Lead distribution in water and its association with sediment constituents of the "Barje" lake (Leskovac, Yugoslavia)

Z. TODOROVIĆ[1], P. POLIĆ[2#], D. DJORDJEVIĆ[3#] and S. ANTONIJEVIĆ[4]

*[1]Faculty of Technology, University of Niš, Bulevar Oslobodjenja 124, Leskovac
(E-mail: todoroviczoran@yahoo.com), [2]Faculty of Chemistry, University of Belgrade,
P. O. Box 158, Belgrade, (E-mail: ppolic@helix.chem.bg.ac.yu), [3]Institute of Chemistry,
Technology and Metallurgy, P. O. Box 815, YU-11001 Belgrade and [4]Hemofarm Concern,
Beogradski put bb, YU-26300 Vršac, Yugoslavia*

The lead concentrations in the water of the "Barje" lake are presented for the years 1995 to 1998. Sequential extraction was applied to estimate the chemical association of lead in the sediments of the "Barje" lake. Several lead fractions showed highly significant correlations with the corresponding substrate (step II: Mn-oxyhydroxides; step III: Fe-oxyhydroxides) suggesting that lead carbonates were incorporated with amorphous iron and manganese hydroxides. An explanation for this relation can be in the same anthropogenic source of these elements.

Keywords: lead, sediments, sequential extraction, correlation analyses.

INTRODUCTION

Heavy metals are major anthropogenic contaminants. Their inputs, which may be in particulate or dissolved form, include urban run-off, industrial effluents, mining operations and atmospheric depositions. Because most heavy metals tend to accumulate in sediments, their presence in the water column is usually the result of recent inputs. Both sorption and desorption are controlled by the nature of the total heavy metal loading, the sediment type, and the surface water characteristics. Although many heavy metals are essential biological elements, they are all potentially toxic to organisms above certain threshold concentrations.

The adsorption and desorption processes are likely to be major factors in controlling the concentration of lead in natural waters and tend to counteract changes in the concentration of lead ions in solution. Adsorption and desorption rates of lead are rapid on mud solids and particles of clay, silica, humic material, and other naturally occurring solids. Changes in physicochemical conditions, especially pH and redox potential, that

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\#   Serbian Chemical Society active member.

occur during dredging and disposal of lead-polluted sediments may increase chemical mobility and, hence, bioavailability of sediment-bound lead. Under anaerobic conditions in the lake's hypolimnion, a marked decrease in the dissolved fraction and a corresponding increase in the suspended fraction were noted.

Among the microelements, lead is one of the most abundant heavy metal in the lithosphere and also ranks third in the world production of heavy metals,[1] which makes it a highly important potential pollutant of aquifers. Lead, like most microelements, is sorbed by various naturally occurring substrates. In percolated water systems, like soils, sediments, aquifers, *etc.*, lead is often preferentially bound to hydrous iron and manganese oxides, due to pronounced adsorption and coprecipitation processes. In sediments, lead also becomes incorporated into carbonates.

The mobilization of metals from sediments is highly uncertain. Transformations in the chemical forms of metals may affect their mobility. The potential leachability, defined as the amount released at constant pH, decreases in the order zinc (58 %), Cd (49 %), Cu (5 %) and Pb (2 %).[2]

Our general goal is to identify and quantify key geochemical and hydrologic processes controlling the forms and amounts of lead exported from watersheds representing diverse geology, hydrology, sediment type, and land use/cover. Specific objectives are to determine mobility and sorption processes in the sediments for predicting their behaviour in ecosystems.

Health effects summary

Acute: Lead can cause a variety of adverse health effects in humans.[3] At relatively low levels of exposure, these effects may include interference with red blood cell chemistry, delays in normal physical and mental development in babies and young children, slight deficits in the attention span, hearing, and learning abilities of children, and slight increases in the blood pressure of some adults. It appears that some of these effects, particularly changes in the levels of certain blood enzymes and in aspects of children's neurobehavioral development, may occur at blood lead levels so low as to be essentially without a threshold. Chronic exposure to lead has been linked to cerebrovascular and kidney disease in humans. Lead has the potential to cause cancer from a lifetime exposure to levels above the action level.

Site description

The accumulation "Barje" is located on the Veternica River, 30 km upstream from Leskovac near the village of the same name. This accumulation is multifunctional: to protect Leskovac from flooding and to manage flood control, to protect the suspended material, to maintain a safe river flow and finally to supply Leskovac with drinking water. The accumulation has a volume of 40.67 million m^3 and extends in the Veternica valley named "Klisura".

