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Transformations of volatile methylated selenium in soil

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Abstract

Microbial volatilization of selenium as dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) from soil is an important part of the Se cycle in nature, but little is known about the stability and transformations of these gases during residence in the soil environment before dissipation to the atmosphere. Experiments monitored by gas chromatography and atomic absorption spectroscopy were made with various clay mineral standards, charcoal, commercial humic substances and soils to determine the sorption and transformations of DMSe and DMDSe injected into the headspace or passed through soil materials. Batch experiments conducted with 2–5 g materials placed into 40 mL Teflon centrifuge tubes equipped with Mininert® gas sampling valves showed that DMSe was slowly sorbed by soil materials and most of the DMSe deficit in the headspace was recovered as $SeO_3^=$ and $SeO_4^=$. In contrast, DMDSe was rapidly partitioned from the gas phase and resulted in an increased recovery of less soluble elemental and selenide-Se forms. These results were confirmed during flow-through soil column studies with both little DMSe sorption and sorption of the majority of DMDSe addition. Additions of selenomethionine (SeMet) to soil to produce DMSe and DMDSe in sealed flasks resulted in an increased partitioning of Se into inorganic Se when compared with a flow-through system designed to limit the contact of Se gases with soil. These results suggest that soil Se volatilization as DMSe and DMDSe results in Se loss to the atmosphere as DMSe with concomitant soil Se immobilization due to the instability of DMDSe.

Keywords: Methylated selenium volatiles; Soil transformations of Se

1. Introduction

Challenger and North (1934) first reported that fungal cultures were able to methylate inorganic Se resulting in dimethylselenide (DMSe). Additional research has shown that bacteria (Francis et al., 1974; Doran and Alexander, 1977), soil microbes (Karlson and Frankenberger, 1988; Frankenberger and Karlson, 1989), microbes in sewage sludges (Reamer and Zoller, 1980) and plants (Lewis et al., 1966) also are capable of methylating Se resulting in DMSe and DMDSe. This research has shown that methylation reactions are important in the natural cycling of Se into the atmosphere from natural and anthropogenic sources, but little is known concerning the environmental fate of the methylated Se species (Mackenzie et al., 1979).

Irrigation practice in the west side of the San Joaquin Valley of California has resulted in salinity, drainage and trace element problems (Tanji et al., 1986). At Kesterson National Wildlife Refuge, Se accumulated to hazardous concentrations for wildlife in the Kesterson Reservoir as a consequence of the disposal of marginal quality drainage waters contaminated with Se. Kesterson Reservoir was isolated from further inputs of Se, but 23 evaporation pond facilities, with a total surface area of 2860 ha operated in the San Joaquin Valley (Tanji et al., 1992). Today, 10 ponds are still active with a surface area of 1900 ha (Tanji, personnel communication). Volatilization of Se through microbial activity has been suggested as a possible method to dissipate Se that contaminates soils and irrigation drainage waters (Frankenberger and Karlson, 1989; Gao and Tanji, 1995).

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Table 1
Properties of soils used

Soils	Sub group	pH[a]	g kg^{-1} Total C[b]	Sand	Clay
Traver 1	Natric haploxeralf	8.1	7.6	449	159
Traver 2	Natric haploxeralf	8.4	3.5	407	170
Twisselman 1	Typic torriorthents	8.1	1.8	274	459
Twisselman 2	Typic torriorthents	8.0	5.3	334	178
Mojave	Typic haplargids	8.1	0.9	869	56
Willows	Typic pelloxererts	8.3	18.5	104	398
Panoche	Typic haplargid	8.1	5.6	360	320
Panhill	Typic torriorthent	7.9	5.8	320	460

[a] The pH values were determined on a 1:2.5 soil to water ratio.
[b] Total carbon content was determined by Coulometric analysis.

