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Selenium speciation analysis at trace level in soils

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ABSTRACT

This paper describes the development of an analytical methodology to determine speciation of selenium present in soils at trace level ($\mu g\,kg^{-1}$). The methodology was based on parallel single extractions and high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC–ICPMS). Two complementary chromatographic separations were used to confirm Se species identity. Different extractants, selected on the basis of sequential extraction schemes, were compared. Ultrapure water, 0.1 mol L^{-1} phosphate buffer (KH_2PO_4/K_2HPO_4) at pH 7 and 0.1 mol L^{-1} sodium hydroxide extractants were finally chosen owing to their efficiency in extracting Se and compatibility with Se species stability. These extractants allow also assessing respectively water-soluble Se (i.e. the most mobile Se fraction), exchangeable Se (i.e. sorbed onto soil component surface) and Se bound to soil organic matter. This methodology gives thus information on Se mobility related to its distribution in soil with preservation of original Se speciation. Detection limits range from 3 to 29 ng(Se) L^{-1} and from 0.1 to 10 μg(Se) kg^{-1}, allowing determination of Se species concentrations in extracts from soils containing native Se at trace level. The methodology was applied to three soils with total Se concentrations between 210 and 1560 μg(Se) kg^{-1}.

1. Introduction

Selenium is an element of environmental interest owing to the narrow range between its nutritionally required and toxic concentrations in many organisms [1]. Its mobility and bioavailability differ greatly depending on individual Se species [2]. In soil compartment, the most mobile Se forms, selenate (Se(VI)) and selenite (Se(IV)), can exist as aqueous species in solution or sorbed onto soil component surfaces [3–8]. Se(0) and metal selenides (Se(−II)) are insoluble and thus poorly mobile [9–11]. The abundance and mobility of organoselenium compounds, generally produced by biologic reduction of oxidized forms (e.g. selenoamino acids, selenoproteins, trimethylselenonium ion or volatile methylated compounds), are not well known [6,12,13]. Information about total Se content is thus not sufficient to assess Se mobility and behavior in soils and the determination of individual species in soils appears necessary.

Analytical methodology and validation for the determination of Se speciation, according to IUPAC recommendations [14], in soils are not available in the literature [1]. In order to understand and evaluate Se distribution and ensuing mobility, sequential extraction schemes (SES) have been generally used. They include three to six successive extractions with washing steps between each extraction, leading to a large dilution factor [15]. These procedures seem thus not adapted to soils containing relatively low Se concentrations ($\mu g\,kg^{-1}$ level). Moreover, they require a series of shaking, centrifuge and filtration processes that increase the risk of Se loss, contamination and Se species redistribution. As a solution, Zhang and Frankenberger [15] suggested the use of parallel single extractions, which were applied to sediments. To determine water-soluble Se fraction, ultrapure water [13,15–20] or KCl or $CaCl_2$ solutions [8,21–23] have been employed. Various authors reported the effectiveness of phosphate solutions (K_2HPO_4 or KH_2PO_4) to recover exchangeable Se, considered generally as sorbed onto soil component surfaces [17,21,24–27]. Martens and Suarez [17] suggested the use of KH_2PO_4/K_2HPO_4 buffer at pH 7 to prevent Se redistribution that may result from the acid pH value (≈4.8) of a KH_2PO_4 solution. According to the results of Balistrieri and Chao [3] and Wright et al. [26], an increase to pH 8 could lead to higher recoveries. Se fraction associated to soil organic matter has been recovered with the help of NaOH [6,7,13,15,16,18,20,23,25], NaOCl [8,26,27] or $K_2S_2O_8$ solutions [17,21,28,29]. However, due to their oxidant characteristics, $K_2S_2O_8$ and NaOCl reagents may lead to Se species redistribution and appear thus not appropriated for Se speciation determination [17]. Moreover, Wright et al. [26] have shown that NaOCl may dissolve metal selenides (>1%). Extraction

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step using HCl or HNO_3 solutions has been also performed but these extractants were associated to different Se fractions by the authors: "strongly" associated to Al, Fe, Mn oxide surfaces [21,22], amorphous materials [21], calcium compounds or minerals [7,18,21], some sulphide minerals [21] or crystalline oxides [8].

Determination of selenium species in soil fractions was reported only in few of these works. Se(IV) selective techniques, i.e. hydride generation hyphenated to atomic absorption spectrometry (HG-AAS) and electrochemical methods, were generally used [8,13,15–17,27,28]. A combination of direct mineralized, reduced and oxidized sample analysis is thus needed to complete Se speciation, increasing the possibilities of element loss or contamination from the reagents and the risk of Se species redistribution. Se(IV), Se(VI) and only total Se(−II) (i.e. metal Se(−II) and organoSe(−II) compounds) are thus determined and organoselenium compounds remain unidentified. Hence, methods, which separate all individual species followed by their direct detection, are preferred. Indeed, they need only minimal sample pre-treatment and allow individual Se species identification [1]. To our knowledge such methods have never been applied to Se species determination in soils.

This study was thus conducted using high performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC–ICPMS) coupling for the determination of Se species extracted from soils after parallel single extractions. Different extractants, selected from SES, were tested and evaluated on the basis of extraction efficiency and compatibility with Se speciation preservation. Finally, the optimized analytical methodology was applied to different soils containing native Se at trace level ($\mu g\,kg^{-1}$), and corresponding data for Se species are reported.

