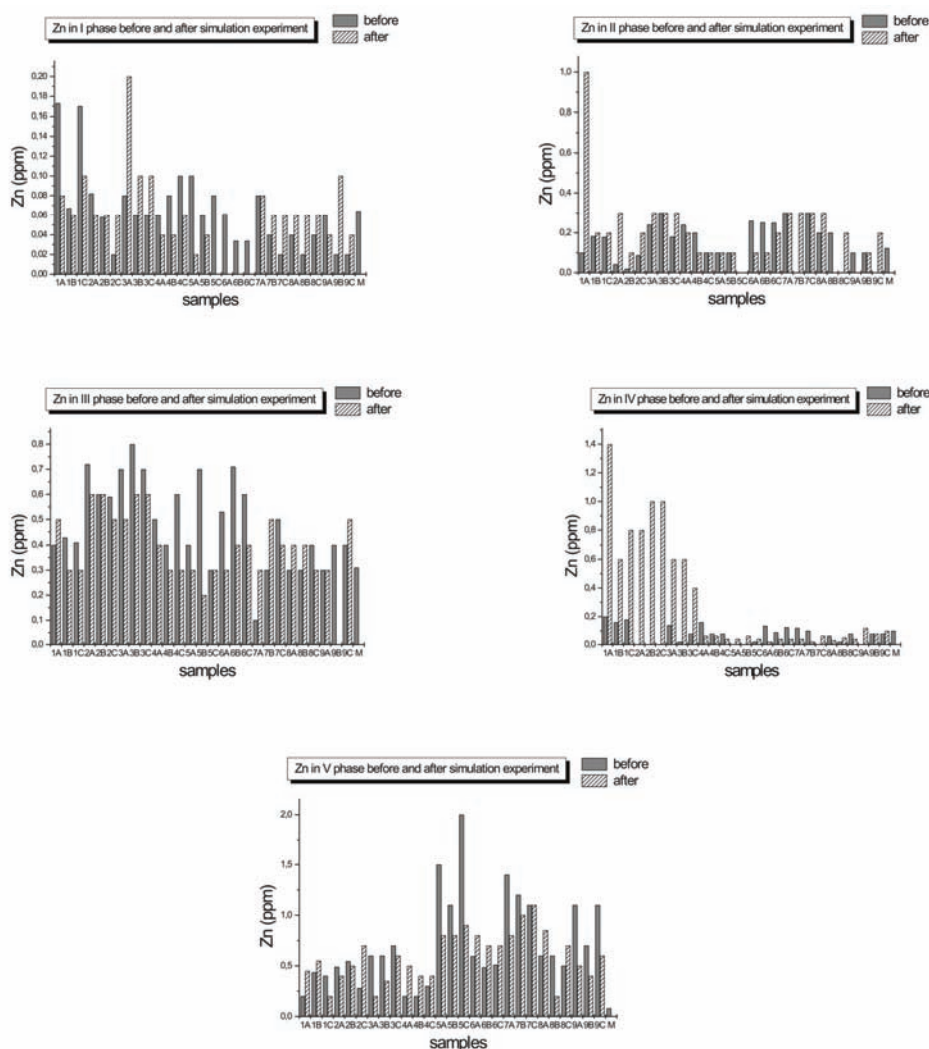


Fig. 2. Concentrations of zinc in all phases (I–V) before and after the simulation experiment.

A huge amount of nickel was incorporated in the mineral matrix. Similar quantities were associated in the first three phases (sorpitive, easily reducible and moderate reducible). There was no nickel in the organic phase. In addition, after simulation experiment, increased concentrations were found in the sorpitive and carbonate phase. These results indicate the contribution of biological processes in the release of nickel.

The results of the first and second phase of the extraction implied that cadmium was partially sorbed on carbonates. The higher concentration found in the second phase samples after the simulation experiment in could be attributed to

the change in pH. These results were compatible with the results obtained for the inundation area of the accumulation Lake Rovni near Valjevo (Serbia).⁶ In addition, the results in the third phase were outside the detection limit.

