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Katta J. Reddy
and
Zhonghua Zhang
Wyoming Water Resources Center
University of Wyoming
Laramie, Wyoming

Michael J. Blaylock
Center for Agricultural Molecular Biology
Rutgers University
New Brunswick, New Jersey

George F. Vance
Plant, Soil and Insect Sciences
University of Wyoming
Laramie, Wyoming

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Water Resources Center, P.O. Box 3067, University of Wyoming, Laramie, Wyoming 82071, Center for Agricultural Molecular Biology, Rutgers University, New Brunswick, New Jersey 08903, and Plant, Soil and Insect Sciences, University of Wyoming, Laramie, Wyoming 82071

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Method for Detecting Selenium Speciation in Groundwater

KATTA J. REDDY,*,[†]
ZHONGHUA ZHANG,[†]
MICHAEL J. BLAYLOCK,[‡] AND
GEORGE F. VANCE[§]

Water Resources Center, P.O. Box 3067, University of Wyoming, Laramie, Wyoming 82071, Center for Agricultural Molecular Biology, Rutgers University, New Brunswick, New Jersey 08903, and Plant, Soil and Insect Sciences, University of Wyoming, Laramie, Wyoming 82071

To better understand the potential toxicity of Se, it is necessary to know the concentration of different Se ionic species (e.g., SeO_3^{2-} and SeO_4^{2-}). The hydride generation atomic absorption spectrophotometry (HGAAS) method of Se analysis cannot separate Se into individual ionic species. Ion chromatography (IC) can determine SeO_3^{2-} and SeO_4^{2-} concentrations simultaneously; however, common anions, such as sulfate (SO_4^{2-}), in groundwater interferes with SeO_3^{2-} and SeO_4^{2-} speciation. The purpose of this study was to measure the concentration of ionic SeO_3^{2-} and SeO_4^{2-} species in groundwater, thereby determining the chemical speciation of dissolved Se. Three groundwater samples with high concentrations of Mg^{2-} and SO_4^{2-} were used in this study. The ionic SeO_3^{2-} and SeO_4^{2-} species in groundwater samples were selectively adsorbed onto copper oxide (CuO) particles by lowering the pH to 5.5. These ionic species were desorbed from the surface of CuO particles by increasing the pH to 12.5. Subsequently, the concentrations of SeO_3^{2-} and SeO_4^{2-} ionic species in solutions were determined with HGAAS and IC. The effect of divalent cations (e.g., Mg^{2+}) on the concentration of SeO_4^{2-} in aqueous solutions was also evaluated. The dissolved Se concentration in three groundwater samples ranged from 22 to 151 μg/L. The CuO particles extracted 97% of SeO_3^{2-} from groundwater samples, suggesting that Se(IV) concentrations were dominated by the SeO_3^{2-} ion. However, CuO particles extracted 80% of SeO_4^{2-} from groundwater samples. These results suggest that Se(VI) concentrations consisted of SeO_4^{2-} and metal SeO_4^{2-} solution species. The dissolved Mg^{2+} in groundwater samples formed a strong neutral ion pair with SeO_4^{2-} ($MgSeO_4^0$), which was not adsorbed by the CuO particles. Overall chemical speciation of dissolved Se, extracted with CuO particles, suggests that groundwater samples consisted of SeO_3^{2-} (6−36%), SeO_4^{2-} (32−65%), organic Se species (14−23%), and neutral ion pairs (9−16%). An important aspect of the proposed method is that CuO can be used in the field to extract both SeO_3^{2-} and SeO_4^{2-} ionic species from groundwater samples, and these species could be desorbed from CuO and measured using HGAAS or IC methods, depending upon the concentrations of these species.

Introduction

Groundwater is a major natural resource in the United States. It is estimated that 50% of the population uses groundwater as its primary source of drinking water (*1*). Therefore, any contamination of groundwater could lead to severe consequences. It has been estimated that 70% of Wyoming's population use groundwater as their source of drinking water. Recently, selenium (Se) concentrations ranging from 3 to 330 μg/L have been detected in shallow post-mining groundwater from coal mines in seleniferous areas of the Powder River Basin, Wyoming (*2, 3*). Selenium is an essential element; however, excessive Se can be toxic to animals and humans. Therefore, Se concentration in drinking water is federally regulated not to exceed 0.01 mg/L (*4*).

