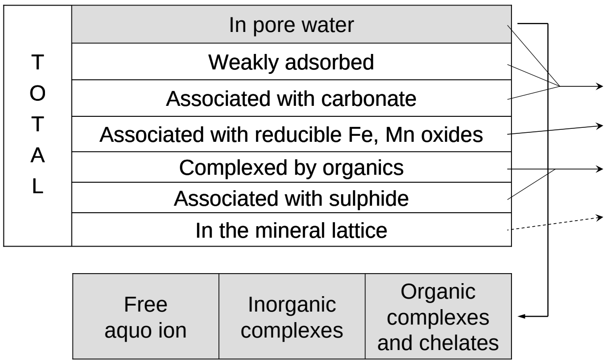
EVALUATION OF ENVIRONMENTAL MOBILITY AND LONGTERM TRANSFORMATION OF HEAVY METAL CONTAMINATION IN SOILS AND SEDIMENTS.

1. INTRODUCTION, ANTECEDENTS.

Potentially toxic elements (PTE) which are in the environmental chemistry literature frequently called as heavy metals are the most important group of the persistent inorganic pollutants. The role of different chemical elements in concern of food production is one of the most important question of the agricultural chemistry research since the middle of the XIXth century. Numerous methodology was elaborated for estimation of nutrition capacity of soils by determination of biologically available fraction of plant nutrition element content. Similar questions were generated since the eighties of the XXth century due to the increasing environmental pollution problems, however in this field, the estimation of human and the ecotoxicological impact became the main goal. This claim has brought new requirements for the methodology and has led to the development of the speciation analytical chemistry which is the primary tool of the evaluation of toxicological effects. These researches have called attention to the fact, that the environmental mobility and biological impact of elements in environmental systems are determined by their chemical species forms. Biological risk assesment of PTE-contaminated areas therefore in principle requires the total speciation of all chemical elements present in the system. This task in practice cannot be solved. As a compromise fractionation of heavy metal content according to environmental mobility and biological availabity became the main trend.

1.1.Risk assessment of PTE contamination by fractionation with sequential extraction methods, methodological problems.

Risk assessment of PTE contamination in the soil/water/atmosphere system was based on fractionation of metallic and metalloid element content of environmental samples according to their environmental mobility. The term „fractionation” was recommended by the IUPAC in 2000 [1]. Mobility of an element according to different solubility of different binding classes can be estimated by solvents sequentially applied which contain increasingly more and more aggressive reagents [2,3]. The first sequential extraction procedure for characterization of mobility of heavy metals in aquatic sediments was developed by Tessier [4] who classified the metal content of sediments according to solubility and binding forms of metallic species as it is presented in the following scheme.



Step	Extractant	Duration of leaching
1	0.11 mol L^{-1} HOAc	16 h
2	0.10 mol L^{-1} $NH_2OH.HCl$ at pH = 2	16 h
3	8.8 mol L^{-1} H_2O_2 followed by 1 mol L^{-1} NH_4OAc at pH = 2	16 h
4	(residual) Aqua regia	

a ***b***

a: *Element fractions in aquatic sediment as classified by Tessier [4], Caroli [2], Kersten et al. [3].*

b: *Original BCR sequential extraction scheme (Ure et al. [6], Quevauviller et al. [7], López-Sánchez et al. [8].)*

