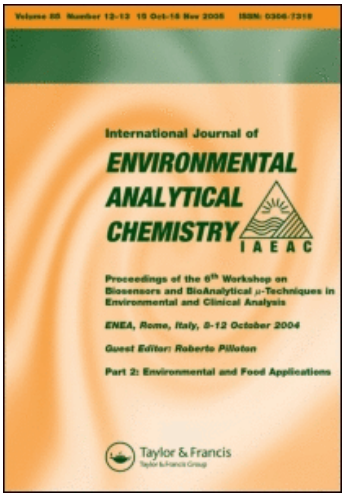

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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Online publication date: 17 September 2010

To cite this Article Zhang, Yiqiang and Frankenberger Jr., William T.(2003) 'Determination of Selenium Fractionation and Speciation in Wetland Sediments by Parallel extraction', International Journal of Environmental Analytical Chemistry, 83: 4, 315 — 326
To link to this Article: DOI: 10.1080/0306731031000076850
URL: http://dx.doi.org/10.1080/0306731031000076850

Intern. J. Environ. Anal. Chem., Vol. 83, No. 4, pp. 315–326

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DETERMINATION OF SELENIUM FRACTIONATION AND SPECIATION IN WETLAND SEDIMENTS BY PARALLEL EXTRACTION

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(Received 25 February 2002; In final form 20 November 2002)

Selenium (Se) fractionation and speciation of wetland sediments is very important in understanding the bioavailability and bioaccumulation of Se in wetland systems. Sequential extraction of Se in sediments is often used in fractionation and speciation studies. Because of the difficulty to accurately determine Se fractions and species in sediment samples containing relatively low concentrations, high light materials and high clay texture by using a sequential extraction procedure, an alternative method was developed by parallel extraction of Se in sediments with deionized (DI) water, NaOH, Na_2SO_3 and H_2O_2–HCl, and determination of Se species by differences. Results showed that adsorbed Se from spiked Se in sediments during DI water extraction can be quantitatively recovered with 0.1 M NaOH and 1 M Na_2SO_3. Mass recovery of Se from sediments between the parallel extraction and a sequential extraction was very close, indicating that sequential extraction can be replaced by parallel extraction in Se fractionation and speciation studies. Selenite [Se(IV)], elemental Se [Se(0)], organic material-related Se (OM-Se) and organic Se were the major forms of Se, respectively accounting for 31.2, 24.4, 25.2, and 11.6% of the total Se in Tulare Lake Drainage District wetland and Stewart Lake sediments. Reduction of selenate [Se(VI)] to reduced Se [Se(IV) + Se(0)] and Se uptake by wetland organisms with incorporation of these organisms into the sediment are two major immobilization processes that accumulate Se in wetland sediments.

Keywords: Parallel extraction; Selenium speciation; Sediment; Wetland

INTRODUCTION

Irrigation in certain parts of the western United States has produced selenium (Se)-impacted drainage water, which is the major Se source causing deformities in wetland waterfowl [1,2]. The biogeochemistry of Se in wetland systems is very complex because Se can exist in four different oxidation states (-II, 0, IV and VI) and as a variety of organic compounds. The bioavailability of Se in wetlands is largely dependent on the speciation of Se present [3,4]. Studies by Besser *et al*. [3] and Wang and Lovell [4] have revealed that organic forms of Se are subject to greater bioavailability and bioaccumulate more rapidly than selenite [Se(IV)] or/and selenate [Se(VI)]. Therefore, information about Se speciation in wetland systems is much more important than total Se to scientists and wetland managers.

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ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0306731031000076850

A wetland system is a complex aggregate of water, sediment and various types of organic materials. Dissolved Se entering the wetland in agricultural drainage water reacts with this aggregate through various adsorption, reduction, and transformation processes, causing Se accumulation in wetland systems as different forms of Se [5–8]. Sediment is the largest reservoir of Se, accounting for more than 90% of total Se in wetland systems [9,10]. Therefore, speciation of Se in wetland sediments is a major reflection of the various biogeochemical processes that occur in wetland systems.