There was no lead extracted in first phase and there was only a small amount extracted in the second phase (only in the pastureland). Small amounts of lead were also found in the fourth and fifth phase of the extraction, mostly in the forest samples. High amount of lead in the third phase implied that this metal was associated with manganese/iron oxy-hydroxides.²⁷ There was good compatibility with the results obtained for the accumulation Lake Rovni, except that after the simulation experiment, there were no increases of lead in the second phase. The same conclusion was reached that manganese oxides were the main substrate for lead.⁶

Cobalt was found in all extraction phases with the exception of the organic phase. Biological processes were noticed in the second phase, as the release of cobalt was several times higher after the simulation experiment.

Small amounts of mercury were found in some samples. They were closed to the limit of detection by the employed method (0.8 ppb).

Based on a comparison of the results obtained before and after the simulation experiments, some conclusions could be drawn: the action of microorganisms could significantly influence the release of microelements; the changes in pH could also be the result of the release of microelements; the release of manganese and iron as substrates could affect the release of microelements associated with them and organic substances and sulphides could play an important role in the binding of microelements.

Hydroxylamine hydrochloride and hydrochloric acid were used in the second phase of the sequential extraction. Silica matrices are often attacked in this extraction procedure and low concentrations of aluminium and silicon could be extracted in this phase.

Due to the existence of several oxides of some microelements, it is sometimes difficult to dissolve them and destroy the mineral matrices. Furthermore, these oxides often have different solubility. This was the case with two types of manganese oxides. Hydrated and amorphous oxides of manganese are readily soluble. On the other hand, the dissolution of crystalline manganese(IV) oxide is slow and depends of the period of the action of the reducing agent.²⁸

Based on the results of the sequential analysis, it was not always possible to differentiate microelements bound to iron oxides and manganese oxides. However, the use of correlation analysis could increase the reliability of the conclusions. Correlation analysis could provide information on whether the microelements in the third phase were associated with iron or manganese oxide. It could also be helpful in distinguishing the microelements associated with carbonates of calcium and magnesium. In the fifth phase correlation analysis, it could help in

the differentiation of the associations of microelements with clay and silica matrices.

The concentration of each microelement was correlated with the concentration of corresponding elements in possible substrates. Calcium and magnesium represent carbonates as substrates. Iron and manganese represent their oxides. Aluminium and silica represent clay and mineral matrices.

Nickel had a positive correlation with Ca (NiICaII, $r = 0.81900$; $p = 0.000$) and negative one with Mn (NiIMnII, $r = -0.6429$; $p = 0.013$). After the simulation experiment, it was apparent that it had positive correlations with Ca (NiII/2CaI/2, $r = 0.64467$; $p = 0.024$), Al (NiII/2AlI/2, $r = 0.68182$; $p = 0.015$; NiIII/2AlI/2, $r = 0.73490$; $p = 0.010$) and Mg (NiIII/2MgIV/2, $r = 0.65074$; $p = 0.030$), while the correlations with Mn were negative (NiI/2MnV/2, $r = -0.7429$; $p = 0.006$).

The concentrations of cadmium in the samples were very low and correlations were found only in the second phase. Positive correlations were found with Ca and Mg (CdIICaII, $r = 0.98424$; $p = 0.18$; CdIIMgII, $r = 0.97055$; $p = 0.000$; CdIIMgIV, $r = 0.83649$; $p = 0.005$) and negative ones with Fe (CdIIFeI, $r = -0.7785$; $p = 0.005$) and Mn (CdIIMnII, $r = -0.7209$).

Positive correlations of cobalt with Mn (CoIMnII, $r = 0.99988$; $p = 0.000$; CoIIMnII, $r = 0.77840$; $p = 0.001$; CoIIMnIII, $r = 0.82430$; $p = 0.000$; CoIVMnIV, $r = 0.78722$; $p = 0.0012$), Si (CoISiIV, $r = 0.86515$; $p = 0.000$; CoIIISiIII, $r = 0.67939$; $p = 0.021$) and Al (CoIIAlIV, $r = 0.78278$; $p = 0.001$; CoIIIAlIV, $r = 0.67642$; $p = 0.022$) were registered, as well as negative ones with Mg (CoIMgI, $r = -0.8831$; $p = 0.020$; CoIMgII, $r = -0.8815$; $p = 0.020$; CoIMgIII, $r = -0.8425$; $p = 0.035$).

