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GROUND WATER CONTAMINATION BY
SOIL SELENIUM MOVEMENT**

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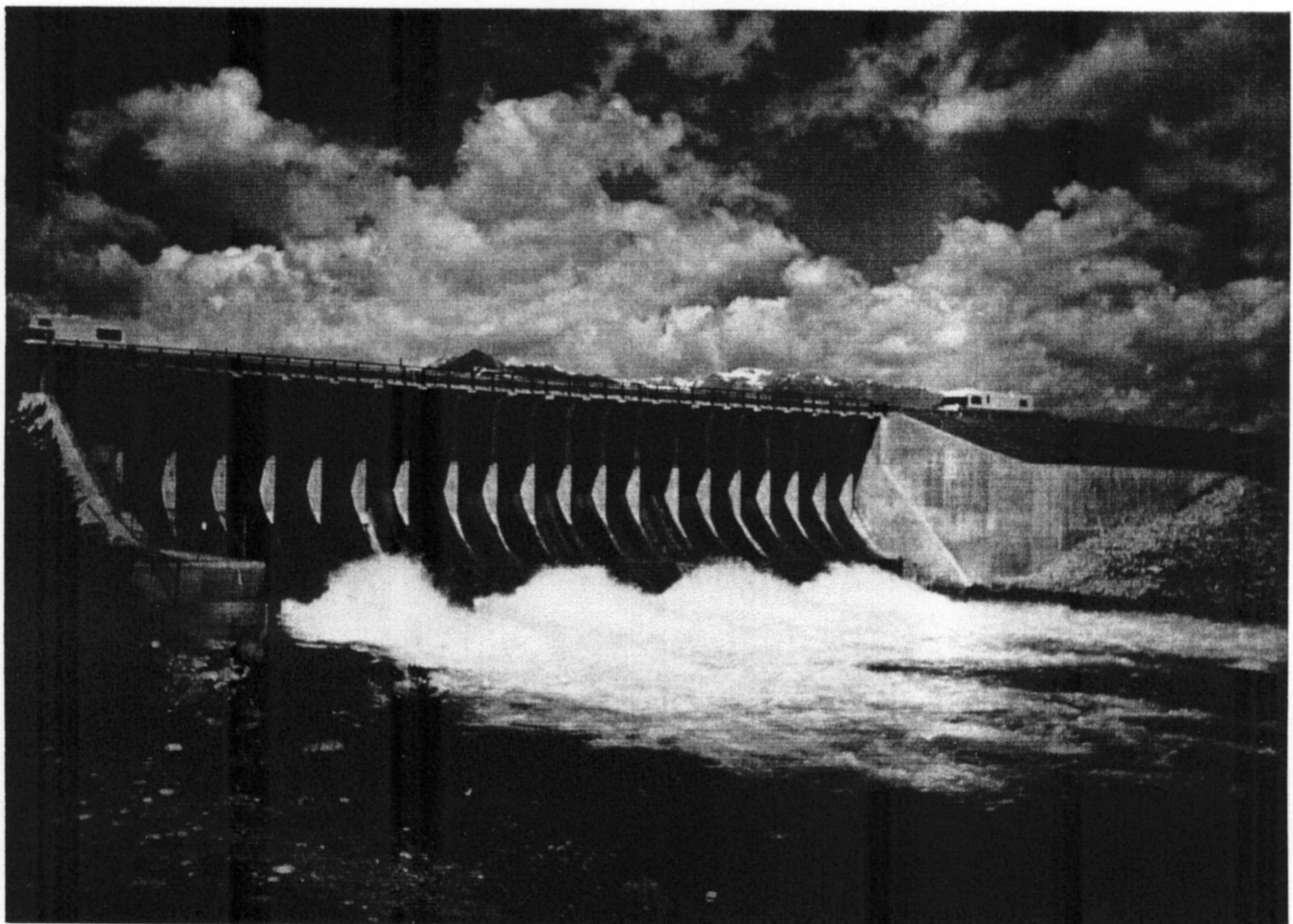
**Shankar Sharmasarkar
and
George F. Vance
Soil and Environmental Chemistry
Department of Plant, Soil and Insect Sciences
University of Wyoming
Laramie, Wyoming**