Based on this essential work several 5-8-step sequential extraction schemes were developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed [5]. The total time demand of these procedures is 5-6 days, while duration of the applied batch leaching steps is determined by long setting up time of partition and other heterogeneous equilibria. The BCR proposal for a 3(+1)-step sequential extraction procedure issued in 1993 is a simplified version of the above mentioned schemes [6], but it is still time consuming and labour intensive. As it can be seen in the scheme, by this method the water soluble, the weakly adsorbed and the carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step, so it does not model the primary natural pathways of mobilization with water dissolution and bicarbonate formation. Due to the numerous operations and reagents applied, there is a risk of contamination during the whole procedure. Readsorption of extracted metals during the phase separation can lead to analyte losses in the extracts. In the extracts the high reagent's concentrations may cause strong matrix effects during the spectrochemical element detection. The CRM 601 sediment reference material issued in 1997 was certified only for fractionation of five element (Cd, Cr, Ni, Pb, Zn) to this procedure [8-9]. During the elaboration of the next (BCR 701) sediment materials, the original BCR procedure was modified to avoid the analyte losses during the second leaching step due to the pH instability [10, 11, 12, 28]. This change, however, can cause difficulties when the consistency with former data is required. The BCR procedure in its original and modified versions was successfully applied to aquatic sediments and soils, however, soil CRM was not issued up to now [13] and standardization of procedure was not achieved up to now. Žemberyová [14] successfully utilized the modified BCR three-step sequential extraction procedure for fractionation of Cd, Cr, Cu, Ni, Pb and Zn in different soil reference materials of Slovak origin. Kubová et al. [15,16] successfully applied the BCR three-step sequential extraction and the dilute HCl single-step extraction procedure for soil-plant metal transfer predictions in contaminated lands. With extension of BCR-fractionation usage to soils and aerial gravitation dust samples one has to calculate with further difficulties [23, 25, 26, 27]. For example, in the modification of the BCR procedure the high carbonate content samples were not considered, in spite of the fact that the amount of acetic acid may not be enough to dissolve the total calcium carbonate content of 1 g sample weighed in according to the BCR protocol. Gravitation dust can significantly contribute to heavy metal contamination of soils and sediments, particularly at sites affected by industrial activity or traffic. However, the application of the BCR procedure to such kind of samples is not free from further difficulties. The available sample quantity is mostly less than that is required to BCR procedure, therefore miniaturized BCR procedure by Dabek-Zlotorzynska et al. [17] and realization of BCR procedure in continuous flow system by Shiowatana et al. [18] was proposed, too. Another problem may arise from the high organic matter content of such samples (dusts, sediments) which can form separate phases during the leaching. To overcome the above mentioned problems the elaboration of a quite different continuous flow sequential extraction procedure was started formerly at our laboratory [19, 31]. The solid samples were mixed in 1:20 (m/m) rate with pure quartz sand (SiO_2) weighed into a column of a supercritical fluid extractor (SFE). Firstly supercritical CO_2, then under the same conditions subcritical H_2O and finally their 1:10 ratio (V/V) mixture were applied as extractants, as can be seen on the following scheme:

Step	**Extractant**	**Chemical information**	**Duration**
1	Supercritical CO_2 (in SFE)	CO_2-soluble mobile organic bound fraction	60 min
2	Subcritical H_2O (in SFE)	Water soluble fraction	60 min
3	H_2O/CO_2 (10:1) (in SFE)	Carbonate bound fraction	60 min
4	HNO_3/H_2O_2 (out of SFE)	Residual	

Further validation with high carbonate containing soil reference samples has proved that the complete dissolution of carbonates during the 3rd step requires longer time (90-180 min) [20, 21]. Firstly organic fraction which can contain organic pollutants, too can be obtained by this procedure. In the 2nd step the water-soluble, and in the 3rd step the carbonate-bound fraction can be collected.

1.2. Evaluation of PTE contamination at the Gödöllő –Isaszeg lake system.

Our research group performed an intensive monitoring on the Gödöllő-Isaszeg lake system and the Rákos creek since 1993. This fishpond system along the Rákos creek from the eighties were used as a receiver of cleaned industrial and communal waste water of Gödöllő. In the lake sediment was detected the heavy metal accumulations arising from these sources and the traces of the radioactive aerosol deposition from Chernobil nuclear accident. The mobility of heavy metals in the sediment layers was evaluated by BCR sequential extraction and for several elements (e.g. Cd, Pb, Cr) significantly higher concentration values were detected in the most mobile BCR-fractions as the allowed threshold [22]. Later to these sediment samples was applied the SFE sequential extraction procedure elaborated by our laboratory [19, 29] and ecotoxicological tests were performed using the aquaeos-phase extracts [30]. Following this the mobility of the contamination was investigated using biofilm samples [24].