Sequential extraction has been successfully used by many researchers to determine fractionation and speciation of Se in sediments [5–8]. Their studies revealed that soluble Se species, exchangeable Se, organically bound Se, elemental Se [Se(0)] and organic material related-Se are the major Se forms found in wetland sediments, which provide valuable information for understanding various biogeochemical processes and bioavailability of Se in wetland systems. Over several years in fractionation and speciation studies of Se in wetland sediments in our laboratory, we have found that it is very difficult to accurately determine Se fractions and species in some sediment samples containing relatively lower concentrations of Se, higher light material and higher clay texture by using a sequential extraction procedure. The reason for this is that sequential extraction of Se in sediment often uses 4–5 extractions that are performed in a set sequence. After each extraction, the residue is washed 1–2 times in order not to affect the next extraction. Therefore, it may not be possible to measure Se species in samples containing low Se due to the large dilution factor. The sequential extraction also requires a series of shaking, centrifuge, and filtration processes. Upon separation, light materials can be removed from the sediment samples, causing a loss of Se in the next series of extractions. The extraction efficiency of sequential extraction is low for samples containing high clay content due to the difficulty of re-suspending the sample residue after each extraction and centrifugation. Because of these problems with sequential extraction, we have developed an alternative method for Se fractionation and speciation in wetland sediments.

The main objective of this study was to develop a parallel extraction method to determine Se fractionation and speciation in wetland sediments, which allows quantitative detection of Se in sediment samples containing relatively low concentrations, high light materials and high clay texture.

METHOD DEVELOPMENT

An efficient extraction procedure for different Se fractions and species in sediment needs to meet two criteria: (i) extractants will not interfere with Se measurements as determined by hydride generation atomic absorption spectrometry (HGAAS), and (ii) target Se can be extracted in each extraction step and speciated. Sequential extraction has been commonly used to determine fractionation and speciation of Se in wetland sediments [5–8]. Tokunaga *et al.* [5] used different extractants to sequentially extract seven different Se fractions in sediments at Kesterson Reservoir, CA. These Se fractions included soluble (KCl extract), adsorbed (K_2HPO_4 extract), carbonate (Na-acetate-K_2HPO_4 extract), soil organic matter (NaOCl extract), easily reducible oxides (NH_2OH–KOH extract), amorphous oxides (NH_2OH/HCl–KOH extract), crystalline oxides (HCl extract), and amorphous aluminosilicates (NaOH extract). On the basis of the importance of different fractions of Se in wetland sediment, Zhang

and Moore [6] modified Tokunaga's sequential extraction procedure by defining sediment Se into five different fractions and used KCl, K_2HPO_4, Na_2SO_3, NaOCl and HCl to sequentially extract soluble, adsorbed, elemental, organic material related and oxides Se, respectively in sediments at Benton Lake, MT. Zawislanski and Zavarin [7] used KCl, Na_2HPO_4, NaOH, Na-acetate-K_2HPO_4 and HNO_3–H_2O_2–HCl to sequentially extract and determine five Se fractions (soluble, adsorbed, organic, carbonate and refractory) in sediments at Kesterson Reservoir, CA. Recently, Gao *et al.* [8] used KCl, K_2HPO_4, Na-acetate, Na_2SO_3 and $HClO_4$–HNO_3 to determine soluble, ligand-exchangeable, carbonate-associated, organic matter associated, and elemental Se in sediments at a California flow-through wetland system.

In this study, a parallel extraction procedure to extract different Se species is operationally defined and proposed in Table I based upon the characteristics of Se species described below. We chose deionized (DI) water, NaOH, Na_2SO_3, H_2O_2 and HCl as extractants and used a parallel extraction procedure to extract different Se species from sediment samples because these solutions meet these two criteria mentioned above. For example, HCl and NaOH are two reagents used in hydride generation acid and sodium borohydride ($NaBH_4$) channels in a hydride generation system. They, therefore, will not interfere with Se measurements by HGAAS. Na_2SO_3 and H_2O_2 will not interfere with Se measurements by HGAAS because Na_2SO_3 can be oxidized to sulfate during oxidization of all Se to Se(VI) by H_2O_2. Surplus H_2O_2 can be easily destroyed to water by heating the H_2O_2 solution under a basic condition [11].

Deionized water, NaOH, Na_2SO_3, H_2O_2 and HCl will extract different Se species based on the physical–chemical characteristics of Se species in sediment samples. Se(VI) is the most oxidized form of Se, and is highly soluble in water [12]. DI water, therefore, can be used to extract most of Se(VI) in the sediment. DI water can also extract water soluble Se(IV) and organic Se. In this study, organic Se is defined as the sum of various organic forms of Se including Se bound organic materials in the DI water and 0.1 M NaOH extracts. In a stability test of three Se species [Se(VI), Se(IV) and selenomethionine] in DI water upon 20 h of shaking at 21°C, all Se species were stable and only about 3% of selenomethionine was converted to Se(IV) (Table II).

