

Soils and sediments testing for contamination by heavy metals – some case studies in Slovakia

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Abstract. Soil (sediment) testing and determination of various chemical forms of metals is important in evaluating their mobility and bioavailability. It can be perceived as an evolving process aimed at improving the assessment of risk associated with heavy metals in soils and plants. Especially the determination of an „available„ fraction of metals, based on single or sequential extraction and soil (pore) solution analyses is now gaining widespread acceptance, as a means to characterise hazards from contaminated soil.

The main task of this contribution is to summarise current testing methodologies illustrated by new analytical results obtained from some case studies in Slovakia. This paper examines new concepts and procedures used for the assessing hazard from metal contamination, including some limitations (analytical, soil) that produce testing results, weakening the relationship between higher content of metals in soil and actual environmental and human health hazards.

Key words: soil/sediment testing, metal speciation, single extraction, sequential extraction, soil solution, plant available metal fraction, soil contamination

Introduction

The accumulation of heavy metals and metalloids in soils and sediments possess many risks to human and ecosystem health. Risks may be expressed either through the food chain or through the groundwater contamination. The evaluation of soils, stream and overbank sediments contamination is an evolving process aimed at improving the assessment of environmental and human health hazards associated with the content of potentially toxic elements in plants and water.

Risks due to soils and sediments pollution by metals are well recognized and major texts have been published by several authors (Alloway, 1990; Kabata - Pendias and Pendias, 1992; Salomons et al., 1995).

Many researches have tried to find out a relation between the concentration of potentially toxic elements in soil/plants system and their effect on organisms (plants and humans) based on total element content or extractable forms of elements (Fergusson, 1990). The most biological effects in soils are rather closely related to the soil solution concentration than to the total metal content. Because of most national inventories of metal concentrations in soils are based on the total metal content a preliminary approach is to find out how this data can be transformed to understand a real effect. This effect-based approach is aimed at elaboration of critical limits based on adverse effect on ecosystems. The implicit assumption is that (ecotoxicological) effects are due to the metal accumulation. However, in most cases, toxic effects are mainly due to the elevated bioavailable (mobile) concentration (de Vries and Bakker, 1998).

A big amount of work has been done in attempting to quantify metals held in different soil/sediment fractions, particularly those thought to be mobile and bioavailable, since these fractions can potentially adversely effect on the ecosystem. The most widely used approach is to choose a chemical extractant (single extraction) or series of extractants (sequential extraction) to remove particular chemical phases (species) of metals from soil and sediments (Tessier et al., 1979; Shuman and Hargrove, 1985; Keefer et al., 1984; Miller et al., 1985).

In most cases, however, toxic effects on micro-organisms and soil fauna is mostly due to an elevated bioavailable concentration in soil (pore) solution (Van Straalen and Bergema, 1995). But physico-chemical properties of solids control activities and concentrations of metals in the solution, therefore, directly affect their availability to plants. In spite of the fact that modern instrumental technique has made possible to analyse most elements in small concentrations in pore solution, there are still many limitations that hamper wider use of the results of pore solution analysis. Those limitations are theoretical, analytical and methodological (Gregor et al., 1997, 1999; de Vries and Bakker, 1998).

The aim of this paper is to illustrate on concrete results, obtained from studies of contaminated soils in Slovakia, mostly within INCO-COPERNICUS project „Long term risk of inadequate management practices on the sustainability of agricultural soils„ (co-ordinated by W. de Vries), the possibility of using soil (and sediments) testing and summarise soil testing methodologies and concepts. The evaluation of different tests and results, towards the hazards involved, is out of the scope of this paper. How-

ever, some theoretical and methodological problems are also tackled, to point out some new trends and concepts which might be useful to apply in geochemical and environmental studies of soils, sediments and sewage sludges.

Methodology

For this study analytical results (single extraction and soil solution) of twenty contaminated soils were chosen. Their soil characteristics are presented in Tab. 1. Sequential analyses were performed on another set of contaminated soil samples from the Hron river basin. The basic characteristics of these soils are presented in Tab. 4.

Sampling. Sampling was done by augering that enabled us to take samples at fixed depths of a plough layer. The spatial variability of soil required to take 25 subsamples at one point in order to prepare composite sample from a plot area of 25 x 25 m.

Soil properties analyses. Fraction < 2 mm was arbitrary used for soil properties analyses by routine methods. Soil reaction was measured potentiometrically in suspensions. For determination of potential soil reaction 1M KCl solution and 20 g sample was used, for determination of active soil reaction redistilled water and 20 g of soil was used. Carbonates were determined by Janko in a lime-meter, in 10 % solution HCl and from 20 g of soil sample. The classical pipette method for soil texture was used (fraction < 2 mm, after the sample dispersion by sodium hexametaphosphate).

Chemical analyses. Soil extraction methods were used followed handbook by Houba et al. (1996) and hence, only principal methods are mentioned here:

Soil extraction with 0.01 M CaCl₂. Soil samples dried at 40°C were extracted at 20°C with 0.01 M CaCl₂. The suspension was stirred for 2 hours and centrifuged. Supernatant was taken for analysis.

Soil extraction with aqua regia. Soil samples were dried at 40°C and extracted with aqua regia at room temperature for 16 hours, followed by boiling under a reflux for 2 hours. Then the extract was filtered. The extracted solution was fulfilled to the standard volume by adding of nitric acid.

Soil extraction with 0.05 M EDTA. Soil samples were dried at 40 °C and extracted with 0.05 M EDTA solution by stirring the suspension for 1 hour at room temperature (20 °C). The extract was filtrated into a polyethylene bottle.

Soil extraction with 0.05 M ammonium oxalate and oxalate acid mixture. Soil samples, dried at 40°C, were extracted with ammonium acetate and acetic acid mixture (pH = 3.0 ± 0.1). The suspension was stirred for 2 hours in a dark room at 20 ± 1 °C. The extract was filtered into a polyethylene bottle.

Methods for soil solution analysis. 25 g of air-dried sample were extracted with 50 ml of 0.002 M CaCl₂.

Sequential extraction scheme used in this work is based on Community Bureau of Reference method (1987) tested in 18 EU laboratories (Mackových et al., 1999). The following metal fractions are distinguished:

- i – exchangeable and carbonate fraction (0.11M acetic acid),
- ii – reducible fraction (Fe and Mn oxides bound) fraction (0.1M hydroxylamine hydrochloric),
- iii – organically (sulphide) bound fraction (8.8 M peroxide + 1M ammonium acetate),
- iv – residual fraction (total decomposition with inorganic acids mixture - HNO₃, HF, HClO₄).

