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Assessment of Isotope Exchange Methodology to Determine the Sorption Coefficient and Isotopically Exchangeable Concentration of Selenium in Soils and Sediments

RICHARD N. COLLINS,* NGOC D. TRAN, ESTELLE BAKKAUS, LAURE AVOSCAN, AND BARBARA GOUGET

Laboratoire Pierre Süe, CEA-CNRS UMR 9956, 91191 Gif sur Yvette, France

Isotope exchange methodology is invaluable to determine the solution−solid-phase distribution (K_d) and isotopically exchangeable concentration (E value) of elements in soils and sediments. This work examined the use of species-specific stable isotope exchange techniques to determine the K_d and E value of selenium (Se), as selenite (SeO_3) and selenate (SeO_4), in nine soils and sediments varying in concentration and source of Se. High-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) was used to quantify the isotope (e.g., ^{76}Se, ^{78}Se, ^{80}Se, and ^{82}Se) concentrations of the soluble Se oxyanions. The two Se oxyanions were detected in the solution phase of all of the soils and sediments. However, upon spiking the suspensions with stable isotope-labeled $^{78}SeO_3$ and $^{76}SeO_4$, it was observed that isotope self-exchange was insignificant to the derivation of Se oxyanion K_d and E values during 24 h (and up to 120 h in four of the samples). These results demonstrate that valid determinations of the E value of Se necessitate that the Se oxyanions are speciated in solution. This is clearly evident for these soils and sediments where it was observed that the E values of SeO_3 and SeO_4 represented, respectively, 5−97% and 3−95% of the total Se E value.

Introduction

Isotope exchange techniques are extremely useful for the determination of the solution−solid-phase partitioning coefficient (K_d) and isotopically exchangeable concentration (E value) of elements in soils and sediments (*1*). The K_d is an excellent indicator of element mobility in the environment (*2*), while the E value provides the most accurate prediction of the concentration of an element in soils and sediments that is potentially accessible to plants (*3−9*). More recently, isotope exchange techniques have also been employed to determine the mechanisms controlling As, Cd, and Zn immobilization (and mobilization) in polluted soils (*10−12*).

Both of these values are generally calculated from measurements of the solution phase of a soil suspension after a defined time of pre- and post-isotope addition equilibration (*1*). In fact, it is immediately apparent from eqs 1 and 2 that the K_d (L/kg of soil) and E value (mg/kg of soil) can be measured in the same solution

$$K_d = \frac{R - r}{r}\frac{L}{S} \qquad (1)$$

$$E = \left(K_d + \frac{L}{S}\right)M \qquad (2)$$

where R is the quantity of a radioactive, or stable, isotope of the element added to the soil suspension (becquerel or milligram), r is the quantity of radioactive, or stable, element added to the soil suspension that remains in solution after a defined time of isotopic equilibration (becquerel or milligram), M is the concentration of soil-derived element in solution (milligrams per liter), and L/S is the liquid-to-solid ratio of the soil suspension (liters per kilogram). The fundamental precept of isotope exchange methodology is that the isotope ratio measured in solution, after the addition of an isotope, is identical to that of the solid-phase pool of element that is isotopically exchangeable.

Despite the apparent simplicity of these techniques, the determination of the K_d and, in particular, the E value of elements can be erroneous if particular attention is not taken methodically and, perhaps more importantly, theoretically in their implementation. Although Hamon et al. (*1*) have largely addressed the key theoretical aspects concerning the appropriate use of E values, it has only recently been realized that the classical approach to determining the K_d and E values of elements that may exist simultaneously in numerous oxidations states in the environment may require significant modification. For example, Hamon et al. (*10*) have reported that the oxidation states of As (As(III) and As(V)) were rapidly isotopically self-exchangeable in two soils, and therefore, regardless of the initial oxidation state of the isotopic tracer, the distribution of the tracer between the solution and the solid phases was identical. As a result, when the total solution concentration of As was used in the calculations, the E value of As(III) and As(V) also appeared to be identical. As the authors note, these results incorrectly represent the K_d, and E value, of either oxidation state of As. Nevertheless, the E value of As (comprising As(III) and As(V)) was still determined by (a) the oxidation states in solution being quantified and (b) the partitioning of one of the oxidation states between the solution and the solid phases being measured.