<div align="center">EXPERIMENTAL</div>

Sediments sampling and sample preparation

Clean techniques must be used to obtain meaningful data for metals. During preparation, all plastic containers should be soaked in 10 % HNO_3 solution for at least one day. Newly purchased plastic bottles must also be acid soaked. After soaking for 24 hours, plastic bottles are rinsed three times using distilled water. All tools used for sampling must be stored in plastic bags after cleaning.

The sampling and analysis of the sediments were done using standard methods. Surface sediment grab samples were take in March, July, September and October 1998 from six different locations (close to the dam of the accumulation, at the water tower, from the middle of the accumulation and from the tributaries: Veternica, Beslićka dolina and Vučji potok). The general characteristics of the sediments analyzed by sequential extractions are outlined in Table I.

TABLE I. General characteristics of sediments analyzed by sequential extractions

Sample	Sampling time	Location	Water content/%	Sediment description
K1	March 1998	Kula	52.02	clay
K3	September 1998	Kula	36.16	clay
K4	October 1998	Kula	28.10	sandy
MD1	March 1998	Middle Lake	48.24	clay
MD2	July 1998	Middle Lake	42.87	clay
MD3	September 1998	Middle Lake	56.68	clay
MD4	October 1998	Middle Lake	58.04	clay
V1	March 1998	Veternica (tributary)	23.97	sandy
V3	September 1998	Veternica (tributary)	42.62	clay
V4	October 1998	Veternica (tributary)	20.34	sandy
VP4	October 1998	Vučji potok (tributary)	24.28	sandy
BD4	October 1998	Beslićka dolina (tributary)	20.66	clay

After sampling, the samples were quickly packed in polypropylene flasks, hermetically closed and frozen, as soon as they reached the laboratory. Subsamples were de-frozen, dried at ambient temperature and to determine the partitioning of trace metals in the sediments, a sequential extraction scheme was followed.

Water samples were collected separately from two locations in the accumulation: at the water tower and in the middle of the accumulation. Because the water qualities at most times depend of the input water quality, the investigation included the tributaries: Vaternica, Crcavački potok, Beslićka dolina, and Vučji potok. Sampling was performed with a sampler, which enabled samples to be taken from various depths, at the same time preventing aeration. The samples were taken from depths of 0.5 m; 15 m and 30 m. Immediately after sampling, the following parameters were measured: water and air temperature, pH, conductance, and the nitrate, nitrite and ammonia concentrations. Other non-filtered samples were preserved by the addition of 5 ml HNO_3 (OPTIMA grade) per liter of sample. All the collected samples were placed in individual plastic bottles or bags and returned to the laboratory.

Sequential extraction

Chemical fractionation by sequential extraction has been developed as a tool in environmental analysis for two main reasons. Firstly, to understand the behaviour and fate of elements. Secondly, to predict aqueous speciation, mainly for toxicological reasons. A number of studies have looked at speciation in aqueous particulates. Those methods have been used to explore geochemical processes relating to contemporary sediments.[4,5]

In this work a modification of the extraction scheme (Table II) desribed elsewhere was used.[6,7] In the first three phases same solid/solution ratio (1:45), as recommended by the cited authors, was applied in the second phase the selective extraction of carbonates was omitted because of fact that their destruction cause the dissolution of hydrated oxides, hence the shaking time was extended to 12 h. Instead of total degradation of the residual fraction after the fourth extraction step, a

procedure for the degradation of the crystallized iron oxide phase was applied to improve the selectivity of the sequential extraction procedure. Under the conditions applied in the employed extraction procedure (fifth step, Table II), most of the crystallized iron oxides present should have been dissolved. The residual silicate matrix, which remains after the extraction steps, can be cosidered as highly immobile and insignificant from the point of view of environmental chemistry.

TABLE II. Experimental extraction conditions

Extr. step.	Extraction reagent	Solid/solution ratio	Shaking time	Temp. ºC	Phase extracted (associated metals)
1	1 M Ammonium acetate	1:45	2 h	20	Adsorbed and ion-exchange bound cations
2	0.1 M $NH_2OH \cdot HCl$, 0.01 M HCl	1:45	12 h	20	Carbonates; Mn oxides; partly amorphous Fe oxyhydrates
3	0.2 M Ammonium oxalate, 0.2 M oxalic acid	1:45	10 h	20	Poorly crystallized Fe oxyhydrates
4	30 % H_2O_2; 0.01 M HCl then	1:15	2 h	85	Organic fraction and sulfides
	1 M Ammonium acetate	1:20	30 min	20	
5	6 M HCl	1:5	9 h digest.	85	Crystallized Fe oxides

The sediment dry weight was determined using a separate portion by drying at 120 ºC until constant weight. The combined extracts and washings after each extraction step were concentrated and the trace elements were determined by flame atomic absorption spectroscopy (SpectraAA-20+Varian). According to the fractionation scheme, the metals are categorized as "exchangeable" (Table III), "bound to carbonates" (Table IV), "bound to iron and manganese oxides" (Table V), bound to organic matter" (Table VI) and "residual" (Table VII).