Metal speciation and metal fractions in soils/sediments

Metals, both naturally occurring and inputted to soils and sediments are present in an extremely large range of forms. They may be distributed among many components of soils or sediments and may be associated with them in many different ways. The nature of this association is often referred to as *speciation*. Soil scientists, geochemists and biologists have attempted to extract and quantify these fractions held in different soil/sediment fractions, particularly those which are thought to be mobile (chemical *species* or *forms*), since they can potentially pollute the groundwater or can get in to the food chain from a plant uptake. In soils and sediments this generally means to identify metals held in any of the following fractions:

- a) soluble
- b) extractable (adsorbed)
- c) organically bound
- d) Mn oxides occluded
- e) amorphous and crystalline oxyhydroxides Fe occluded
- f) bound in carbonates
- g) residual (total)

The potential availability (mobility) of elements in different fractions of soil/sediments is illustrated in Fig. 1.

A big effort has been expended in attempting to quantify metals held in different fractions, particularly those fractions that are thought to be mobile and bioavailable. The most common and single physical separation technique is to filter solution through micropore membranes of the pore size 0.45 µm, thus it is rather a coarse differentiation between „soluble,, and „particulate,, metals.

The fundamentals and concepts of soil testing have been reviewed by McLaughlin et al. (2000). Basically two main groups of procedures are used at present:

- a) single chemical extraction,
- b) sequential chemical extraction.

Assessing „plant available,, or „mobile,, amounts of metals in soils (sediments) by single extraction methods

For many years chemical extractants have been tested by soil scientists and geochemists to estimate „plant available,, („mobile,,) fractions of metals.

The development of these tests was mainly in response to the needs to monitor the metal uptake by plants in contaminated soils, in bottom sediments, soils loaded with sewage sludges and pesticides. Single extractions are generally used to extract the following fractions of potentially toxic metals (Berrow and Buridge, 1980):

- a) metals in soil solution (ionic, molecular, chelated and colloidal forms),
- b) exchangeable forms (readily exchangeable),
- c) in adsorption complexes (firmly bound),
- d) reducible-easily bound in sesquioxides (coprecipitated) and in hardly soluble salts,
- e) fixed in crystal lattices of secondary minerals (predominantly clay minerals).

In order to extract metals from the soil/sediments, the basic dissolution, chelation, desorption/ion exchange and oxidation/reduction processes are used prior to elemental determination.

Metals present in the solid phase as discrete phases (sulphides, carbonates, phosphates, oxides, or coprecipitated with sesquioxides) can be released by *dissolution processes*. Usually less soluble compounds require more vigorous extractant (usually inorganic acids).

Table 1: Selected soil characteristics

Sample	Site	Soil unit FAO (1970)	pH/CaCl ₂ (1 : 5)	Carbonates (%)	Humus (%)	Clay (%)	CEC (cmol.kg ⁻¹)
ICSK-1	Slovenská Lúpča	Fluvisol	6.63	0.4	5.46	14.22	20.45
ICSK-2	Gemerská Poloma	Gleyic Fluvisol	6.92	1.6	4.17	3.84	17.39
ICSK-3	Družstevná pri Hornáde	Fluvisol	6.74	0.3	3.08	17.89	20.20
ICSK-4	Veľká Lodina	Fluvisol	7.14	6.4	2.99	4.61	14.49
ICSK-5	Kluknava	Cambisol	5.51	0	3.33	13.01	15.40
ICSK-6	Markušovce	Fluvisol	6.35	0.12	4.08	7.54	16.45
ICSK-7	Gelnica	Fluvisol	5.70	0	7.08	2.74	14.05
ICSK-8	Fiačice - Ľubňa	Fluvisol	6.87	0.5	3.99	7.78	17.40
ICSK-9	Kozárovce	Fluvisol	7.05	7.3	3.17	14.64	20.29
ICSK-10	Starý Tekov	Fluvisol	5.82	0	3.12	21.89	22.90
ICSK-11	Hontianske Tesáre	Fluvisol	5.54	0	1.65	17.51	15.85
ICSK-12	Domaniky	Fluvisol	6.13	0	2.17	11.35	17.95
ICSK-13	Iľija	Pseudogley	5.46	0	6.67	17.50	35.65
ICSK-14	Stará Kremnička	Fluvisol	6.70	0.52	2.17	9.69	13.75
ICSK-15	Bzenica	Fluvisol	6.03	0	5.99	11.34	20.50
ICSK-16	Tekovská Breznica	Fluvisol	7.00	4.2	2.32	7.17	14.49
ICSK-17	Kalná nad Hronom	Fluvisol	6.66	0.1	3.74	19.37	25.35
ICSK-18	Pezinok	Phaeozem	6.75	0.4	5.67	12.32	23.90
ICSK-19	Limbach	Cambisol	7.08	4.5	6.17	6.07	14.49
ICSK-20	Slovenský Grob	Fluvisol	7.06	0.3	4.64	17.47	20.80

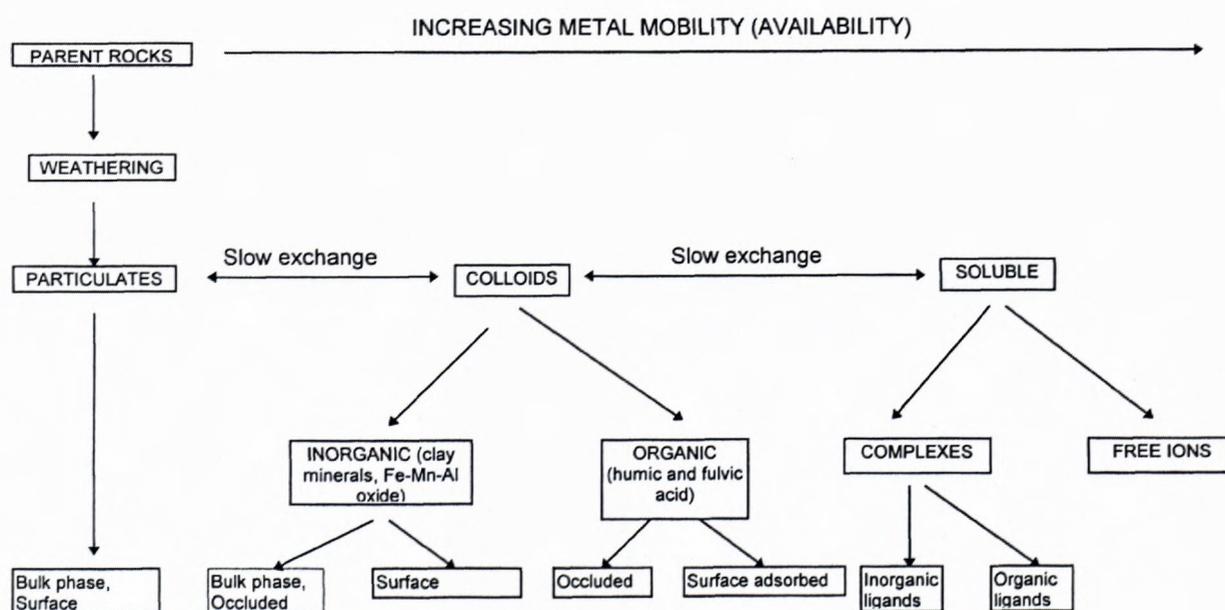


Fig. 1 The potential metal mobility (availability) of different fractions of soil/sediments.