These complications are not only relevant to As but potentially to any other element that may simultaneously exist in numerous oxidation states in the environment, such as Se. Although the aqueous redox reactions of inorganic Se (selenite and selenate) are known to be extremely slow (*13*), redox-active mineral phases in soils and sediments can promote rapid changes in the redox chemistry of Se (*14*). Therefore, the application of isotope exchange methodology to measure the K_d and E value of Se may possibly necessitate the examination of its aqueous speciation and, if more than one chemical form is present, the isotopic exchangeability of these Se species. Selenium is an essential element to animals; however, toxic concentrations of Se can be found in the environment resulting in serious hazards to ecological health. The most cited example is the Se contamination of wetlands in the western United States that have received agricultural drainage waters from seleniferous soils (*15−17*). In the environment, Se can exist in four oxidation states (−II, 0, +IV, +VI). However, in solution, Se is primarily found as

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* Corresponding author phone: +61 (0)2 9385 5045; fax: +61 (0)2 9313 8624; e-mail: richard.collins@unsw.edu.au. Current address: Centre for Water and Waste Technology, School of Civil and Environmental Engineering, the University of New South Wales, Sydney 2052, Australia.

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TABLE 1. Selected Properties of Soils and Sediments Used in This Study[a]

	particle size distribution					water-extractable elements							
	sand (%)	silt	clay	pH	EC (dSm)	Ca (m mol$_c$/L)	Mg	K	Na	Cl	NO$_3$	SO$_4$	total Se (mg/kg)
						French sediments							
FR1	1	87	12	6.4	7.5	23	1.0	0.8	0.3	0.1	0.0	36	1130
FR2	1	92	7	6.8	1.7	4.6	0.1	0.3	0.2	0.0	0.1	5.1	482
FR3	1	91	8	6.7	2.1	4.9	0.4	0.6	0.2	0.1	0.1	7.4	347
FR4	4	95	1	6.6	2.8	7.4	0.4	0.7	0.3	0.2	0.2	13	337
FR5	29	54	17	6.8	0.4	0.7	0.0	0.5	0.1	0.0	0.1	0.3	44.3
						American soils and sediments							
WY2	42	34	24	7.1	8.8	31	49	0.6	24	0.3	16	97	18.0
CO4	37	29	33	8.4	0.6	2.3	0.4	0.3	1.1	0.3	0.6	1.0	12.0
KP11	21	40	39	8.1	16	21	21	1.6	170	71	36	108	5.0
SL01	27	37	36	7.8	3.0	16	17	0.3	7.0	4.1	9.5	10	3.3

[a] All values for the American soils and sediments, with the exception of total Se, were determined by Goodson et al. (*18*) and are reproduced with permission of the New Phytologist Trust.

selenite (Se(IV)) or selenate (Se(VI)), although the presence of inorganic and organic selenides (Se(−II)) is possible.

The aim of this experimental work was, therefore, to define the appropriate conditions needed to accurately determine the K_d and E value of Se in a range of soils and sediments. As selenium has six stable isotopes (^{74,76,77,78,80,82}Se), high-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) was used to (a) identify, and quantify, the soluble species of Se in a range of soils and sediments and (b) to conduct species-specific stable isotope measurements of selenite (SeO_3) and selenate (SeO_4). In this manner, the kinetics of isotope exchange between the oxidation states of Se, and also between the solution and solid phases of soil suspensions, could be simultaneously determined.

Materials and Methods

Soils and Sediments. Nine soils and sediments were used to examine the isotopic exchangeable characteristics of Se (Table 1). Four of the samples originate from the western United States and have been thoroughly described by Goodson et al. (*18*). In this paper, these soils have been designated with the same names as in the publication of Goodson et al. (*18*)., more precisely, −SL01, KP11, CO4, and WY2. The first two samples are derived from California, whereas the samples CO4 and WY2 are derived from, respectively, Colorado and Wyoming (*19*). The other five sediment samples (designated FR1 to FR5) were collected from the Nord-Pas de Calais region of northern France. This area has been subject to atmospheric metal pollution from a nearby Zn smelter. The sediments were dredged from local canals and subsequently deposited into large shallow basins in 1976. Samples were taken to a depth of 15 cm, air-dried, and sieved to 2 mm before analyses and experiments were conducted.