TABLE III. Exchangeable fraction determined by CH_3COONH_4-extraction (mg kg^{-1} dry sediment)

Metal	K1	K3	K4	MD1	MD2	MD3	MD4	V1	V3	V4	VP4	BD4
Fe	3600	12.4	1.9	4070	10.7	13.5	57.2	6.4	10.6	23.2	4.5	6.3
Mn	1220	218	0.7	1060	281	539	535	7.7	143	119	7.5	24.9
K	254	107	9.6	3000	137	162	167	16.9	92	40.1	31.5	20.7
Ni	5.7	0.5	0.3	6.5	0.7	0.9	0.7	0.3	0.9	1.1	<0.05	0.2
Pb	11.4	0.3	0.6	6.0	<0.05	<0.05	<0.05	<0.05	<0.05	1.8	0.6	0.7
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	1.0	0.2	0.1	0.9	0.0	0.5	0.0	0.3	0.2	1.1	0.3	0.4
Zn	7.3	0.2	<0.01	4.8	0.3	1.1	0.5	0.4	0.5	2.6	0.1	0.5

TABLE IV. Easily reducible fraction determined by NH$_2$OH–HCl-extraction (mg kg$^-$ dry sediment)

Metal	K1	K3	K4	MD1	MD2	MD3	MD4	V1	V3	V4	VP4	BD4
Fe	3210	1840	178	3380	4470	6730	7000	1080	3820	816	483	849
Me	108	125	163	92	169	325	424	145	158	22	117	250
K	49.7	67.8	34.2	48.1	23.1	38.3	36.1	15.6	23.0	17.5	20.5	41.5
Ni	1.9	5.2	2.6	3.0	2.8	4.5	5.9	2.1	5.0	0.8	0.3	0.5
Pb	5.4	3.2	2.3	8.0	6.3	7.7	8.9	2.9	4.2	2.1	2.7	2.2
Cd	0.04	0.05	<0.01	0.11	0.13	0.16	0.22	0.07	0.19	<0.01	0.04	0.01
Cu	2.7	2.9	1.1	2.4	1.2	1.8	2.0	1.2	0.4	1.3	1.0	0.6
Zn	9.3	5.0	1.9	4.5	7.9	14.0	14.1	5.0	13.8	2.4	2.3	2.9

TABLE V. Moderately reducible fraction determined by (NH$_4$)$_2$C$_2$O$_4$–H$_2$C$_2$O$_4$ -extraction (mg kg^{-1} dry sediment)

Metal	K1	K3	K4	MD1	MD2	MD3	MD4	V1	V3	V4	VP4	BD4
Fe	8760	6080	2740	8370	8980	12300	12300	3430	7470	1880	2050	2960
Mn	117	63.8	41	79	109	132	133	31.9	56.6	18.2	30.8	49.2
K	31.1	24.2	20.5	27.8	49.1	33.8	33.8	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	6.2	7.3	4.1	5.6	5.0	10.1	7.4	<0.05	<0.05	<0.05	<0.05	1.8
Pb	8.3	4.0	4.1	14.8	18.2	13.5	19.7	2.6	12.4	<0.05	4.1	1.8
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	25.9	13.7	4.8	29.6	19.8	28.2	29.6	6.5	21.2	5.0	4.8	6.1
Zn	28.0	9.7	2.1	12.1	27.3	33.8	40.7	5.9	23.9	5.6	2.1	3.7

TABLE VI. Organic (including sulfides) fraction determined by H$_2$O$_2$ then CH$_3$COONH$_4$-extraction (mg kg^{-1} dry sediment)

Metal	K1	K3	K4	MD1	MD2	MD3	MD4	V1	V3	V4	VP4	BD4
Fe	103	85.5	22.6	87.9	83.0	85.7	86.9	19.5	133	17.2	19.5	28
Mn	22.8	6.9	1.4	18.5	23.9	27.0	19.1	4.2	13.7	2.2	3.1	7.5
K	161	141	48	134	124	135	130	42.3	137	28.2	41	76
Ni	3.6	2.0	0.7	4.6	4.1	3.9	4.3	0.7	5.3	0.6	<0.05	<0.05
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	<0.01	<0.01	0.30	0.40	1.70	1.10	<0.01	0.70	1.30	0.60	<0.01	<0.01