Table 2: Heavy metal concentrations ($\text{mg}\cdot\text{kg}^{-1}$) in contaminated soils obtained by different (single) extraction methods: i - the total (pseudototal) content obtained by aqua regia extraction, ii - the mobile fraction concentration obtained by 0.05 M EDTA, iii - the mobile fraction concentration obtained by ammonium oxalate and oxalate acid, iv - the „mobile“ (available) fraction concentration obtained by 0.01 M CaCl_2 .

Sample	Extraction method	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
ICSK-1	i	20.95	0.5	30	57	0.080	26	62	123
	ii	0.35	0.3	< 0.1	23	< 0.005	2	25	9
	iii	5.85	0.1	1.6	32	< 0.005	4	4	18
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-2	i	54.80	0.2	35	135	0.050	44	24	123
	ii	0.10	0.2	< 0.1	40	0.019	7	8	9
	iii	19.30	0.2	1.6	56	< 0.005	9	2	18
	iv	< 0.01	< 0.05	< 0.1	< 0.5	0.005	< 0.5	< 0.5	< 0.3
ICSK-3	i	18.80	0.4	33	113	0.110	36	33	110
	ii	0.40	0.2	< 0.1	44	< 0.005	5	11	10
	iii	10.00	0.1	1.4	74	< 0.005	7	3	25
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-4	i	46.80	0.4	29	228	0.100	46	50	137
	ii	1.50	0.2	< 0.1	137	0.030	3	20	15
	iii	29.30	0.1	1.0	192	< 0.005	5	3	37
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-5	i	36.80	0.6	38	70	0.200	40	43	177
	ii	1.80	0.3	< 0.1	29	0.009	3	18	30
	iii	19.20	0.2	1.0	39	< 0.005	3	3	45
	iv	0.09	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	0.6
ICSK-6	i	20.10	0.3	28	76	0.940	26	17	70
	ii	0.50	0.2	< 0.1	35	0.061	3	7	7
	iii	9.50	0.1	1.2	49	< 0.005	4	1	14
	iv	0.02	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-7	i	87.50	0.7	17	589	0.180	25	170	243
	ii	0.60	0.3	< 0.1	260	0.048	2	58	30
	iii	50.50	0.2	1.3	372	< 0.005	3	29	61
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	0.6
ICSK-8	i	12.50	0.3	28	21	0.080	27	16	67
	ii	0.20	0.2	< 0.1	11	0.009	5	6	6
	iii	6.40	< 0.1	1.8	12	< 0.005	6	< 1	12
	iv	< 0.01	< 0.05	< 0.1	< 0.5	< 0.005	4.6	< 0.5	< 0.3
ICSK-9	i	39.20	0.7	25	117	0.120	17	62	158
	ii	1.00	0.5	< 0.1	59	0.024	3	22	35
	iii	23.70	0.1	0.8	71	< 0.005	3	3	46
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-10	i	42.70	0.6	29	130	0.140	19	72	119
	ii	0.50	0.4	< 0.1	60	0.038	3	25	12
	iii	21.50	0.1	1.3	76	< 0.005	2	9	19
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-11	i	17.50	13.7	23	201	0.030	14	1303	1704
	ii	0.10	8.4	< 0.1	81	0.019	< 1	467	400
	iii	9.20	2.2	0.4	135	< 0.005	< 2	243	595
	iv	< 0.01	1.16	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	52.3
ICSK-12	i	16.90	20.5	19	236	0.030	11.0	1301	2445
	ii	0.10	16.8	< 0.1	140	< 0.005	< 1	585	853
	iii	9.70	3.7	0.4	178	< 0.005	< 2	373	994
	iv	< 0.01	1.59	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	165.6

Table 2: to be continued

Sample	Extraction method	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
ICSK-13	i	119.50	1.1	19	39	0.030	8	220	178
	ii	0.90	0.7	< 0.1	9	0.006	1	102	26
	iii	45.70	0.1	0.7	12	< 0.005	< 2	24	31
	iv	0.04	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-14	i	102.50	0.2	15	42	0.560	6	68	76
	ii	1.10	0.1	< 0.1	14	0.088	< 1	17	9
	iii	53.70	0.1	1.5	19	< 0.005	< 2	12	19
	iv	0.04	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-15	i	62.00	2.0	15	90	0.060	12	322	427
	ii	1.10	1.3	< 0.1	43	0.054	2	147	94
	iii	28.30	0.2	0.8	52	< 0.005	3	29	128
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-16	i	39.20	1.9	22	107	0.090	10	134	339
	ii	1.40	1.2	< 0.1	44	0.046	1	69	65
	iii	22.50	0.2	3.5	63	< 0.005	3	11	117
	iv	0.11	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-17	i	48.50	1.2	27	193	0.140	19	122	215
	ii	0.60	0.9	< 0.1	105	0.076	4	56	40
	iii	31.40	0.1	1.7	131	< 0.005	4	15	51
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-18	i	68.90	0.9	66	49	0.010	77	28	173
	ii	3.00	0.6	0.2	21	0.001	21	10	14
	iii	49.10	0.2	3.1	24	< 0.005	22	3	21
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-19	i	4.70	0.3	9	138	0.010	7	33	81
	ii	0.30	0.1	0.2	103	< 0.005	1	12	13
	iii	1.50	< 0.1	0.7	94	< 0.005	< 2	1	16
	iv	0.01	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-20	i	61.80	0.3	51	26	0.020	30	21	80
	ii	0.50	0.1	< 0.1	6	< 0.005	4	4	2
	iii	39.70	< 0.1	1.1	11	< 0.005	5	2	9
	iv	0.07	< 0.05	< 0.1	< 0.5	< 0.005	0.7	< 0.5	< 0.3

The mechanism of *complexation* is following: a metal is paired with a ligand supplied by a metal ligand salt, allowing metal desorption and helping to retain the metal ion in a solution in a complex form (McLaughlin et al., 2000). The weak chelating agents (EDTA, DTPA, TEA) are used most often. It seems reasonable that at least the more widespread use of DTPA reagent for testing „availability„ of Ni, Zn, Cu and Cd in contaminated soils is based on an internationally standardised method.