High-purity water (>18 MΩ/cm resistance) extracts of the soils and sediments (1:1 wt/wt) were used for measurements of pH, electrical conductivity, and concentrations of major anions and cations. The anions and cations were separated using routine ion chromatography methodology and quantified by eluent-suppression conductivity detection (Dionex, Sunnyvale, CA). Because of the difficulties encountered with acid-digesting the soil and sediment samples, instrumental neutron activation analysis (INAA), performed at Laboratoire Pierre Süe, was used to quantify total Se concentrations.

General Protocol for Determination of K_d and E Values of SeO_3 and SeO_4. The enriched Se isotopes (99.5% ^{76}Se and 94.6% ^{78}Se) used in these experiments were purchased from Eurisotop, Saint Aubin, France. Stock solutions of isotopically enriched $^{78}SeO_3$ were obtained by dissolving the elemental Se in concentrated HNO_3 at 60 °C, while stock solutions of isotopically enriched $^{76}SeO_4$ were prepared by dissolving the elemental Se in 30% H_2O_2 and 2 M KOH. The latter solution was then heated to 90 °C and evaporated to dryness. This procedure was repeated thrice before the white precipitate was dissolved in a small volume of concentrated HNO_3. These stock solutions were diluted with high-purity water to a final Se concentration of 1000 mg/L, and the Se oxidation state was verified by the HPLC-ICP-MS methodology described next. These analyses confirmed that the previous procedures resulted in 100% transformation of the elemental Se isotopes to either SeO_3 or SeO_4.

The K_d and E values of SeO_3 and SeO_4 in the soils and sediments were measured by batch experiments. Approximately 2.5 g of air-dry soil was added to 50 mL centrifuge tubes with the addition of 25 mL of high-purity water. The soil suspensions (in triplicate) were shaken at room temperature on an elliptical shaker (225 rpm) for 24 h to attain constant solution concentrations of SeO_3 and SeO_4. At this time, 100−200 μL of appropriately diluted isotopically enriched SeO_3 and SeO_4 (resulting in an isotope spike of between 0.8 −and 25 μg of Se/g of soil) was added to the tubes and shaken for a further 24 h to equilibrate the isotope with the soil-derived isotopically exchangeable Se in the soil suspensions. The quantity of stable isotope added to the soil suspensions was approximated to have >1 μg/L of the isotope remaining in solution after isotopic equilibration (the limits of detection for SeO_3 and SeO_4 were, respectively, 0.17 and 0.33 μg/L).

After a total of 48 h of shaking, the tubes were centrifuged to aid phase separation, and the supernatant was filtered (0.22 μm) into 15 mL polyethylene bottles. These solutions were refrigerated, for a maximum of 3 weeks, until analysis by HPLC-ICP-MS.

HPLC-ICP-MS Analyses of SeO_3 and SeO_4 in Solution. Anion exchange chromatography was used to separate SeO_3 and SeO_4 in the soil solutions. Separation was achieved using a 4 mm AS11 anion exchange column (Dionex, Sunnyvale, CA) using a mobile-phase flow rate of 2 mL/min and a NaOH gradient from 0.8 −to 25 mM in 2 min followed by a 3 min re-equilibration time period at 0.8 mM NaOH. An injection volume of 25 μL was used for all samples and standards.

The column was coupled directly to the nebulizer of the ICP-MS (Series X7, Thermo Electron Corporation, Cergy-Pontoise, France), via PEEK tubing, and chromatograms of counts per second (cps) for each isotope of Se against time were recorded. Collision cell technology (CCT) was used to suppress isobaric interferences, caused by the argon (Ar) plasma, with the Se isotopes. The $^{80}Se^+$ isotope ion was used to calculate total Se concentrations in the sample solutions, and this measurement was verified by monitoring the $^{82}Se^+$

TABLE 2. Average Se Oxyanion Solution Concentrations, Isotopic K_d, and E Values Determined in Soil and Sediment Suspensions[a]

