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LONGTERM STUDY OF TRANSFORMATION OF POTENTIALLY TOXIC ELEMENT POLLUTION IN SOIL/WATER/SEDIMENT SYSTEM BY MEANS OF FRACTIONATION WITH SEQUENTIAL EXTRACTION PROCEDURES

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ABSTRACT

In first part of the paper a review is given on fractionation methodologies by sequential extraction methodologies applied for risk assessment of environmental pollution by potentially toxic elements (PTE). Main sources of PTE release are the mining-, industrial-, agri-food production-, traffic- and communal-waste. In this latter the medical and health care sources may emerge due to therapeutic and diagnostic applications (Ag, As, Au, Ba, Bi, Cd, Ga, Gd, ¹³¹I, Ir, Li, Mn, Fe, Os, Pd, Pt, Rh, Ru, Sb, Sn, Ti, V), to nanomedicines, to ayurvedic herbal medicines with possible contaminant PTEs and non-controlled dietary supplements. The magnitude of adverse effects caused by PTEs in the soil-water-sediment system depends on the various chemical species that can arise. Long-term biological impacts are strongly influenced by mobilization-immobilization processes in the aquatic environment. These can be studied through sequential extraction procedures modelling their pathways. In Europe the simplified extraction scheme proposed by BCR in 1993 and modified in 2001 is mostly used for this purpose. By this approach samples are gradually decomposed and four different fractions of PTEs can be identified, *i.e.*: *i*) water-soluble and carbonate-bound fraction; *ii*) fraction associated with reducible Fe- and Mn-oxides; *iii*) organic complexed fraction and sulphides; *iv*) fraction soluble in oxidative acids. The sediment-based Certified Reference Material (CRM) BCR 701 was produced to check the accuracy of the fractionation procedure. The standardization process was hindered by methodological problems, *i.e.*: *i*) the solvents used in the BCR system do not mirror completely the natural mobilization processes and partly modify the original chemical species; *ii*) the time demand of the batch leaching extraction steps is exceedingly long (4-5 days); *iii*) the above CRM, certified for the fractionation of Cu, Cd, Cr, Ni, Pb and Zn, is available only for sediment and cannot be applied to other environmental matrices and other PTEs. The studies aimed at improving the BCR methodology are summarized, in particular to: *i*) develop continuous flow systems; *ii*) accelerate the BCR leaching steps by sonication; *iii*) extend the BCR procedure to other environmental matrices (soils, red mud, composts, biofilms) and further PTEs by multielemental (ICP-OES) detection.

In second part of the paper a case study is presented for evaluation of long-term changes of the environmental mobility of PTE contaminations in the fish pond system of Gödöllő town. For vertical and horizontal mapping of PTE content of accumulated sediment layers core samples were taken in 1994, 1995 and 2013. In the sediment layers total soluble PTE content was related to the BCR fractionation. The Chernobyl origine radionuclides were detected by γ -spectroscopy. The BCR sequential extraction procedure for tracking the long-term fate of PTE contamination of different origine in surface water/sediment/ systems showed a much potential. By

repetition of fractionation of PTEs after 20 years clearly reflects the change of PTE concentrations in different fractions. The decrease of PTE concentrations can be explained by leaching the most mobile fractions by water exchange over the sediment and/or by remediation activity.

KEYWORDS

Potentially toxic elements
 Fractionation
 BCR sequential extraction
 ICP-OES multielemental detection of pollutants
 Risk assesment

ABBREVIATIONS

BCR: European Community Bureau of Reference
 CRM: Certified Reference Material
 DC-ARC: Direct Current Arc
 DOM: Dissolved organic matter
 FAAS: Flame Atomic Absorption Spectrometer
 ICP-MS: Inductively Coupled Plasma Mass Spectrometry
 ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry
 MR: Magnetic resonance
 PTE: Potentially toxic element
 SFE: Supercritical Fluid Extraction
 XR: X-ray

INTRODUCTION

Potentially toxic elements (PTE) are the most important persistent inorganic pollutants. PTEs are mostly metals or metalloids and their environmental mobility and biological impact is determined by the chemical speciation of these elements in the environmental systems [1]. Main sources of PTE release are the mining-, industrial-, agri-food production-, traffic- and communal-waste. In this latter the medical and health care sources may emerge as it follows [2-4]:

- In therapeutic applications: Ag, As, Au, Bi, Ga, Li, Pt, Ru, Sb, Sn, Ti, V;
- Antitumor agents: Pt, (trials: As, Ga, Ru, Ti, Os, Ir, Rh, Pd);
- Contrasting agents: MR: Gd, Mn, Fe; XR: Ba; Radiography: ^{131}I ;
- Nanomedicine: Ag, Au, FeO, CdS, CdSe;
- Ayurvedic herbal medicines with possible contaminant PTEs: Ag, Al, As, Cd, Cs, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Se, Sr, U, V, Zn, W;
- Dietary supplements: Cu, Zn, Cr, Se.

The fate of potentially toxic elements (PTE) pollution became very hot question in Hungary after two disastrous environmental events: Tisza River contamination in 2000 and Ajka red mud disaster in 2010. PTE load in soil/water/sediment system is responsible for acute ecotoxicity which is determined by actual speciation of PTEs. Longterm biological impacts can be influenced by mobilization/immobilization and transport processes in the aquatic environment (Fig. 1.a.), which can be followed by fractionation based on sequential extraction procedures modelling the pathways of these processes (Fig. 1.b.) [5-7].