Gao and Tanji (1995) documented two major processes that affect the volatilization of Se from contaminated soils or sediments. The two steps are first, the formation of DMSe and other volatile species of Se and second, the volatilization of Se through the air–water interface. Karlson et al. (1994) determined the Henry's Law constant for DMSe as 0.058 indicating that at equilibration, the DMSe concentration in the water interface is about 17 times greater than the concentration in air. This partitioning points out a possible third step involved in Se volatilization as a remediation method, which would be microbial utilization of the DMSe in solution before volatilization. Doran and Alexander (1977) isolated bacterial species from soil that could utilize DMSe and DMDSe as sole carbon sources, but did not report the formation of Se products from DMSe and DMDSe mineralization. Zieve and Peterson (1985) utilizing a ^{75}Se labeled volatile, generated from the metabolism of inorganic sodium ^{75}Se selenite by *Candida humicola*, reported that sorption of volatile ^{75}Se by soils was related to organic matter content (90–290 g organic matter g soil^{-1}) or addition of montmorillonite. A chemical Se fractionation after a 30-d exposure showed significant differences in solubility of sorbed ^{75}Se among the three soils investigated. Martens and Suarez (1997a) reported that two California soils amended with selenomethionine (SeMet) and incubated in a static soil environment rapidly volatilized both DMSe and DMDSe. The generated gases first increased in concentration in the headspace and then decreased with time, suggesting that soils can sorb both Se gases, with DMDSe adsorption occurring at a much faster rate than DMSe. The very low vapor pressure of DMDSe (0.38 kPa, 25°C) compared to DMSe (32.03 kPa, 25°C) may account for the faster adsorption rate and may limit the contribution of DMDSe to the vapor phase (Chasteen, 1998).

Our study was initiated to determine the extent of DMSe and DMDSe sorption in a range of soils and soil minerals and to determine the species of Se resulting from adsorption.

2. Materials and methods

2.1. Materials

The soils listed in Table 1 were obtained from various parts of California. Soil pH was determined on a 2.5:1, water to soil ratio, total C content was determined by dry combustion with a Coulometric C analyzer (UIC, Inc., Joliet, IL, USA), and texture by the hydrometer method of Gee and Bauder (1986). The clay minerals were used as obtained from the Source Clay Mineral Repository, University of Missouri (Wyoming montmorillonite SWY-1, Silver Hill illite IMT-1) and Ward's Clay Mineral Standard's Collection (kaolinite No. 5) after passing through a 100 μm diameter sieve.

A standard solution of DMSe was obtained from Strem Chemical Co. (Newburyport, MA), and DMDSe was obtained from Aldrich (Aldrich Chemical Co. St Louis, MO). The coconut charcoal was obtained from Fisher (Pittsburgh, PA) and the humic substance was purchased from Aldrich.

2.2. Instrumentation

Selenium analysis was performed by hydride generation atomic absorption spectroscopy (HGAAS) using a Perkin Elmer 3030B spectrophotometer (Perkin–Elmer Corp., Norwalk, CT) equipped with a Varian Model VGA-76 (Varian Associates, Mulgrave, Victoria, Australia) vapor generation apparatus. An Se electrodeless discharge lamp (Perkin–Elmer) operated at 6 W was used as the radiation source. The operational conditions were as follows: acetylene flow, 2.4 l min^{-1}; air flow, 6.0 l min^{-1}; purge gas flow, argon, 90 ml min^{-1}; sample flow, 1.0 ml min^{-1}; 6 M HCl flow, 1.0 ml min^{-1}; reagent flow, 0.6% $NaBH_4$–0.5% NaOH, 330 μl min^{-1}; wavelength, 196 nm; and slit width, 2.0 nm. Quality assurance procedures for Se analysis by HGAAS were employed as follows: duplicate samples were analyzed with calibration, reagent blanks, and NIST Se standard reference material 3149 (National Institute of Standards and Technology, Gaithersburg, MD) spikes (20 ng Se ml^{-1}) to check for interferences at the beginning and end of each HGAAS run. Acceptable data quality objectives were as follows: spikes, 90–103% recovery; precision, 10%; detection limit, 200 μg kg^{-1}.

The Se gas composition of the soil headspace was analyzed on a Varian 3700 g.c. equipped with a DB-5 capillary column (J.W. Scientific, Folsom, CA) with a

Table 2
Speciation of soil selenium resulting from DMSe injected into the headspace of different soils and materials after incubation for 10 days 25°C[a]