	SeO_3			SeO_4		
	soln concn (μg of Se/L)	K_d (L/kg)	E value (μg of Se/kg)	soln concn (μg of Se/L)	K_d (L/kg)	E value (μg of Se/kg)
FR1	19.8 (0.3)	9520 (180)	188000 (7 000)	67.3 (0.5)	1.1 (0.2)	755 (11)
FR2	19.6 (0.3)	3420 (130)	67300 (3 600)	29.9 (0.8)	9.1 (0.4)	575 (2)
FR3	17.2 (0.3)	4770 (170)	81900 (1 700)	14.3 (0.4)	7.4 (0.2)	249 (7)
FR4	4.7 (0.3)	9390 (570)	44500 (1 600)	20.8 (0.2)	14.4 (0.4)	509 (1)
FR5	20.4 (0.0)	412 (14)	8620 (270)	20.0 (0.1)	0.9 (0.0)	222 (2)
WY2	4.2 (0.1)	255 (13)	1100 (40)	454 (13)	6.4 (1.7)	7440 (530)
CO4	5.6 (0.1)	40 (2)	280 (1)	3.7 (0.1)	2.9 (0.5)	48 (1)
KP11	9.6 (0.7)	8.6 (1.6)	178 (1)	253 (3)	5.1 (0.1)	3740 (56)
SL01	6.0 (0.0)	66 (1)	460 (6)	38.6 (1.9)	1.5 (0.0)	433 (12)

[a] Equations used to determine the K_d and E values are described in the text. Values in parentheses represent the standard deviation of triplicate samples.

isotope ion. Upon ICP-MS analysis of 100 μg of Se/L concentrations of a SPEX Se standard (Metuchen, NJ) and five solutions containing the following Se species——SeO_3, SeO_4, seleno-L-METHIONINE, SELENO-L-cystine, and seleno-methylseleno-L-cysteine (Sigma-Aldrich, Steinheim, Germany)——no discernible difference in the interspecies $^{74}Se/^{80}Se$, $^{76}Se/^{80}Se$, $^{77}Se/^{80}Se$, $^{78}Se/^{80}Se$, and $^{82}Se/^{80}Se$ isotope ratios was observed (Table S1, Supporting Information). Although these ratios were different to those reported for the natural abundance of Se (*20*), due to the mass bias introduced by the instrument, it was, therefore, assumed that these isotope ratios were representative of the natural abundance of Se. As a result, the SeO_3 and SeO_4 standards were used to quantify the isotope ion concentrations in the samples. In addition, when Se isotope ratios were calculated, these standards were used to normalize, assuming a linear function of mass bias to mass difference (linear regression $R^2 = 0.93$ for the isotope ratios stated previously), the measured Se isotope ratios to the natural abundance isotope ratios of 0.189 and 0.479 for, respectively, $^{76}Se/^{80}Se$ and $^{78}Se/^{80}Se$ (*20*).

All of the Se isotope ions were monitored using a dwell time of 10 ms, and the transient peaks produced by SeO_3 and SeO_4 were integrated with a 1400 ms integration time (700 ms on each side of the peak maxima). It should be noted that the isotope ratios of the transient peaks were also determined on-line with the same integration time limits. All peaks were background corrected using an average integrated cps (icps) calculated on a 5000 ms section of the chromatogram where no peaks were observed. Isotope concentrations of the Se species were quantified using linear calibration curves calculated from the response of four to five external standards varying in Se concentration from 0.5−130 μg/L, and sample analyses were bracketed with standard analyses to correct for instrumental drift and mass bias.

X-ray Absorption Spectroscopy. Selenium K-edge X-ray absorption near-edge structure (XANES) spectroscopy analyses of the French samples were performed on beamline FAME (BM30B) of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The Se model compounds used for this study were the following: hexagonal (gray) elemental selenium, sodium selenate, sodium selenite, selenium sulfide, selenium dioxide, dimethyl selenide in solution, selenomethionine, S-methyl seleno L-cysteine, and seleno-DL-cystine. The experimental details for obtaining these analyses and the subsequent data treatment have been reported by Sarret et al. (*21*).

Results and Discussion

Solution-Phase Speciation of Se in the Soil and Sediment Suspensions. The two Se oxyanions—SeO_3 and SeO_4—were detected in the solution phase of all of the suspensions after 48 h of shaking (Table 2). A sample HPLC-ICP-MS chromatogram is provided in the Supporting Information as Figure S1. No other peaks containing Se were observed in the HPLC-ICP-MS chromatograms for any of the suspensions. As SeO_3 and SeO_4 existed simultaneously in the solution phase of all of these soil and sediment samples, accurate calculations of the Se E value, therefore, require that these concentrations are used in the employed equation.