Correlation analysis for lead was not performed, as the concentrations found in sediments were too low.

Correlations of zinc with other elements are shown in Fig. 3. There are two types of correlation diagrams: before and after the simulation experiments. These diagrams differ slightly, which could be the consequence of the activities of microorganisms at the bottom of the lake.

Positive correlations of zinc with Si (ZnIISiII, $r = 0.67490$; $p = 0.001$; ZnIIISiIII, $r = 0.66781$; $p = 0.000$), Al (ZnIIAlIII, $r = 0.69583$; $p = 0.000$; ZnVAlI, $r = 0.64197$; $p = 0.000$), Mn (ZnIIIMnIII, $r = 0.63930$; $p = 0.000$; ZnIVMnIV, $r = 0.73287$; $p = 0.000$) and Fe (ZnVFeV, $r = 0.64472$; $p = 0.000$) were found. A negative correlation of zinc with Ca (ZnIICaII, $r = -0.6503$; $p = 0.001$) was found. It could be concluded that zinc was bound to or sorbed on manganese and iron oxy-hydroxides but that it was also built in the silicate matrix. The negative correlation with Ca could imply that only a small amount of zinc was associated with carbonates.

Correlation diagrams obtained after the simulation experiment are shown in Fig. 4.

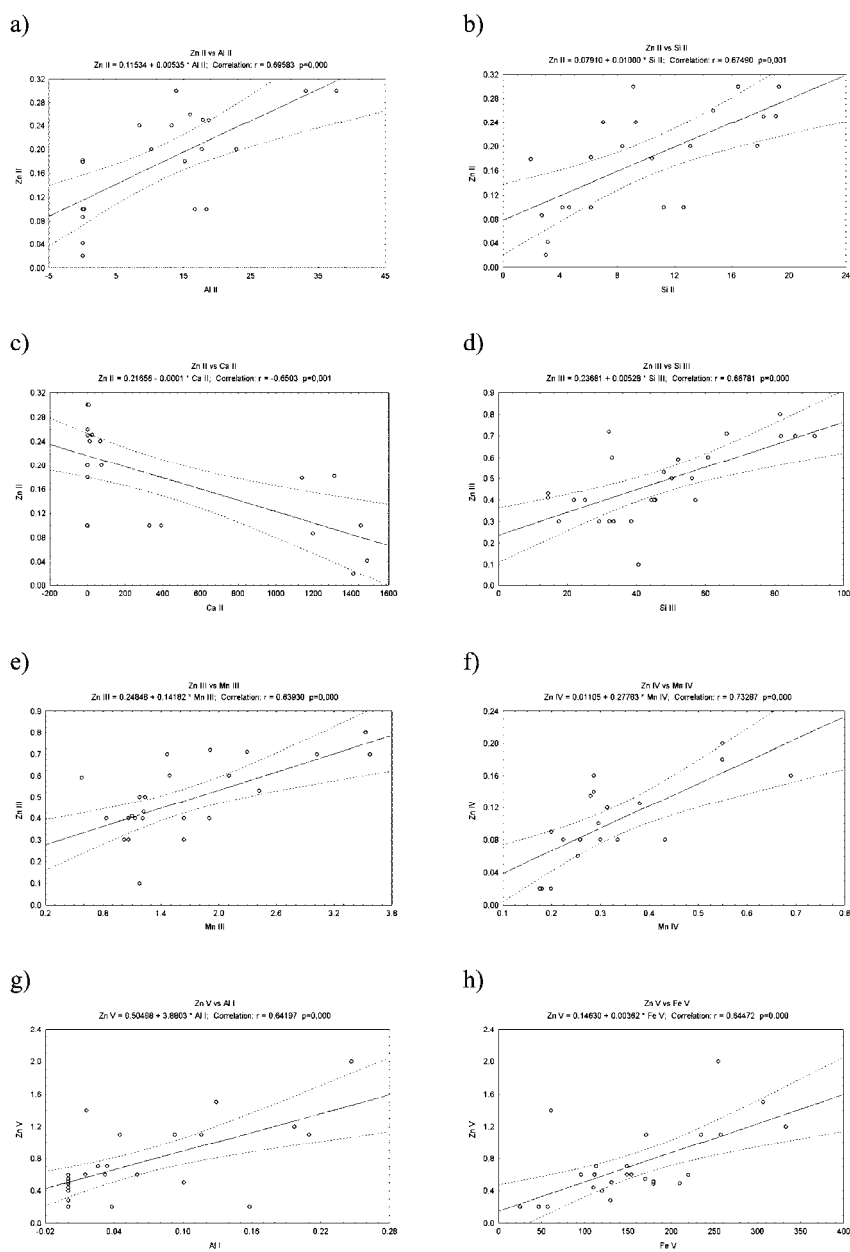


Fig. 3. Correlation diagrams before the simulation experiment: a) Zn in the second phase vs. Al in the second phase; b) Zn in the second phase vs. Si in the second phase; c) Zn in the second phase vs. Ca in the second phase; d) Zn in the third phase vs. Si in the third phase; e) Zn in the third phase vs. Mn in the third phase; f) Zn in the fourth phase vs. Mn in the fourth phase; g) Zn in the fifth phase vs. Al in the first phase and h) Zn in the fifth phase vs. iron in the fifth phase).