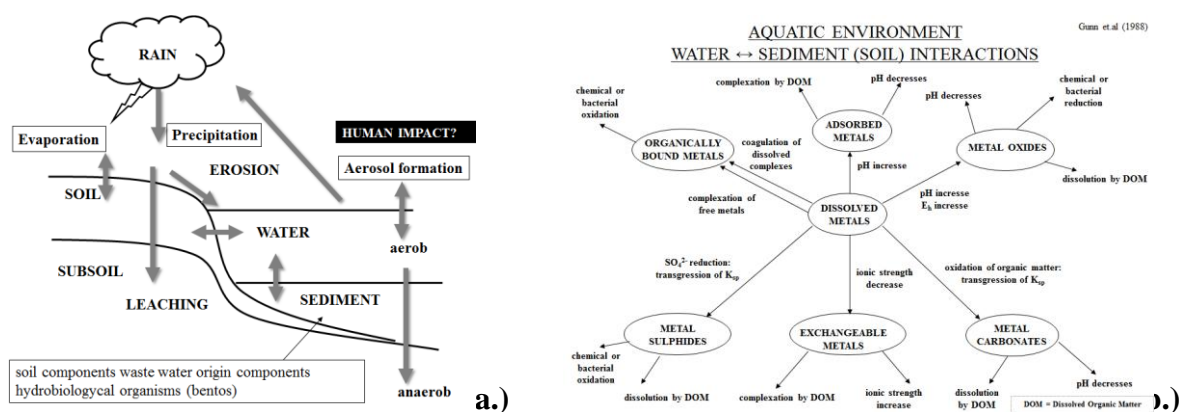


Fig. 1. (a.): The transport routes in soil/water(sediment)/atmosphere systems; **(b.):** The pathways of mobilization/immobilization processes of PTEs in aquatic environment [6]

The first sequential seven-step extraction procedure was developed by Tessier et al. [5] who classified the PTE-content of aquatic sediments according to solubility and binding forms of metallic species as it presented in Fig. 1.(b.). After this essential work several 5-8 step sequential extraction schemes were developed based on the dissolution/or decomposition of original chemical structures of PTEs in the sediment [8]. In the original classification of Tessier [5] the following seven group of PTEs can be distinguished:

1. Water soluble in pore water (free aqua ions, inorganic complexes, organic complexes).
2. Weakly adsorbed to solid phases.
3. Associated with carbonate.
4. Associated with reducible Fe and Mn oxides.
5. Complexed by organics (humic components).
6. Associated with sulphide.
7. Residue soluble in strong oxidative acids only.

Determination of total soluble element content in strong oxidative acids can be additionally performed with the original solid sample, the result of this determination can be compared with summarized result of the seven sequential extraction steps.

Total time demand of the multistep batch leaching techniques combined with phase separation of extracts is 7-10 days while the heterogen dissolution equilibria can be reached by 16-20 hours shaking in each extraction step. That is why the European Community Bureau of Reference (BCR) proposed a simplified 3(+1) step extraction scheme as it follows:

1st step: The water soluble, the weakly adsorbed and the carbonate-associated metal fractions are extracted simultaneously by 0.11M acetic acid;

2nd step: The metal fractions associated with reducible Fe and Mn oxides are dissolved with hydroxylamine-hydrochloride at pH=2.

3rd step: Organic complexed and sulphides are dissolved after oxidization by H₂O₂ in ammonium acetate;

(+1) step: Residual fraction dissolved in oxidative acids (HNO₃/H₂O₂, or aqua regia).

After 16 hours batch leaching steps the solid residuum and the extracts are separated by centrifugation. During the phase separation the readsorption of dissolved ions may cause analytical inaccuracy. For element detection spectrochemical methods (FAAS, ICP-OES, ICP-MS) were proposed but their application is strongly influenced by the matrix effects caused by the various composition of extractant solvents. Therefore the sediment reference sample to validation of BCR procedure issued in 1997 (BCR-601) could be certified for fractionation of five PTEs (Cd, Cr, Ni, Pb, Zn) only [9, 10]. In 2001 was issued the BCR-701 sediment reference sample certified for fractionation of six elements (Cd, Cr, Cu, Ni, Pb, Zn)

and simultaneously the BCR sequential extraction protocol was also modified to avoid the analyte losses during the second leaching step due to the pH instability [11-16]. These changes should be considered in long term studies of PTE-contamination when consistency with former data is required [17]. The original and the modified BCR-procedures were successfully applied for risk assessment of PTE contaminations in aquatic sediments and soils, however, CRM sample for fractionation of PTE-content of soils was not issued up to now [17-27]. Application in environmental risk assessment of PTE-fractionation based on the classification of Tessier [5] should require more and more the standardization of the sequential extraction procedures but the methodological problems hindered this up to now. These problems and researches directed for their solutions are summarized in Table 1.

Table 1: Researches directed for the improvement of BCR sequential extraction procedures.

Shortcomings of BCR-procedure	Development trends, Progress
Does not fit to the chemistry of natural mobilization ↔ immobilization pathways	<p>→ Better modelling the chemistry of environmental mobilization by carbonization applying CO₂, H₂O, H₂O/CO₂ solvents sequentially in supercritical extractor [28].</p> <p>→ Leaching large size (1-10 kg capacity) rock-, sediment-, soil cores with solvent flow modelling natural hydrogeological conditions (water, salt solutions with 0,1-10 L/day) [29].</p>
1 st step of BCR procedure is leaching with an acidic reagent. It may alter the intact forms of metallic species, therefore from the extract cannot be identified the original species and it cannot be used for ecotoxicological tests.	→ Application of sediment pore water, cold water- or subcritical water-extraction for ecotoxicological testing [30, 31].
The multi-step batch leaching is time consuming minimum 5 days.	→ Acceleration of batch leaching by sonication or microwave treatment [32, 33].
Selectivity and completeness of extraction steps strongly influenced by the reagent-solvents ratio and technical conditions of leaching (e.g. shaking rpm).	<p>→ Elaboration of continuous flow techniques:</p> <ul style="list-style-type: none"> • Elaboration of flow-through extraction chambers equipped with membrane filters for sequential extraction of 0,25 – 5 g or 5-25 mg solid sample which can connected directly to element analytical detectors [34,35]. • Sequential extraction in Supercritical Fluid Extractor (SFE) by supercritical CO₂, subcritical H₂O and subcritical (H₂O+CO₂) mixture [36, 37]. • Application of rotation coiled column-planet centrifuge for continuous flow fractionation of trace metals in soils and sediments [38, 39].
There is a hard risk of (cross)contamination due to the numerous operation and reagents' applications.	→ Reduction of number of operations and reagent-applications which was achieved by continuous flow systems [34-45].

Shortcomings of BCR-procedure	Development trends, Progress
Primary application was elaborated for sediments. Soils and other matrices were less considered, therefore CRM is only for sediment available to BCR procedure, validated for fractionation six elements (Cd, Cr, Cu, Ni, Pb, Zn).	→ Extension of application and validation to other matrices: soils, rocks, sewage sludge, red mud, gravitation dust, compost, biofilm [32, 46-50]. → For fractionation of P, As, Se and other PTEs in above matrices were elaborated other fractionation procedures with different extraction reagents [51-54].
High (organic) reagent concentration of extracts causes high matrix effects in spectrochemical sources particularly in the case of calibration of multielemental ICP-OES and ICP-MS techniques.	→ Reduction of matrix effects by matrix separation or matrix matched calibration, application of internal standardization. Extension of calibration to all possible PTEs occurring in different solid environmental media [55].