Further experiments were performed with four of the soil samples, encompassing the wide range of soil and sediment types, to examine the solution speciation, and concentration, of Se as a function of shaking time. As can be seen in Figure S2 of the Supporting Information, the concentration of these two oxyanions did not significantly (one-way ANOVA, $p < 0.05$) change between 24 and 120 h in any of these samples, thereby indicating that SeO_3 and SeO_4 had achieved a partitioning equilibrium. As such, it was assumed that a pre-isotope addition shaking time of 24 h was sufficient for K_d and E value determinations of all the soil and sediment samples.

Solid-Phase Speciation of Se in Soils and Sediments. The solid-phase speciation of Se in the samples was probed, when possible, with the use of XANES spectroscopy. For example, the concentrations of Se in the American samples were too low to obtain spectra for this element. As such, only XANES spectra for the French samples are shown in Figure 1. The position of the main peak for all of the samples was found to be identical to that of Se(IV), indicating that this oxidation state dominates the solid-phase speciation of Se in these samples. Although the position of the main peak for SeO_2 is identical to that of SeO_3 (because they have the same (IV) oxidation state), the lack of the second characteristic peak of SeO_2 in the sediment samples indicates that its presence is unlikely. In fact, with the exception of the FR5 sample (due to the low concentration of Se), the spectra of the sediments are very similar to that of the Na_2SeO_3 reference spectrum. Perhaps the major difference between the reference Na_2SeO_3 spectrum and the sediment spectra is that the main peak of the sediment samples commences at a lower energy, which may infer the presence of reduced Se chemical forms (e.g., Se(−II)) or selenite-metal precipitates (e.g., $Fe_2Se_3O_9$) (*22*). Confirmation of a $Fe_2Se_3O_9$ contribution to the XANES spectra is difficult, however, as this technique is not suited to differentiating between adsorbed and precipitated forms of SeO_3.

Upon linear combination fitting of the sediment XANES spectra with the Se reference materials, it was observed that the lowest NSS values (i.e., the best fit) were generally obtained, regardless of the sample, with only two reference materials (selenite and seleno-L-methionine). The percentage of Se(IV), as selenite, was estimated to range from 43 to 83% with Se(−II), as seleno-L-methionine (C−Se−C), making up the remainder (Figure 1). The reduced form C−Se−C could be replaced with other reference materials having the Se(−II) oxidation state with minimal impact on the NSS values.

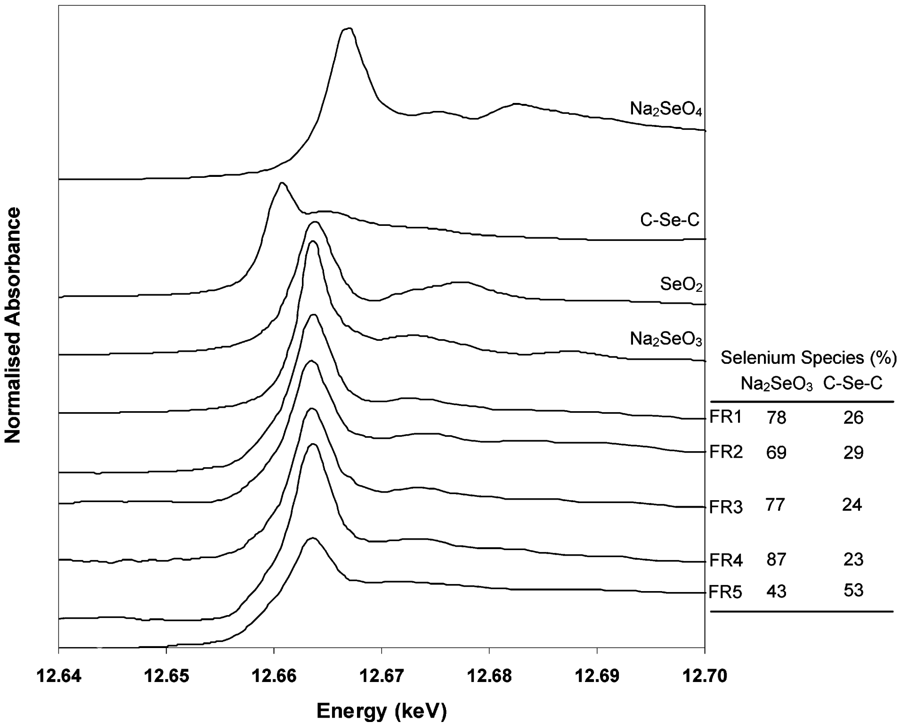

FIGURE 1. Se K-edge XANES spectra for some reference materials and the French sediments. The spectrum shown for C−Se−C is that of seleno-L-methionine. The table presents the percentage of Se species in the sediment samples as determined by linear combination fitting of the Se K-edge spectra with the reference Se materials.