2. Materials and methods

2.1. Reagents and samples

All reagents used were analytical grade. The solutions were prepared with ultrapure water obtained from a Milli-Q System (18.2 Ω cm). D,L-Selenomethionine (SeMet), L-selenocystine ($SeCys_2$), methane seleninic acid (MeSeOOH), sodium selenite (Se(IV)) and sodium selenate (Se(VI)) were obtained from Sigma–Aldrich (SigmaUltra, ≥99.0%). Stock standard solutions containing 1000 mg(Se) L^{-1} were prepared in ultrapure water, except $SeCys_2$, which was dissolved in 0.2% HCl for stabilisation. They were stored in the dark at 4 °C. Working standard solutions were prepared daily by dilution in ultrapure water.

An English meadow clay loam soil (Rothamsted), containing 423 μg(Se) kg^{-1} of native selenium according to INRA analysis (Arras, France), was used for methodology optimization. It was air dried, sieved (<2 mm) and grinded in zirconium oxide bowl during 7 min at 30 Hz (Retsch MM200, Fisher Bioblock Scientific) before mineralization or extraction.

Two reference soil materials were used to validate the mineralization procedure and total selenium determination by ICPMS. The ZC-73001 (NCS, National Analysis Center for Iron and Steel, Beijing, China) soil reference material has total Se certified value of 210 ± 20 μg(Se) kg^{-1}. The San Joaquin 2709a (NIST, National Institute of Standards and Technology, USA) soil reference material has a total Se indicative value of 1500 μg(Se) kg^{-1}. These two reference soils were chosen as corresponding total Se concentrations enclosing the Rothamsted one.

2.2. Soil mineralization procedure

Soils were mineralized by microwave-assisted acid digestion (Ethos Touch Control, Milestone). To avoid cross-contamination, all microwave vessels (PTFE) were washed according to the procedure described in Table 1-a. They were then rinsed with ultrapure water prior to sample digestions. Mineralization procedure is presented in Table 1-b. Digested samples were diluted to a final volume of 50 mL and boric acid was added to neutralize HF and avoid erosion of quartz parts of ICPMS sample introduction device. They were stored in polypropylene tubes at 4 °C until analysis. Sample digestion was realized in triplicate and a blank was added in each mineralization run.

Table 1
Vessel washing and mineralization procedures.

	Heating program
(a) Vessel washing	
ultrapure water: 5 mL	Stage 1: 10 min, 1000 W, temperature/pressure
HF: 2 mL–HNO_3: 6 mL	ramp until 200 °C/10 bar
HNO_3: 5 mL	Stage 2: 10 min, 1000 W, 200 °C/10 bar
(b) Soil	
Soil: 250 mg	Stage 1: 20 min, 1000 W, temperature/pressure
HF: 2 mL–HNO_3: 6 mL	ramp until 200 °C/40 bar
Blank	
	Stage 2: 20 min, 1000 W, 200 °C/40 bar

2.3. Parallel single extraction procedure

Six selective chemical solutions were tested on the basis of SES: ultrapure water, calcium chloride (5×10^{-4} mol L^{-1}), phosphate buffer (KH_2PO_4/K_2HPO_4, 0.1 mol L^{-1}) with pH 7 or 8, nitric acid (1 mol L^{-1}) and sodium hydroxide (0.1 mol L^{-1}).

Each extraction was realized in triplicate with following operating conditions: soil was placed in polypropylene centrifuge tube with extractant solution ($v : m = 5/150$ mL mg^{-1}), the mixture was mechanically stirred at 250 rpm (KS15, Edmund Bühler GmbH) during 24 h (room temperature). Then, the suspension was centrifuged at 15,000 × *g* for 30 min at 4 °C (Jouan). The supernatant was taken up and stored in a polypropylene tube at 4 °C until analysis. The residual solid phase was mineralized as described in Table 1-b in order to quantify unextracted selenium.

2.4. Total selenium determination by ICPMS

Total selenium was determined with an Agilent 7500ce ICPMS instrument equipped with an octopole collision/reaction cell. Sample introduction system was constituted of a concentric nebulizer (Meinhard Associates, CA, USA) and a Scott double pass spray chamber cooled to 2 °C. The parameter settings were as follows: Ar plasma gas flow, 15 L min^{-1}; Ar auxiliary gas flow, 0.86 L min^{-1}; Ar nebulizer gas flow, 1–1.1 L min^{-1}; H_2 gas flow, 4 L min^{-1}; radio frequency forward power, 1500 W; nickel sampler and skimmer cones, according to Darrouzès et al. [30]. These parameters were optimized daily using a solution of 1 μg L^{-1} of gallium, yttrium, thallium and cerium. Acquisition parameters were: integration time, 100 ms per isotope; 10 replicates; monitored *m*/*z* 77 and 78. External calibrations in reconstituted extractants and standard additions were performed the same day in order to control matrix effects during Se quantification. Results indicated that standard additions were needed to compensate for matrix effects in extractant solutions.

Sample pre-treatments. Supernatants and digested solutions (total soil and residual solid phase) were filtered at 0.45 μm. As the sensitivity of the ICPMS detection can be decreased by high salt or acidity of samples, the samples were diluted as a function of salt concentration or acidity, i.e. twentyfold dilution for phosphate buffer supernatants and digested samples, and tenfold dilution for sodium hydroxide supernatants. All samples were acidified with concentrated HNO_3 at 2% before analysis.