Selenite has a strong affinity to sorption sites of sediment and soil constituents [13–17]. Se(IV) adsorption results through the replacement of the surface hydroxyl groups with Se(IV) [18–20]. At pH > 10–12, Se(IV) adsorption in different soils is

TABLE I Parallel extraction procedure for Se fractionation and speciation in wetland sediment

Fractions(1–6)	*Extractants*	*Se fractions and species**
1. Soluble	DI water	Water soluble Se(VI), Se(IV) and organic Se
2. 0.1 NaOH extractable	0.1 M NaOH	0.1M NaOH extractable Se(VI), Se(IV) and organic Se
3. Elemental	1 M Na_2SO_3 (pH 7 and pH 13)	Se(0) and 0.1M NaOH extractable Se(VI), Se(IV) and organic Se
4. Organic material (OM)	30% H_2O_2	OM-Se, Se(0) and 0.1M NaOH extractable Se(VI), Se(IV) and organic Se
5. Residue	6 N HCl	mainly Fe–Mn oxides Se
6. Total	30% H_2O_2 and 6 N HCl	Total Se

*: Calculation of Se fractions and speciation in sediment samples: Water soluble Se(VI), Se(IV) and organic Se = fraction 1; Total Se(VI), Se(IV) and organic Se = fraction 2; Se(0) = fraction 3 – fraction 2; OM-Se = fraction 4 – fraction 3; Residue Se = fraction 6 – fraction 4.

TABLE II Stability of three Se species (50 μg/L) in deionized water and 0.1 M NaOH solution during a 20-h shaking at 21°C

Se solutions	*Se(IV)*	*Se(VI)*	*Organic Se*	*Total Se*
Se in deionized water				
Se(IV)	49.8 ± 0.3*	−0.07	−0.17	49.6 ± 0.3
Se(VI)	BDL*	50	BDL	50.0 ± 0.1
Selenomethionine	1.48 ± 0.09	0.32	47.6	49.4 ± 0.2
Se in 0.1 M NaOH				
Se(IV)	49.6 ± 0.1	0.52	−0.47	49.6 ± 0.4
Se(VI)	BDL	49.9	BDL	49.9 ± 0.6
Selenomethionine	1.88 ± 0.17	0.07	47.4	49.4 ± 0.6

*Mean±SD ($n = 4$); BDL: below detection limit.

close to zero [16–20]. In an efficient extraction study for Se(IV), Zhang *et al.* [21] found that Se(IV) was more efficiently extracted by 0.1 N NaOH than 0.1 M Na_2HPO_4. In a stability test of three Se species [Se(VI), Se(IV) and selenomethionine] in a 0.1 M NaOH solution with 20 h of shaking at 21°C, all Se species was stable and less than 4% of selenomethionine was converted to Se(IV) (Table II). 0.1 M NaOH can also extract organic Se, and Se(VI). Because this direct NaOH (0.1 M) extraction can extract water soluble Se species, the concentration difference of Se species between the direct NaOH (0.1 M) extraction and the DI water extraction should be equal to the Se species extracted by 0.1 M NaOH after water soluble Se is removed from the samples.

Elemental Se is a thermodynamically stable form under anoxic conditions, and it is relatively insoluble [22]. Se(0) can be extracted with a high concentration of Na_2SO_3 [23]. After all Se(0) is extracted by 1 M Na_2SO_3 (pH 7) extractant, the 1 M Na_2SO_3 extractant (pH 7) can be adjusted to pH 13 using 5 M NaOH for continuing extraction. This combined extraction should extract Se(0) and all 0.1 M NaOH extractable Se. Therefore, the concentration difference of Se species between this direct 1 M Na_2SO_3 extraction and the direct 0.1 M NaOH extraction should be equal to Se(0) in the samples. In a sequential extraction study, Gao *et al.* [8] reported that extracted Se by 1 M Na_2SO_3 included KCl, PO_4-, NaOAc- and NaOH-extractable Se. The Se(0) concentration in sediment samples can be calculated by the difference total Na_2SO_3 extractable Se and the sum of KCl, PO_4-, NaOAc- and NaOH-extractable Se.

Hydrogen peroxide is a strong oxidant, which can oxidize organic Se, Se(0), organic material-related Se (OM-Se) and Se(IV) to Se(VI). OM-Se is defined as the Se in sediment organic materials after 0.1 M NaOH extractable organic Se is removed from the samples. Therefore, the concentration difference of Se between the direct H_2O_2 extraction and the direct Na_2SO_3 extraction should be equal to OM-Se after Se(VI), Se(IV), Se(0), 0.1 M NaOH extractable organic Se are removed from the samples.

Total Se can be determined in sediments by using a two-step (H_2O_2–HCl) digestion procedure [24]. The concentration difference of Se between this extraction and the direct H_2O_2 extraction should be equal to the residue Se.

