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ANALYTICAL INVESTIGATION CONCERNING THE METHODS FOR EXTRACTION OF EXCHANGEABLE FORMS OF HEAVY METALS FROM THE SEDIMENT FROM THE DANUBE DELTA

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Abstract. This paper proposes a chemical single extraction method for exchangeable forms of heavy metals applied to specific types of sediments from the Danube delta (Uzlina, Murighiol). The total contents of heavy metals (Cd, Cu, Cr, Mn, Pb and Zn) determined in the sediments from this location are within the normal levels of concentration according to the values indicated in the Romanian Order No 756/97. It was found a higher content of Fe, Mn and Cu in surface water just because of influence of exchangeable forms. The Standard NF X 31 – 120/1992 was found to be able to give a good information about exchangeable forms of heavy metals in the Danube delta sediment. In these sediments Cr is not in exchangeable forms, being bound poorly and strongly by crystalline iron oxides, organic matter, and in residual forms. Pb is bound in two different fractions: exchangeable fraction and bound by Mn oxides and organic matter. Different levels of concentration of exchangeable forms for Zn, Cu, Fe and Mn was determined in the analysed sediments.

Keywords: analytical methods, exchangeable forms, heavy metals, sediments, the Danube delta.

AIMS AND BACKGROUND

The level of heavy metals in the environment seriously is increased during the last few decades due to human activities. Since the toxicity of heavy metals is related to their existing species, their specification is increasingly attracting more attention. However, the determination of specific chemical species is difficult and sometimes impossible. Thus, the so-called exchangeable or carbonate-bound forms, defined by the operational procedure, could be a good compromise to provide the environmental information, and have been commonly applied through different single and sequential extraction procedures, in environmental studies.

The content of trace metals in soil and sediment can be toxic when metals are in highest level of concentration or when the heavy metals are in exchangeable forms. According to the European Community Regulations, Directive No 67/548/EEC (Ref. 1), metals and their various compounds must be analysed or

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monitored because of their toxic properties that can induce chronic or acute diseases, by swallowing, inhaling or cutaneous penetration in reduced quantities and even death due to higher level of concentration.

The release of heavy metals into the aquatic environment is known to cause detrimental effects to the environment. Most of the heavy metals, entering water bodies, become associated with particulates and as a result of setting time, accumulate in bottom sediments of the receiving water.

The occurrence of heavy metals in soils and sediments can theoretically include the following fractions:

- free ions or complexed in the pore water;
- adsorptive or exchangeable bound on soil component surfaces, mainly on iron and manganese oxides and hydroxides, clay minerals and organic matter;
- precipitated as chemical compounds (hydroxides, carbonates and sulphides);
- co-precipitate on iron and manganese oxides and hydroxides, carbonate, phosphate and sulphide minerals;
- organically complexed (on organic solid phases);
- residual, occluded in detritic minerals, especially silicates.

This paper proposes a single chemical extraction method for determination of the exchangeable forms of heavy metals applied to specific types of sediments from the Danube delta (Uzlina, Murighiol). Even if usually the heavy metals (Cd, Cu, Cr, Mn, Pb and Zn) determined in the sediments from this location are within the normal level of concentration according to the values indicated in the Romanian Order No 756/97 (Ref. 2), it was found a higher content of Fe, Mn and Cu in surface water just because of influence of exchangeable forms.

A single chemical extraction was chosen. Advantages for a single extraction versus sequential extraction are:

- it is a rapid procedure;
- the conservation of sample is critical only after first extraction;
- the risk to redistribution of trace elements among phases during extraction procedure does not exist.

Sediments from two sites of the Danube delta were analysed by two different standards (ISO 14870/1999 and NF X31–120/1992) and two other analytical methods. The main objectives of this study consists of evaluation of the extraction technique on organic-rich sediments and determination of the geochemistry and mobility of potentially biotoxic trace metals in the environment.

EXPERIMENTAL

The sediment samples were taken in the period April–September 2003 from two locations (Uzlina and Murighiol) situated in the Danube delta. The sediment samples were air-dried and sieved to particle size < 2 mm. For the determination of the total heavy metal content, 1g of air-dried sediment was digested with 2 ml nitric acid (65%) and 6 ml hydrochloric acid (37%) in a microwave digestion apparatus (the Ethos milestone laboratory system). The total content of heavy metals was determined by flame atomic absorption spectrometry using an ATI UNICAM spectrometer with two types of combustion mixture: an air-acetylene mixture (for Cd, Cu, Fe, Mn, Pb and Zn) and a nitrogen protoxide-acetylene mixture (for Cr) (Ref. 3).