The *desorption/ion exchange processes* for extraction of metals from soil/sediments has not been used until now due to the very low analytic concentration, resulting from the extraction based on these processes. With the improvement of analytical instrumentation the detection limits were considerably lowered which allowed to detect very low concentration in the extracted solution. Mostly neutral salt solutions are used (NaNO₃, Ca(NO₃)₂, Mg(NO₃)₂, NH₄NO₃, MgCl₂, CaCl₂). Generally, concentration of metals extracted by Cl salts are higher, than those extracted by corresponding nitrate salts.

Oxidation processes (with peroxide or acid solution of HNO₃, HCl, HClO₄, HF or aqua regia) can release metal sulphides and metals bound to organic materials. For heavy metals bound to (co-precipitated with) secondary sesquioxides (Fe, Mn, Al), *reducing agents* are used such as acidified hydroxylamine hydrochloride (NH₂OH.HCl), acidified ammonium oxalate and dithionite/citrate solution (see also sequential extraction schemes).

The heavy metal concentrations in Slovakian contaminated soils obtained by different (single) extraction methods are presented in Tab. 2. It is clear from presented results that concentration of metals in different extractants is mainly a function of metal ability to be bound in different soil compounds. Higher concentration of several studied elements (As, Cu, Cr, Hg and Zn) in the ammonium acetate (+oxalate acid) fraction is due to selective binding of these elements to secondary Fe oxides. Especially high concentration of As in this fraction, as compared to the total content, points to the high selectivity of As to Fe oxides. Predominantly in alluvial soils redox

processes may partly deliberate As which can be than transported to the groundwater. Similar tendencies are evident for zinc (Tab. 2).

Very high portion of extractable Cd in contaminated soils is present in the fraction obtained by 0.05 M EDTA extraction. This extractant is used for extracting „available,, forms of the metal in soil to predict plant metal uptake. Our study, supported also by sequential extraction, points to the fact that Cd usually enters the highly „mobile,, fraction in contaminated soils independent of pH (our soils were mostly neutral - see Tab. 1). Cd contaminated soils show a good correlation between the total content and EDTA extractable concentration (Fig. 2). There have been assumptions, supported by some findings, that the behaviour of Cd in soil and its bioavailability differ according to Cd origin. Cd added to soils from anthropogeneous sources is more bioavailable (Kabata-Pendias and Pendias, 1992). Similar results were obtained also for lead contaminated soils in which both EDTA extractable and the fraction thought to be bind in Fe oxides are high.

CaCl₂ extraction has been suggested as the best predictor of phytoavailable metals in soils (Houba et al., 1996). A good correlation has been found only in limited number of soil types. Soils tested in our experiments are hardly to evaluate, as different soil types have been used, and no correlation between soil and plants has been detected. Anyhow, in some cases high concentrations of available Cd have been detected in soils (ICSK-11, 12).

Many authors have reported a good correlation between extractable metal content and metals uptake by

plants. However, the comparison between positive and negative results of such tests revealed in some cases insignificant correlation between extracted metals and metal content in tested plants. Some extractants are useful to extract metals and predict metal availability in neutral and calcareous soils (DTPA) but not in acid soils. Davies (1992) found a good correlation between the plant uptake and the amount of potentially toxic metals in contaminated soils using a strong extractant such as EDTA.

An overview of different results (positive or negative) published by Ross (1994) has shown that it is extremely difficult to summarise these findings since so many test solutions, different bioassay test plants, different soils and different extraction techniques have been used. Our results show that the prediction of plant metal content based on a single extraction is very questionable. Single extractants can neither give a useful information on the metal speciation in soils/sediments.

Selective sequential extraction (dissolution) procedures

Metal fractionations using sequential extraction techniques have been used to extract heavy metals from contaminated stream sediments (Tessier et al., 1979) and metals applied in waste sludge. Such extraction usually starts with the weakest, least aggressive and ends with strongest and most aggressive extractant. Sequential extractants are generally used to characterise five or six of the above stated fractions (see part: Metal speciation...). The weakest extractants in the system are the most spe-

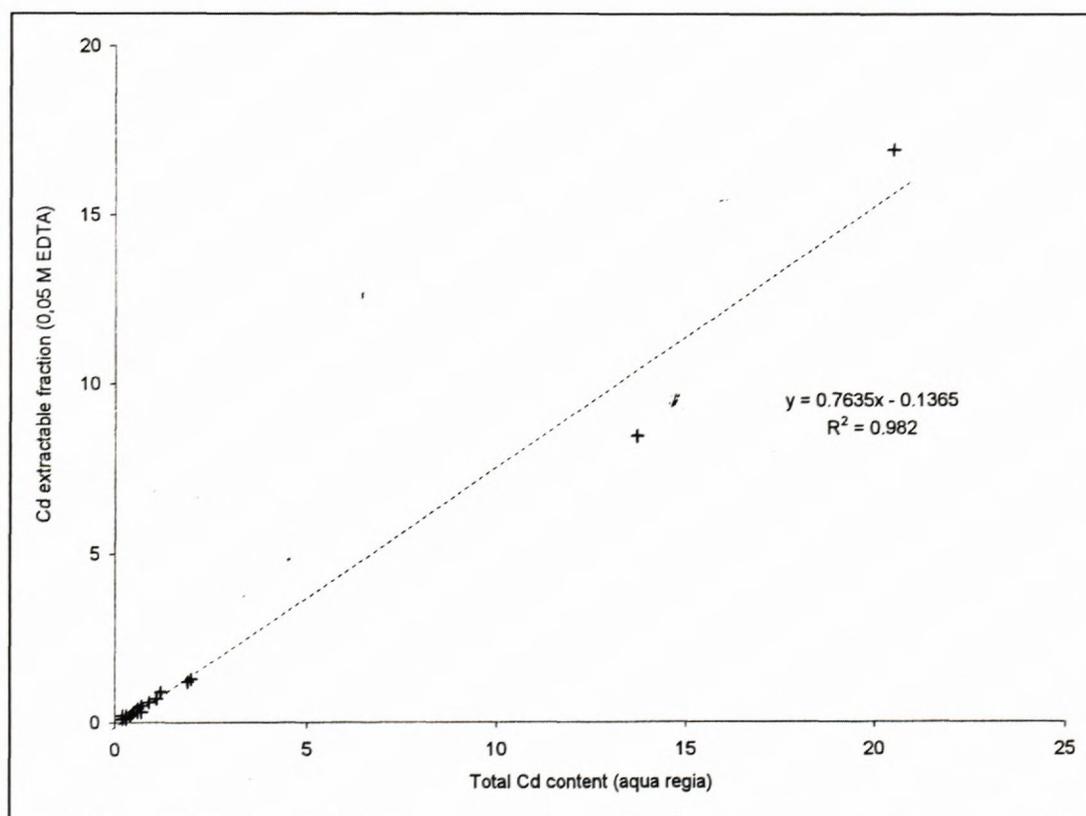


Fig. 2 Relationship between total and EDTA Cd contents in soils (mg.kg^{-1})

cific, the later, stronger extractants, the least specific, but because they come later in the sequence, only one or two groups of compounds may remain that they can dissolve (Becket, 1989; Ross, 1994). A very large number of sequential extraction schemes have been used. The principal schemes of sequential chemical extractions are presented in Tab. 3.