In spite of these methodological problems the application of BCR-sequential extraction seems to become the standard methodology in risk evaluation of PTE-contaminations while it offers a possibility for quantitative characterization of environmental mobility by the ratio of 1st most mobile fraction of PTEs to total PTE-load [56]. On the polluted areas tracking the immobilization and the migration of PTEs can be performed by the repetition of BCR fractionation [57-59]. In this paper these possibilities will be presented through a case study which was started in 1993 on the lake-chain created by a rivulet Rákos arising from north and running through the town of Gödöllő [59]. Fish ponds and watermills have been established south of Gödöllő with the water of the stream for centuries, forming a nine-unit string of lakes in the valley of the Rákos. At the beginning of this study (1993) the first lake unit served as receiver of the sewage cleaner of Gödöllő and the rain collector of a military machine factory was introduced into the seventh lake unit. The lake system was used as a recreational area for angling, but the environmental damage could be observed visibly (silt accumulation, eutrophization, etc.) and therefore the local authorities initiated the evaluation of environmental status of lakes to support the revitalization. It was immediately found the utilization of lakes is greatly endangered by the settled mud layer, which could take up about 70% of the water storing capacity of the lake basins. This sediment layer was used as a cumulative indicator of pollution (plant nutrients, PTE species and pathogenic microbes). A suitable sampling strategy was developed, core sediment samples were taken from each unit considering the waterflow governance along the lakes allowing determination of the spatial (horizontal and vertical) distribution the different PTEs, plant nutrients and pathogens in the sediment layer. The estimation of total element concentrations in solid phase was performed by DC-ARC spectrography and the total dissoluble element fraction was determined after 2 M HNO₃ extraction by means of ICP-OES. The different radionuclides were detected by γ -spectroscopy. This complex analytical approach together with soil hygienic investigations has made it possible to prove the origine and level of pollution in the lakes. It was established that in the 1st lake-unit the accumulation of PTEs and nutrients (phosphates) is characteristic to the communal sewage sludge and in the 7th unit the PTEs of industrial origine were accumulated over the hygienic threshold. By γ -spectroscopy the appearance of ¹³⁷Cs isotope of Chernobyl origine until depth of 30-35 cm was detected near to the tolerable limit values. Considering the date of Chernobyl accident this distribution provides a time scale to calculation the rate of sedimentation process. The vertical distribution of pollutant PTEs was similar to the ¹³⁷Cs, that means that their accumulation became more intensive during the period of 1986-1996 years [60]. The BCR fractionation of PTEs (residual) in sediment cores taken from 1st and 7th lakes was performed in 1998 and later the supplementary fractionation in supercritical extractor with supercritical CO₂, subcritical H₂O and subcritical H₂O/CO₂ solvents was also performed [17, 28, 36, 60]. In 1998 several PTE concentrations were significantly higher in

the most mobile BCR fraction as the soil-hygienic threshold values and the biological tests of aqueous extracts has shown significant ecotoxicological effects. After this initial study the cleaned waste water inlet to the 1st lake was ceased and from the 7th lake the sediment layer was partially swept. To detect the impacts of these operations in 2013 the present comparative study was started for tracking the changes of PTE concentrations and mobile fractions.

MATERIALS AND METHODS

Sampling

Survey map of Gödöllő and the scheme of the sediment sampling is presented on **Fig. 2(a)** and **(b)**.

1. In October 1994 mixed sediment samples were taken from the upper 0-20 cm of sediment layer with a long-handled dipper. A small part of the wet samples was used for soil hygienic investigations and the other part was dried at 105 °C and homogenized to element analytical investigations for horizontal mapping the PTE accumulations. The lake-units are numbered with Roman numerals according to water flow direction.
2. In July 1995 sediment core samples were taken from the lakes where the PTE accumulations were detected (N_oI and N_oVII) with a 5-cm-diameter sampler piston developed for lake-deposit-sampling by Livingstone and modified by Braun [61, 62]. The samples were pushed out of the sampler tube and carried to the laboratory in clingfilm. The core samples were cut into 5-10-cm slices with a plastic knife and later dried at 105 °C and homogenized in an achate mortar. This samples were used for vertical mapping of radionuclides and PTE accumulations.
3. In October 2013 the sampling 2. was repeated approximately at the same points for present tracking study.



Fig. 2. (a.): The map of Gödöllő
(b.): Scheme of sediment sampling in the lake system

Element analytical methods

- The total soluble PTE content of mixed samples taken at first sampling was extracted by 2 M HNO₃ according to non standardized method applied in Hungarian Soil Laboratory Network at that time. 5 g homogenized sample was weighed into a plastic

flask, 50 cm³ 2 M HNO₃ was added, and the flask was circularly shaken for 2 h. After filtering the solution were analysed with a Jobin-Yvon 24 sequential ICP-OES spectrometer. Operational parameters: incident power 1 kW; outer Ar-flow 12 L min⁻¹; intermediate Ar-flow 0.2 L min⁻¹; nebulizer Ar-flow 1.1 mL min⁻¹; Meinhardt-type nebulizer uptake rate 1 mL min⁻¹. Detected elements: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn, V. Prior to ICP-OES measurement solid mixed samples were analysed by DC-ARC emission spectrography as it described in our earlier publication [60].