The ranges of the total content of heavy metals and other determinations for Uzlina and Murighiol sediments in the period April–September 2003 are presented in Table 1.

Table 1. Characteristics of Uzlina and Murighiol sediments

Indicator	M.U.	Uzlina	Murighiol	Normal value (the Romanian Order No 756/97)
Zn	mg/kg d.m.	100 ÷ 160	65 ÷ 153	300
Cu	mg/kg d.m.	35 ÷ 90	31 ÷ 51	200
Pb	mg/kg d.m.	25 ÷ 40	25 ÷ 51	90
Cd	mg/kg d.m.	< 0.5	< 0.5	3.5
Fe_{total}	% d.m.	2.3 ÷ 3.1	1.5 ÷ 1.8	–
Cr_{total}	mg/kg d.m.	38 ÷ 46	26 ÷ 46	90
Mn	mg/kg d.m.	580 ÷ 765	360 ÷ 485	900
P_{total}	mg/kg d.m.	440 ÷ 2020	811 ÷ 2645	–
NO_3^-	mg/kg d.m.	105 ÷ 200	118 ÷ 175	–
Mineral oil	mg/kg d.m.	36 ÷ 125	36 ÷ 153	< 100
$C_{organic}$	% d.m.	3.8 ÷ 4.2	2.9 ÷ 3.6	–
N (the Kjeldahl method)	mg/kg d.m.	540 ÷ 760	350 ÷ 670	–

The determination of the total content of heavy metals by using a mixture of concentrated acids is not able to give a good information about the ecological risk on the aquatic ecosystems of the Danube delta. In view of this, it was necessary to use reactants with low chemical aggressivity, which have the role to render soluble only the exchangeable forms of heavy metals.

The methods chosen and their applicability are presented in Table 2.

Table 2. List of the methods used in the present study

Method	Extractant	Applicability
SR ISO 14970/1999 (Ref. 4)	0.05 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA	Cu, Mn, Zn, Cd, Ni, Pb
NF X 31–120/1992 (Ref. 5)	0.01 M EDTA + 1 M CH_3COONH_4	Cu, Mn, Zn, Fe, Pb, Cd, Cr, Ni
Frank Liebe, S. Laudw 1999 / Lakanen si Ervio, 1997 (Ref. 6)	0.025 M EDTA + 1 M CH_3COONH_4 + 0.1 M $NH_2OH.HCl$	Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn, Sr, Ti, V, Zn
Method recommended by the recently introduced ANZECC and ARMCANZ interim sediment – quality guidelines – Australia 2003 (Ref. 7)	1 M HCl	Ag, As, Cd, Cu, Hg, Pb, Se, Zn

A set of mixtures of chemical reagents were used under various extraction conditions (pH, extraction time, reactant/sample ratio):

- A mixture of 0.005 M DTPA+ 0.01 M $CaCl_2$ + 0.1 M TEA; buffer solution pH = 7.3; 1:2 ratio of sediment to buffer solution; 2 h at 30 rot./min and 20°C (Ref. 4);
- A mixture of 0.01 M EDTA + 1 M CH_3COONH_4; buffer solution pH = 7; 1:10 ratio of sediment to buffer solution; 2 h at 40 rot./min and 20°C (Ref. 5);
- A mixture of 0.025 M EDTA + 1 M CH_3COONH_4 + 0.1 M $NH_2OH.HCl$; buffer solution pH = 4.6; 1:10 ratio of sediment to buffer solution; 2 h at 40 rot./min and 20°C (Ref. 6);
- 1 M HCl at 1:10 ratio, 10 min at 40 rot./min and 20°C (Ref. 7).

Table 3. Extractants and fractions and binding form

Fraction and binding form	Extractant
Mobile fraction and easily mobile fraction	0.005 M DTPA+ 0.01 M $CaCl_2$ + 0.1 M TEA, pH = 7.3
	0.01 M EDTA + 1 M CH_3COONH_4, pH = 7
In Mn oxides occluded fraction and organically bound fraction	0.025 M EDTA + 1 M CH_3COONH_4 + 0.1 M $NH_2OH.HCl$; pH = 4.6*
In poorly crystalline iron oxides occluded fraction and organically bound fraction	1 M HCl*
In well crystalline iron oxides occluded fraction and residual fraction	aqua regia*

* Because we do not use sequential extraction, the content of heavy metals extracted with these reactants included preceding fractions.

Heavy metals were extracted with these solutions, shaken for different periods of time and finally the Cd, Cu, Cr, Fe, Mn, Pb and Zn concentrations in the extracts were determined with flame atomic absorption spectrometry, using a SOLAR ATI UNICAM equipment. In Table 3 are presented the extractants, and fraction and binding form.