TABLE VII. Immobile fraction determined by 6 M HCl-extraction (mg kg^{-1} dry sediment)

Metal	K1	K3	K4	MD1	MD2	MD3	MD4	V1	V3	V4	VP4	BD4
Fe	11600	9100	14400	10300	9270	11800	12200	4800	7880	3400	6000	6600
Mn	152	78.7	72.8	151	140	152	149	51.1	85.58	35.4	95.7	152
K	7940	6600	5500	5740	5190	5990	5390	2560	3840	1790	4140	4870
Ni	32.6	20.2	10.6	28.2	25.2	29.9	30.2	7.5	15.9	5.3	7.9	4.6
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	20.7	15.7	11.6	16.6	16.1	18.6	17.3	4.9	10.6	2.8	7.9	5.5
Zn	94.8	57.3	35.6	29.6	73.5	82.3	82.6	25.1	53.1	16.6	35.9	35.4

RESULTS AND DISCUSSIONS

The concentrations of lead in the various water samples are presented in the Table VIII. The maximum lead concentration of 0.085 mg/L was in the sample taken from the middle of the accumulation at a depth of 30 m in July 1998. It is interesting that the lead concentrations were less in spring than in autumn and the maximum concentrations were at the location at the water tower. Of the main tributary the lead concentration in the sample from Veternica (0.039 mg/L) was higher than in the samples taken from the other tributaries (0.004 mg/L).

TABLE VIII. Concentration of lead (mg/L) in the water of "Barje" lake for the samples taken from depths of 0.5 m, 15 m and 30 m and from tributaries (Vet. = Veternica, Bes. d. = Beslićka dolina; Vuc. p. = Vučji potok, and Crc. p. = Crcavački potok)

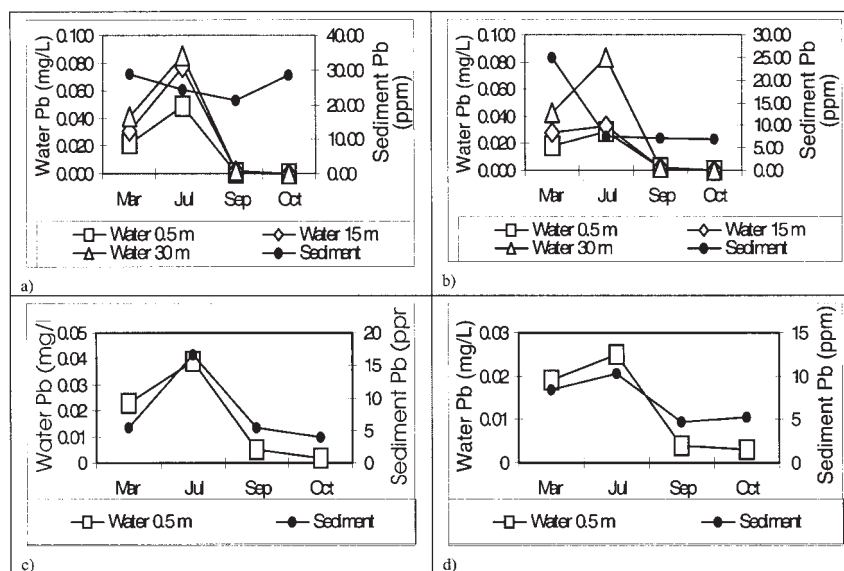|	Water tower			Middle of the accumulation			Tributaries			
	0.5 m	15 m	30 m	0.5 m	15 m	30 m	Vet.[1]	Bes. d.[2]	Vuc. p.[3]	Crc. p.[4]
May 95	0.022			0.016			<0.001			
Aug. 95	0.005			0.003			0.037			
Sep. 95	0.022			0.016						
May 96	0.022			0.016						
Sep. 96	<0.001			<0.001			0.003			
Dec 97	0.008			<0.001						
March 98	0.018	0.028	0.043	0.022	0.031	0.041	0.023			
July 98	0.029	0.033	0.083	0.049	0.077	0.085	0.039			
Sep. 98	0.002	0.002	0.002	0.001	0.002	0.002	0.005	0.001	0.004	0.006
Oct. 98	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	0.003	<0.001

Fig. 1. The lead concentrations in the water and sediments during 1998: a) in the middle of the accumulation, b) at the water tower, c) at the main tributary, Veternica, d) tributary, Vučji potok.

Sediment–water partitioning models have an important contribution to make to field-scale lake studies of sediments containing heavy metals, and have important implications for the deposition of heavy metals.[8] On the basis of the waters and sediments data, it can be concluded that the highest lead concentrations in the sediments were found in the spring in spite of the fact that the concentrations of lead in the water sample were maximum in the summer. The highest lead concentrations in water were found during the summer time because stratification of the lake has occurred and the oxygen concentrations in the waters at the bottom of the lake had become depleted.