EXPERIMENTAL

Sample Treatment and Extraction

Twelve sediment samples used in this study were collected from three wetlands. Five samples were collected from five different cells (Cell 1, 3, 6, 7 and 9) in Tulare Lake

Drainage District wetlands (TLDD), CA in July 2000 and six samples (SL, S1, S2, S3, S4 and S5) were collected from different sites of Stewart Lake (SL), UT in September 2000. One sample (pond 4) was collected from Kesterson Reservoir pond 4 (Pond 4), CA in October 1997. All sediment samples were air-dried at room temperature (21°C) and ground to 100 mesh prior to extraction.

The fractionation and speciation of Se in the sediment samples were performed in triplicates at room temperature (21°C) using a procedure described in Table I, in which four parallel extractions were used to extract different Se species.

(1) DI water extraction: DI water extracts water soluble Se(VI), Se(IV) and organic Se in sediment samples. In this extraction, 1 g of sediment samples were placed in 40-mL Teflon centrifuge tubes, followed by 30 mL of DI water. The centrifuge tubes were tightly capped and placed horizontally in a gyrotory shaker and shaken for 20 h. Then, the tubes were centrifuged at 17300 × g (R.C.F) for 20 min. The supernatant from each tube was passed through a 0.45-μm Supor membrane filter (Gelman Sciences) into a 40-mL glass vial.

(2) 0.1 M NaOH extraction: This extraction extracts 0.1 NaOH extractable Se, which includes most of Se(VI), Se(IV) and organic Se in sediment samples. In this extraction, 1 g sediment samples were placed in 40-mL Teflon centrifuge tubes, followed by 30 mL of 0.1 M NaOH. The centrifuge tubes were tightly capped and placed horizontally in a gyrotory shaker and shaken for 20 h. The centrifuge and filtration procedures were the same as the DI water extraction described above.

(3) 1 M Na_2SO_3 extraction: 1 M Na_2SO_3 extracts Se(0) and 0.1 NaOH extractable Se in sediment samples. In this extraction, 1 g sediment samples were placed in 40-mL Teflon centrifuge tubes, followed by 30 mL of 1 M Na_2SO_3. In a previous recovery test of red Se(0) in a 1 M Na_2SO_3, we found that a relatively long-time shaking was needed to recover 95% of Se(0). This red Se(0) was made by the chemical reaction of Se(IV) with ascorbic acid, dried at room temperature (21°C) and ground to 100 mesh prior to the test. Therefore, the centrifuge tubes were tightly capped and placed horizontally in a gyrotory shaker and shaken for 40 h. After that, the 1 M Na_2SO_3 extractant was adjusted to pH 13 by using 5 M NaOH, and the tube was shaken again for 20 h. The centrifuge and filtration procedures were the same as the DI water extraction described above.

(4) H_2O_2 (30%) extraction: 30% H_2O_2 oxidizes organic Se, Se(0), OM-Se and Se(IV) to Se(VI). In this extraction, 0.3–0.5 g sediment samples were placed in 40-mL Teflon centrifuge tubes. Then, 0.5 mL of 30% H_2O_2 were added. After effervescence stopped, an additional 0.5–1 mL of H_2O_2 was added. This procedure was repeated several times. Then, 10–20 mL of H_2O_2 were added to the tube. The sample was heated in a hot water bath at 60°C until the sediment residue in the tube had settled to the bottom of the tube. Then, several drops of 1 M NaOH were added to the tube to facilitate the decomposition of the surplus H_2O_2. After the slurry was cooled to the room temperature, the tubes were centrifuged at 17300 × g (R.C.F) for 20 min. The supernatant from each tube was transferred to a 60-mL polyethylene bottle. The sample was then rinsed and re-suspended once with DI water and centrifuged. The final combined supernatant of the sediment sample was adjusted to 40–50 mL with DI water, and then passed through a 0.45-μm Supor membrane filter into another polyethylene bottle.

After the H_2O_2 extraction, 5 mL of 6 N HCl were added to the tube, mixed with the sediment residue, and heated in a hot water bath at 95°C for 3–4 h. After cooling to

room temperature, the separation of the supernatant and sample residue was performed using a procedure described above.

Selenium Recovery Tests

Although the parallel extraction technique was developed on the basis of sequential extraction techniques and the characteristics of Se species in sediment described above, two important tests were needed in order to accept the procedure proposed in Table I. The first was to test the recovery of spiked Se during extractions. To initiate this test (see Figure 1), we spiked 0.2 mL of 15 μg/mL Se (IV) in three batches of sediment samples to examine (i) the adsorption of spiked Se during the DI water extraction (Figure 1, P1); (ii) the recovery of adsorbed Se during the 0.1 M NaOH extraction (Figure 1, P2); and (iii) the recovery of adsorbed Se during 1 M Na_2SO_3 extraction (Figure 1, P3).