RESULTS AND DISCUSSION

In the ISO standard[4] it is mentioned that a single DTPA extraction is not able to exchange all mobile forms. It was necessary to do a double extraction with DTPA. Some experimental values for DTPA (single and double) extraction and EDTA extraction for Uzlina and Murighiol sediments are presented below. These results very clearly show that the analyses for Zn, Cu and Pb after the two extractions with DTPA are identical with the analyses using a single extraction with EDTA. For manganese the extraction with DTPA was 2 ÷ 3 times lower than with EDTA. Cr was not found in exchangeable forms, being poorly and strongly bound by crystalline iron oxides and in residual forms.

Table 4. Comparison between DTPA and EDTA extraction for Uzlina sediments for a period of two months

Indicator	Uzlina (June 2003)				Uzlina (July 2003)			
(mg/kg d.m.)	DTPA single	DTPA single+ double	EDTA	aqua regia	DTPA single	DTPA single+ double	EDTA	aqua regia
Zn	9.9	14	15.5	164.4	9.6	14.8	15	148
Cu	17.6	20.3	23.9	90	13.6	16	18.3	53
Mn	5.4	12.2	32	764	5.7	11.1	32.3	622
Fe	83.9	113	42.1	24590	84	106	41.6	26830
Pb	4.9	5.8	6.3	30.1	5.4	7	7.5	25.7
Cr	< 1	< 1	< 1	42.5	< 1	< 1	< 1	46.1

Table 5. Comparison between DTPA and EDTA extraction for Murighiol sediments for a period of two months

Indicator	Murighiol (August 2003)				Murighiol (September 2003)			
(mg/kg d.m.)	DTPA single	DTPA single+ double	EDTA	aqua regia	DTPA single	DTPA single+ double	EDTA	aqua regia
Zn	22.7	45.8	47	153	16.2	23.7	25.2	109
Cu	8	12.1	11.3	49	4.9	9.5	8.9	36
Mn	11	19.7	34	424	7.5	13.6	27.8	218
Fe	88.6	142	34	16250	110	173	65	17463
Pb	10.2	14.9	15.7	51	8.9	17.7	18	36.4
Cr	< 1	< 1	< 1	32.2	< 1	< 1	< 1	26.3

It is evident that iron extraction with DTPA was much better than with EDTA, but in Table 2 iron is not specific for SR ISO 14970/1999. In conclusion, we can say that EDTA extraction (Standard NF X 31–120/1992) is able to give a good information about exchangeable forms of the Danube delta sediments. The chemical substances used in this standard are not expensive comparable with DTPA+TEA solution, and the procedure is more simple due to the better ratio than DTPA standard.

Next are presented the experimental data for other 2 methods used for extraction. In these experiments Cr was extracted only by 1M HCl. The conclusion was that Cr is bound in poorly crystalline iron oxides fraction and organic fraction, in different proportions and mostly is bound in well crystalline iron oxides fraction and residual fraction.

Another observation is that the total content of lead could be extracted by using these two methods. Pb is bound in Uzlina and Murighiol sediments in two fractions: mobile and easily mobile fractions and Mn oxides fraction and organically bound fraction.

Table 6. Comparison between EDTA+CH_3COONH_4+$NH_2OH.HCl$ and 1 M HCl extraction for Uzlina sediments

Indicator (mg/kg d.m.)	Uzlina (June 2003)			Uzlina (July 2003)		
	EDTA+ CH_3COONH_4+ $NH_2OH.HCl$	1 M HCl	aqua regia	EDTA+ CH_3COONH_4+ $NH_2OH.HCl$	1 M HCl	aqua regia
Zn	42	73.4	164.4	29.4	70	148
Cu	41	44.5	90	33	35.5	53
Mn	605	767	764	476	614	622
Fe	2832	10530	24590	2953	11270	26830
Pb	29.8	29.9	30.1	24.6	23.9	25.7
Cr	< 1	8.3	42.5	< 1	7.2	46.1

Table 7. Comparison between EDTA+CH_3COONH_4+$NH_2OH.HCl$ and 1 M HCl extraction for Murighiol sediments

Indicator (mg/kg d.m.)	Murighiol (August 2003)			Murighiol (October 2003)		
	EDTA+ CH_3COONH_4+ $NH_2OH.HCl$	1 M HCl	aqua regia	EDTA+ CH_3COONH_4+ $NH_2OH.HCl$	1 M HCl	aqua regia
Zn	55.3	120	153	74	84.5	109
Cu	14.5	29.7	49	23.5	28.8	36
Mn	343	400	424	189	205	218
Fe	2159	8350	16250	3706	8940	17463
Pb	47.4	49.7	51	35.7	36	36.4
Cr	< 1	6.3	32.2	< 1	4.6	26.3