PROCEEDINGS

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APPLICATION OF PARTIAL FRACTIONATION AND SPECIATION TECHNIQUES FOR PREDICTING GROUND WATER CONTAMINATION BY SOIL SELENIUM MOVEMENT

Shankar Sharmasarkar^{1*} and George F. Vance¹

ABSTRACT: Selenium (Se) was partially fractionated and speciated to understand its mobility and contamination behavior in soils of contrasting properties. Five Se fractions were obtained by sequentially extracting the soils with 0.25 M KCl, 1 M KH₂PO₄, 4 N HCl, (KClO₃ + 12 N HCl) and concentrated (HNO₃ + HClO₄ + HF), respectively. Each fraction was analyzed for total Se by atomic absorption spectrophotometry with hydride generation (AAS-HG) after a digestion with 30% H₂O₂ + 12 N HCl. Solution selenite was analyzed before this pre treatment. Selenate was calculated from the difference of these two results. The overall findings suggest selenate as the potential contaminant of ground water. However, selenite or both Se species may be mobilized depending on soil conditions and sources of Se.

KEY TERMS: Partial fractionation, speciation, selenite, selenate, contamination.

INTRODUCTION

Selenium (Se) is an element of environmental importance because of its potential toxicity to animals and humans. Selenium occurs naturally in soils (Adriano, 1986), aquifers (Cooke and Bruland, 1987), fly-ash (Campbell et al., 1978), and agricultural drainage (Deverel et al., 1984). The environmental chemistry of Se was reviewed by Lakin (1973). McNeal and Balistrieri (1989) have discussed the geochemistry and occurrence of Se in details.

In natural systems Se exists in one or more oxidation state: Se⁻² (selenide), Se⁰ (element), Se⁺⁴ (selenite), and Se⁺⁶ (selenate). In surface coal mine environments, Se⁺⁴ and Se⁺⁶ are the main species of concern in relation to ground water contamination (Sharmasarkar et al., 1992). One way of understanding ground water contamination of Se from soil environments is by partial fractionation and subsequent speciation. The fractionation technique has been reviewed and applied by Chao and Sanzalone (1989), though there had been some earlier criticism (Gruebel et al., 1988). Application of atomic absorption spectrophotometry with hydride generation (AAS-HG) for Se speciation was

¹Graduate Student and Assistant Professor of Soil and Environmental Chemistry, Department of Plant, Soil and Insect Sciences, P.O. Box 3354, University of Wyoming, Laramie, WY 82071.

*Corresponding author.

evaluated by Fio and Fujii (1990) and Blaylock and James (1993). The importance of solid selenium speciation in a reclaimed abandoned mine environment was recently studied by Sharmasarkar and Vance (1993). However, information is still lacking on the combined application of partial fractionation and speciation. For addressing this aspect, the current paper examines the application of partial fractionation and speciation techniques in understanding the potential ground water-contamination behavior of Se in soils.

MATERIALS AND METHODS

A reclaimed coal mine profile (0-132 cm), having six horizons of contrasting soil chemical properties, was sampled from the northeastern Powder River Basin of Wyoming. The profile was selected to study selenium mobilization behavior in a diverse environment. The sample site was located on an upland position within a coal mine site. Soil samples were air-dried, finely ground (<0.25 mm), and stored at room temperature in polythene bags until analysis.