- The total soluble PTE content of sliced core samples taken at second sampling was extracted by microwave supported digestion with concentrated nitric acid/hydrogen-peroxide mixture according to Hungarian Standard for sewage sludge analysis [63]. The element analysis of solutions was performed with Jobin-Yvon 24 ICP-OES spectrometer as described above.
- The fractionation of PTE content of sliced core samples taken at second sampling was performed according to the original BCR 3(+1) scheme [15]. The residual fraction was extracted by aqua regia. The validation was performed with BCR-601 CRM sample. The element detection (Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) in the extracts was performed by a Perkin Elmer ELAN 6000/PE type ICP-MS instrument. The calibration was performed with multielemental Merck standard solutions, as internal standards In and Re were applied [60].
- The total soluble PTE content of sliced core samples taken at third (recent) sampling was extracted by microwave supported digestion with concentrated nitric acid/hydrogen-peroxide mixture according to Hungarian Standard to environmental soil analysis [64].
- The fractionation of PTE content of sliced core samples taken at third sampling was performed according to the modified BCR 3(+1) scheme. The residual fraction was extracted by microwave supported digestion with concentrated nitric acid/hydrogen-peroxide mixture according to Hungarian Standard to environmental soil analysis [64]. The validation was performed with BCR-701 CRM sample. For element detection in different extracts, the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer was employed, which is able to record the entire UV-VIS spectrum range by rapid scanning CCD detection. It also makes possible a flexible analytical line selection for 75 elements. The operational parameters: incident power 1.2 kW; outer Ar-flow 15.94 L min⁻¹; intermediate Ar-flow 0.32 L min⁻¹; nebulizer Ar-gas pressure 2.86 bar; Meinhardt-type nebulizer cyclonic spray chamber solution uptake rate 0.85 mL min⁻¹. Detected elements: Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn. The multielemental calibration was optimized by matrix-matched calibration to BCR-extractant solvents and by application of Yttrium internal standard. The validation was performed with BCR-701 CRM sample [55].
- Radiochemical analysis of 2. and 3. sampling was performed by γ -spectroscopy. The dried and homogenized samples were filled in an airtight 38 cm³ plastic box similar to Marinelli containers and a solid state detector (Canberra HPGe) 1333 keV half-width detector was used connected to a multichannel analyzer. The activities of radionuclides were determined in Bq/kg units. In present studies the activity of Chernobyl-origine ¹³⁷Cs-activity was compared in the layers.

RESULTS AND DISCUSSION

During this longterm environmental study both the analytical methodology and the regulation has been continuously changed. Under such circumstances the comparability of data series has to be sustained by retrospective crossvalidations or in the explanation of experiences the

changes have to be considered. Therefore the data of mapping of total soluble PTE-content of first sampling can not be directly compared with total soluble PTE measurements in second and first sampling. As an example on **Fig. 3.(a.)** the distribution of Cd-content in the upper sediment layer is presented obtained at first sampling at the points given on **Fig. 2.(b.)**. On **Fig. 3.(b.)** the total soluble Cd concentrations measured during the first, second and third sampling in the 0-10 cm layer are presented next to each other at the corresponding sampling points. It can be observed the order of magnitude of measured Cd-contents during the first, second and third sampling is equal at points lying in Lake I., but at points lying in Lake VII. this equality is not valid in all cases and significant decrease can be observed in 2013. This observation reflects to the fact that in 2003 the sediment layer from the Lake VII. was partially removed.

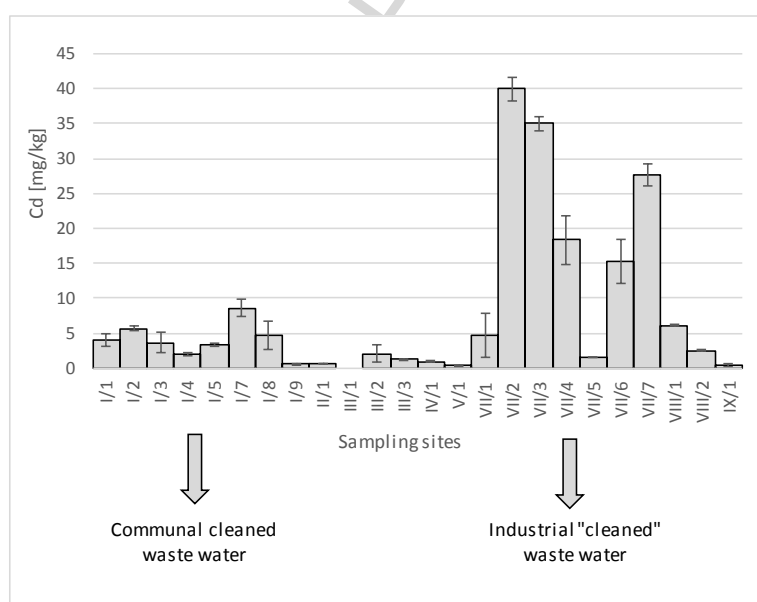
The results of vertical mapping of total soluble PTE concentration in sediment core samples taken in second (1998) and third (2013) sampling are summarized in the **Table 2**. The tendency of decrease of PTE-concentrations in soil core samples taken from Lake VII. in 2013 can be observed for all elements, except for vanadium and zinc.

The results of vertical mapping of ^{137}Cs -activity concentration measured in 1996 and 2016 in core samples taken at I/1 and VII/10 sampling points are presented on **Fig. 4.(a.)** and **(b.)**. The activity concentrations measured in 1996 are corrected to 2016 considering the decay rate. On figures a one order of magnitude decrease of activity concentration can be observed in 2013 at both places which is not attributable to the radioactive decay. This decrease can be explained by dissolution and transport of Cs^+ -with water flow through the lakes.

Table 2. Results of vertical mapping of total soluble PTE concentrations (mg/kg) in sediment core samples taken in second (1998) and third sampling. (RSD of three parallel concentration determination was in all case less than 3 %)