Selenium exists in different oxidation states in natural environments. These include the following: for Se(IV): SeO_3^{2-}, $HSeO_3^-$, $H_2SeO_3^0$, $CaSeO_3^0$, and $MgSeO_3^0$; for Se(VI): SeO_4^{2-}, $HSeO_4^-$, $H_2SeO_4^0$, $CaSeO_4^0$, and $MgSeO_4^0$; and for Se(−II): Se^{2-}, HSe^- H_2Se^0, $CaSe^0$, and $MgSe^0$. Additionally, dissolved organic Se compounds are known to exist in natural environments (*5*). Thermodynamic calculations show that Se(−II) species should be found in reducing environments, Se(IV) species in moderately oxidizing environments, and Se(VI) species in oxidizing environments (*6*). The determination of ionic SeO_3^{2-} and SeO_4^{2-} species in groundwater is important because Se species vary in their toxicity potential to aquatic species, animals, and humans. Moreover, such information is also required for any calculations involving adsorption, solid phase control, or indeed mobility of dissolved Se in groundwater.

Hydride generation atomic absorption spectrophotometry (HGAAS) is the most commonly used method for the speciation of Se in aqueous solutions, primarily because HGAAS can detect as low as 1 μg/L Se. The HGAAS method will measure Se as total Se and Se(IV), from which Se(VI) and organic Se can be determined by difference or by altering the pretreatment steps (*7*). However, the concentration of Se(IV) and Se(VI) may be different from that of individual SeO_3^{2-} and SeO_4^{2-} ionic species because Se(IV) and Se(VI) also include solution complexes and ion pairs. The HGAAS procedure, however, cannot separate Se into individual ionic species. Ion chromatography (IC) can measure the concentration of SeO_3^{2-} and SeO_4^{2-} simultaneously in aqueous solutions. The IC limit of quantification for Se analysis has been reported to be 181 μg/L (*8*). However, common anions (e.g., SO_4^{2-}) in aqueous solutions will interfere with SeO_3^{2-} and SeO_4^{2-} analysis with IC (*9*).

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* Corresponding author e-mail address: Katta@uwyo.edu; Fax: (307)766-3785.

[†] Water Resources Center.

[‡] Center for Agricultural Molecular Biology.

[§] Plant, Soil and Insect Sciences.

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Roden and Tallman (*10*) found that passing groundwater samples through a column of XAD-8 resin at pH 1.6–1.8 can remove organic compounds without altering Se(IV) and Se(VI) chemistry. Fio and Fujii (*11*) extended this technique and separated soil solution Se into Se(IV), Se(VI), and organic Se. Wang and others (*12*) developed fluorometry methods to determine nanograms of Se per liter in natural waters. Although these methods are useful for laboratory characterization of aquatic and soil solutions, they require extensive sample pretreatment and are not practical for field applications. Additionally, these methods cannot extract dissolved SeO_3^{2-} and SeO_4^{2-} ionic species directly from aqueous solutions.

Recent work in our laboratory has led to the observation that certain oxides, e.g., CuO, selectively adsorb ionic SeO_3^{2-} and SeO_4^{2-} species in the presence of other anions at pH 5.5 and desorb them 100% at pH 12.5. In this paper, we tested and used this hypothesis to measure the concentration of ionic SeO_3^{2-} and SeO_4^{2-} species in groundwater samples containing SO_4^{2-} concentration as high as 11 000 mg/L. From the measurement of SeO_3^{2-} and SeO_4^{2-} ionic species and total dissolved Se as well as organic Se measurements, we calculated the chemical speciation of dissolved Se in groundwater samples.