It is clear from the table, that there are some differences in opinions concerning appropriate use of extractants. There is some agreement only about the *kinds* of extractants needed for each fraction. For example, soluble and easily exchangeable fractions are often extracted using dilute salt solutions replacing cations, while organically bound fractions are released using oxidising agents. Reducing agents are used to release metals bound in Fe and Mn oxides. Strong acids are used to assess residual or occluded metals in soils.

Up to now a range of problems and limitations were associated with sequential extraction. The major problem results from the fact that extractants are not as selective as it is stated. Another problem is related to a large number of different extracting techniques which make difficult to compare results from different studies.

Apart from those problems Salomons and Forstner (1984) pointed to three another serious problems that must be considered when using selective sequential extraction procedures:

- labile metal phases could be transformed during sample preparation,
- readsorption or precipitation processes could occur during extraction,
- the duration of extraction and the soil/solution ratios play important roles as far as the quantity of extracted metals.

Metal fractionation using sequential extraction techniques (Community Bureau of Reference, 1987) has been used in our study to identify the metals fate in contaminated alluvial soils of the Hron river basin. Results presented in Tab. 4 emphasise the possibility to predict the groundwater contamination through the soils (Čurlík et al., 2000). In the cited work soil characteristics are described in more details. Based on this study, only simple postulates are made here.

Mainly the soil organic matter and secondary Fe and Mn oxides are responsible for the soil metal retention. These soil components are unevenly distributed down the

Table 3: Five principal sequential extraction schemes for assessing metal fraction in soils/sediments. Numbers refer to stages in the extraction scheme

Fraction	Tessier et al. (1979)	Miller et al. (1986)	Sposito et al. (1982)	McLaren and Crawford (1973)	* BCR (1987)
Soluble		1 H ₂ O			
Exchangeable	1 1 M MgCl ₂	2 0.5 M Ca(NO ₃) ₂	1 0.5 M KNO ₃	1 0.05 M CaCl ₂	1 0.11 M Acetate acid
Acid Soluble		4 HOAc 0.1 M Ca(NO ₃) ₂			
Adsorbed		3 Pb(NO ₃) ₂	2 H ₂ O	2 2.5% HOAc	
Organic	4 0.02 M HNO ₃ 30 % H ₂ O ₂ 3.2 M NH ₄ OAc	5 0.1M K ₄ P ₂ O ₇	3 0.5 M NaOH	3 1M K ₄ P ₂ O ₇	3 8.8 M H ₂ O ₂ 1 M NH ₄ OAc
Fe Mn oxide	3 0.04 M NH ₂ OH.HCl in 25 % HOAc				2 0.1 M Hydroxylamine + hydrochloric
Mn oxide		6 0.01 M NH ₂ OH.HCl + 0.1 M HNO ₃			2 0.1 M Hydroxylamine + hydrochloric
Fe oxide		7 Ammonium Oxalate Acid in UV light		4 Ammonium Oxalate Acid	2 0.1 M Hydroxylamine + hydrochloric
Carbonate	2 1 M NaOAc		4 0.05 M Na ₂ - EDTA		1 0.11 M Acetate acid
Residual	5 2 x 70 % HNO ₃ 40 % HF/72 % HClO ₄	8 HNO ₃ + HF	5 4 M HNO ₃	5 Conc. HF	4 HNO ₃ +HF+HClO ₄

* BCR – Community Bureau of Reference (1987)

Table 4: Results of heavy metals concentrations ($\text{mg}\cdot\text{kg}^{-1}$) in different soil fractions obtained by sequential extraction analyses: i-exchangeable (carbonate) fraction (0.11 M Acetic acid), ii-fraction held in Fe-Mn oxide (0.1 M Hydroxylamine + hydrochloric), iii-organically bound (sulphidic) fraction ($8.8 \text{ M H}_2\text{O}_2 + 1 \text{ M NH}_4\text{Oac}$), iv-residual fraction (soil samples decomposition with inorganic acid mixture $\text{HNO}_3 + \text{HF} + \text{HClO}_4$).

Elements	Extraction method	Samples					
		LV-1		LV-2		LV-3	
		A hor.	C hor.	A hor.	C hor.	A hor.	C hor.
As	i	0.2	< 0.1	0.1	< 0.1	0.1	< 0.1
	ii	17.1	8.3	5.8	2.2	11.9	3.6
	iii	1.2	1.0	1.1	0.7	1.7	1.1
	iv	32.3	20.1	11.8	11.4	30.9	22.1
Cd	i	1.28	0.18	0.38	0.14	0.42	0.15
	ii	0.36	0.18	0.22	0.13	0.22	0.16
	iii	0.06	< 0.01	0.03	0.02	0.04	0.02
	iv	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cr	i	< 1	< 1	< 1	< 1	< 1	< 1
	ii	2	4	4	2	2	2
	iii	3	2	4	3	4	3
	iv	55	60	49	57	61	44
Cu	i	14	3	3	< 1	12	1
	ii	54	18	19	7	57	13
	iii	34	5	10	2	32	5
	iv	37	14	33	18	52	26
Hg	i	< 0.001	0.002	0.003	0.001	< 0.001	0.001
	ii	0.001	< 0.001	< 0.001	0.001	0.002	< 0.001
	iii	0.933	0.174	0.357	0.007	0.877	0.120
	iv	0.486	0.144	0.260	0.131	0.281	0.129
Ni	i	3	2	2	2	2	1
	ii	3	6	2	4	4	5
	iii	2	< 1	1	< 1	2	1
	iv	9	9	10	9	11	8
Pb	i	< 2	< 2	< 2	< 2	< 2	< 2
	ii	58	58	47	10	55	13
	iii	7	7	8	4	10	4
	iv	14	14	13	11	15	9
Sb	i	0.4	< 0.1	0.1	0.3	0.2	< 0.1
	ii	1.0	0.3	0.2	0.1	0.6	0.2
	iii	0.6	0.1	0.2	0.1	0.3	0.2
	iv	34.2	11.5	11.2	4.3	25.8	8.4
Zn	i	82	9	16	3	13	4
	ii	121	23	28	12	27	17
	iii	31	10	14	17	17	10
	iv	63	47	61	46	78	49
As	i	0.3	< 0.1	0.4	0.1	0.2	0.1
	ii	13.1	12.9	14.1	8.5	0.9	1.6
	iii	1.0	1.2	1.0	0.6	1.0	0.4
	iv	22.7	28.2	13.6	9.7	20.2	22.6
Cd	i	1.62	1.69	0.15	0.12	0.09	0.08
	ii	0.73	1.35	0.26	0.11	0.17	0.06
	iii	0.05	0.08	0.03	0.03	0.03	0.01
	iv	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cr	i	< 1	< 1	< 1	< 1	< 1	< 1
	ii	2	4	2	2	1	1
	iii	3	2	5	3	3	1
	iv	40	38	48	49	46	37
Cu	i	7	10	< 1	< 1	< 1	< 1
	ii	35	55	10	7	2	2
	iii	18	16	5	2	2	2
	iv	23	23	19	15	19	8

