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Fractionation of arsenic in soil and sludge samples: continuous-flow extraction using rotating coiled columns versus batch sequential extraction

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Abstract

Fractionation of arsenic and other trace elements (TE) in environmental solid samples is usually achieved by application of batch sequential extraction procedures (SEP). In the present work a rotating coiled column (RCC) earlier used mainly in countercurrent chromatography has been applied to study continuous-flow fractionation (CFF) of As compared to conventional batch SEP. A particulate solid sample (soil or sludge) was retained in the rotating column as the stationary phase under the action of centrifugal forces while different eluents were continuously pumped through. The eluents were applied in correspondence with an optimized SEP for As addressing non-specifically sorbed, specifically sorbed, bound to amorphous and crystalline Fe oxides fractions extractable by $(NH_4)_2SO_4$, $NH_4H_2PO_4$, NH_4-oxalate buffer, NH_4-oxalate buffer + ascorbic acid at 96 °C, respectively. For all samples the recoveries of As in the non-specifically sorbed fraction obtained by CFF were considerably higher than in the corresponding fraction of the batch SEP. This finding is consistent with a quickly obtained equilibrium between the solid phase and the ammonium sulphate solution in batch where no further extraction takes place. The repeated extraction occurring due to the continuous removal of the eluate in the CFF procedure enables a more complete extraction of the non-specifically adsorbed pool. For the two consecutive steps, both methods delivered virtually the same results. In contrast, since no heating was used in RCC batch SEP more efficiently extracted As bound to crystalline Fe oxides at step 4. As a result, the residual fraction was overestimated after CFF. The CFF procedure can be completely automated. In addition, investigating the elution curves allows one to study the kinetics of As (and related elements of interest) release, to test efficacy of extractants and to assess the maximum pool size of target fractions.

Keywords: Continuous-flow fractionation; Sequential extraction; Arsenic; Soil; Sludge

1. Introduction

Different trace elements (TE) coming to the natural systems from both anthropogenic and geological sources are widely distributed in the environment. Interaction of potential contaminants with inorganic and organic constituents of soils, sediments or sludge can lead to their immobilization and accumulation. Slow or fast mobilization of pollutants under changing environmental conditions causes serious problems for living organisms inducing a perturbation of the ecosystem. Hence, risk assessment related to environmental solids as sinks for TE is one of the most important issues in ecology, agriculture, and environmental management.

Mobility, bioavailability, and toxicity of TE depend strongly on their chemical form and type of binding. Consequently, determination of total TE concentrations is insufficient to estimate potential risks of remobilization and uptake of liberated TE by biota. Thus, analytical techniques and leaching (or fractionation) procedures for distinguishing different forms of TE are required. An approach that has been widely applied is the fractionation of TE into operationally defined forms under the sequential action of different extractants [1]. Such sequential extraction procedures (SEP) provide information on the physicochemical lability of the TE binding forms. These operationally defined forms can help to

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estimate the amounts of TE in different fractions that could be mobilized due to changes in chemical properties of soil.

Since 1970s a considerable number of SEP have been proposed for TE fractionation [2,3]. Most of these procedures are based on the scheme introduced by Tessier et al. [4]. Although these procedures were originally used in the chemical analysis of soils, they have been employed on a wide variety of contaminated environmental samples including sediments, road dust, and sewage sludge.

With regard to the fractionation of elements that predominantly occur as anionic species, such as As or P, specific SEP have been proposed [2,5,6]. Wenzel et al. [7] introduced an improved five-step SEP for the fractionation of As based on a new combination of reagents commonly used for the sequential extraction of metals, Se and P. The sequence of extractants includes: $(NH_4)SO_4$; $(NH_4)H_2PO_4$; NH_4-oxalate buffer; NH_4-oxalate buffer + ascorbic acid; HNO_3/H_2O_2 (microwave digestion).