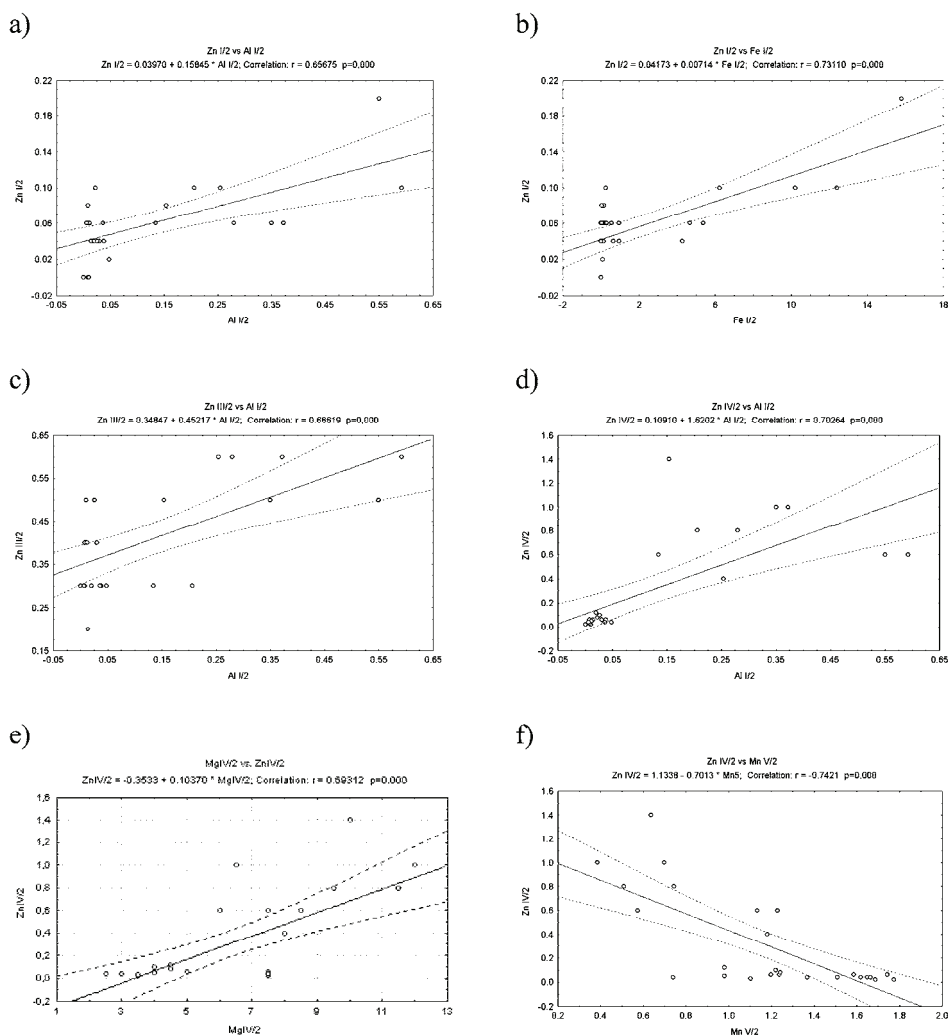


Fig. 4. Correlation diagrams after the simulation experiment: a) Zn in the first phase vs. Al in the first phase; b) Zn in the first phase vs. Fe in the first phase; c) Zn in the third phase vs. Al in the first phase; d) Zn in the fourth phase vs. Al in the first phase; e) Zn in the fourth phase vs. Mg in the fourth phase and f) Zn in the fourth phase vs. Mn in the fifth phase.

After the simulation experiment, there were some positive correlations between Zn and Al ($ZnI/2AlI/2$, $r = 0.65675$; $p = 0.000$; $ZnIII/2AlI/2$, $r = 0.66619$; $p = 0.000$; $ZnIV/2AlI/2$, $r = 0.70264$; $p = 0.000$), Fe ($ZnI/2FeI/2$, $r = 0.73110$; $p = 0.000$) and Mg ($ZnIV/2MgIV/2$, $r = 0.69312$; $p = 0.000$), and a negative correlation with Mn ($ZnIV/2MnV/2$, $r = -0.7421$; $p = 0.000$).

Based on results presented in Figs. 3 and 4, it could be concluded that after the simulation experiment, zinc was associated only in the silica and clay matri-

ces (Figs. 4a–4d). The negative correlation with manganese (Fig. 4f) implied that microorganisms acted on the redox cycles of manganese.

Low concentrations of lead were found in the extracts. This is in accordance with the theory that lead can be efficiently removed from water.^{28,29} Lead was not correlated with any of the examined elements.

Nickel was extracted in the first, second and third phase of the sequential extraction before the simulation experiment and in the first and second phase after the simulation experiments. Similar results were obtained for the correlation analysis before and after the simulation experiments. Before the simulation experiments, most of the nickel was associated with calcium, but after it was associated with calcium and magnesium. The correlations of nickel with manganese were negative. There were better correlations after the simulation experiments than before it. The results of correlation analysis were in accordance with results obtained by sequential extraction. The main conclusion is that sequential extractions have good selectivity for nickel. These results also indicated that the main substrates for nickel are carbonates and that there were no associations with iron and manganese oxides.