Table 4 (continued)

Elements	Extraction method	Samples					
		LV-1		LV-2		LV-3	
		A hor.	C hor.	A hor.	C hor.	A hor.	C hor.
Hg	i	< 0.001	0.006	0.003	< 0.001	0.002	< 0.001
	ii	0.002	0.003	< 0.001	0.001	0.001	< 0.001
	iii	0.592	0.617	0.035	0.009	0.104	0.021
	iv	0.146	0.174	0.092	0.130	0.093	0.079
Ni	i	2	1	1	1	1	< 1
	ii	4	5	7	5	6	4
	iii	3	< 1	3	2	< 1	< 1
	iv	9	10	10	10	11	7
Pb	i	2	< 2	< 2	< 2	< 2	< 2
	ii	75	102	23	11	14	6
	iii	7	7	4	3	5	4
	iv	16	17	10	8	11	8
Sb	i	0.5	0.3	0.1	0.2	0.1	0.5
	ii	0.5	0.7	0.2	0.1	< 0.1	0.1
	iii	0.2	0.1	< 0.1	< 0.1	0.1	< 0.1
	iv	18.1	20.0	10.5	5.8	4.5	4.7
Zn	i	71	63	3	3	2	< 1
	ii	130	152	23	15	12	7
	iii	27	32	10	9	6	7
	iv	66	73	58	49	51	39

LV-1 – Kozárovce (Gleyic Fluvisol, pH/KCl – 6.72), LV-2 – Hronský Beňadik (Fluvisol, pH/KCl – 6.41), LV-3 – Starý Tekov (Fluvisol, pH/KCl – 5.4), LV-5 – Tekovský Hrádok (Fluvisol, pH/KCl – 7.31), LV-6 – Mýtne Ludany (Phaeozem, pH/KCl – 6.93), LV-8 – Hronské Kľačany (Phaeozem, pH/KCl – 7.04).

soil profiles depending on the soil processes. But metal affinities to different soil fractions may play an important role for the proportion of metals held in so called „mobile„ forms.

As it was stated above, *arsenic* is mostly present in the residual fraction. Second place belongs to the fraction held in Fe and Mn oxides. Hence, the distribution of As in soil profiles partly corresponds to the formation (cumulating) of secondary oxyhydroxides within the depth.

Cadmium shows marked tendency to concentrate in the most mobile (exchangeable) fraction and partly in the reducible fraction (in Fe, Mn-oxides).

Chromium is mostly present in the residual fraction which points to the low mobility of his element in the soil (mostly Cr³⁺).

Copper, which is able to form chemical compounds of different solubility, can be present in different soil fractions, as it is apparent from the sequential extraction. Highly mobile (soluble) forms of copper are usually present in small amounts in the soil solution. Copper is also fixed to secondary sesquioxides.

Mercury is strongly held in organic matter. Therefore in all contaminated soils the highest concentration of mercury has been revealed in the organically bound fraction. Fortunately, this is the reason for the low potential toxicity of mercury in soils (except of methylated forms).

Nickel can be partly mobile in soils. Small portion of nickel in exchangeable fraction points to a possibility that this metal can be transferred from sources of contamination to the groundwater or from soils to plants.

Lead is concentrated mostly in secondary sesquioxes (Fe, Mn, Al), humus and clay. It is postulated that potential of lead toxicity related to the soil is low. The results point to the high portion of Pb concentrated in secondary oxides.

Antimony is usually dispersed in soil. In contaminated soils of the Hron river basin Sb is distributed to a long distance from known contamination sources (Nízke Tatry Mts., Štiavnické vrchy Mts. and Kremnické vrchy Mts.). Antimony is a weak migrant when oxidised. But its concentration in plants, and small concentration in the very mobile fraction (exchangeable), far from primary contamination sources, point to a possible water transport of Sb similarly to As, to which it is geochemically linked (Alloway, 1990; Fergusson, 1990).

Zinc is present in soil in several fractions (Alloway, 1990): water-soluble, exchangeable, fixed to organic matter, clay and nonsoluble metal oxides. From the sequential extraction it is clear that higher proportion of Zn is bound to secondary oxides (Fe, Al?, oxides).

Various sequential extraction schemes have been developed, including the one of the European Commission (formerly BCR) which was used in our study. This

scheme can be improved only in the presented way to be predictable for a plant uptake of metals or for an adverse effect on human health or eco-toxicity, but such results are still missing (McLaughlin et al., 2000).

Metal concentration in pore (soil) solution

Apart from the occurrence of elements in the solid phase of soil/sediment little is known about their concentration and speciation in a pore (soil) solution. The knowledge about pore solution concentration and the solubility of elements is of a great importance in studies of their biogeochemical cycles and their availability to plants. Plants essentially take up heavy metals from soil via solution. On the other hand, heavy metals from the

solution may be transferred (leached) to the groundwater and cause its contamination.

The pore solution is the most important constituent influencing chemical and biological activities in soils/sediments. Soil organisms without water die or become dormant. Mineral transformation becomes slow and chemical weathering is limited.

In spite of the overall acceptance of these general statements there is no meaningful definition of the pore solution. From the viewpoint of soil chemistry the pore (soil) solution is defined as „the aqueous liquid phase in whose the composition is influenced by flows of matter and energy between it and its surroundings and by the gravitational field of the Earth (Sposito, 1989).

Table 5: Major inorganic components in pore (soil) solution (Sumner, 2000).

Category	Major component (10^{-4} to 10^{-2} mol.l $^{-1}$)	Minor components (10^{-6} to 10^{-4} mol.l $^{-1}$)	Others
Cations	Ca $^{2+}$, Mg $^{2+}$, Na $^{+}$, K $^{+}$	Fe $^{2+}$, Mn $^{2+}$, Zn $^{2+}$, Cu $^{2+}$, NH $_4^{+}$, Al $^{3+}$	Cr $^{3+}$, Ni $^{2+}$, Cd $^{2+}$, Pb $^{2+}$
Anions	HCO $_3^{-}$, Cl $^{-}$, SO $_4^{2-}$	H $_2$ PO $_4^{-}$, F $^{-}$, HS $^{-}$	CrO $_4^{2-}$, HMoO $_4^{+}$
Neutral	Si(OH) $_4^0$	B(OH) $_3^0$	

Table 6: Major organic components found in pore (soil) solution (Sumner, 2000).