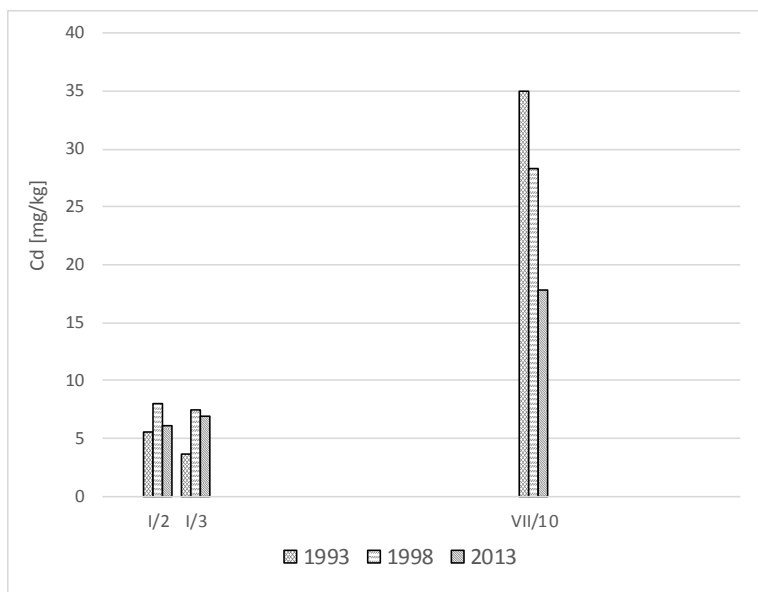
Sample	Layer [cm]	Cd		Co		Cr		Cu		Fe		Mn		Ni		Pb		V		Zn	
		1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013
I/1	0-10	4.99		9.54	10.2	156	83.0	323	222	29000	26100	658	474	138	129	88.8	55.7	29.5	37.6	535	434
	10-20	7.44	7.16	10.4	9.85	172	51.1	367	46.2	32000	23800	632	849	157	37.4	86	35.5	31	30.4	587	160
	20-30	6.06	4.20	5.98	4.86	40.9	27.4	121	10.9	13600	12400	376	224	54.1	13.3	34.3	9.93	20.0	14.2	247	37.1
	30-40	1.04	3.58	5.18	4.83	17.8	25.0	38.6	7.65	11800	11400	370	197	18.8	12.4	25.4	6.69	19.7	11.1	130	27.1
	40-50	0.28	4.50	6.21	7.49	19.2	27.3	33.0	9.18	13800	17000	383	519	15.2	14.9	28.8	9.54	21.3	11.8	123	33.4
	50-60	0.26	3.23	6.55	4.83	20.9	24.9	32.9	7.97	15800	11400	360	184	16.8	13.2	30.9	6.55	22.0	7.81	133	28.3
	60-70	0.41	2.96	10.3	3.76	32.2	29.7	50.5	6.54	28000	8900	644	135	28.1	13.0	50	5.98	29.3	12.2	239	22.4
I/2	0-10	8.08	6.07	7.03	4.92	125	65.8	176	128	22300	13000	1140	453	165	34.7	53.2	33.3	6.66	14.3	28.4	292
	10-20	11.0	7.66	9.56	4.76	65.0	165	129	385	32700	15600	1010	583	106	81.5	50.4	41.4	10.4	10.4	49.5	633
	20-30	0.98	17.7	12.9	5.73	38.9	244	69.0	569	33100	24300	794	518	40.5	139	53.4	49.1	11.3	19.5	51.2	787
	30-40	23.9	9.47	10.8	5.31	57.4	37.2	148	81.6	44800	13300	1750	276	128	38.1	50.8	26.3	11.7	17.9	50	160
	40-50	0.38	3.64	8.59	4.23	30.3	23.6	18	21.3	21100	10900	235	283	29.5	11.7	18.4	20.1	9.04	11.3	42.2	80.9
	50-60		4.40		7.25		46.1		45.4		20700		441		23.1		37.3		24.6		168
	60-70		4.53		6.65		34.0		16.4		16100		358		16.4		17.8		18.5		57.3
70-80		4.83		8.39		42.6		20.6		21100		924		21.5		23.6		22.8		59.3	
I/3	0-10	7.42	6.90	11.7	7.66	37.1	84.0	104	182	29100	10500	1500	442	66.5	74.0	54	24.0	10.7	13.0	51.7	344
	10-20		5.20	2.86	6.64	11.6	33.3	14.7	47.8	9800	7500	198	325	10.0	47.7	15.3	13.9	3.58	13.0	16.2	111
	20-30	0.23	4.90	6.4	7.74	22.3	14.5	33.3	10.0	17700	9000	292	1190	23.1	10.9	54.2	9.85	6.87	14.6	48.4	25.3
	30-40	0.31	4.16	8.09	7.64	30.7	13.3	42.3	7.40	21900	10800	504	910	40.8	10.6	43.5	8.28	8.03	14.7	41	20.8
	40-50		5.67	8.18	7.28	29.7	17.9	14.5	9.85	19200	10900	410	173	51.9	11.8	20.5	9.84	7.59	20.6	36.6	24.4
VII/9	0-10	22.5	11.4	28.5	8.40	1080	245	155	41.8	74800	11100	321	211	317	38.5	197	60.8	12.0	11.1	101	318
	10-20	1.78	23.2	5.9	11.5	85	637	24.5	83.2	18900	12600	158	207	63.5	66.9	18.7	111	4.49	10.5	44.4	657
	20-30		17.7		32.3		532		131		27600		214		134		154		28.3		676
	30-40		9.39		12.2		53.1		24.7		16200		265		42.1		28.2		24.7		54.1