Materials and Methods

Collection and Chemical Analyses of Groundwater Samples. Three groundwater samples were collected from reclaimed coal mine sites in the Powder River Basin, Wyoming. Groundwater samples were filtered through 0.45 μM fiber glass filters and were analyzed for cations and anions. More details regarding the collection and analyses of groundwater samples are reported elsewhere (*13*). A Perkin-Elmer Model 5000 atomic absorption spectrometer equipped with a VGA-76 hydride generation system was used to determined Se species by the selective digestion procedure.

The concentration of Se(IV) in samples was determined by generating H_2Se with a $NaBH_4$ solution [0.6% (w/v) $NaBH_4$; 0.5% (w/v) NaOH] and 7 M HCl (undigested). Another aliquot of the sample was heated for 20 min at 85 °C with 7 M HCl to reduce Se(VI) to Se(IV). The concentration of Se in this solution is considered as the sum of Se(VI) and Se(IV) (digested). The difference between the concentration of Se in digested and undigested samples is the concentration of Se(VI). The total Se concentration in samples was determined by oxidizing organic matter with H_2O_2 for 20 min at 85 °C and was then digested with 7 M HCl for another 20 min at 85 °C. The difference between total Se and digested Se concentrations was assumed as the concentration of organic Se. Details regarding detection limits and the limit of quatification for the HGAAS method for Se analysis are reported in Cutter (*7*).

The IC used in this study was a Dionex 2000i with Al-450 software (Version 2.12); 50-μL sample loop, AG-5 guard column, and AS4A separator column were used to determine SeO_3^{2-} and SeO_4^{2-} with a 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ eluent mixture at a flow rate of 2 mL/min and 0.013 M H_2SO_4 regenerant solution. Electrical conductivity was used as the detection method. Before Se analysis, SeO_3^{2-} and SeO_4^{2-} standard solutions were prepared and analyzed with IC to determine the retention time, peak height, and peak area. More details regarding detection limits and the limit of quatification for the IC method for Se analysis are reported in Blaylock and James (*8*).

Selection of CuO. Initially, $BaCl_2$ and $Ba(OH)_2$ solutions were used to precipitate SO_4^{2-} from alkaline aqueous solutions; however, along with SO_4^{2-}, SeO_3^{2-} and SeO_4^{2-} also coprecipitated. Later, Cu^{2+} (cupric) was selected to precipitate SO_4^{2-} from alkaline aqueous solutions because $Cu^{2+}-SeO_3^{2-}$ and $-SeO_4^{2-}$ solution species are not significant in aqueous solutions and because $Cu^{2+}-SeO_3^{2-}$ and $-SeO_4^{2-}$ solid phases are highly soluble. The $CuCl_2$ solution was added to aqueous solutions containing SO_4^{2-}, SeO_3^{2-}, and SeO_4^{2-}. Then, SO_4^{2-} was precipitated as hydroxysulfate by adding NaOH to the solutions. This procedure appeared to work for some samples; on further investigation, the addition of $CuCl_2$ and NaOH to solutions was not completely effective in removing SO_4^{2-}.

In some $CuCl_2$ solutions, increasing the pH by adding NaOH precipitated CuO (tenorite). Excessive Cu^{2+} in solutions slowly lowered the pH to around 6.0 through hydrolysis reactions. At this point, we could not detect SeO_3^{2-} and SeO_4^{2-} in solutions; when solution pH was increased to 12, SeO_3^{2-} and SeO_4^{2-} were detected. For further studies, CuO was prepared by adding concentrated NaOH solution to $CuCl_2 \cdot 2H_2O$ solutions. The precipitate was washed with distilled deionized H_2O several times, heated at 250 °C for several hours, and identified as tenorite by X-ray diffraction analysis (XAD 2000, Scintag Inc.). We estimate that the surface area of this material will be greater than 40 000 m^2/kg.

pH Effect on Adsorption and Desorption of SeO_3^{2-} and SeO_4^{2-} by CuO. A total of 2 mg/L SeO_3^{2-} and SeO_4^{2-} each was added to solutions containing 7.5 g of CuO particles. The pH of the solutions was adjusted to 13.5 with NaOH solution. The pH of the solution was reduced gradually by adding HCl. After reacting for 4 h at a given pH, 1 mL of the solution was removed with a syringe containing a 0.45 μM millipore filter and measured for SeO_3^{2-} and SeO_4^{2-} using IC. The effect of CuO particle concentration on the adsorption of SeO_3^{2-} and SeO_4^{2-} was examined using the above procedure, except the concentration of CuO particles was varied.