Following the procedures outlined by Chao and Sanzolone (1989), soil samples (duplicates) from each horizon were fractionated sequentially using 0.25 M KCl, 1 M KH_2PO_4 , 4 N HCl, ($\text{KClO}_3 + 12 \text{ N HCl}$) and concentrated ($\text{HNO}_3 + \text{HClO}_4 + \text{HF}$). We used 1 M KH_2PO_4 , instead of 0.1 M KH_2PO_4 (used by Chao and Sanzolone, 1989), since the former has been defined as the suitable extractant for available Se in the standard operation procedure for Se analysis in mine soils (Spackman et al., 1994). Each fraction was analyzed for total Se by atomic absorption spectrophotometry with hydride generation (AAS-HG) after digestion (30% $\text{H}_2\text{O}_2 + 12 \text{ N HCl}$, 90°C, 30 min.). Solution selenite was analyzed before this pre treatment. Selenate was calculated from the difference of these two results. The concentrations of total Se in the samples from each horizon of the profile under investigation was also measured after a complete digestion of the soil samples in mixed acid (concentrated $\text{HNO}_3 + \text{HClO}_4 + \text{HF}$) at 150°C for 18 hr.

RESULTS AND DISCUSSION

Some general soil chemical properties of the profile are described in Table 1. The soil data showed contrasting chemical properties between different horizons of the profile studied. The pH varied from 3.6 to 8.7 indicating both acidic and alkaline soil conditions within the profile. The variability in pH is an important factor governing Se mobility and availability for ground water contamination. A fairly broad range in electrical conductivity values (0.5-2.6 dS m^{-1}) indicated variation of soluble salt content throughout the profile. A high sand distribution (55-84%) was also observed throughout the whole profile. This suggested that the profile might have a greater Se leaching potential to the water table. The silt and clay contents varied between 5-23% and 8-22%, respectively. The total soil Se ranged from 0.258 to 0.359 mg kg^{-1} .

Table 1. General soil chemical properties .

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH*	Elect. Cond.* (dS m ⁻¹)	Total Se (mg kg ⁻¹)
0-15	59	19	22	8.7	0.6	0.258
15-30	84	5	11	8.6	0.5	0.269
30-56	69	18	13	3.6	2.6	0.359
56-76	80	12	8	8.4	0.7	0.281
76-107	68	18	14	4.2	2.3	0.312
107-132	55	23	22	4.3	2.1	0.275

*soil:water = 1:2.

Results of partial fractionation are presented in Table 2. Applying this technique we have successfully extracted 85-98 % of the total Se.

Table 2. Selenium distributions in various fractions.

Depth	KCl	KH ₂ PO ₄	HCl	KClO ₃ +HCl	Mixed Acid	Sum	Se recovery*
-----cm-----	-----mg kg ⁻¹ -----						-----%-----
0-15	0.020	0.024	0.026	0.092	0.075	0.237	92
15-30	0.020	0.060	0.055	0.059	0.057	0.251	93
30-56	0.017	0.136	0.068	0.050	0.042	0.313	87
56-76	0.016	0.083	0.038	0.073	0.031	0.241	85
76-107	0.009	0.048	0.105	0.079	0.033	0.274	88
107-132	0.004	0.050	0.121	0.055	0.040	0.270	98

*Se recovery = sum x 100 / total

There was a good linear fit of the sum of Se fractions with the total Se concentrations ($R = 0.92$, Figure 1). The high percent Se recovery, and the high R value indicated that the partial fractionation technique could be considered as a precise and accurate method for studying extractable Se.

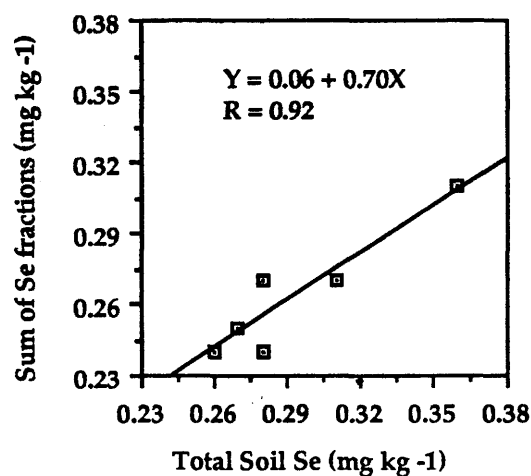


Figure 1. Linearity between total Se and sum of Se fractions.