Source	Major components (10^{-5} to 10^{-3} mol.l $^{-1}$)	Minor components ($<10^{-5}$ mol.l $^{-1}$)
Natural	carboxylic acids, amino acids, simple sugars	carbohydrates, phenols, proteins, alcohols, sulfhydryls
Anthropogenic		herbicides, fungicides, insecticides, PCBs, PAHs, petroleum, hydro- carbons, surfactants, solvents

By this definition the pore solution is an open system that exchanges matter and energy with other subsystems (air, water, biota). Also, because the solution is defined as a phase it implies that the pore solution has uniform properties and can be isolated from soils (sediments). These requirements of uniformity (stable composition, temperature) can be met only on small time-space area because of the variable nature of the pore solution. The pore solution is not a distinct entity but rather it is a continuum of phases, ranging from that held in colloids, through the immobile water in micropores, to free water percolating through macropores.

As the pore solution is highly variable its composition can be discussed only in general terms. The concentration of inorganic constituents in the pore solution is controlled by pH, Eh and solid phase composition.

Commonly found inorganic components in pore solution are given in Tab. 5. Trends in composition are similar but natural and anthropogenic factors can have big influences on this composition. The composition of soluble organic components in the pore solution reflects the composition of organic matter in the solid phase. Major organic components found in pore (soil) solution are present in Tab. 6. All studies of metals in pore solution suffer from two major problems:

- finding suitable techniques for detecting extremely low concentrations,
- differentiation between free metal ions in solution and soluble organo/metallic complexes.

Other problems are associated with obtaining of an unaltered solution. The moisture of field soils and fresh sediments can range from air dried to saturated over short period of time. Most techniques for obtaining samples of solutions function poorly when water content is below the saturation.

Methods for obtaining the pore solution can be broadly categorised in three groups: *aqueous extracts*, *column displacements* and *pressure extraction*. An alternative method is to use saturated soil paste (USDA, 1954).

Obtaining *aqueous extract* includes adding water to samples, to the point of saturation or beyond, equilibrating and removing solution.

Column displacement consists of forcing a fraction of pore solution to move from the soil (sediment) by leaching by an aqueous solution or with nonsoluble organic solvent. This procedure can be modified to include pressure from the top or vacuum applied to the bottom of the column.

Neither the variation in the total electrolyte concentration nor the activity ratios of specific ion components

Table 7: Soil solution concentrations (soil solution extraction by 0.002 M CaCl₂)

Sample	pH	EC mS/m	Cl ⁻ µg/l	(SO ₄) ²⁻ µg/l	(HCO ₃) ⁻ µg/l	N-NO ₂ µg/l	N-NO ₃ µg/l	N-NH ₄ µg/l	N-tot. µg/l	Ca µg/l	Mg µg/l	Na µg/l	K µg/l	Al µg/l	Fe µg/l	As µg/l	Cd µg/l	Cr µg/l	Cu µg/l	Hg µg/l	Ni µg/l	Pb µg/l	Zn µg/l
ICSK-1	6,7	21,95	13570	5200	183	378	< 90	3885	13945	90,374	19480	2700	20040	37	62	20	2	< 2	48	0,1	14	< 10	93
ICSK-2	7,3	21,47	14810	9400	153	566	4179	2139	13583	121,45	8530	2090	3010	< 20	20	2,7	5	3	74	0,1	152	< 10	720
ICSK-3	6,8	18,63	12340	3400	122	2750	2146	1926	18576	63,735	31410	3480	13340	< 20	20	6,7	3	< 2	77	0,1	44	13	210
ICSK-4	7,4	16,74	9880	3800	122	798	2733	1148	10342	86,229	17010	610	9550	< 20	10	12,6	< 2	2	62	< 0,1	35	12	110
ICSK-5	6,0	21,47	17280	11200	37	1684	6438	1829	15441	84,610	10090	3430	37290	35	40	18,1	2	< 2	129	< 0,1	52	< 10	300
ICSK-6	6,8	16,74	9880	4600	122	1236	2485	1193	8618	109,19	12690	1340	1790	< 20	30	2,4	< 2	< 2	31	0,1	16	< 10	80
ICSK-7	6,4	14,38	9880	13400	37	1833	9849	4053	16354	81,736	7910	1630	5240	32	60	10,4	2	2	269	0,3	44	< 10	270
ICSK-8	7,1	16,74	14810	4000	153	1784	3840	1779	18243	95,655	26880	870	3419	< 20	40	1,4	< 2	2	26	< 0,1	21	< 10	110
ICSK-9	7,2	21,5	11110	6600	183	1964	1694	2252	6715	107,21	18510	4070	7680	46	10	40,8	2	3	73	< 0,1	13	< 10	68
ICSK-10	6,3	12,91	20980	6800	37	1145	474	1548	7924	74,775	15570	9450	4550	95	20	10,5	< 2	< 2	66	0,3	17	< 10	58
ICSK-11	6,5	11,56	23450	5400	18	37	< 90	676	7356	81,204	9520	5860	15770	47	16	1,5	7	< 2	50	0,3	10	< 10	466
ICSK-12	6,1	8,84	20980	11200	37	37	1649	1070	5795	63,177	1383	4960	14420	27	22	1,1	32	2	86	0,9	19	< 10	2790
ICSK-13	6,7	34,28	13570	8600	183	< 6	< 90	5348	9458	118,78	15480	1350	31860	125	67	11,1	26	< 2	40	1,3	35	26	209
ICSK-14	6,8	12,97	11110	5000	37	79	836	1070	14257	65,199	22550	2660	20940	< 20	283	2,9	138	8	56	1,2	36	< 10	189
ICSK-15	7,2	28,51	13570	6400	214	1322	565	1661	10444	96,263	22160	2280	29670	53	41	11,9	19	3	68	1,0	< 10	< 10	75
ICSK-16	6,9	17,85	16040	2400	122	1023	3569	1126	15851	93,912	15940	5980	6780	< 20	20	26,7	5	< 2	46	1,3	< 10	< 10	106
ICSK-17	6,8	39,61	18510	87500	183	1065	9510	760	22341	126,98	24750	7930	4920	< 20	42	6,5	7	2	77	0,7	< 10	< 10	101
ICSK-18	6,9	31,62	25920	19200	183	1309	2259	1126	17248	112,89	21400	16810	2480	176	99	13,3	8	< 2	46	0,9	17	< 10	137
ICSK-19	7,0	20,07	6170	2000	122	956	2711	2167	8114	101,12	5290	985	40960	224	103	7,0	3	4	97	0,4	< 10	12	57
ICSK-20	6,8	21,85	25920	3800	122	518	271	1281	5799	97,471	14770	9000	3180	56	43	6,7	5	4	33	0,6	16	< 10	46

of the pore solution can be adequately resolved when water to sample ratios vary from field moisture contents to ratio >1. This is the main limitation to the use of water extracts as models for pore solution (Sumner, 2000).