Sample	Layer [cm]	Cd		Co		Cr		Cu		Fe		Mn		Ni		Pb		V		Zn	
		1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013	1998	2013
	40-50		4.42		5.25		29.4		12.2		9500		202		16.7		16.1		12.9		25.4
	50-60		0.48		2.38		25.7		9.38		7400		151		11.7		13.0		16.0		18.0
	60-70		0.30		2.77		14.7		7.46		5400		118		8.17		17.8		8.86		10.8
	70-80		0.33		3.20		19.1		8.25		5800		88.5		11.0		15.8		14.1		12.6
	80-90		0.34		2.72		21.2		8.67		5800		73.5		9.84		10.3		18.8		17.6
VII/10	0-10	28.3	17.8	11.5	8.13	917	737	126	120	30700	20600	316	302	92	91.5	183	211	34.1	17.7	1280	869
	10-20	34.6	2.07	11.2	5.75	1020	53.2	131	29.5	26900	14200	311	321	85.8	30.5	192	26.8	37.1	16.3	1300	88.6
	20-30	19.4	0.52	7.80	5.36	571	27.9	74.8	9.71	18400	12200	211	246	54.4	13.4	118	11.2	28.9	8.12	707	31.7
	30-40	15.7	0.86	5.73	7.61	526	43.2	64.9	14.7	13600	17700	173	280	45.4	22.6	109	16.7	22.5	21.5	641	43.9
	40-50	1.78	0.42	4.73	3.41	193	29.4	38.7	9.84	7800	12900	103	437	20.5	14.6	38.8	13.3	16.9	10.8	195	24.1
	50-60	4.28	0.53	9.39	2.25	332	12.7	81.1	6.87	17400	12000	184	676	47.1	7.52	88.2	15.6	24.9	6.46	347	12.2
	60-70	0.52	0.46	4.32	1.96	31.2	15.7	10.7	7.44	12600	10600	165	564	17.5	8.49	15.4	10.4	21.9	5.92	68.7	13.4
	70-80	0.54		4.72		34.0		12.8		12800		143		13.5		11.7		24.2		45.2	
	80-90	0.65		7.1		48		17.6		16400		164		19.4		15.1		28.2		69.1	
VII/11	0-10	0.81	40.4	2.78	9.98	22.1	1970	10.2	230	11500	28100	316	304	14.2	118	22.2	379	3.53	23.5	15	1640
	10-20	0.55	18.6	5.90	13.6	22.1	1460	14.5	120	20000	28300	619	261	20.8	129	19.2	146	7.37	24.2	35	1150
	20-30	0.47	0.84	8.42	4.27	30.4	43.0	17.3	18.3	23100	12300	384	172	27.2	17.7	20.3	27.0	9.98	11.6	47	56.5
	30-40	6.90	0.60	7.97	5.48	26.5	32.6	16.3	13.7	21000	17400	635	246	21.6	16.4	20.5	16.4	8.19	17.6	39.6	34.9
	40-50	1.71	0.54	7.16	7.55	55.7	49.7	29.6	18.2	18500	23700	779	548	44.2	24.0	34.2	18.7	9.35	25.9	42.7	50.4
	50-60		0.58		9.04		60.1		15.1		18800		217		28.2		19.0		18.3		44.5
	60-70		2.43		4.93		140		20.9		14000		222		26.7		35.4		12.7		95.8
VII/12	0-10	8.04	1.77	7.89	5.09	401	146	46.7	30.3	31800	12200	284	244	102	30.8	76.2	33.8	7.39	10.7	72.4	128
	10-20		0.33		1.69		16.8		7.79		4600		194		5.19		10.6				21.2
	20-30		0.26		2.47		13.8		5.06		4700		103		6.80		9.49		0.78		14.0
	30-40		0.15		1.72		11.3		4.62		4000		107		5.59		8.68				12.9
	40-50		0.12		1.62		7.41		3.55		2600		113		4.20		9.01				7.23
	50-60		0.10		1.84		3.64		2.76		1800		94.0		3.11		7.74				3.91
	60-70		0.21		2.34		11.7		6.38		2700		32.4		8.33		10.6		24.3		6.31
	70-80		0.50		2.21		75.7		10.4		3600		46.7		16.1		8.28		31.4		9.90
	80-90		0.33		2.13		106		6.30		3400		61.3		10.2		4.84		33.2		9.68



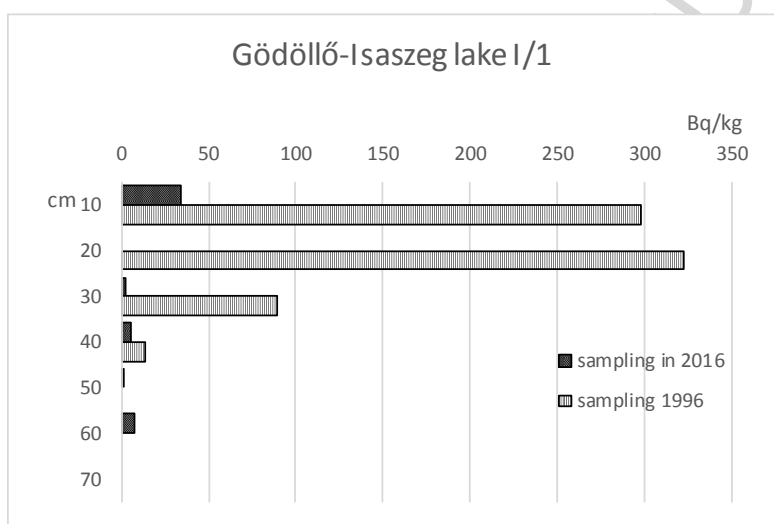
a.)

Fig. 3.(a.): Distribution of Cd-content in the upper sediment layer obtained at first sampling.



b.)

Fig. 3.(b.): Total soluble Cd concentrations measured during the first, second and third sampling in the 0-10 cm layer are presented next to each other at the corresponding sampling points.



a.)

Fig. 4.(a.): Vertical distribution of ^{137}Cs -activity concentration in sediment cores taken at I/1 sampling site in 1996 and 2016.

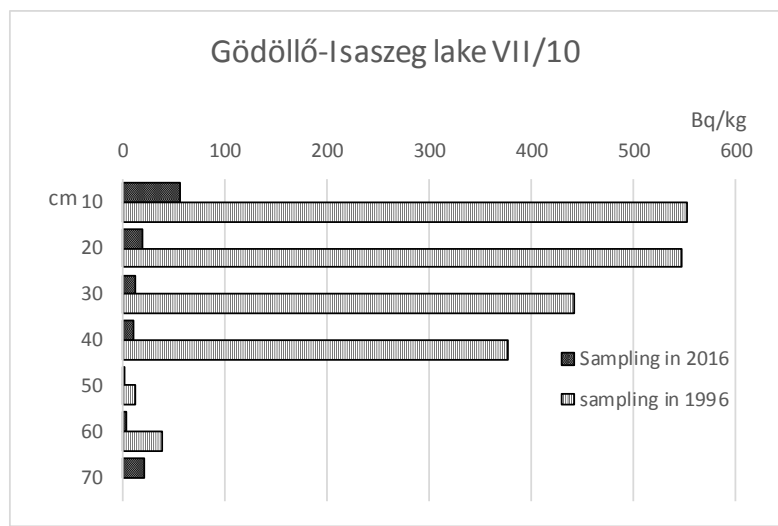
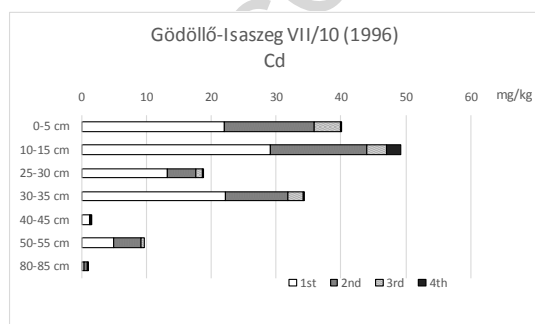


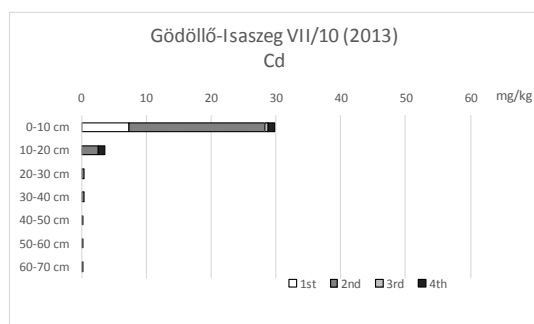
Fig. 4.(b.): Vertical distribution of ^{137}Cs -activity concentration in sediment cores taken at VII/10 sampling site in 1996 and 2016.