Results of the Se speciation analysis are listed in Table 3. The following discussion will concentrate on the individual fractions and their content of Se^{+4} and Se^{+6} .

Table 3. Speciation of selenium fractions.

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	Se ⁺⁴	Se ⁺⁶	Se ⁺⁴	Se ⁺⁶	Se ⁺⁴	Se ⁺⁶	Se ⁺⁴	Se ⁺⁶	Se ⁺⁴	Se ⁺⁶
Depth	Aqueous		Exchangeable		Acid leachable		Organic		Siliceous	
---cm---	-----mg kg ⁻¹ -----									
0-15	*ND	0.020	0.024	0.001	0.007	0.020	0.060	0.032	0.050	0.025
15-30	*ND	0.019	0.031	0.029	0.033	0.022	0.021	0.038	0.037	0.020
30-56	0.008	0.010	0.051	0.085	0.044	0.024	0.039	0.012	0.040	0.002
56-76	0.004	0.012	0.015	0.068	0.027	0.011	0.014	0.059	0.014	0.017
76-107	0.006	0.003	0.010	0.038	0.066	0.039	0.033	0.046	0.024	0.010
107-132	0.004	*ND	0.011	0.039	0.022	0.099	0.030	0.026	0.022	0.018

*ND : Not detected

Selenium in KCl, KH_2PO_4 , HCl, ($\text{KClO}_3 + 12 \text{ N HCl}$) and concentrated ($\text{HNO}_3 + \text{HClO}_4 + \text{HF}$) extracts represent water soluble (aqueous), adsorbed (exchangeable), acid extractable (acid leachable), organic bound and siliceous fractions, respectively. The soluble and exchangeable fractions are of greater concern to ground water quality.

The distribution of Se in different fractions varied from one horizon to another (Figure 2). At the surface horizon (0-15 cm), organic bound Se was found to be very high; from 15 to 76 cm depth, exchangeable Se was the dominant fraction; beyond 76 cm, acid leachable portion was maximum. Thus depending on soil conditions, Se would be solubilized from different sources.

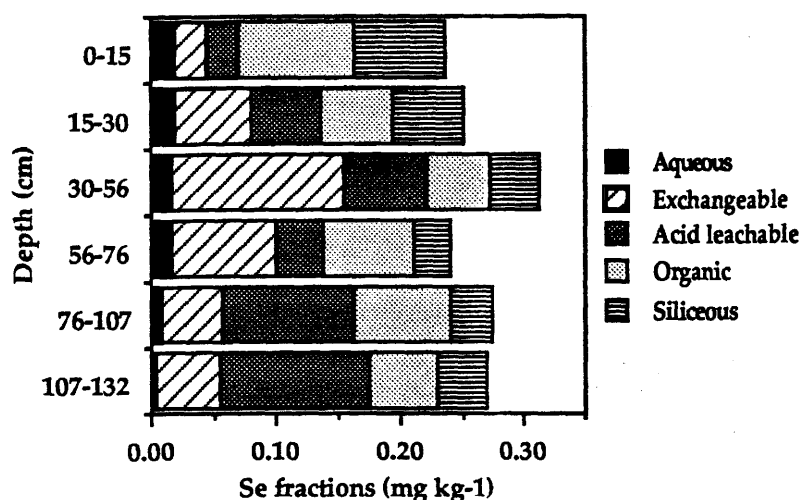


Figure 2. Partial fractions of soil Se at various depths.

Selenium in the KCl fraction was high in the 0 to 30 cm depths, and decreased thereafter. In this fraction, Se^{+6} was found to be dominant, suggesting it to be the

potential soluble species available for leaching. Concentration of Se^{+6} decreased from upper to lower horizons, and at the greatest depth it is below detection limit (Figure 3).