The second test was to determine whether the amount of Se detected from the procedure described in Figure 1 was similar to the mass recovery of Se from a sequential extraction procedure. In conducting this test, we carried out four different extraction procedures (Figure 2, P1–P4). Duration, the amount of sediment samples and extractants used in the sequential extraction were the same as the parallel extraction described in Table I.

Two sediment samples (Pond 4 and SL) were selected to test the mass recovery of Se in different extraction procedures and the recovery of spiked Se in sediment samples because these two sediment samples contained relatively high Se concentrations (14.3–17.9 μg/g) and the residue of these two samples can be easily resuspended after each extraction. All extractions in these tests were run in triplicates.

Selenium Species Analysis

Selenium species in the DI water and 0.1 M NaOH extracts were determined using a speciation method developed by Zhang *et al.* [25] after a slight modification. This modification includes the adjustment of solution pH to 10.3 instead of 10 and the addition

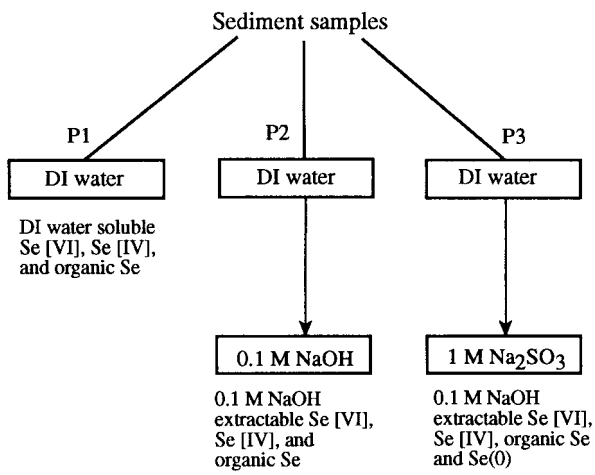

FIGURE 1 A procedure to determine the recovery of spiked Se in wetland sediments.

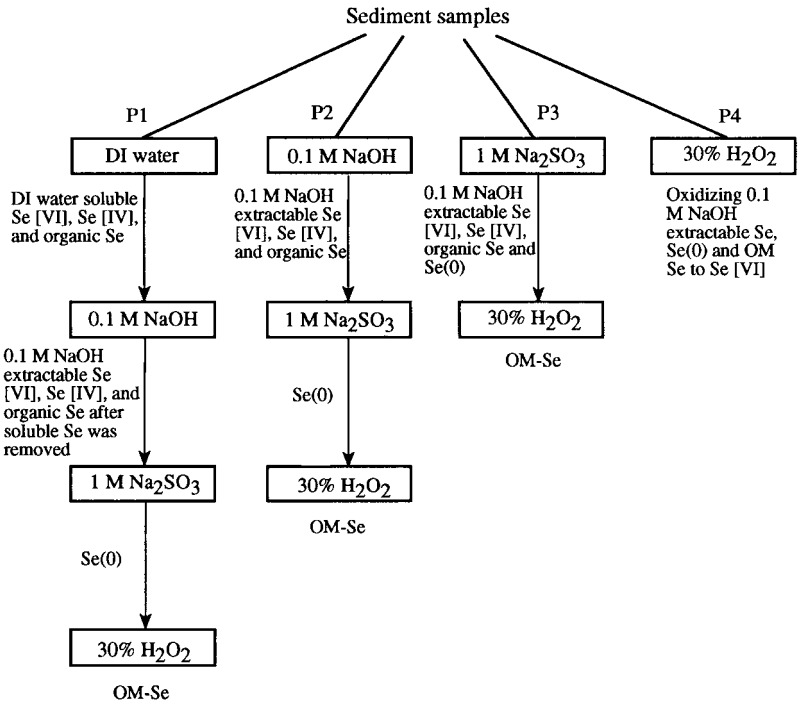

FIGURE 2 Four different extraction procedures (P1–P4) to determine the mass recovery of Se in wetland sediments.