On **Fig. 5.(a.)** and **(b.)** are presented the results of BCR fractionation of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn in VII/10 sediment core samples taken in 1995 and 2013. At this point was the highest PTE load detected in 1995, therefore the success of sediment removal performed in 2003 can be evaluated. On the basis of diagrams the followings can be established:

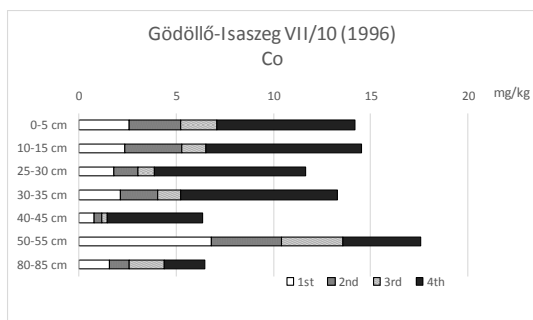
- Concentration of Cd, Co, Cr, Cu, Ni, Pb, Zn in deeper layers significantly decreased in 2013, but in the 0-10 cm upper layer it is still high and some cases it exceeds the soil hygienic threshold values.
- Concentration of Fe and Mn in all layers significantly increased in 2013, probably it can be explained with oxidative circumstances during the 2003 sediment-removal operation.
- The ratio of 1st BCR fraction has significantly decreased for elements. It can be attributed to the fact, that the most mobile fraction after the disruption of inlet of contaminants can be dissolved and transported by effluent water.
- The ratio of 2nd BCR fraction had significantly increased for elements. It can be explained by formulation of insoluble iron- and manganese-oxides during the 2003 sediment-removal operation.
- In general it can be established that the removal of PTE contamination from lake seven was not complete in 2003.



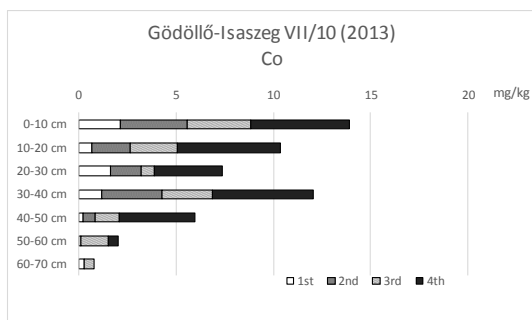
a.)



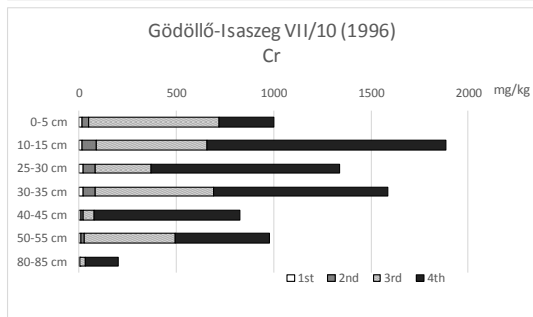
b.)



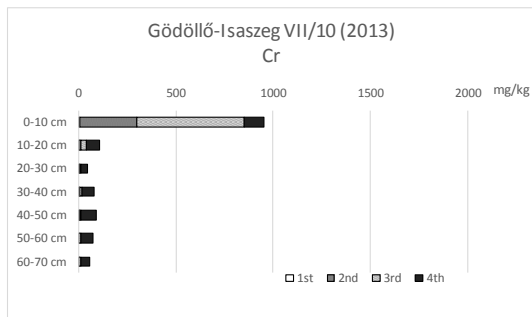
a.)



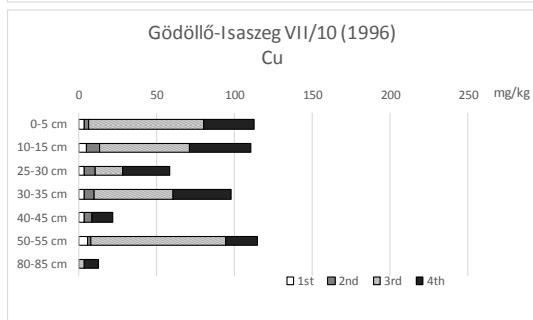
b.)



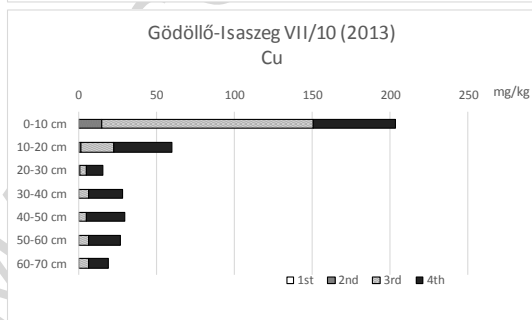
a.)



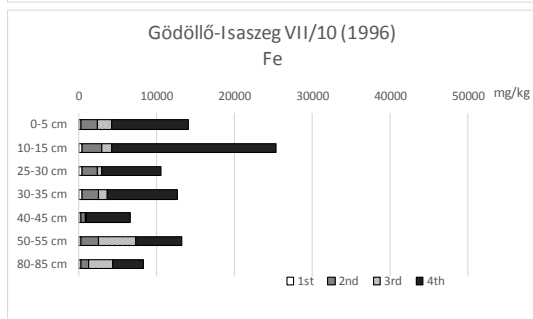
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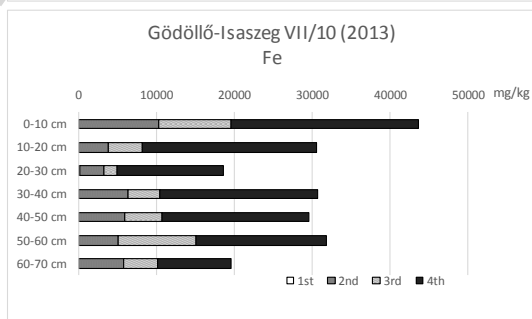
a.)