The SeO_3^{2-} and SeO_4^{2-} desorption procedure was similar to that of the adsorption experiments, except that the initial pH of the solution was adjusted to less than 5.5. The pH of the solution was gradually increased with NaOH. After reacting for 24 h at a given pH level, 1 mL of solution was removed with a syringe containing a 0.45 μM millipore filter and measured for SeO_3^{2-} and SeO_4^{2-} with IC.

Extraction of SeO_3^{2-} and SeO_4^{2-} from Groundwater Samples with CuO. The groundwater samples were spiked with 2 mg/L standard SeO_3^{2-} and SeO_4^{2-} and were acidified to pH 5.5 with concentrated HCl. The concentrations of Se(IV), Se(VI), and organic Se in spiked and unspiked samples were determined with HGAAS following the selective digestion procedure. Twenty milliliters of the spiked and unspiked groundwater samples was transferred into 50-mL centrifuge tubes containing 0.6 g of CuO particles.

After reacting for 4 h, solutions were centrifuged, and the supernatant was separated from the CuO particles by decantation. A 20-mL sample of NaOH solution (pH > 12.5) was added to each centrifuge tube to desorb the Se species from the CuO particles, and solutions were reacted overnight and then centrifuged. The concentration of SeO_3^{2-} and SeO_4^{2-} in the supernatant solutions was determined by HGAAS and IC. All analyses were performed in triplicate,

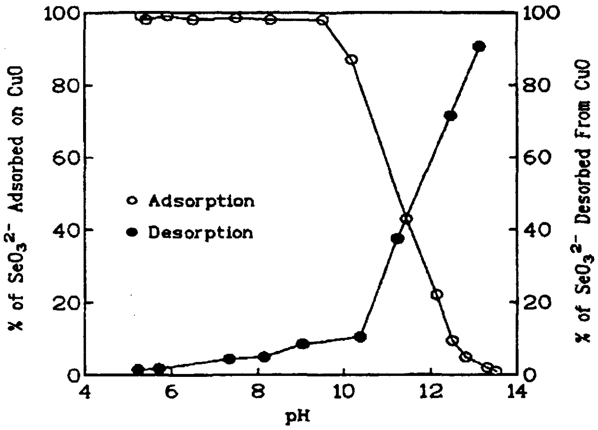

FIGURE 1. Adsorption and desorption of SeO_3^{2-} by CuO particles in 0.05 M NaCl solution as a function of pH.

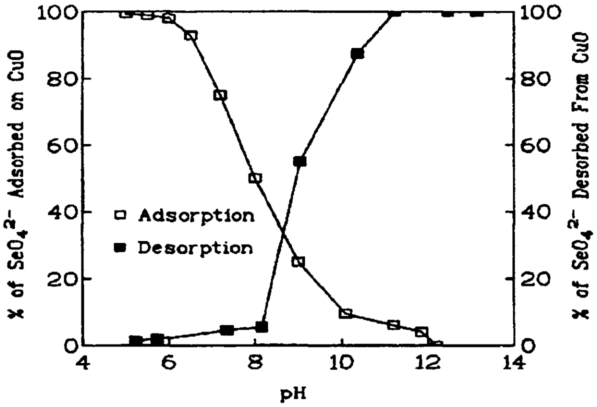

FIGURE 2. Adsorption and desorption of SeO_4^{2-} by CuO particles in 0.05 M NaCl solution as a function of pH.