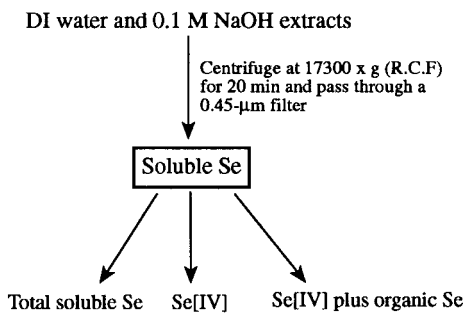

FIGURE 3 A procedure to determine Se species in the DI water and 0.1 M NaOH extracts. Calculation of Se is as follows: Se(VI) = total soluble Se – Se(IV) plus organic Se; and Organic Se = Se(IV) plus organic Se – Se(IV).

of 0.2–0.5 mL 0.2 M potassium persulfate ($K_2S_2O_8$) to each sample when the sum of Se[IV] and organic Se was determined. The purpose of the adjustment in pH was because the 0.1 M NaOH extract contained relatively higher dissolved organic materials than water. When organic materials and organic Se were oxidized by $K_2S_2O_8$, the pH in solution slightly decreased. A slight increase in pH from 10 to 10.3 can compensate for the decrease in pH of the samples during oxidation of organic Se to Se(IV). In brief, this speciation was carried out as follows (Figure 3): Se(IV) in the extracts was determined in a pH 7 buffer solution. The sum of Se(IV) and organic Se was determined when the

organic Se in the extracts was oxidized to Se(IV) by $K_2S_2O_8$, which was indicated by precipitation of Mn oxides. Total Se was determined by oxidizing all Se to Se(VI) by $K_2S_2O_8$, followed by reduction to Se(IV) in 6 N HCl. Se(VI) concentration in the DI water and 0.1 M NaOH extracts was calculated as the difference between total Se concentration, and the sum of Se(IV) and organic Se concentration determined. The organic Se concentration was calculated as the difference between Se(IV) concentration and the sum of Se(IV) and organic Se.

For determination of total Se in the Na_2SO_3 and H_2O_2 extracts, Na_2SO_3 was oxidized to sulfate by H_2O_2, and then surplus H_2O_2 was decomposed to water under a basic condition in a hot water bath [11]. Total Se in the sediment was determined in a solution mixed with the H_2O_2 and HCl extracts in the parallel extraction after Se in the H_2O_2 extract was determined. Se concentrations in all prepared solutions were determined by HGAAS [25]. All Se concentrations in samples are reported on a room temperature (21°C) dry-sediment basis. Detection limit was 0.5 μg Se (IV)/L in solution.

RESULTS AND DISCUSSION

Selenium Recovery Tests

Selenate, Se(IV) and organic Se (e.g. selenomethionine) are commonly used as spiked Se in speciation studies. Se(VI) is highly soluble in water and its adsorption to sediment is much lower than Se(IV) [15,26]. Free selenomethionine is not a stable form of organic Se in soil [27]. Se(IV) has a strong affinity to sorption sites of sediments. After the DI water extraction, a significant amount of Se(IV) can be adsorbed to the sediment. Recovery of the adsorbed Se(IV) in the sediment can be obtained by the 0.1 M NaOH and 1 M Na_2SO_3 extractions. Therefore, only Se(IV) was selected as spiked Se in this work.

The results of recovery of spiked Se(IV) in different extracts are shown in Table III. After 20 h of shaking with DI water (Figure 2, P1), about 72% and 28% of the spiked Se(IV) were recovered in the Pond 4 and SL sediments, respectively. When the DI water was adjusted to pH 13 (0.1 M NaOH), and then shaken for another 20 h

TABLE III Recovery of spiked Se (μg/g) in different extracts as described in Figure 1

Samples	*Se in extracts**	*Spike Se**	*Se measured**	*Recovery* (%)*
Procedure 1 (P1)				
Pond 4	1.02 ± 0.02	3.00 ± 0.01	3.19 ± 0.04	72
SL	1.78 ± 0.02	3.00 ± 0.01	2.61 ± 0.07	28
Procedure 2 (P2)				
Pond 4	3.21 ± 0.03	3.00 ± 0.02	6.32 ± 0.03	104
SL	7.18 ± 0.08	2.99 ± 0.01	9.69 ± 0.13	84
Procedure 3 (P3)				
Pond 4	8.40 ± 0.17	2.99 ± 0.01	11.4 ± 0.22	100
SL	14.2 ± 0.32	2.99 ± 0.00	17.3 ± 0.12	104

* Se in extracts: Se in sediment was extracted without spiked Se; Se measured: Se in sediment was extracted with a spiked Se; Recovery of spiked Se (%) = [(Se measured − Se in extracts)/spiked Se] × 100.

(Figure 2, P2), the accumulated Se(IV) was completely recovered as Se(IV) in the Pond 4 sediment and about 84% was recovered in the SL sediment, revealing that hydroxyl (OH) groups can quantitatively replace the adsorbed Se(IV) on the surface of sediments [18–20]. In another test with these two sediment samples, there was no retention of Se(IV) in the sediment when spiked Se(IV) was directly added in a 0.1 M NaOH extraction solution (data not shown). When the DI water was adjusted to 1 M Na_2SO_3 at pH 7 (Figure 2, P3), and then shaken for another 40 h, followed by 20 h of shaking at pH 13, the accumulated Se in both sediments was completely recovered as total Se. These results revealed that spiked Se can be quantitatively recovered with the 0.1 M NaOH and 1 M Na_2SO_3 extractions.