The correlations of the lead concentration in the surface water with the water temperature, turbidity, color, pH, conductivity, permanganate consumption, oxygen demand (BOD5), oxygen saturation, dissolved oxygen, anions (NO_2^-, SO_4^{2-}), cations (NH_4^+, Mg^{2+}, Ca^{2+}), total hardness and values of the UV extinction at 254 nm are shown in Fig. 2.

There is no direct correlation between lead concentration and temperature because of stratification, which is caused by a layering effect produced by unequal warming of the lake waters.

The negative correlations with dissolved oxygen, oxygen saturation and nitrite concentrations are to be expected because of the well know phenomenon that oxygen depletion causes high metals levels. Increased organic and nutrient loads apparently cause oxygen depletion. The high values of turbidity, color, conductivity, permanganate consumption and values of the UV extinction at 254 nm, as well as the positive correlations with lead concentrations support this statement.

The positive correlations with the calcium, magnesium concentrations and total hardness suggest that carbonates are substrates for lead in the lake sediments.

Lead found in association with carbonate minerals, precipitated as stable solid compounds, or co-precipitated with hydrous iron oxides, would be less likely to be mobilized by resuspension of sediments or biological activity. Lead absorbed to mineral surfaces (*e.g.*, clay) or organic materials would be more easily bioaccumulated or released in the dissolved state is the sediments were disturbed, such as during flooding.

In order to define the types of association of the various forms of lead, the lead contents in the sediments were correlated with the contents of macroelements such as Mg, K, Fe and Mn. It is known that K and Mg are indicators for hydrated alumosilicates, but Mg also represent carbonates. Fe and Mn, depending on the extracted phases, represent hydrated or crystallized iron and manganese oxides.

Reciprocally, by correlating the contents of the microelements, it was additionally intended to confirm to what extent each microelement represents a certain substrates. The contents of lead and microelements were correlated in order to precisely define the lead substrates. Also, it can be assumed that the obtained results also give insight into interactions occurring in the sediments.

The exchangeable fraction consists of metals that are readily leached by a neutral salt. In oxidized sediments, as opposed to the reduced sediments, the exchangeable fractions (Table III) are significant, illustrating that metals tend to be mobilized when the sediments are brought into upland conditions.
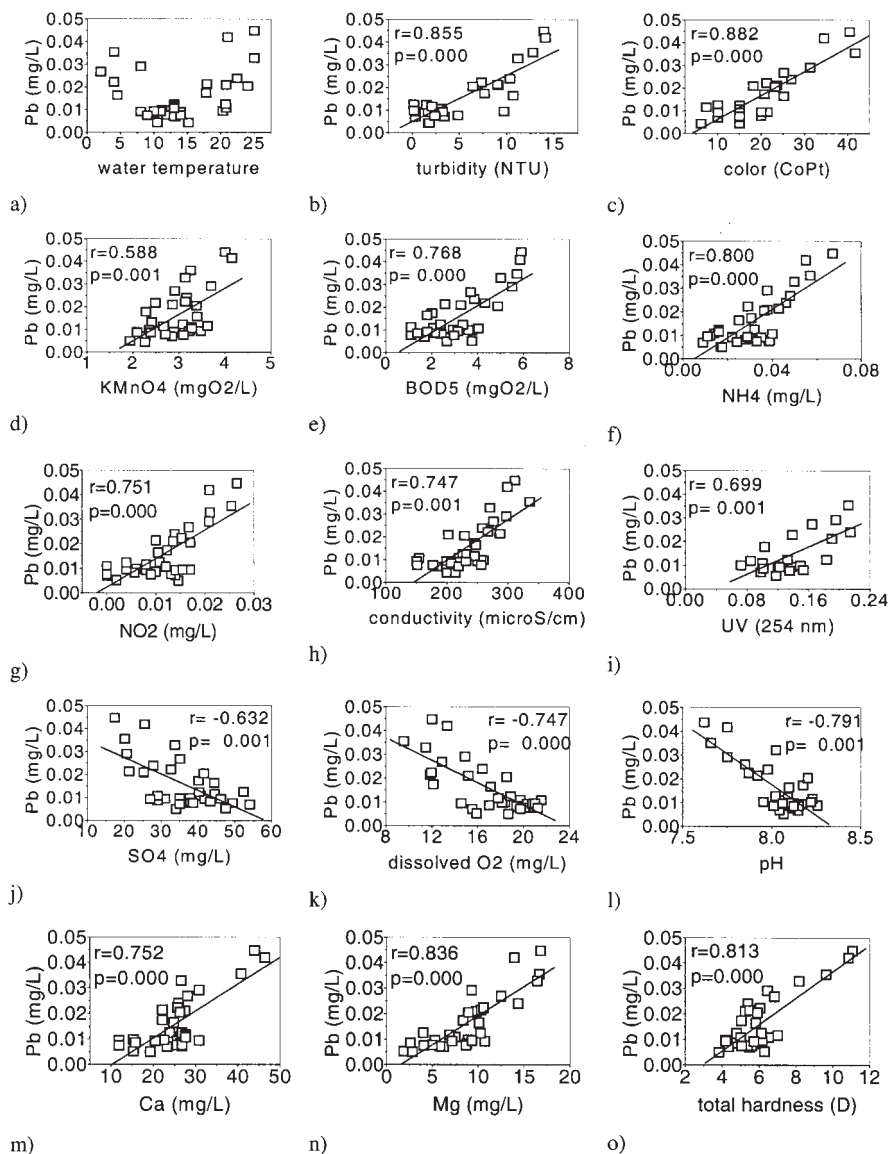
Fig. 2. Surface water lead correlation diagrams. *y*-Axis surface water lead concentrations (mg/L), and *x*-axis: a) water temperature, b) turbidity, c) color, d) permanganate consumption, e) oxygen demand (BOD5), f) ammonia conc., g) nitrite conc., h) conductivity, i) UV extinction (254 nm), j) sulfate conc., k) dissolved oxygen, l) pH, m) Ca^{2+} conc., n) Mg^{2+} conc., o) total hardness.