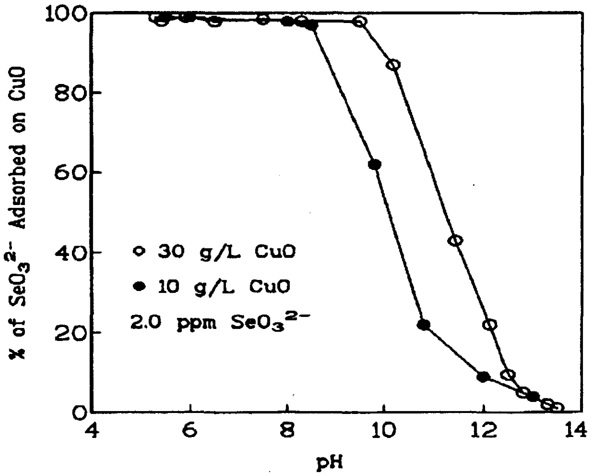

FIGURE 3. Adsorption of SeO_3^{2-} in 0.05 M NaCl solution as a function of CuO particle concentration and pH.

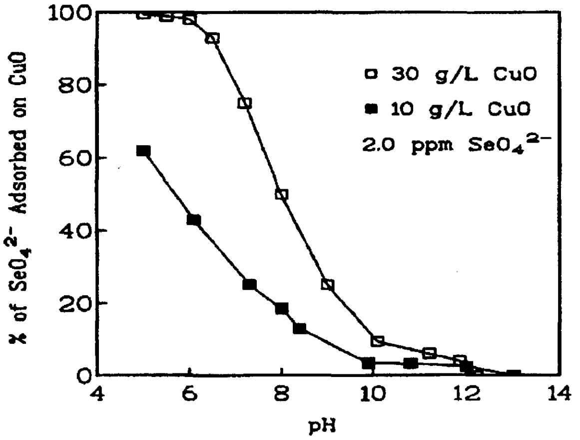

FIGURE 4. Adsorption of SeO_4^{2-} in 0.05 M NaCl solution as a function of CuO particle concentration and pH.

and from triplicate analyses standard deviations were calculated.

Results and Discussion

pH Effect on Adsorption and Desorption of SeO_3^{2-} and SeO_4^{2-} by CuO. The adsorption and desorption of SeO_3^{2-} by CuO particles as a function of pH is shown in Figure 1. At pH 9.5, CuO particles adsorbed 100% of SeO_3^{2-} from aqueous solutions. As pH increased, the percent of SeO_3^{2-} adsorbed by CuO particles decreased, and at pH 12.5, most of the SeO_3^{2-} was in solution. An increase in anion adsorption by oxides with decreasing pH is a typical feature of the anion adsorption process. Results in Figure 1 also show that SeO_3^{2-} adsorption by CuO particles is a reversible process. These results agree with the studies reported for SeO_3^{2-} adsorption by goethite (α-FeOOH) as a function of pH (*14, 15*).

Adsorption and desorption of SeO_4^{2-} by CuO particles as a function of pH is presented in Figure 2. Results show CuO particles removed 100% of the SeO_4^{2-} from solutions at pH 6.0. As pH increased, SeO_4^{2-} adsorption decreased, and nearly all the SeO_4^{2-} was in solution at pH 11.0, suggesting that SeO_4^{2-} adsorption by CuO particles is also a reversible process. Benjamin (*14*) studied the adsorption of SeO_4^{2-} by an amorphous iron oxyhydroxide as a function of pH and reported only 85% adsorption at pH 4.5. He also reported that divalent cations such as Cu^{2+} in solution caused a significant increase in the adsorption of SeO_4^{2-} by $Fe_2O_3{\cdot}H_2O$. Balistrieri and Chao (*15*) reported the slight adsorption of SeO_4^{2-} (<20%) in a system containing 300 mg/L goethite at pH 6.0. However, results in this study show that lower concentrations of CuO particles can adsorb close to 100% of the SeO_4^{2-} from aqueous solutions at pH 6.0. A possible explanation is that zero point of charge (ZPC) for CuO occurs at higher pH (9.5) than the ZPC of goethite, which occurs at the lower pH range (6 and 7) (*16*).

Adsorption and desorption results also show that SeO_3^{2-} is strongly adsorbed onto the surface of CuO particles compared to SeO_4^{2-}. For example, at pH 11.0, only 50% of SeO_3^{2-} was desorbed from the surface of CuO particles (Figure 1). At the same pH, 100% of the SeO_4^{2-} desorbed from the surface of the CuO particles (Figure 2). A possible explanation is that SeO_3^{2-} forms a strong inner-sphere surface complex in contrast to a weak outer-sphere surface complex formed by SeO_4^{2-} (*17*).