Soil/material	μg Se recovered						
	Phosphate buffer			Headspace			
	SeO_3	SeO_4	Se-II	$K_2S_2O_8$	HNO_3	Se[b]	Sum
Traver 1	3.35	0.85	1.35	2.70	2.45	3.90	14.60 (2.35)
Traver 2	1.00	1.15	0.00	0.05	0.00	13.25	15.45 (1.56)
Twisselman 1	5.45	3.00	1.05	0.80	0.50	4.80	15.00 (1.25)
Twisselman 2	2.00	2.75	0.05	0.20	0.50	6.50	13.00 (3.14)
Mojave	3.90	2.00	1.20	0.00	0.00	8.30	15.30 (0.95)
Willows	3.40	1.95	1.30	0.00	0.35	8.00	15.00 (1.35)
Panoche	1.55	1.50	0.40	2.25	0.85	9.10	15.65 (0.88)
Panhill	2.10	1.75	0.30	0.45	0.45	8.24	13.29 (1.89)
Montmorillonite	0.00	0.00	3.25	0.00	0.00	12.15	15.40 (1.25)
Kaolinite	0.00	0.00	2.60	0.00	0.00	13.35	15.95 (0.35)
Illite	0.00	0.00	2.00	0.00	0.00	13.55	15.55 (0.28)
Humic acid[c]	0.00	0.00	0.00	0.00	0.00	0.0	14.30 (1.25)
Charcoal[c]	0.00	0.00	0.00	0.00	0.00	0.0	15.30 (0.56)

[a] Soils and materials were incubated in 40 ml Teflon Oak Ridge centrifuge tubes equipped with a Mininert valve for introduction of 15.75 μg DMSe–Se and subsequent gas sampling. Value in parentheses indicate standard deviation of the mean.
[b] Reported as DMSe–Se.
[c] Selenium sorbed was recovered in methanol wash of material as determined by HGAAS.

250 μm inner diameter, 25 nm film thickness, and a 30-m length. The operational conditions were as follows: f.i.d., 115°C; column temperature, 60°C; injector, 80°C; carrier gas (He) 1.0 ml min^{-1}; make up gas 30 ml min^{-1}; H_2, 30 ml min^{-1}; air, 300 ml min^{-1}. Peak areas and retention times were determined with a Hewlett–Packard 3396 recording integrator.

2.3. Procedures

Sorption of Se gases was determined by injection of a known concentration of DMSe (170 n*M*) and DMDSe (75 n*M*) [with a 1-mL gas-tight series 2 Pressure-Lok gas syringe (Alltech Associates, Deerfield, IL)] into the headspace of duplicate 40-mL Teflon centrifuge tubes equipped with Mininert® gas sampling valves containing 5 g of soil (oven-dry basis) or 2 g of charcoal, humic substance or clay minerals (see Table 2). Soil water was allowed to equilibrate at 34 kPa moisture tension before gas addition. At the specified times, 100 μl air samples were removed from the tubes and injected into the g.c. for analysis. The experiments were ended on day 1 (DMDSe) and day 10 (DMSe) and the soil or soil material was extracted using the Se speciation procedure of Martens and Suarez (1997b). Briefly, the soils were extracted with 25 ml (pH 7.0) 100 m*M* KH_2PO_4–K_2HPO_4 (P-buffer) and shaken for 1 h on a horizontal shaker (120 oscillations min^{-1}). The sample was then centrifuged for 20 min at 10,000 *g* and the supernatant decanted. After the P-buffer extraction, the soils were extracted with 100 m*M* $K_2S_2O_8$ (90°C) for 2 h, centrifuged for 20 min at 10,000 *g* and the supernatant collected for analysis. In addition, the P-buffer and persulfate extracted samples were treated with 2.5 ml 17 M HNO_3 for 0.5 h (90°C) then diluted with 20 ml water and heated for an additional 1.5 h, centrifuged (20 min; 10,000 *g*) and the supernatant collected for analysis. The P-buffer selectively removed soluble selenate (Se + VI), ligand-exchangeable selenite (Se + IV) and organic selenide (Se-II), the $K_2S_2O_8$ extraction removed tightly-held Se + IV and Se-II and the nitric acid extractions released insoluble elemental Se (Se°) fractions, respectively (Martens and Suarez, 1997b). Non-decomposed, sorbed DMSe and DMDSe-Se (Se-II) would be accounted for by the P-buffer extraction.