The quantity of extracted lead in the second phase (Table IV) was about 31.1 % for the lake and 43.2 % for the tributaries.

The second easy reducible fraction is determined after extraction with acidic NHOH–HCl. In principle, this step should selectively dissolve carbonates and thereby

release the associated metals. Conceptually, this reagent is designed to release hydrated, amorphous and partially crystallized manganese oxides while dissolution of crystallized manganese(IV) oxide is appreciably slowly and incomplete. Amorphous iron oxides are also dissolved but to a lower degree.

The highly significant correlations Mg1-Pb2 ($r = 0.912$; $p = 0.000$; lin. corr.); Mg2-Pb2 ($r = 0.847$; $p = 0.000$; lin. corr.); Mg3-Pb2 ($r = 0.839$; $p = 0.000$; lin.corr.); Mg4-Pb2 ($r = 0.935$; $p = 0.000$; lin. corr.); Mg5-Pb2 ($r = 0.805$; $p = 0.000$; lin. corr.); Mg3-Pb3 ($r = 0.912$; $p = 0.000$; lin. corr.); Mg4-Pb3 ($r = 0.901$; $p = 0.000$; lin. corr.) confirm the carbonate nature of the lead.

As was expected, a significant quantity of lead probably originates from amorphous hydroxides, which were extracted in the second phase, but to a smaller amount of lead also comes from crystallized manganese oxides, which were extracted, in the third phase.

The definition for this extraction procedure already anticipates that Mn2 represents hydrated manganese oxides.

The possibilities that iron oxides could be extracted in the second phase have been already discussed. The positive correlations of Pb2 with the macroelements Mg1, Mg2, Mg3, Mg4, Mg5, and with Fe2, Fe3, (Fig. 3), suggest that lead carbonates were incorporated with amorphous iron and manganese hydroxides. An explanation for this relation can be found in the same anthropogenic source.

The most significant lead correlations for each extraction steps are shown in Fig. 3.

A stronger reducing agent, a mixture of oxalic acid and ammonium oxalate pH 3, was necessary for the reductive dissolution of partly crystallized hydrated iron oxides and the associated microelements. In the dark, the oxalate agent reductively dissolves amorphous iron and aluminum oxyhydrates, while silicates, crystallized iron oxides, and substrates of aluminum stay almost intact. If a sample is exposed to light, crystallized iron oxides can dissolve. One of the main disadvantages of the oxalate agent is the dissolution of organic substances and amorphous aluminum precipitations of barium and calcium oxalates, which particularly complicate the metal extraction.[10]

The quantities of lead extracted in the third phase (Table V), were similar for all analyzed samples (average 57.7 % for the lake and 43.2 % for the tributaries).

In the third extraction step, as has already been discussed, the oxalate reagent extracts relatively "mobile", or reducible iron hydroxides. Significant correlations of Pb3 with the macroelements Mg3, Mg4, Fe2, Fe3, Mn3 and Mn4, as well as with the following microelements: Cd2, Cu3, Ni4 and Zn3 (Fig. 2), were found which can prove the abovementioned assumption about the incorporation of heavy metal carbonates into amorphous iron and manganese hydroxides.