1.3. Evaluation of PTE contamination at the Upper Tisza Region in 2000

The Hungarian part of the Tisza River is highly contaminated by metals from mining activities in Romania. Mining in Maramures County (former Máramaros) traditionally exploits host ores of base metals (Cu, Zn and Pb) and precious metals (Au and Ag). Besides mining, metal pollution in upper Tisza catchment has also a long history [32]. Nowadays the processing of old tailings pond material using cyanide in the recovery of Ag and Au is spread over this region. Mining activities use dangerous and toxic chemicals like cyanide which is prime source of contamination. Besides this, wastewater may contain some other heavy metals associated with fine-grained sediments. However, metal concentration of river water is not remarkable 30 km downstream from the point sources [33], sediment-associated metals are dispersed at much greater distances. In January and March 2000 two tailings dam failed in Baia Mare (Nagybánya) and Baia Borsa (Borsabánya) and resulted cyanide and metal pollution in the Lápos - Szamos - Tisza and metal pollution in the Visó - Tisza river systems [34]. The short term effects of the pollution events were studied by many of researchers, and the Lápos-Szamos-Tisza and Visó-Tisza river systems were found to be contaminated by Cu, Zn, Pb and Cd [33, 35, 36, 37, 38, 39]. The mining accidents were followed by floods; therefore the metal pollution of the floodplains were also observed [40, 41]. Deposition of contaminated sediment on floodplains during flood events and the mobilization of the pollutants may increase the plant available metal content of the upper soil layer. The mobility and phyto- availability of metals depend on their chemical compositions [42]. Hence, the floodplain soils and river sediment were measured by sequential extraction procedures (SEP) [35, 43, 44] and Lakanen-Erviö extraction [45,46]. Remarkable rate of Cd and Zn contents of polluted sediments (Lápos, Szamos and Tisza Rivers) were in mobile form [35]. Besides this, the Cd and Zn contents of the floodplain soils (Szamos and upper Tisza) could be found in an easily available form [40].

1.4. Aims of Present Project

The research aims of present project were determined in three directions:

- Development and critical evaluation of methodolgy of risk assesment of PTE contamination by fractionation with sequential extraction techniques, improvement the reliability of these analytical techniques supporting the standardization of remediation planning.
- Evaluation of longterm changes of PTE-contamination at the Gödöllő-Isaszeg lake system sediment, it was regarded as a model area for testing the methodological developments.
- Evaluation of longterm changes of PTE-contamination in 2000 in the sediment/soil/ plant system at Upper Tisza Region.

The results achieved in theproject are reported in three lots according to these three main goals and the publications will be referred in the project publication list [PL].

2. RESULTS and PROGRESS

2.1. Development and critical evaluation of methodolgy of risk assesment of PTE contamination by fractionation with sequential extraction techniques, improvement the reliability of these analytical techniques supporting the standardization of remediation planning.

Analytical methodological developments for characterization of environmental mobility of heavy metal contamination in soil and sediment was based on our former OTKA 72926 project closed in 2012, its results were published in printed form in 2013 (Horváth et al. [24]). These results were built in our present project research in which we tried to improve the reliability of BCR sequential extraction procedure, to extend its application and validation for different environmental sample types occuring in assesment of PTE contamination and to develop our alternative-supplementary SFE sequential extraction procedure. The main results can be summarized in the followings:

- The validation and calibration of the (3+1) step BCR sequential extraction procedure to aquatic sediment, soil, mining waste, gravitation dust and biofilm samples using the available Certified Reference Material (CRM) and preparing own Laboratory Reference Samples (LRS) was performed. First the influence of extractant solvents applied in the steps of BCR procedure on parameters of multielemental ICP-OES analytical calibration was studied and a spectral data base was built in for the possible spectral interferences when a whole UV-VIS range recorded by CCD scanning detector. Following this for all contaminant elements at least two interference-free analytical lines were selected and the extractant-solvent matrix effects were reduced by increasing the plasma incident power and by application of yttrium internal standard. After this optimalization we should achieve acceptable recoveries for BCR-701 certified reference sediment sample. Laboratory Reference Sample (LRS) for soil fractionation was prepared an validated by this optimized method. These results were presented in several conferences,two papers in journals already were published [PL15, PL18] and one is still in preparation.
- Joint to the above investigations a study of the results of one step leaching methods (water, $CaCl_2$-DTPA, KCl-EDTA, Lakanen-Erviö, HNO_3/H_2O_2 microwave digestion) proposed in Hungarian agrochemical and environmental soil analysis standards, was compared with two sequential extraction methods (BCR and McGrath) applying four different physical properties (clay, sandy loam, sand, loam) soil sample of Hugarian Soil Information Monitoring (TIM) collection. The relationship between the easily available fractions and the one step leaching methods were significantly influenced by the soil properties. These results were presented in five conferences and a paper is in preparation for submission in a journal.
- Another methodological study was performed for acceleration of BCR procedure by sonication treatments. By the combination of sonication and shaking the extraction-time-demand could be significantly reduced with a 85% recovery. The above results were presented in five conference lecture and one paper was published in a journal [PL38].
- Adaptation of our formerly elaborated „SFE" continuous flow sequential extraction procedure for extracting the original elemental species to sample types of our present investigations has been performed. The normal preparative column in the supercritical fluid extractor was replaced by a smaller volume column to reduce the sample mass and solid dilution ratio and the blank values. Investigations on the problems in collection of fractions have been continued on the basis of our experiences from the previous years. The time of extraction has been optimized for samples of various carbonate content, that was verified by a first order kinetics model based on the results. The results were presented in three conference lectures and a paper is in preparation for publication in a journal.