Nevertheless, a mixture of selenite and seleno-L-methionine consistently produced the lowest NSS values. As such, it was conservatively concluded that the solid-phase Se of these sediments consisted primarily of Se(IV), as SeO_3, and Se(−II) and therefore indicates that the E value of SeO_4 should not be large.

SeO_3 and SeO_4 Isotope Self-Exchange Kinetics. The four samples used to assess the stability of the solution concentrations of SeO_3 and SeO_4, as a function of shaking time, were also used to observe, after the addition of the isotope tracer, the isotope self-exchange between SeO_3 and SeO_4. This experiment was accomplished by the simultaneous addition of ^{78}Se-labeled SeO_3 and ^{76}Se-labeled SeO_4. In this fashion, the kinetics of isotope exchange between the two oxidation states was monitored by measuring the $^{78}SeO_4/^{80}SeO_4$ and $^{76}SeO_3/^{80}SeO_3$ isotope ratios in solution. For example, if the $^{78}SeO_3$ isotope tracer was isotopically exchangeable with SeO_4, then an increase in the $^{78}SeO_4/^{80}SeO_4$ isotope ratio would be observed. In these experiments, all of the suspensions were shaken for 24 h before the addition of the isotope tracers.

The results in Figure 2 show that neither the $^{76}SeO_3/^{80}SeO_3$ nor the $^{78}SeO_4/^{80}SeO_4$ aqueous isotope ratios significantly (one-way ANOVA, $p < 0.05$) differed between 24 and 120 h after the addition of the isotope tracers. In addition, these values were not significantly (Student's paired t-test, $p < 0.05$) different to the isotope ratios measured before the addition of the isotopes ($t = 0$ h) (Figure 2). Therefore, no detectable isotope exchange between these two oxyanions was observed during 120 h. Similar results were also observed for the remaining soil samples after 24 h of post-isotope addition equilibration (data not shown). These data also suggest that the reduction or oxidation reactions involving these oxyanions are either unimportant or kinetically inert in these soils, during this time period, when using these experimental conditions.

K_d and E Values of SeO_3 and SeO_4. Given that isotope self-exchange between the two oxyanions was not detectable during 24 h in any of the samples, and up to 120 h in four of the samples, the K_d and E values of SeO_3 and SeO_4 can be determined with the general eqs 1 and 2 when the oxyanions are speciated in solution. As such, the R and r terms become, respectively, the quantity of the isotope-labeled Se oxyanion added to the soil suspension (becquerel or milligram) and the quantity of isotope-labeled Se oxyanion remaining in solution after a defined time of isotopic equilibration (becquerel or milligram). In fact, if the oxidation state of the isotope-labeled Se is known and if only the K_d value is required, it is not even necessary to speciate the oxidation states in the soil suspension. This is, therefore, a rather simple measurement with the use of radioactive isotopes but, as in the present case, is more complex when stable isotopes are used. For example, with the use of enriched stable isotopes, a correction must be made to subtract the concentration of the stable isotope that was originally in solution (i.e., derived

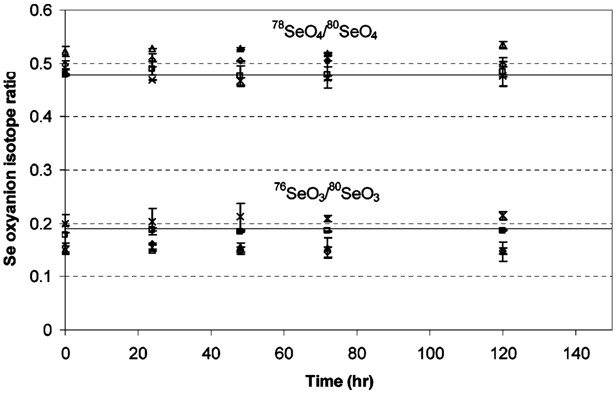

FIGURE 2. Mean aqueous isotope ratios of SeO_3 or SeO_4 in triplicate soil and sediment suspensions as a function of shaking time after the addition of $^{78}SeO_3$ and $^{76}SeO_4$. The symbols (open symbols only) used to represent the samples are identical to those in Figure 2 of the Supporting Information, and the error bars signify the standard deviation. The solid lines correspond to the natural abundance isotope ratios of $^{78}Se/^{80}Se$ (0.479) and $^{76}Se/^{80}Se$ (0.189) (*20*).