High significant correlations Pb3-Fe2 ($r = 0.907$; $p = 0.000$; lin. corr.); Pb3-Fe3 ($r = 0.905$; $p = 0.000$; lin. corr.); Pb3-Fe4 ($r = 0.776$; $p = 0.001$; lin. corr.); Pb3-Mn3 ($r = 0.854$; $p = 0.000$; lin. corr.) and Pb3-Mn4 ($r = 0.864$; $p = 0.000$; lin. corr.) confirm the close tie between lead incorporation and the iron and manganese extracted in the investigated sediments.

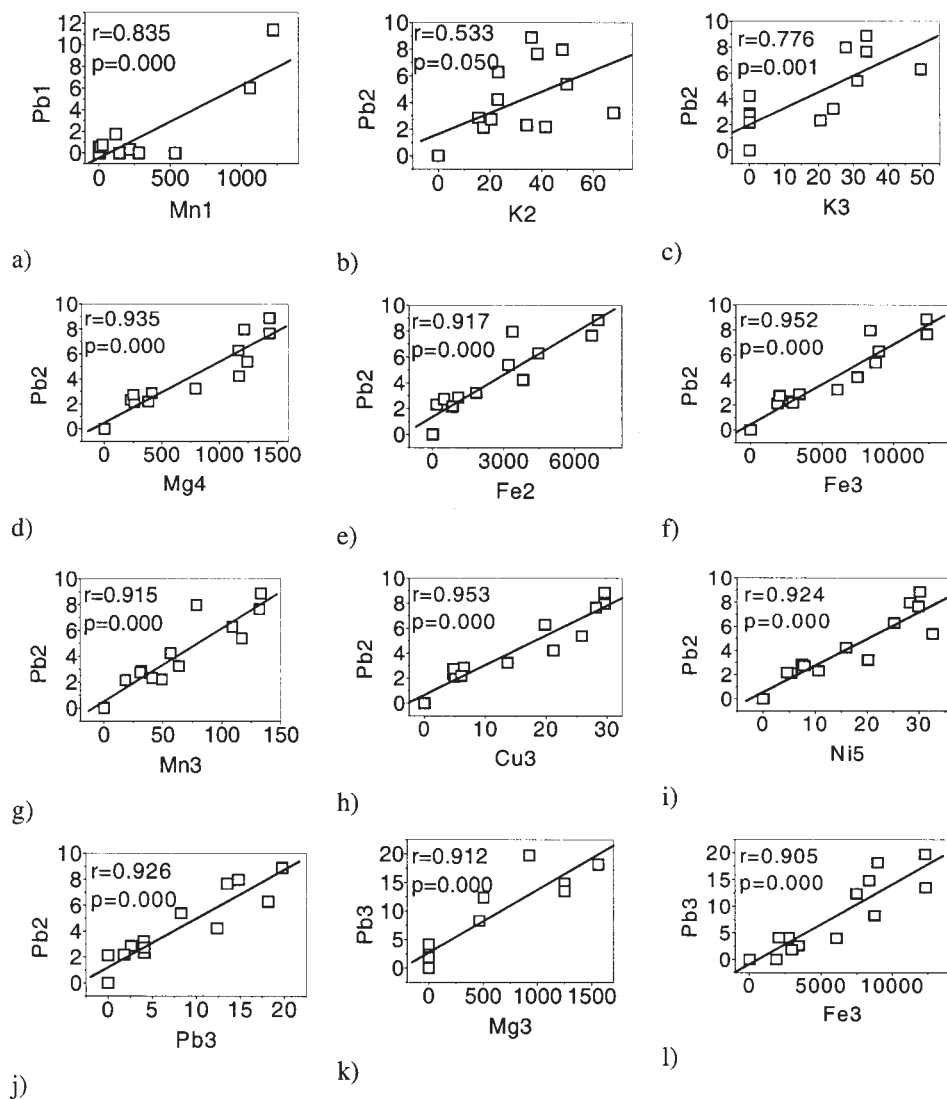The negative correlation Pb3 with K5 and Mg5 confirm that Pb3 are not of silicate nature.

Fig. 3. The most significant lead correlations with macro and microelements (ppm, based on dry sediment): a) Pb1-Mn1, b) Pb2-K2, c) Pb2-K3, d) Pb2-Mg4, e) Pb2-Fe2, f) Pb2-Fe3, g) Pb2-Mn3, h) Pb2-Cu3, i) Pb2-Ni5, j) Pb2-Pb3, k) Pb3-Mg3, l) Pb3-Fe3.