Figures 3 and 4 show the effect of CuO particle concentration on the adsorption of SeO_3^{2-} and SeO_4^{2-} as a function of pH. The concentration of CuO particles had a greater effect on the adsorption of SeO_4^{2-} than the adsorption of SeO_3^{2-}. As the CuO particle concentration increased, the adsorption edges probably shifted to higher pH values because of the greater area of available binding sites. This trend has been previously observed for SeO_3^{2-} adsorption on goethite by Balistrieri and Chao (*15*).

Extraction of SeO_3^{2-} and SeO_4^{2-} from Groundwater Samples with CuO. Partial chemical composition of groundwater samples is presented in Table 1. The pH

TABLE 1

Partial Chemical Data of Groundwater Samples from Reclaimed Coal Mine Sites in the Powder River Basin, Wyoming[a]

	SP2	SP4	CA649B
calcium	470	427	545
magnesium	693	2080	391
sodium	339	1180	347
potassium	18	38	33
aluminum	2.54	0.03	0.01
iron	0.007	0.001	0.006
sulfate	4980	11300	2960
chloride	46	340	65
molybdenum	0.006	0.005	0.006
total selenium, (μg/L)	22 (±3)	151 (±6)	107 (±5)
DOC	14	88	87
E_h (mV)	450	360	400
pH	5.5	7.1	6.3

[a] Units are mg/L unless otherwise indicated.

TABLE 2

Selenium Speciation of Groundwater Samples Determined with HGAAS[a]

sample	Se(IV)	Se(VI)	organic Se	total Se
SP2 unspiked	8 (±2)	9 (±4.5)	5 (±3.4)	22
SP2 spiked	1809 (±15.9)	1781 (±18.7)	104 (±8.4)	3694
SP4 unspiked	10 (±2.1)	110 (±7.6)	31 (±4.8)	151
SP4 spiked	1789 (±15.2)	1967 (±10.9)	134 (±8.3)	3890
CA649B unspiked	7 (±1.7)	85 (±8.3)	15 (±3.9)	107
CA649B spiked	1848 (±16.7)	1927 (±11.2)	112 (±9.1)	3887

[a] Hydride generation atomic absorption spectrometry. Units are in μg/L.

ranged from 5.5 to 7.1; total Se concentrations were between 22 and 151 μg/L; and the concentration of As, Cd, Cr, Pb, and Zn were all less than 0.001 mg/L. A high concentration of SO_4^{2-} (2960–11 300 mg/L) in groundwater samples prevented direct determination of SeO_3^{2-} and SeO_4^{2-} with IC. Dissolved Se speciation in spiked and unspiked samples, as determined by HGAAS, is summarized in Table 2. Results for unspiked samples show that 6–36% of the total dissolved Se is in the form of Se(IV). The Se(VI) concentrations ranged between 41 and 79% of the total dissolved Se. Organic Se concentrations ranged between 14 and 22% of the total dissolved Se.

The SeO_3^{2-} and SeO_4^{2-} concentrations extracted with CuO particles are presented in Table 3. For unspiked samples, the results indicate that CuO particles extracted 97% of SeO_3^{2-} from groundwater samples when compared with the concentration of Se(IV) present in the samples. These results suggest that Se(IV) in groundwater samples is dominated by the SeO_3^{2-} ion. High concentration of SO_4^{2-} in groundwater did not affect the extraction of SeO_3^{2-} by the CuO particles. However, the CuO particles extracted only 80% of SeO_4^{2-} from unspiked groundwater samples. Similar results were observed for spiked samples. The observed 80% adsorption of SeO_4^{2-} for unspiked and spiked samples would suggest that (1) dissolved SO_4^{2-} may compete for adsorption sites on CuO and (2) other Se species such as $MgSeO_4^0$ and/or $CaSeO_4^0$ may be present in the groundwater samples, which may not be adsorbed by the CuO particles.