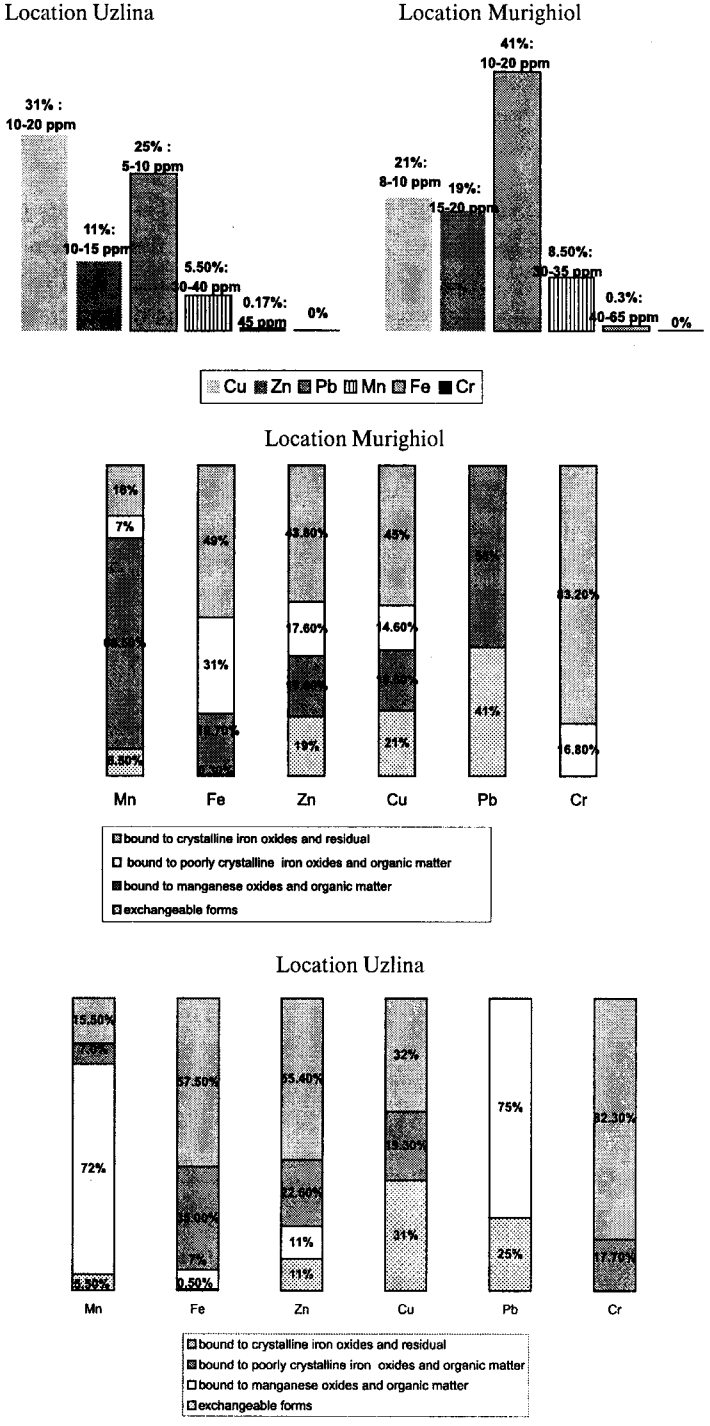

Fig. 1. Concentrations of exchangeable forms of heavy metals

The concentrations of exchangeable forms of Cu, Zn, Pb, Mn, Fe and Cr (ppm d.m. and % d.m.) extracted by a mixture of 0.01 M EDTA + 1 M CH_3COONH_4 (selected method) are presented in Fig. 1.

CONCLUSIONS

The EDTA extraction – Standard NF X 31–120/1992 is able to give a good information about exchangeable forms of the Danube delta sediment. Cr was not found in exchangeable forms, being bound by crystalline iron oxides (poorly and strongly), organic matter and in residual forms. Pb is bound in two different fraction: mobile and easily mobilisable fraction, Mn – oxides fraction and organically bound fraction.

In Uzlina sediments were found exchangeable forms in different concentrations: Cu (10÷20 ppm), Zn (10-15 ppm), Pb (5-10 ppm), Mn (30-40 ppm), Fe (45 ppm).

In Murighiol sediments were found exchangeable forms in different concentrations: Cu (8÷10 ppm), Zn (15-20 ppm), Pb (10-20 ppm), Mn (30-35 ppm), Fe (40-65 ppm).

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