



Longterm study of transformation of potentially toxic element pollution in soil/water/sediment system by means of fractionation with sequential extraction procedures



György Heltai^{a,*}, Zoltán Győri^c, Ilona Fekete^a, Gábor Halász^{a,b}, Katalin Kovács^a, Anita Takács^a, Norbert Boros^d, Márk Horváth^{a,b}

^a Szent István University, Department of Chemistry, Páter K. u. 1, H-2103 Gödöllő, Hungary

^b Szent István University, Regional Knowledge Center, Páter K. u. 1, H-2103 Gödöllő, Hungary

^c Debrecen University, Nutrition Institute, H-4032 Debrecen, Egyetem Space 1, Hungary

^d Debrecen University, Department of Environment and Chemical Engineering, Ótemető u., 2-4, H-4028 Debrecen, Hungary

ARTICLE INFO

Article history:

Received 3 August 2016

Received in revised form 27 January 2017

Accepted 28 January 2017

Available online 2 February 2017

Keywords:

Potentially toxic elements

Fractionation

BCR sequential extraction

ICP-OES multielemental detection of pollutants

Risk assessment

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.

© 2017 Elsevier B.V. All rights reserved.

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.

* Corresponding author.

E-mail addresses: heltaigyorgy@gmail.com (G. Heltai), gyori.zoltan@unideb.hu (Z. Győri), fekete.ilona@mkk.szie.hu (I. Fekete), halasz.gabor@mkk.szie.hu (G. Halász), kovacs.katalin.eva@halgato.szie.hu (K. Kovács), takacs.anita87@gmail.com (A. Takács), nboros@eng.unideb.hu (N. Boros), horvath.mark@mkk.szie.hu (M. Horváth).

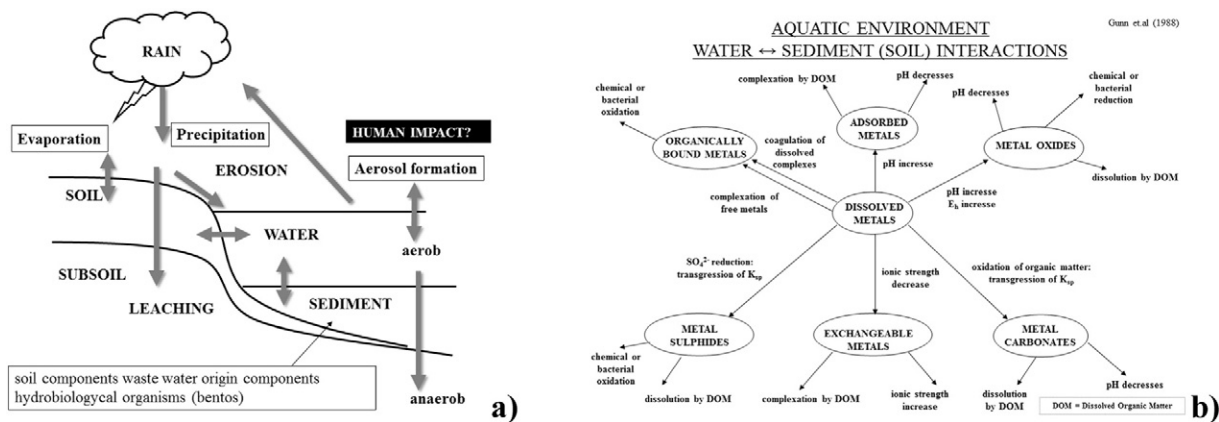


Fig. 1. (a.): The transport routes in soil/water (sediment)/atmosphere systems; (b.): The pathways of mobilization/immobilization processes of PTEs in aquatic environment [6].

1. 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: ¹³¹I;
- 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. 1a.), which can be followed by fractionation based on sequential extraction procedures modelling the pathways of these processes (Fig. 1b.) [5–7].

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 groups 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).

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	<ul style="list-style-type: none"> → Better modelling the chemistry of environmental mobilization by carbonization applying CO₂, H₂O, H₂O/CO₂ solvents sequentially in supercritical extractor [28]. → 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]. → Application of sediment pore water, cold water- or subcritical water-extraction for ecotoxicological testing [30,31].
1st 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. The multi-step batch leaching is time consuming minimum 5 days. Selectivity and completeness of extraction steps strongly influenced by the reagent-solvents ratio and technical conditions of leaching (e.g. shaking rpm).	<ul style="list-style-type: none"> → Acceleration of batch leaching by sonication or microwave treatment [32,33]. → Elaboration of continuous flow techniques: • 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. 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).	<ul style="list-style-type: none"> → Reduction of number of operations and reagent-applications which was achieved by continuous flow systems [34–45]. → 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.	<ul style="list-style-type: none"> → 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].

Download English Version:

<https://daneshyari.com/en/article/5138952>

Download Persian Version:

<https://daneshyari.com/article/5138952>

[Daneshyari.com](https://daneshyari.com)