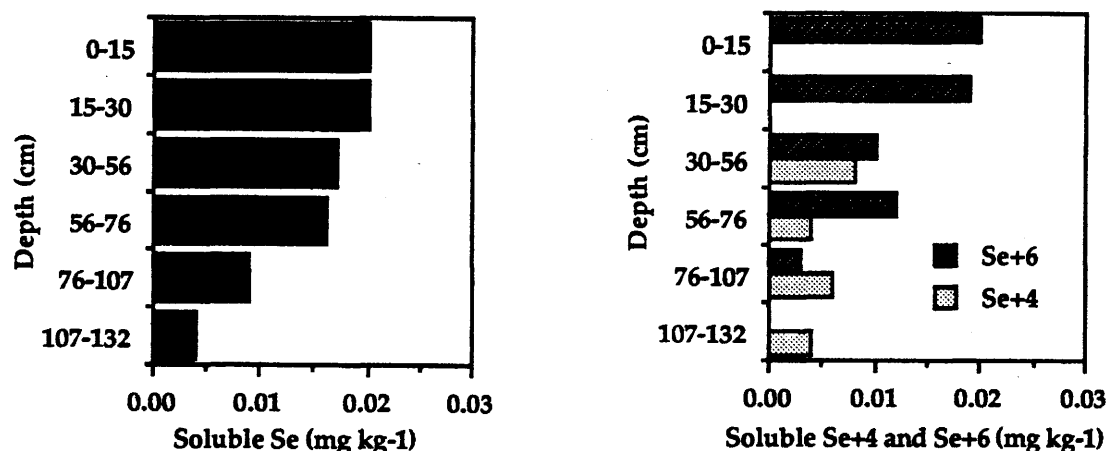


Figure 3. Distribution of soluble Se, Se^{+4} and Se^{+6} at various depths.

Phosphate extractable Se was highest in the horizon having the lowest pH (30-56 cm), which is probably due to the formation of complexes at exchangeable sites of soil minerals; while the surface horizon (0-15 cm) has the highest pH and the lowest level of exchangeable Se. In this fraction, Se^{+6} was detected in higher proportion than Se^{+4} , suggesting Se^{+6} may become more available (Figure 4). Phosphate generally replaces the inner-sphere-complexed selenite through the ligand exchange mechanism. However, considerably high proportion of selenate in the exchangeable fraction indicated that a part of the selenate must have been extracted by the phosphate, probably through the dissolution process of the selenate complexes caused by phosphate anion.

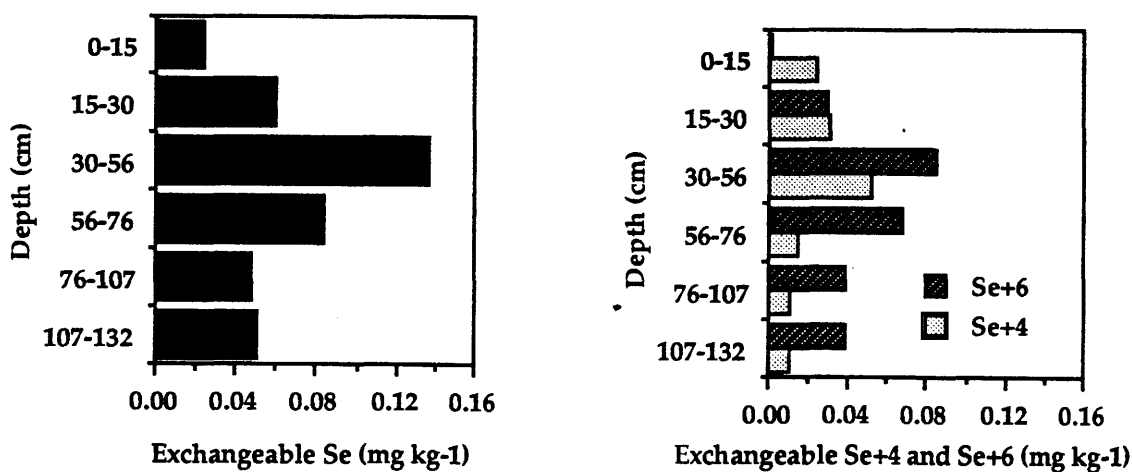


Figure 4. Distribution of exchangeable Se, Se^{+4} and Se^{+6} at various depths.