Small amounts of cadmium were extracted in second phase and only in a few samples. These results showed that cadmium was associated with carbonates before the simulation experiments. After the simulation experiments, the amounts associated with carbonates were smaller. Obviously, the action of microorganisms resulted in the release of cadmium. Cadmium had positive correlations with calcium and magnesium but negative with iron and manganese. After the simulation experiments, there were no significant correlations. There was good agreement of the results obtained by sequential extraction with the correlation analysis. It could be concluded that cadmium was associated with carbonates, with no associations existing with iron and manganese.

Cobalt was found in the first, third and fifth phase of the sequential extractions. These results indicated that cobalt was associated with iron or manganese oxides but that it was also incorporated in the silicate matrices and clays. The results of the correlation analysis also indicated that cobalt was non-specifically sorbed on different substrates. Good correlation was found for cobalt with manganese and aluminium. Moreover, after the simulation experiments, good correlations were found for cobalt with calcium, magnesium, iron, silicon and aluminium. Analysis of these results indicated that cobalt was an easily removable element that could be reabsorbed after the primary dissolution. Manganese oxides and clay were the substrates of cobalt before the simulation experiment and they were replaced with carbonates and mineral matrices afterwards. The explanation for such behaviour could be very complicated and it might involve different adsorptivity of the substrates and the activity of microorganisms.