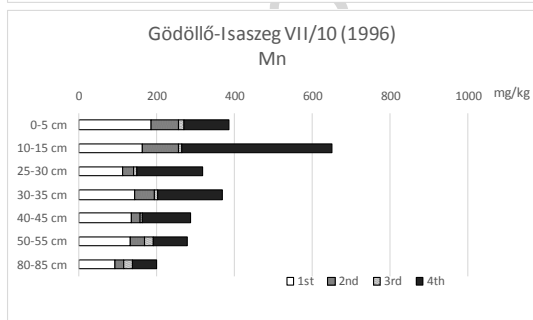
b.)



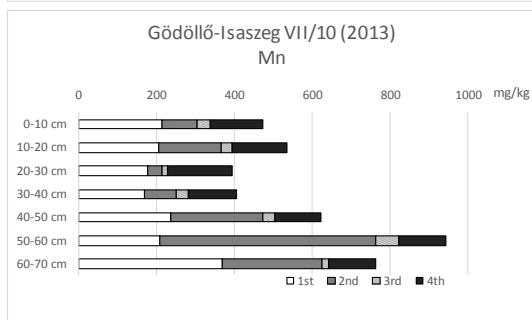
a.)



b.)



a.)



b.)

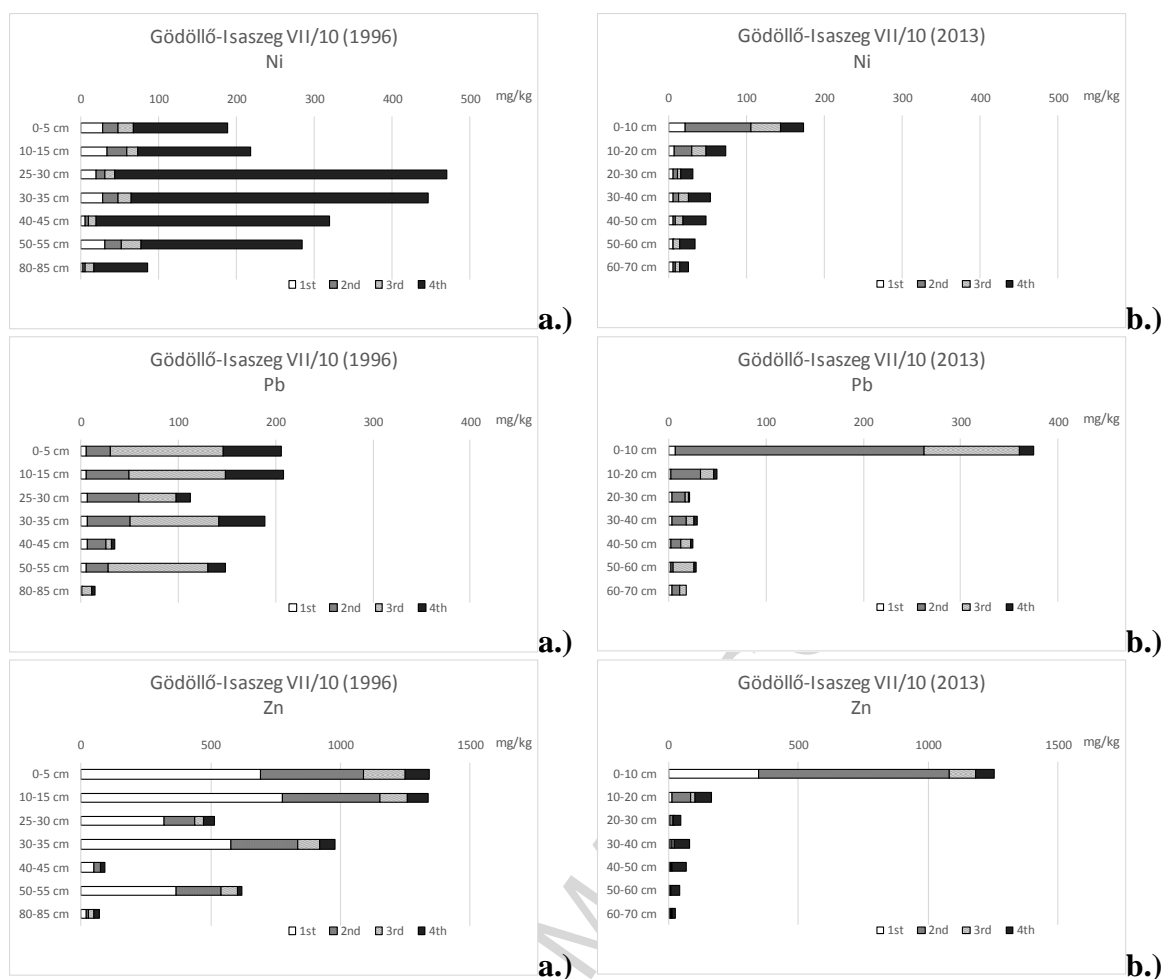


Fig. 5.(a.): The results of BCR fractionation of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn in VII/10 sediment core sample taken in 1995.

Fig. 5.(b.): The results of BCR fractionation of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn in VII/10 sediment core sample taken in 2013.

CONCLUSION

The BCR sequential extraction procedure for tracking the long-term fate of PTE contamination of different origin in surface water/sediment/ systems showed a much potential. By repetition of fractionation of PTEs after 10 and 20 years clearly reflects the change of PTE concentrations in different fractions. The decrease of PTE concentrations can be explained by leaching the most mobile fractions by water exchange over the sediment and/or by remediation activity.

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HIGHLIGHTS

- Detailed review is given on fractionation methodologies by sequential extraction methodologies applied for risk assessment of environmental pollution by potentially toxic elements (PTE). Considering the all sources of PTE pollution involved the health care release.
- The researches for improvement of the BCR 3+1 step fractionation are reported.
- A case study is presented for evaluation of long-term changes of the environmental mobility of PTE contaminations in a polluted lake system.
- The BCR sequential extraction procedure for tracking the long-term fate of PTE contamination of different origine in surface water/sediment/ systems showed a much potential.