To determine the sorption of the Se gases, DMSe and DMDSe, as they passed through the soil, glass tubes (2.5 cm I.D.) were fitted with a single hole rubber stopper at the bottom and connected by glass to a 250-mL Erlenmeyer flask. Two-5 g samples of soil at 34 kPa moisture potential were placed in duplicate glass tubes, separated by a Whatman no. 42 hardened ashless filter paper and each layer packed to a bulk density of 1.34 g cm^{-3}. The top of the glass tube (15 cm height) was fitted with a rubber stopper connected to a charcoal trap for collection of Se gas that passed through the two layers of soil. Exposed glass, tubing and rubber surfaces were treated with Fluoroglide™ Teflon spray (Aldrich) to limit surface exposure of added gases. A purified air supply was attached to the Erlenmeyer flask and the Se gas (13 μg DMSe-Se; 8 μg DMDSe-Se) was introduced into the air stream (flow rates of 10 ml air min^{-1}) just as it entered the Erlenmeyer flask to dilute the Se gas for passage through the soil. After 6 h, the charcoal cartridge was removed, stored at −20°C, and replaced with a new cartridge for the remaining incubation period. At day 7, both charcoal cartridges were emptied into 40 ml centrifuge tubes and the Se extracted with 10 ml of a H_2O_2–HNO_3 solution (80 ml 30% H_2O_2 l^{-1}; 58.8 ml 17 M HNO_3 l^{-1}) incubated at room temperature for 1 h. The samples were then centrifuged (10,000 *g*; 20 min), the supernatant removed, and subsequently analyzed by HGAAS after 6 M HCl reduction.

To evaluate the sorption of Se gases released by natural processes in soils, duplicate 5 g samples of the Panoche soil were incubated (34 kPa moisture potential) in 125 ml screw top Erlenmeyers after treatment with SeMet (10.4 μg SeMet-Se g^{-1} soil) and incubated for 7 days at 25°C in two systems. The first system

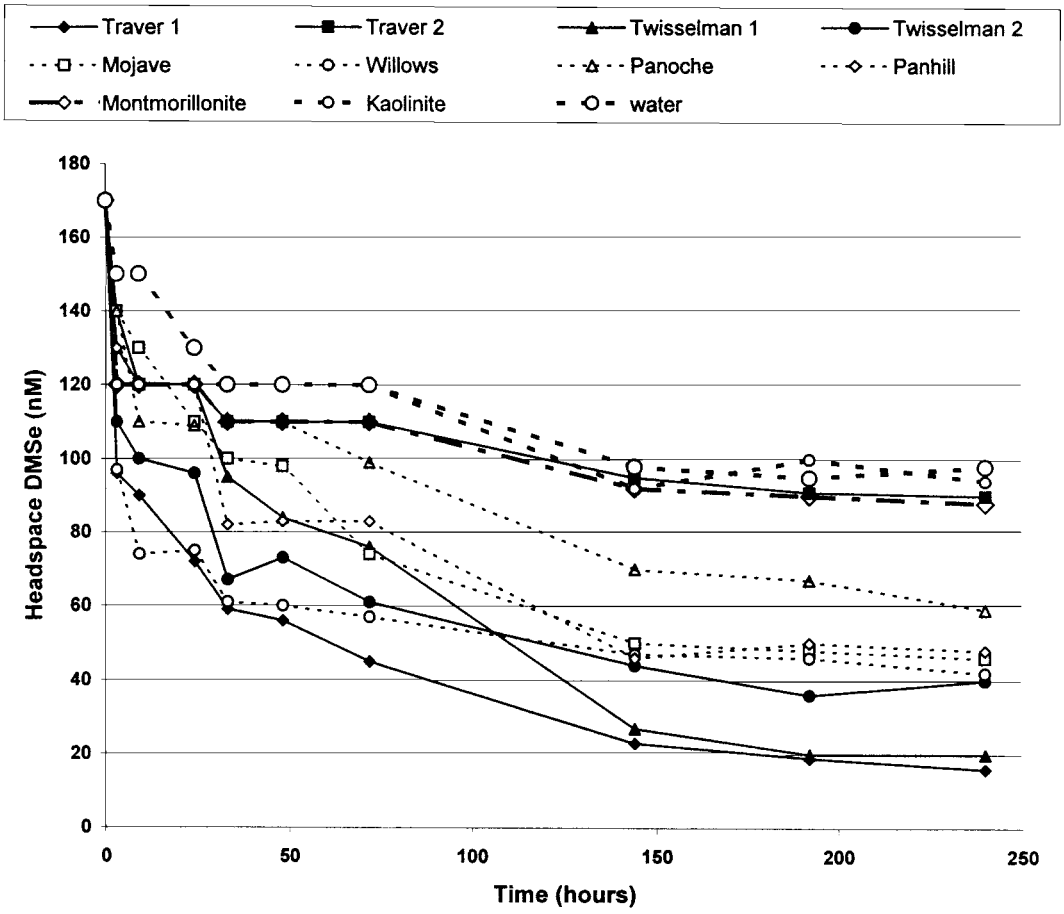

Fig. 1. Concentration of DMSe remaining in headspace above soils and clay minerals incubated for 10 days (25°C) after injection of 170 n*M* DMSe.