Selenium concentrations determined with different extraction procedures are present in Table IV. The sum of Se fractions from the four extraction procedures was very similar, ranging from 13.8 to 14.3 μg/g in the Pond 4 sediment and 17.4 to 17.6 μg/g in the SL sediment. The sum of Se fractions was also very close in the first two fractions (DI water and 0.1 M NaOH) and in the first three fractions (DI water, 0.1 M NaOH and 1 M Na_2SO_3). All these tests show that a sequential extraction can be replaced by parallel extraction with different extractants and concentrations of Se can be determined by the difference.

The advantages of this parallel extraction method not only overcome the drawbacks (described in the Introduction section) of sequential extraction, such as a large dilution factor, loss of light material during filtration and less extraction efficiency for some samples containing high clay content due to the difficulty in resuspending the sample residue after each extraction and centrifugation, but also this parallel extraction method can be easily operated. For example, a sequential extraction procedure needs to continuously extract Se for several days, and each extraction has to be separated (centrifuged and/or filtrated) and resuspend the residue 2–3 times. Whereas in this parallel extraction, each extraction can be performed at different times, each extraction is only centrifuged one time, and the residue samples do not need to be resuspended. Also, Se species in the DI water and 0.1 M NaOH extracts can be determined on the same day after centrifugation and filtration. This removes the problems caused by changes in Se species during storage of extract solutions.

TABLE IV Mass balance of Se (μg/g) released from the different extraction procedures as described in Figure 2

Samples	*DI water*	*0.1 M NaOH*	*1 M Na_2SO_3*	*H_2O_2*	*Sum**
Procedure 1 (P1)					
Pond 4	1.02 ± 0.02	2.57 ± 0.03	4.99 ± 0.34	5.72 ± 0.07	14.3
SL	1.78 ± 0.02	5.95 ± 0.04	7.29 ± 0.18	2.41 ± 0.04	17.4
Procedure 2 (P2)					
Pond 4		3.36 ± 0.03	4.68 ± 0.10	5.79 ± 0.08	13.8
SL		7.23 ± 0.01	7.57 ± 0.19	2.64 ± 0.28	17.4
Procedure 3 (P3)					
Pond 4			8.33 ± 0.17	5.73 ± 0.07	14.1
SL			14.7 ± 0.58	2.70 ± 0.05	17.4
Procedure 4 (P4)					
Pond 4				14.0 ± 0.2	14.0
SL				17.6 ± 0.2	17.6

*Sum of Se in DI water, 0.1 M NaOH, 1 M Na_2SO_3 and H_2O_2 extracts.

Selenium Species in Wetland Sediments

Concentrations of Se species in different sediments are present in Table V. In the SL sediment, Se concentration was high, ranging from 5.71 to 22.2 μg/g, whereas in the TLDD sediment, Se was relatively low (1.14–3.92 μg/g). Among total Se in all sediment samples, Se(IV), Se(0), OM-Se and organic Se were the major Se forms, respectively accounting for 31.2, 24.4, 25.2, and 11.6% of the total Se. Se(VI) and residue Se was low, each less than 5%.

Percentage of Se species concentration differed in these two wetland sediments (Tables V and VI). In the DI water extract of the TLDD sediment, Se(IV) and organic Se were the major forms of Se, accounting for 62.4 and 30.5% of the total soluble Se, respectively and Se(VI) was low, about 6.9%. Whereas in the SL sediment, Se(VI) and Se(IV) were important forms of Se, accounting for 50.8 and 45.1% of the total soluble Se, respectively and organic Se only accounted for 4.1%. In the 0.1 M NaOH extract after water soluble Se was removed from sediment, Se(IV) and organic Se also were the major forms of Se in the TLDD sediment, accounting for 53 and 43.2%, respectively and Se(VI) was less than 4%. In the SL sediments, Se(IV) was the only dominant Se form, accounting for 86%, and Se(VI) and organic Se were all less than 7.5%. Of the