High levels of acid extractable Se were obtained from horizons at 76-132 cm depths. All these horizons had low pH values (Table 1). There was an increasing trend in the amount of this fraction with depth, except in the 56-76 cm, where pH was higher (Table 1). Thus, during any acid leaching process, higher amounts of Se would be mobilized at greater depths, which might increase the potential for ground water contamination. In this fraction, Se^{+4} dominated throughout the profile, except for the surface and the bottom-most horizons, where Se^{+6} would be predominately mobilized (Figure 5).

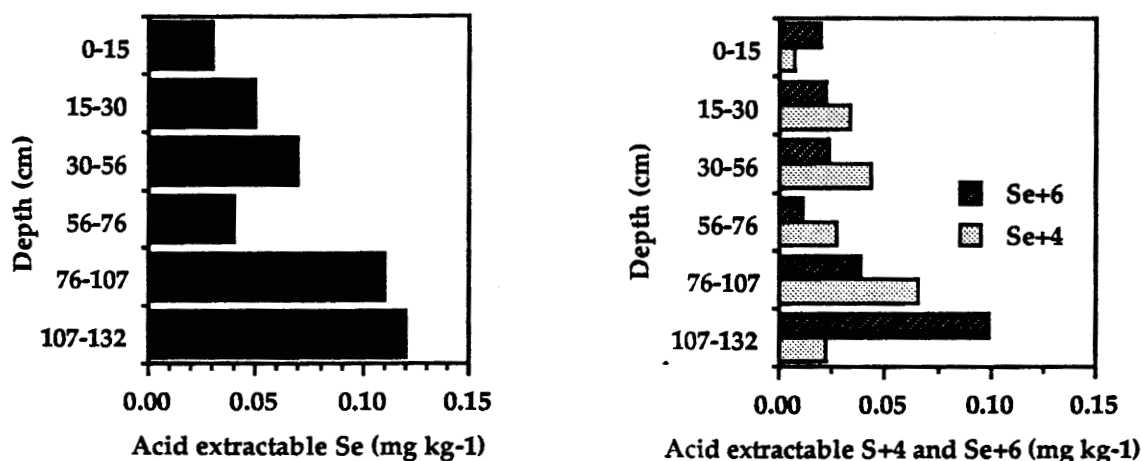


Figure 5. Distribution of acid extractable Se, Se^{+4} and Se^{+6} at various depths.

Organic bound Se was maximum in the surface horizon (0-15 cm), indicating Se accumulation at the surface due to organic residues of plant origin. A mixed distribution of Se^{+4} and Se^{+6} was observed throughout the whole profile (Figure 6). This suggested that during the mineralization process of organic matter, both Se species would contribute simultaneously to Se mobility.

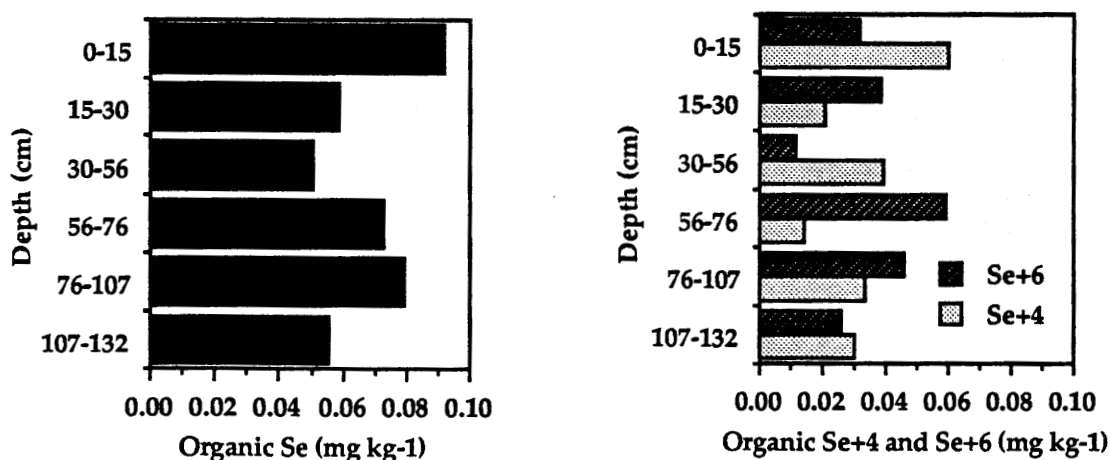


Figure 6. Distribution of organic Se, Se^{+4} and Se^{+6} at various depths.