was a static system equipped with a Mininert valve for gas sampling and gas chromatographic analysis and the second system was a flow-through system with purified air (10 ml min^{-1}) to limit the contact of the Se gases with the soil. The Se gases generated in the flow-through system were captured on a charcoal trap and Se captured was analyzed as previously noted.

3. Results and discussion

The soils we used were chosen to include pairs of soils that were taxonomically similar except for their physical properties (Table 1). Zieve and Peterson (1985) reported Se gas sorption with soils, that ranged from 90 to 290 g organic matter kg^{-1} soil, was related to organic matter content. In general, agricultural soils and especially California soils do not approach this amount of organic matter content. The soils we chose reflect physical conditions typical in California agricultural soils that may be exposed to volatile Se.

Addition of DMSe to the headspace of the soils and clay minerals resulted in an initial rapid decrease in DMSe concentration in the headspace during the first 3 h due to sorption and then a slower decrease over the remaining time of the experiment due to possible mineralization of sorbed DMSe (Fig. 1). Zieve and Peterson (1985) concluded from the use of irradiated soils that soil microorganisms did not affect the initial sorption of Se gas, but may increase long-term sorption through mineralization. After 10 d, most of the Se not remaining as headspace DMSe was found in the phosphate-soluble Se pool suggesting microbial oxidation to Se+IV and+VI (Table 2). With the exception of the Traver 1 (52%) and the Panoche (53%) soils, 74–100% of the Se speciated in the soils after incubation of added DMSe for 10 days was found as phosphate-soluble Se. Traver 1 and Twisselman 1 and 2 soils showed the largest decrease in headspace DMSe concentration and highest formation of inorganic Se (Table 2). Wang and Burau (1995) reported abiotic oxidation of DMSe by MnO_2 via a two electron change to dimethylselenoxide (Se°). Oxidation of DMSe to Se+VI and+IV as reported here, requires cleavage of the Se-C bond, while oxidation to dimethylselenoxide would not (Wang and Burau,

Table 3
Speciation of soil selenium resulting from DMDSe injected into headspace of different soils and materials after incubation for 24 h at 25°C[a]

Soil/material	µg Se recovered						
	Phosphate buffer			Headspace			
	SeO_3	SeO_4	Se-II	$K_2S_2O_8$	HNO_3	Se[b]	Sum
Traver 1	0.75	0.65	0.31	7.38	2.73	0.00	11.82 (2.85)
Traver 2	0.46	0.52	0.00	6.21	1.25	4.16	12.60 (1.67)
Twisselman 1	0.36	0.70	0.00	4.32	0.82	6.40	12.60 (1.56)
Twisselman 2	0.64	1.54	0.97	8.57	1.98	0.00	13.00 (0.56)
Mojave	0.00	0.86	0.00	4.39	0.18	7.17	12.60 (1.23)
Willows	0.89	2.37	0.05	7.54	2.14	0.00	12.95 (0.85)
Panoche	0.45	0.96	0.44	8.46	2.11	0.00	12.42 (1.12)
Panhill	0.87	1.57	0.67	4.32	1.56	3.06	12.05 (1.25)
Montmorillonite	0.25	4.35	0.12	6.32	1.32	0.00	12.36 (1.35)
Kaolinite	0.12	3.23	0.52	8.23	0.12	0.00	12.22 (1.56)
Illite	0.38	5.12	0.00	7.37	0.41	0.00	13.28 (0.25)
Humic acid[c]	0.00	0.00	0.00	0.00	0.00	0.00	12.86 (0.98)
Charcoal[c]	0.00	0.00	0.00	0.00	0.00	0.00	13.06 (0.35)

[a] Soils were incubated in 40 ml Teflon Oak Ridge centrifuge tubes equipped with a Mininert valve for introduction of 13.20 µg DMDSe–Se and subsequent gas sampling. Value in parentheses indicate standard deviation of the mean.
[b] Reported as DMDSe–Se.
[c] Selenium sorbed was recovered in methanol wash of material as determined by HGAAS.