A new continuous-flow extraction system for the fractionation of trace metals and As has been recently proposed by Shiowatana et al. [8,9]. The extraction was performed in a mixing chamber (10 ml volume) closed by a membrane filter while reactants were subsequently passed through. Apart from simplicity, the system has many other advantages. However, the eluent being in contact with the particulate matter is only partially renewed with time and the flow rate is not stable throughout the experiment.

In the present paper the potential of using rotating coiled columns (RCC) for the continuous-flow fractionation of As is discussed. So far, RCC have been mainly applied in countercurrent chromatography (CCC). The technique is based on the retention of one stationary phase of a two-phase liquid system in a RCC under the action of centrifugal forces while the mobile liquid phase is being continuously pumped through [10]. Solutes are subjected to a partition process between the two phases and eluted in order of their partition coefficients. A few devices providing retention of the stationary phase in the field of mass forces in the absence of a solid support have been suggested. Among the various possible designs, the planetary centrifuge retains the liquid stationary phase effectively and enables the fastest and most efficient separation to be achieved. A column (or a column unit) of a certain configuration rotates around its axis and simultaneously revolves around the central axis of the device with the aid of a planetary gear.

Recently it has been shown that RCC can be used for the separation of both solutes and particles not only in liquid–liquid systems but in liquid–liquid–solid and liquid–solid systems as well [11–15]. A procedure has been developed for the dynamic fractionation of heavy metals in soils. The sample of soil was retained in a rotating column as the stationary phase whereas aqueous solutions of complexing reagents, mineral acids and salts were used as mobile phase [13,15].

The same approach may be applied to the continuous-flow fractionation of As in environmental solids. In the present study we compared the fractionation of As in RCC and traditional batch sequential extraction on a series of soil and sludge samples using the reagents of the Wenzel et al. procedure [7].

2. Experimental

2.1. Samples and reagents

Experimental samples were taken from river sludge at different sites after the inundation in Germany (2002) and from As-contaminated forest soils in Austria. The samples were passed through a 90 μm screen prior to analysis. The total element concentrations in these sub-fractions were determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF, Spectro X-Lab 2000) using wax pellets prepared in the mass ratio soil:wax equal to 4:1. Important physicochemical characteristics were determined according to standard procedures [16] and are reported in Table 1.

All chemicals used were analytically grade reagents.

2.2. Continuous-flow fractionation of As using RCC

The continuous leaching of As was performed on a planetary centrifuge with a vertical one-layer coiled column drum fabricated in the Institute of Spectrochemistry and Applied Spectroscopy (Dortmund, Germany). This prototype was presented in a previous publication [17]. The planetary centrifuge has a revolution radius $R = 140$ mm and a rotation radius $r = 50$ mm. The β value ($\beta = r/R$) is 0.36. Two axis of the instrument are parallel. The column was made of a PTFE tube with an inner diameter of 1.5 mm and total inner capacity of 20 ml. The tube length was about 10 m. The rotation and revolution speeds (ω) were 600 rpm. The mobile phase pumping rate (F) was 1 ml min^{-1}.

Before commencing the leaching procedure, the spiral column was filled with water, after which the solid sample (about 0.5 g) was introduced into the column (in the stationary mode) as a suspension in 10 ml of 0.05 mol l^{-1} $(NH_4)_2SO_4$. Then, while the column was rotated, aqueous solutions of different reagents, used as the mobile phase, were continuously fed to the column inlet. The solid sample was retained inside the rotating column as the stationary phase under the action of a centrifugal force field throughout the experiment. The recovery of As in four leachable fractions was achieved by successive change the eluents according to the Wenzel et al. scheme [7] shown in Table 2. Fifty millilitres of each eluent were pumped through the column and collected in 10 ml fractions. The continuous extraction in RCC required about 4 h for each sample. After termination of the leaching procedure, the residue of the solid sample was removed from the column for analysis of the residual As fraction. Three replicates were done for each sample.

It should be noted that the particulate matter was not destroyed under the action of the asymmetrical force field generated in planetary centrifuges (rotation speed up to 1000 rpm,