Zinc, the element to which special attention was paid in this study, was extracted in the third and fifth phases before the simulation experiments. After the simulation experiments, zinc was extracted in the fourth and fifth phases. These results show that zinc was associated with iron oxides and possibly with manganese(IV) oxide. It was also incorporated in silicate and clay matrices. Correlation analysis resolved the doubt about the association of zinc in the second and third phase because there were only positive correlation of zinc with silicon, aluminium and iron before the simulation experiments. In addition, there was a negative correlation between zinc and calcium. After the simulation experiments, there was a positive correlation of zinc with magnesium, iron and aluminium. The correlation with manganese was negative. These results confirmed that carbonates were not a substrate for zinc. The doubt about the oxides in third phase of the extraction was clarified by the negative correlation of zinc with manganese. Therefore, iron oxide was a substrate for zinc.

CONCLUSIONS

A combination of double sequential extraction with correlation analysis was found to be useful for the prediction of substrates of heavy metals.

Most of the heavy metals were sorbed on the most abundant substrates. Some of them migrated easily from the solid phase to water. The results of the presented study indicated that changes in pH intensified the dissolution of most microelements, such as nickel, cadmium and lead. The increase in the concentrations of cobalt and zinc was not affected by changes of pH, as they were not associated with carbonates.

Changes in redox potential affected higher concentrations of nickel and zinc, as they were associated with manganese and iron oxy-hydrates.

Only small quantities of some elements (Ni, Co) were non-specifically bound and they could be released by changing the ionic strength.

The major processes in inundated land could be dissolution as a result of changes in ionic strength, redox potential or pH. The activity of microorganisms could also play an important role in the dissolution processes. Co-precipitation from water to another substrate could also occur. From the comparison of results for zinc before and after the simulation experiment, it could be concluded that before the simulation experiments the main substrates were iron and manganese oxides and after the organic substances because of the activity microorganisms.

These results are important for the provision of good quality water in the future accumulation Lake Bogovina (Serbia).

ИЗВОД

СИМУЛАЦИОНИ ЕКСПЕРИМЕНТ КАО МЕТОДА ЗА ПРОУЧАВАЊЕ МОБИЛНОСТИ
ТЕШКИХ МЕТАЛА ИЗ ПОТОПЉЕНОГ ЗЕМЉИШТАЂОКИЦА ПЕТРОВИЋ¹, МАРИЈА ТОДОРОВИЋ², ДРАГАН МАНОЈЛОВИЋ² И ВОЛИН Д. КРСМАНОВИЋ²¹"Винча" Институт за нуклеарне науке, Лабораторија за радиоизографију, б. бр. 522, 11 001 Београд и²Хемијски факултет, Универзитет у Београду, б. бр. 51, 11158 Београд 118, ПАК: 105305

Симулациони оглед је употребљен за проучавање интеракције речне воде са различитим земљиштем (оранице, воћњаци, ливаде, пашњаци и шумско земљиште). Резултати добијени секвенцијалном екстракцијом пре и после симулационог експеримента упоређивани су како би се одредили супстрати тешких метала у потопљеном земљишту и проценила њихова мобилност. Узорци различитих екохемијских типова земљишта, који су узети у региону будућег акумулационог језера Боговина (Србија), испитивани су на десет елемената помоћу ААС, GFAAS и ICP. Секвенцијална екстракција у пет фаза примењена је за испитивање природе асоцијације тешких метала и идентификацију њихових супстрата. Корелациона анализа је употребљена за одређивање супстрата тешких метала. Добра корелација између микроелемената и одређених макроелемената указује на њихове супstrate. Већина микроелемената је показивала добру корелацију са манганом и гвожђем. Само неки од микроелемената су имали добру корелацију са калцијумом. Цинк и кадмијум су имали један супстрат пре, а други после симулационог огледа.

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