TABLE V Speciation of Se (μg/g) in different wetland sediments

Samples	*Se(IV)*	*Se(VI)*	*Organic Se*	*Se(0)*	*OM-Se*	*Residue Se*	*Total Se*
TLDD wetlands							
Cell 1	1.02	0.120	0.879	0.449	1.42	0.028	3.92
Cell 3	0.886	0.055	0.215	0.818	0.620	0.037	2.63
Cell 6	0.381	0.043	0.127	0.189	0.360	0.042	1.14
Cell 7	0.476	0.047	0.748	0.200	0.790	0.012	2.27
Cell 9	0.600	0.014	0.744	0.624	1.05	0.031	3.06
Stewart Lake							
S1	1.95	0.575	0.060	2.05	0.702	0.375	5.71
S2	4.86	0.442	0.310	7.63	4.73	0.572	18.5
S3	5.55	0.810	0.746	1.86	3.43	0.238	12.6
S4	7.10	1.97	0.414	8.12	3.62	0.994	22.2
S5	3.45	0.67	0.519	2.29	0.829	0.450	8.21

TABLE VI Speciation of Se (μg/g) in the DI water extract, and the 0.1 M NaOH extract after soluble Se species was removed from samples

	Soluble Se				*0.1 M NaOH extractable Se*			
Samples	*Se(IV)*	*Se(VI)*	*Organic Se*	*Total Se*	*Se(IV)*	*Se(VI)*	*Organic Se*	*Total Se*
TLDD wetlands								
Cell 1	0.358 ± 0.005	0.023	0.118	0.499 ± 0.005	0.659	0.097	0.761	1.52
Cell 3	0.136 ± 0.003	0.014	0.079	0.229 ± 0.004	0.750	0.041	0.136	0.927
Cell 6	0.153 ± 0.003	0.018	0.052	0.223 ± 0.003	0.228	0.025	0.075	0.328
Cell 7	0.216 ± 0.002	0.04	0.122	0.378 ± 0.004	0.260	0.007	0.626	0.893
Cell 9	0.126 ± 0.003	0.012	0.089	0.227 ± 0.002	0.474	0.002	0.655	1.13
Stewart Lake								
S1	0.291 ± 0.007	0.509	0.027	0.827 ± 0.005	1.66	0.066	0.033	1.76
S2	0.336 ± 0.002	0.308	0.023	0.667 ± 0.004	4.53	0.134	0.287	4.95
S3	0.305 ± 0.006	0.375	0.031	0.711 ± 0.024	5.24	0.435	0.715	6.39
S4	0.905 ± 0.019	1.57	0.100	2.58 ± 0.04	6.20	0.391	0.314	6.91
S5	0.416 ± 0.006	0.216	0.037	0.669 ± 0.006	3.04	0.454	0.482	3.98

other two major forms of Se, Se(0) and OM-Se were 17 and 32.1% of total Se in TLDD sediment, respectively. In contrast, Se(0) was relatively high in the SL sediment, accounting for 31%, and OM-Se was relatively low, about 18.3%.

Selenium bioaccumulation in both wetlands was caused by agricultural drainage water which contained high Se(VI) concentrations[8,28]. Dissolved Se(VI) reacts with wetland systems through various biogeochemical processes, causing Se accumulation in wetland. Reduction of dissolved Se(VI) to Se(IV) and Se(0) is one of the major immobilization processes for accumulating Se in wetland sediment. Inorganic reduced Se [Se(IV) + Se(0)] accounted for 44.5% of the total Se in the TLDD sediments and up to 69% in the SL sediments, showing that the anoxic character of the wetland bottom sediment supports the Se(VI) reduction process. Se uptake by wetland organisms and incorporation of these organisms into the sediment is also an important immobilization process that accumulates Se in the sediment. In this study, we found that OM-Se and organic Se accounted for up to 52% of total Se in the TLDD sediment and about 21.6% in the SL sediment. These results suggest that reduction of Se(VI) to Se(0) was the most important immobilization process for accumulating Se in the SL sediment, whereas Se uptake by wetland organisms and incorporation of these organisms into sediments is the more important process in the TLDD wetlands.

SUMMARY AND CONCLUSIONS

This study showed that a sequential extraction procedure can be replaced by parallel extraction with different extractants. Recovery of spiked Se in sediments can be quantitatively recovered with 0.1 M NaOH and 1 M Na_2SO_3. Mass recovery of Se from sediments between the parallel extraction and a sequential extraction was very close, ranging from 13.8 to 14.3 μg/g in the Pond 4 sediment and 17.4 to 17.6 μg/g in the SL sediment. Se(IV), Se(0), OM-Se and organic Se were the major forms of Se, respectively accounting for 31.2, 24.4, 25.2, and 11.6% of the total Se in wetland sediments. Reduction of Se(VI) to reduced Se [Se(IV) + Se(0)] and Se uptake by wetland organisms with incorporation of these organisms into the sediment are two major immobilization processes that accumulate Se in wetland sediments.

Acknowledgments

We thank Delbert Smith and Steve Noyes in the U.S. Bureau of Reclamation for providing Stewart Lake sediment samples. This research was funded by the UC Salinity and Drainage Program.

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