Also the microelements such as cadmium (Pb2-Cd2 ($r = 0.822$; $p = 0.000$; lin. corr.); Pb3-Cd2 ($r = 0.894$; $p = 0.000$; lin. corr.)), copper (Pb2-Cu3 ($r = 0.953$; $p = 0.000$; lin. corr.); Pb2-Cu5 ($r = 0.857$; $p = 0.000$; lin. corr.); Pb3-Cu3 ($r = 0.889$; $p = 0.000$; lin. corr.); Pb3-Cu5 ($r = 0.777$; $p = 0.001$; lin. corr.)); nickel (Pb2-Ni2 ($r = 0.718$; $p = 0.004$; lin. corr.); Pb2-Ni3 ($r = 0.760$; $p = 0.001$; lin. corr.); Pb2-Ni2 ($r = 0.854$; $p = 0.000$; lin. corr.); Pb2-Ni5

($r = 0.924$; $p = 0.000$; lin. corr.); Pb3-Ni4 ($r = 0.900$; $p = 0.000$; lin. corr.); Pb3-Ni5 ($r = 0.844$; $p = 0.000$; lin. corr.)) and zinc (Pb3-Zn2 ($r = 0.795$; $p = 0.000$; lin. corr.); Pb3-Zn3 ($r = 0.869$; $p = 0.000$; lin. corr.); Pb2-Zn5 ($r = 0.726$; $p = 0.003$; lin. corr.) which were well correlated with lead can prove that the mentioned microelements were incorporated as carbonates with amorphous iron and manganese hydroxides.

CONCLUSION

The results concerning the lead concentrations gave a basis for quantitative and qualitative postulates about the geochemical, hydrological and antropogenic factors that are in effect in the investigated "Barje" basin. The maximum lead concentration of 0.085 mg/L was found in the sample taken at the location in the middle of the accumulation in July 1998 at a depth of 30 m. It is interesting that the lead concentrations were less in the Spring than in the Autumn and that maximum concentrations were at the location at water tower. Of the main tributary the Veternica lead concentration (0.039 mg/L) was higher than in the other tributaries (0.004 mg/L). Probably in July, the reducing conditions rose from the bottom to the surface causing dissolution of amorphous iron oxides and partly crystallized iron oxyhydrates with contained incorporated lead.

As all the lead contents were extracted in the first three phases, and not in the fourth or fifth extraction steps, it can be concluded that all the lead is mobile and only a very small amount is sorptive associated. Large amounts of lead are incorporated in amorphous manganese and iron hydroxides (33.1 %), while the largest amount of lead is incorporated in crystallized iron oxides (62.9 %). The positive correlations of Pb2 with macroelements Mg1, Mg2, Mg3, Mg4, Mg5, and with Fe2, Fe3, suggest that lead carbonates were incorporated in amorphous iron and manganese hydroxides. An explanation for this fact can lie in their same anthropogenic source.

И З В О Д

РАСПОДЕЛА ОЛОВА У ВОДИ И ЊЕГОВА АСОЦИЈАЦИЈА СА ЕЛЕМЕНТИМА У СЕДИМЕНТУ ЈЕЗЕРА "БАРЈЕ" (ЛЕСКОВАЦ, ЈУГОСЛАВИЈА)

З. ТОДОРОВИЋ [1], П. ПОЛИЋ [2], Д. ЂОРЂЕВИЋ [3] и С. АНТОНИЈЕВИЋ [4]

[1]*Технолошки факулȳеȳ, Универзиȳеȳ у Нишу, Булевар Ослобођења 124, 16000 Лесковац, E-mail:todoroviczoran@yahoo.com,* [2]*Хемијски факулȳеȳ, Универзиȳеȳ у Беоīраду, ȳ. ȳр. 158, 11001 Беоīрад, E-mail: ppolic@helix.chem.bg.ac.yu,* [3]*Инсȳиȳуȳ за хемију, ȳехнолоīију и меȳалурīију, ȳ. ȳр. 815, 11001 Беоīрад и* [4]*Хемофарм, Беоīрадски ȳуȳ бб, 26300 Вршац*

Представљена је концентрација олова за језеро "Барје" од 1995 до 1998. године. Секвенциона екстракција је примењена за проучавање хемијских асоцијација олова у седиментима језера "Барје". Високо сигнификантне корелације појединих фракција олова са одговарајућим супстратима (друга фаза: Mn оксихидроксидима; трећа фаза: Fe оксихидроксидима) показује да су олово-карбонати инкорпорирани са аморфним хидроксидима гвожђа и мангана. Објашњење се може потражити у истом антропогенијском извору.

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