Pressure extraction is defined as the use positive pressure or vacuum, eventually centrifugation, to remove the pore solution.

Field methods include several types of lysimetric studies.

From above stated it is obvious that at least:

- the definition of pore solution is idealised and more functional definition is needed before the concentration/activities of free metal ions in pore solution will be used for the assessment of critical limits;
- the adjustment of design, execution and interpretation of pore solution study methods is strongly recommended;
- the derivation of the total dissolved metal concentration from the total pore concentration should be based on clear understanding of the pore solution. The partition of metals concentration between solid phase and solution should be clearly related to transfer functions.

The solubility of heavy metals under field conditions is strongly linked to soil parameters such as pH, SOM and DOC (Romkens and Salomons, 1998).

The studied soils have acidic to neutral character (pH 5.51 – 7.14) with CEC ranging from 13.75 – 35.65 cmol.kg⁻¹ (Tab. 1). As it was stated in methodological part of this paper, in this study the soil solution was extracted by 0.002 M CaCl₂.

It should be noted that the obtained results (Tab. 7) have very high concentrations of Ca²⁺ and Cl⁻. It is clear that the results are influenced by the background solution. This conclusion is supported also by the relatively low HCO₃⁻ concentration which should be related to Ca²⁺ content in these soils.

The content of SO₄²⁻ is relatively high and points to the fact that some elements in solution were leached due to acid sulphate weathering of sulphides (and hence, sulphatic complexation of metals may play some role in metals transfer).

The nutrient element concentrations in soil solution (K, Mg, Na) show some relation to the parent rocks or to the application of fertilisers (agricultural soils).

The Al and Fe concentration in soil solution does not give clear evidence to soil properties. Higher Fe concentration occurs in soils with some gleyic features.

The potential toxic elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) show relatively high concentrations in soil solution. The limit value for As in the groundwater (5 µg.l⁻¹) is exceeded in more than half of the samples. Arsenic, which occurs as oxoanions in soils, may show an increase in concentration in soil solution with rising pH. This might be the case of soils with gleyic carbonatic processes.

The total content of Cd in studied soils ranges from 0.3 to 20.5 mg.kg⁻¹. Cd solution concentrations range from < 2 (detection limit) to 138 µg.l⁻¹, which is extremely high. The critical limit proposed for Cd concen-

tration in soil solution (precautionary principle) is 10 µg.l⁻¹ (Čurlík et al. 2000) and it is exceeded in several soils contaminated by Zn-Pb (ICSK 11-16). As it was stated by Romkens and Salomons (1998) no single relation appears to exist between the total Cd content and the solution concentration. In the forest soils frequently higher Cd content in soil solutions is due to lower pH values and higher soluble organic fraction content.

The concentration of Cr in soil solution is relatively low and point to known aspects of low solubility/mobility of Cr³⁺ compounds.

The Cu solution concentrations range from 31 to 269 µg.l⁻¹. These concentrations are high and may have an adverse effect to plants (de Vries and Romkens, 2000; In Čurlík et al. 2000). Higher Cu concentrations in pore solutions may be controlled by DOC (dissolved organic carbon), as pointed by Romkens and Salomons (1998), and in alkaline soils (Fotovat and Naidu, 1998). Cu solution concentration in studied contaminated soil is above the limit for groundwater quality standard (20 µg.l⁻¹).

Suggested critical limit for mercury concentration in soil solutions is 0.1 µg.l⁻¹ (Čurlík et al., 2000). In spite of the fact that studied soils are not Hg - contaminated (see Tab. 2 – total content) its solution concentrations are mostly above the limit.

In several soils the solution concentrations for nickel are above the current groundwater quality standards (20 µg.l⁻¹). This may lead to leaching of Ni to groundwater.

The proposed critical limit for lead in soil solution is 50 to 80 µg.l⁻¹ (Čurlík et al., 2000). The results show that lead is a bad migrant and its concentrations in soil solutions are not high.

Current Dutch groundwater quality standard for Zn is 65 µg.l⁻¹ (Romkens and Salomons, 1998). The solution concentrations of Zn in soils are much above the standard.

The solubility of potentially toxic elements under field conditions is thought to be linked to soil parameters (Romkens and Salomons, 1998). To obtain more reliable estimates more results related to metal solubility and leaching still need to be obtained.

Conclusions

Recent advance in soil and sediment testing for potentially toxic elements is due to the improvement of analytical methods, especially the detection of low element concentrations, but also due to better understanding of the behaviour of metals related to soil (sediment) properties.

Recent developments of the testing methods continue in three directions: *single extraction* with soft extractant, *sequential extraction* with multi-solution extraction and *soil (pore) solution testing*, which is thought to be the best predictor of plant available metals. For all the mentioned methods, which are widely used, no meaningful measures exist for metal bioavailability till now. An improvement of these methods needs first of all an increase of the information level on the mobility (toxicity) of extracted species of elements.

The results presented in this work show that contaminated soils may possess some danger for plants in topsoils and for the enhanced leaching towards the groundwater in subsoils. Mobile fraction concentrations of different contaminated Slovakian soils, obtained by single extractant, are high for heavy metals (Cd, As, Cu, Zn) but no calibration data exists as far as the real toxicity to plants. The mobile Cd fraction concentration is clearly not related to soil properties (pH) but more closely to the total Cd content or to the form of Cd occurrence in soils (anthropogenic).

The results of sequential extraction analyses of contaminated alluvial soils of the river Hron basin show that some potentially toxic elements (Cd, Cu, Zn and possibly As, Sb) are present in most mobile fractions. These elements are brought from different remote sources (mining areas). This gives some evidence about a possible adverse effect for plants and groundwater (groundwater - soil interaction).

Soil (pore) solution testing results based on the soil solution extraction method show that As, Cd, Cu, and partly Zn and Hg exceeded current groundwater quality standards or critical limits (for Cd, Hg) proposed during the Bratislava meeting (Čurlík - Šefčík and Viechová, 2000). High concentrations of potentially toxic elements in soil (pore) solutions can be harmful for plants and the groundwater. The acidification of diffusely contaminated soils may speed up the mobility (leaching) of these elements and their transfer to plants (or groundwater).

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