To determine the effect of SO_4^{2-} concentration on the adsorption of SeO_4^{2-} by the CuO particles, different concentrations of SO_4^{2-} (0, 100, 300, 700, 1200, and 2200 mg/L) were added to solutions containing 0.6 g of CuO particles and approximately 1.0 mg/L SeO_4^{2-}. After reacting for 4 h, supernatant solutions were analyzed for SeO_4^{2-} by HGAAS. Results from this experiment suggested that SO_4^{2-} had little or no effect on the adsorption of SeO_4^{2-} by the CuO particles. If both SO_4^{2-} and SeO_4^{2-} behave similarly or compete for the adsorption sites on CuO particles, one would expect low adsorption or no adsorption of SeO_4^{2-}, especially with groundwater samples having a very high SO_4^{2-} and SeO_4^{2-} ratio. For example, sample SP4 has a total Se concentration of 151 μg/L compared to 11 300 mg/L SO_4^{2-} (SO_4^{2-}:total Se = 74 000:1), and 79% of the SeO_4^{2-} was extracted with the CuO particles from the unspiked sample. These results suggest that CuO particles have a high affinity for SeO_4^{2-} even in the presence of high SO_4^{2-} concentrations.

Magnesium concentrations in the groundwater are high as compared to Ca^{2+}, Na^+, and K^+. It may be possible that Mg forms a $MgSeO_4^0$ ion pair in solution. To test this hypothesis, 1 mg/L SeO_4^{2-} was reacted with different concentrations of Mg^{2+} (400, 700, 1000, 1500, and 2000 mg/L). Each solution was reacted for 0.5 h followed by measuring the Se(VI) by IC. Most ion pairs will dissociate in the IC column and be detected. Only strong ion pairs will pass through the IC column, undetected. If $MgSeO_4^0$ is a strong ion pair, it will pass through the IC column and measured Se(VI) concentration will decrease with increasing Mg^{2+} concentrations. Data obtained from this experiment are presented in Table 4. When no Mg^{2+} was added to the solutions, we recovered 1 mg/L SeO_4^{2-}. As Mg^{2+} concentration increased, measured SeO_4^{2-} concentration in solutions decreased from 1.0 to 0.76 mg/L, suggesting that SeO_4^{2-} in solution probably consisted of a $MgSeO_4^0$ ion pair. Thus, observed 80% adsorption for SeO_4^{2-} in groundwater samples may be attributed to the presence of $MgSeO_4^0$ because strongly bonded neutral species may not be adsorbed by the oxide particles (*18*).

TABLE 3

Determination of SeO_3^{2-} and SeO_4^{2-} in Groundwater Samples Extracted with CuO Particles[a]

	IC[b]				HGAAS[b]			
	unspiked		spiked		unspiked		spiked	
sample	SeO_3^{2-}	SeO_4^{2-}	SeO_3^{2-}	SeO_4^{2-}	SeO_3^{2-}	SeO_4^{2-}	SeO_3^{2-}	SeO_4^{2-}
SP2	ND[c]	ND	1820 (±20)	1640 (±30)	8 (±1.6)	7 (±2.4)	1780 (±50)	1520 (±40)
SP4	ND	ND	1750 (±10)	1500 (±40)	9 (±2.3)	87 (±5.3)	1720 (±40)	1450 (±30)
CA649B	ND	ND	1800 (±20)	1710 (±40)	7 (±2)	70 (±6.1)	1770 (±50)	1650 (±50)

[a] Units are in μg/L. [b] Ion chromatography (IC) and hydride generation atomic absorption spectrometry (HGAAS). [c] Not detected (ND).