2.2. Evaluation of longterm changes of PTE-contamination at the Gödöllő-Isaszeg lake' sediment.

As it was outlined in the antecedents in the Gödöllő-Isaszeg lake system the study of PTE contamination was started in 1993 so we have an appropriate reference data baseto comparison of changes during two decades, therefore it was appropriate as a model area for testing the above methodological developments. For vertical and horizontal mapping of PTE content of accumulated sediment layers core samples were taken in1994, 1995 and 2013. In the sediment layers total soluble PTE content determined according to the MSZ-2147050:1998 standard was related to the BCR fractionation. The order of magnitude of measured total soluble PTE contents in 1995 was equal at points lying in Lake I., but at points lying in Lake VII. this equlity was not valid in all cases and significant decrease could be observed in 2015. The Chernobyl origine radionuclides were detected by γ-spectroscopy in 1995 and 2015. Repetition of BCR-fractionation of PTEs after 20 years clearly reflected the change of PTE concentrations in different fractions. The decrease of PTE concentrations could be explained by leaching the most mobile fractions by water exchange over the sediment and/or by remediation activity. This results were presented at several conferences and a paper was published in a journal [PL36].

2.3. Evaluation of transformation of elements in the contaminated soil of the Upper Tisza Region in 2000.

In our former studies between 2000-2002 direct effects of flooding on the upper soil layer were evaluated. Element analytical data obtained for pseudo total (MSZ-2147050:1998 standard) and Lakanen-Erviö extracts of soil layer samples are available, but no sequential extraction data was produced at that time. For retrospective comparison of changes of environmental mobility five sampling sites were selected (Tivadar, Vásárosnamény, Tiszacsege, Tiszaug, Rakamaz) where the soil samples from 2000 were preserved and at the same 28 points 100 cm soil core samples were taken and sliced on layers. The determination of pseudo total element contents was performed in soil samples from 2000 and 2013 respectively. Due to the discrepancies of analytical results between 2000 and 2013 the determination of pseudo total element contents and the soil sampling at several places was repeated in 2015. Determination of element contents of plant samples collected in 2013 and 2016 on the above sampling areas was performed too. These results cocerning on pseudo total element content were presented on four conferences and in one journal paper [PL15].

During the last year of the project the retrospective comparative study of environmental mobility of PTE contamination was performed at four selected sites (Tivadar, Vásárosnamény, Rakamaz, Tiszacsege), where we had archived samples collected between 2000-2002. The current project offered us a chance to examine them again together with the new samples taken at the same places. In order to do this the appropriate fractionation analytical methods could be used. In the given years (2000) to these samples the McGrath-Cegarra (1992) method was used as it was implemented after the Győri Zoltán's Rothmasted Research Scholarship(1993). The BCR method has become widely applied lately and currently it is the most common procedure in the world for analyzing sediment. During the present research project we performed the determination of the "pseudo total" element content by MW digestion in (HNO_3+H_2O_2) mixture, by the Lakanen-Erviö (1971) extractant (for bio availability) and the comparison of the McGrath-Cegarra and the BCR sequential extraction procedures (SEPs) both on the "old" and the new 2015 samples. During the evaluation of soil pH (H_2O, nKCl) it was established that pH of the upper 10 cm layer of the soil has not changed in the past 15 years. The assessment of the results of the Lakanen-Erviö extractant and the previous ones revealed that there was no significant change in the concentration of the extracted element contents in the past 15 years on any of the sample taking sites. This means that there was no forceful impact that would have triggered a major change. The same conclusion can be applied for the total element content as well. However, we have to note that the standard deviation of the data exceeds 15 %.

The fractionation measurements were performed in the last periode of the project, their evaluation and publication is still in process, therefore in the following the preliminary results are summarized.