from the soil). The solution concentration of the stable isotope derived from the soil can be determined in two ways: (a) by the natural abundance ratio with another isotope of the element of interest (e.g., ^{76}Se/^{80}Se) or (b) by measuring the solution concentration of the isotope without the addition of the stable isotope spike (e.g., an unspiked soil suspension). The data in Figure 2 indicate that the $^{76}SeO_3/^{80}SeO_3$ and the $^{78}SeO_4/^{80}SeO_4$ isotope ratios were similar to the natural abundance ratios, but not always statistically (Student's paired t-test, $p < 0.05$). Although these oxyanion-specific isotope ratios would not be used in these experiments to determine the K_d and E values (as $^{78}SeO_3$ and $^{76}SeO_4$ were used as the isotope tracers), they do indicate that the pertinent isotope ratios would need to be determined for each soil or sediment sample. We, therefore, chose the latter methodology (b) when measuring the K_d and E values of SeO_3 and SeO_4 in all the soil and sediment samples. This means, therefore, that isotope concentrations (and not isotope ratios) were used to calculate the K_d and E values. As such, the following equation (modified from eq 1) was used to determine the K_d of SeO_3 and SeO_4:

$$K_d = \frac{R - (r_{\text{spiked}} - r_{\text{control}})}{(r_{\text{spiked}} - r_{\text{control}})}\frac{L}{S} \qquad (3)$$

where R is the quantity of the isotope-labeled Se oxyanion added to the soil suspension, r_{spiked} is the quantity of the Se oxyanion remaining in solution (having the same isotope as the tracer) measured after isotopic equilibration, and r_{control} is the quantity of the Se oxyanion (having the same isotope as the tracer) measured in the solution phase of the unspiked soil suspension.

When determining the E value, it is not necessary to speciate the oxidation state of Se if only one oxidation state exists in solution. As seen in Table 2, this was not the case in any soil or sediment. Therefore, a valid, and accurate, determination of the E value of Se in these samples requires that the solution concentrations of SeO_3 and SeO_4 are used for the term M in the general eq 2 in conjunction with the K_d values determined from eq 3. In the present experiments, measurements of $^{80}SeO_3$ and $^{80}SeO_4$ were used for the total Se oxyanion solution concentrations, and these concentrations were verified by monitoring the solution concentrations of $^{82}SeO_3$ and $^{82}SeO_4$.

The results for the K_d and E values of SeO_3 and SeO_4 in the soils and sediments are tabulated in Table 2. A concern related to the use of stable isotopes for determining these two parameters, however, is that the quantity of the isotope spike added to the suspensions is large relative to that which would be used for radioactive isotopes. As a result, the possibility arises that this quantity may significantly change the distribution coefficient of the soil-derived isotopically exchangeable element. However, by comparing the ^{80}Se and ^{82}Se concentrations of the Se oxyanions in triplicate control samples, where no isotope was added, to the spiked samples, no evidence for this mechanism was observed (i.e., the ^{80}Se and ^{82}Se solution concentrations of the Se oxyanions were the same in the control and spiked samples). This would, therefore, indicate that the K_d values measured here with the isotope-labeled Se oxyanions reflects that of the soil-derived Se oxyanions.

As has been observed for homogeneous mineral phases (*23*, *24*), the K_d values of SeO_3 were generally much higher than those of SeO_4, indicating that SeO_3 is largely associated with the solid phase of most of these soils and sediments. In fact, with the exception of sediment KP11, the SeO_3 K_d values were at least 1−3 orders of magnitude greater than those of SeO_4. This was particularly significant in the French sediments. From the limited number of reported SeO_3 K_d values (12−10 600 L/kg) for soils (*25*), the wide range of SeO_3 K_d values observed in the present experiments is not unusual. Nakamaru et al. (*25*) have reported that the K_d values of SeO_3 were positively correlated with soil extractable Al and Fe concentrations. In addition, Parida et al. (*26*) and Balistrieri and Chao (*24*) have also reported similarly high SeO_3 K_d values (e.g., >1000 L/kg) in the presence of various iron oxyhydroxides. These studies would, therefore, tend to suggest that these mineral phases are present in considerable quantities to control the K_d values of SeO_3 in the French sediments. It is also of interest to note that the SeO_4 K_d values only varied by a factor of 15 (0.9−14.4 L/kg), indicating that physicochemical variations in the solid and solution phases of these soils and sediments had a minor influence on the partitioning of this oxyanion.