TABLE 4

Effect of Mg^{2+} on SeO_4^{2-} Concentration in Solutions[a]

Mg^{2+}	Se(VI)	% $MgSeO_4^0$
0	1.0	0
400 (CA649B)	0.89	11
700 (SP2)	0.83	17
1000	0.81	19
1500	0.78	22
2000 (SP4)	0.76	24

[a] Information in parentheses is the corresponding Mg^{2+} concentration of groundwater sample. Units are in mg/L

TABLE 5

Selenium Speciation in Groundwater Samples Collected from Reclaimed Coal Mine Sites from the Powder River Basin, Wyoming[a]

sample/species	SP2	SP4	CA649B
SeO_3^{2-}	8 (36)	9 (6)	7 (6)
SeO_4^{2-}	7 (32)	87 (57)	70 (65)
organic Se	5 (23)	31 (20)	15 (14)
$MgSeO_4^0$	2 (9)	24 (16)	12 (11)
other	NS	NS	3 (3)
total	22 (100)	151 (99)	107 (99)

[a] Units are in $\mu g/L$. Values in parentheses are percent of total Se. NS = not significant.

Because CuO particles extracted SeO_3^{2-} and SeO_4^{2-} ionic species and $HSeO_3^-$ and $HSeO_4^-$ species are not significant in slightly acidic to alkaline solutions and knowing the concentration of dissolved organic Se and total dissolved Se, we could calculate the chemical speciation of dissolved Se in groundwater samples. Chemical speciation of dissolved Se concentration in unspiked groundwater samples is presented in Table 5. These results show that for SP2 dissolved Se was dominated by SeO_3^{2-} (36%) and SeO_4^{2-} (32%), followed by organic Se (23%) and $MgSeO_4^0$ (9%). For the other two samples (SP4 and CA649B), dissolved Se was dominated by SeO_4^{2-} (57–65%) followed by organic Se (14–20%), $MgSeO_4^0$ (11–16%), and SeO_3^{2-} (6%).

Currently, speciation of dissolved Se concentration in groundwater is not well understood. This is partially due to the fact that this element is regulated as total Se and the EPA approved analysis is HGAAS, which cannot determine individual Se species (*19*). However, measurement of individual Se species is required for determining the contribution of dissolved Se in groundwater to toxicity problems. Commonly, concentrations of SeO_3^{2-} and SeO_4^{2-} ionic species in aqueous systems are calculated indirectly with chemical speciation models using dissolved inorganic Se, pH, and redox potential measurements. The CuO method described in this study extracted SeO_4^{2-} and SeO_3^{2-} ionic species directly from groundwater in the presence of other anions.

The proposed CuO method extracted as low as 7 (±2) $\mu g/L$ SeO_3^{2-} and SeO_4^{2-} from the aqueous solutions. However, its detection limits will be dictated by the method selected for Se analysis (i.e., HGAAS, fluorometry, or IC). The CuO method is simple, effective, and can potentially be used to extract the concentrations of ionic SeO_3^{2-} and SeO_4^{2-} species in alkaline surface water, soil solutions, coal mine spoil solutions from seleniferous regions, and alkaline fly ash and/or hazardous waste solutions. Another important aspect of this method is that CuO could be used in the field to extract both SeO_3^{2-} and SeO_4^{2-} ionic species from samples, and then later these species could be desorbed and determined with HGAAS, fluorometry, and/or IC depending upon the concentration of these Se species.

Summary and Conclusions

Selective adsorption phenomena of CuO for dissolved Se provided an approach to extract SeO_3^{2-} and SeO_4^{2-} ionic species from groundwater samples in the presence of other anions. At pH 5.5, both SeO_3^{2-} and SeO_4^{2-} ionic species were adsorbed onto the surface of CuO particles, and these species were desorbed by raising the pH to 12.5. The concentrations of SeO_3^{2-} and SeO_4^{2-} ionic species in solutions were determined with both HGAAS and IC. Divalent metal ions such as Mg^{2+} in groundwater samples formed a strongly bonded neutral ion pair with SeO_4^{2-}, which was not adsorbed by the CuO particles. Chemical speciation results showed that dissolved Se in groundwater samples consisted of SeO_4^{2-}, organic Se, $MgSeO_4^0$, and SeO_3^{2-}. To determine low concentrations ($\mu g/L$ levels) of SeO_3^{2-} and SeO_4^{2-} ionic species in solutions, extraction with CuO followed by HGAAS or fluorometry will be useful.

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