On these soils the PTE concentrations were low and the result of 3 mg/kg was eventually measured for zinc only with the McGrath method with two extractants (0.1 M $CaCl_2$, 0.05M NaOH). The 0.05 M NaOH extractant solution showed clearly the quantity of organic-bound elements. The measurement data gained by residual fraction show the differences between sample taking sites most prevalently. We have to note here that after fractionation them with strong extractants, soils concentration are not significantly higher than the values of residual sequential extraction with aqua regia, which indicates that in case of this extraction the examined elements can be found predominantly in this fraction. During the extraction of elements by the BCR method it was observed that by acetic-acid dissolution showed a considerable amount of zinc (soluble in exchangeable weak acid) in all 4 sites. The order was Tivadar, Rakamaz, Vásárosnamény, Tiszacsege based on increasing Zinc concentration (6, 23, 37, 51 mg/kg). The concentration was at 2-3 mg/kg with Lead but site influence was not detectable. In case of Cadmium concentration was the highest at Vásárosnamény (0.4 mg/kg). For all the 4 elements the lowest concentration was found at Tivadar samples. At the second step of BCR extraction using hydroxyl-ammonium-chloride reagent (reducible fraction) we could dissolve a larger amount PTE from the soil, which means the concentration of copper was 5-15 mg/kg, lead 20-60 mg/kg, zinc 17-100 mg/kg and cadmium was 0.1-1 mg/kg. Copper content was the lowest at Tivadar (6 mg/kg) followed by Rakamaz (10 mg/kg), Tiszacsege (12 mg/kg) and Vásárosnamény (15 mg/kg). The order was the following for Lead: Tivadar-Tiszacsege-Rakamaz-Vásárosnamény while for Zinc it was Tivadar- Rakamaz – Tiszacsege – Vásrosnamény. This means samples from Vásárosnamény were the highest in copper, lead and zinc and the lowest in the samples from Tivadar. This result proves that in case of Tivadar we have to consider that the contamination was transported by the River Tisza while at Vásáronamény the combined impact of both the River Tisza and Szamos (remains of North-Transylvanian mine and heavy industrial activities) can be found. The third step of extraction was done after H_2O_2-oxidization by ammonium-acetate. The soluble element content (oxidable) as they are characterized by a concentration of 0.4 – 0.45 mg/kg Cadmium on all the 4 sites that of Copper was between 6 and 7 mg and 4-8 mg for Lead. The fraction contained less Copper, Lead and Zinc in Vásárosnamény, Rakamaz and Tiszacsege than the second fraction. The value of these elements in Tivadar was the equivalent of the values in the second extraction step. The residual fraction by aqua regia the measured element content was lower than in case of McGrath extraction. This explaned by the fact that during BCR extraction more elements can be solved in the first three steps.

The results gained by BCR-fractionation method showed clearly that soil contaminated by flood sediment with PTEs (potentially toxic elements) content can be used as the object of studies comparing extraction methods. By comparing these results with the ones gained from the analysis of highly fertile Chernozem soil developed on Loess, we can determine that the element content of the latter one is the same in the first as on the contaminated soil, but the second and third extractions highlight the large differences that can be measured between a contaminated a non-contaminated soils. As the PTE content of this Chernozem is only a one-third of the contaminated floodplain area soils. **The sequential extraction of samples of the sample taking sites on the soils of floodplain areas highlighted the importance of the results gained by examination sequences with different extractants. The data resulting from the two applied methods different extractants with the BCR method (element fractions) vary highly. In terms of the binding ability of the element content, by using SEPs it can be determined, that there was no change detected in this period 2000-2015. Publication of these results was started recently on conferences** [PL32, PL33, PL34].

3. CONCLUSIONS

As a summary we may conclude that by the present project we could achieve a significant progress in improvement of the reliability and applicability of fractionation methodologies serving for risk assesment of PTE contamination in soil/water/sediment systems and [PL18, PL38] these methodological results can be utilized in standardization of planning of remediation technologies and in evalation of field fertilization experiments that are more than 30 years old. Two review type papers was published in journals on state of art these developments containing our results too [PL7, PL24]. In two case study for evaluation of longterm changes of PTE contamination at Gödöllő-Isaszeg lake system [PL36] and Upper Tisza Region [PL15] these methodological developments proved very useful. Two PhD student joint to this project have achieved significant progress in their PhD work connected with analytical and methodological developments in our research plan. The significant part of the results of the projects was already published in journals, but due to the time consuming measurements further publications in journals are still in preparation as it was signed above.

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