When the E values are calculated for the French sediments, it is seen that SeO_3 accounts for >97% of the total Se E value. This is in agreement with the linear combination fitting data of the Se K-edge XANES spectra for these sediments (Figure 2), which estimated that SeO_4 was not a major solid-phase species in these sediments. The SeO_3 E values in the French sediments, however, only account for 13−24% of the total Se. If this percentage is expressed as a function of the total concentration of SeO_3, estimated by the linear combination fitting of the Se K-edge XANES spectra, this percentage increases to 15−45% with the largest increase being observed in the sediment FR5. As such, a large proportion of SeO_3 in these sediments exists in a form that is not highly reactive with the solution phase and, in fact, supports the existence of precipitated SeO_3 forms, such as $Fe_2Se_3O_9$ (*22*). This, in turn, would partly explain the apparent slow oxidation of the reduced forms of Se to SeO_4 in these sediments during the last 30 years.

The E values for the American soils and sediments were somewhat more variable, and the E value of SeO_4 was sometimes larger than that of SeO_3. For example, the SeO_4 E value represented 95 and 87% of the total Se E value in, respectively, the sediment KP11 and soil WY2 and was also 48% for the soil SL01. In addition, the percentage of the Se E value in regards to the total concentration of Se for these three samples was much higher than that observed for the French sediments. For example, the combined E value of Se in the KP11 sediment was 80% of the total Se concentration. In contrast, however, the combined E value in the CO4 soil was <3% of the total concentration of Se. It has been hypothesized by Goodson et al. (*18*) that the Se in this soil is derived from Cretaceous shale parent material. Therefore, given previous studies on these soils (*27*) and the extremely low E value of either Se oxyanion in this soil, it is likely that this Se is covalently bound to organic materials.

It has been demonstrated in this paper that SeO_3 and SeO_4 were not isotopically self-exchangeable in any of the soils and sediments during 24 h of isotope exchange. This, in turn, supports the validity of earlier K_d values reported for this element, or more correctly, these oxyanions, in the presence of soils and homogeneous mineral phases (*23*−*26*). However, due to the simultaneous presence of SeO_3 and SeO_4 in the solution phase of the present samples (Table 2), it was necessary that the (a) aqueous oxyanions (soil- and spike-derived) were speciated for valid E value measurements and (b) K_d and E values of both oxyanions were obtained to provide accurate results on the reactivity of this element between the solid and the solution phases of the soils and sediments. The effects of not complying with (a) and (b) can be illustrated with some examples taken from the data in Table 2. For example, if the K_d of SeO_3 in the WY2 sample is used in conjunction with the total solution concentration of Se (i.e., the concentrations of SeO_3 and SeO_4), an E value of 121 000 μg of Se/kg is calculated. This is almost 7 times greater than the total concentration of Se in this soil (Table 1). Although not as pronounced, similar erroneous results, in direct proportion to the solution concentration of SeO_4, are obtained for all of the other samples. The second case can be demonstrated with the French sediments. For example, if only the data for SeO_4 are determined and then taken to represent the reactivity of Se in these samples, the K_d and E values of this element will be underestimated, respectively, by 3 and 1−3 orders of magnitude. Obviously, such serious errors will result in the mobility and potential bioavailability of this element being severely misrepresented. Although these situations are probably the most extreme examples, they do demonstrate the potential impact of the errors involved if the speciation of Se is not taken into consideration when determining these two parameters. In a more general context, it is, therefore, stressed that the oxidation states of these types of elements, and their kinetics of isotope self-exchange, be measured in future studies before K_d and E values are determined.

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Supporting Information Available

Measured Se isotope ratios for a range of commercially available Se compounds (Sigma-Aldrich, Steinheim, Germany) obtained with the Thermo Electron Corporation Series X7 ICP-MS, an example HPLC-ICP-MS chromatogram, and the results demonstrating the Se oxyanion equilibrium partitioning. This material is available free of charge via the Internet at http://pubs.acs.org.

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