Siliceous Se accumulated at the surface and decreased gradually with depth, except for the bottom-most horizon (107-132 cm) where there was a slight increase. This fraction also contained both Se species which were scattered throughout the profile (Figure 7).

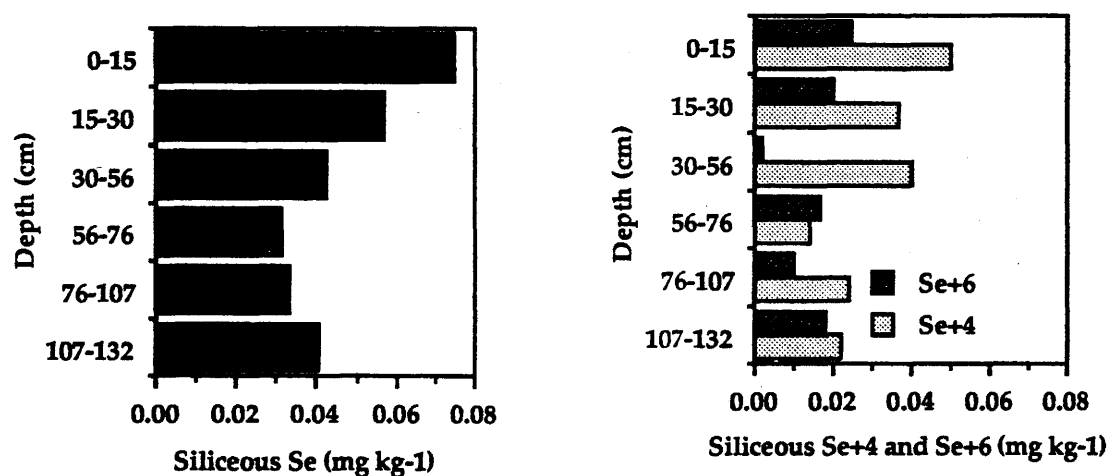


Figure 7. Distribution of siliceous Se, Se⁺⁴ and Se⁺⁶ at various depths.

SUMMARY AND CONCLUSIONS

Though the soil samples were from the same profile, the wide variability in their chemical and physical properties resulted in a diverse distribution of selenium and its potential mobilization behavior. However, the high percentage of sand in all the horizons implied that the profile had a high potential for Se translocation. In aqueous solutions, Se⁺⁶ was found to be the potential specie for leaching. Higher levels of exchangeable Se were found in low pH horizons, where again Se⁺⁶ could be potentially mobilized. The low pH soils also had high acid extractable Se levels, which would only percolate during any acid leaching process. Organic bound Se was found to accumulate at the surface. A mixed distribution of Se⁺⁴ and Se⁺⁶ in this fraction suggested the contribution of both species to Se contamination during the mineralization of organic matter. Siliceous Se could be mobilized through a long process of weathering, and from this fraction also both Se⁺⁴ and Se⁺⁶ would contribute to Se movement. The overall findings indicated that Se⁺⁶ is of greater concern to ground water contamination; however, depending on soil conditions, both Se⁺⁴ and Se⁺⁶ species might be mobilized from different Se sources.

The general results of this study suggested that partial fractionation and speciation techniques could be used as important tools in predicting the geochemical mobilization and subsequent fate of Se towards ground water contamination. However, we recommend that similar studies in different aqueous environments should be conducted in order to obtain a better understanding of the aquatic chemistry of selenium.

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