1995), suggesting microbial activity is the major factor involved in the decomposition of sorbed DMSe. The remaining soils and clay minerals sorbed smaller amounts of the added DMSe. Rapid sorption of DMSe additions to commercial humic substances (< 36 h) or charcoal (< 5 min) was recovered as DMSe by use of a methanol wash indicating there was no microbial mineralization during the 7 day incubation. Karlson and Frankenberger (1988) reported that DMSe was rapidly sorbed to charcoal and could be quantitatively recovered by use of a methanol wash. In our experiments, there was no statistical relationship between soil carbon content ($r = 0.013$; $n = 8$) and clay content ($r = 0.03$; $n = 8$) and n*M* DMSe sorbed. Zieve and Peterson (1985) reported that Se gas was rapidly sorbed in the three soils with high amounts of organic matter (90 to 290 g kg^{-1}). Our results confirm that humic materials and charcoal with high amounts of carbon rapidly sorbed Se gases, and suggest that very high amounts of carbon present in certain soils or sediments could act as a sink for DMSe. However, with the low organic matter content of most California soils, DMSe partitioning would follow Henry's Law and subsequent DMSe mineralization.

In contrast to the relatively slow sorption of DMSe (CH_3–Se–CH_3), addition of DMDSe (CH_3–Se–Se–CH_3) to the headspace of the same soils resulted in a

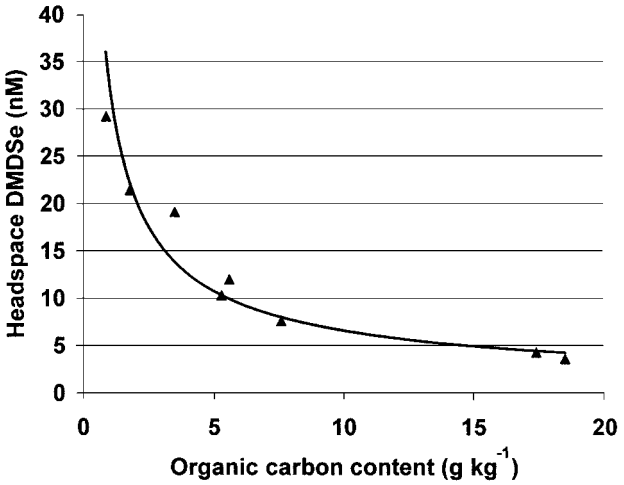

Fig. 2. Relationship between headspace DMDSe concentrations and organic carbon content of the soils and illite clay mineral tested after 6 h incubation (25°C) after injection of 75 n*M* DMDSe.

rapid decrease in headspace DMDSe concentrations and recovery of sorbed Se as less soluble forms of Se (Table 3). A first-order relationship between headspace DMDSe concentration measured after 6 h of incubation and the organic C content of the soils and illite tested indicates the importance of organic matter for sorption of DMDSe (Fig. 2). In contrast to DMSe addition, less than 25% of the sorbed DMDSe-Se was recovered as phosphate-soluble Se, with most found as tightly-held selenite, selenide and elemental Se. It was noted that the specimen clay minerals tested sorbed little of the DMSe gas, but were very reactive sorbing DMDSe (Tables 2 and 3). There was, however, no statistical relationship between soil clay content and n*M* DMDSe sorbed after 5 min ($r = 0.21$; $n = 8$) and 6 h ($r = -0.05$; $n = 8$) incubation. Martens and Suarez (1997a) reported that the diselenide bridge of selenocystine (Se-II) was unstable in aqueous solutions with formation of red elemental Se°. Selenocystine was also found to be very unstable when applied to soils with most of the Se recovered as non-selenocystine organic selenide (Se-II) and elemental Se° when incubated for time as short as 6 h (Martens and Suarez, 1997a). The lack of microbial oxidation of sorbed DMSe by clay minerals in the previous study and the results of Martens and Suarez (1997a), suggests that the instability of sorbed DMDSe, not microbial decomposition, is the major factor partitioning DMDSe-Se in soils and clay minerals.

Zieve and Peterson (1985) reported that soil organic matter and montmorillonite were effective for sorbing biologically-produced Se gas. They did not analyze the Se gas composition produced by *C. humicola*, but assumed the volatile gas was (^{75}Se)DMSe. Our results suggest that the biological ^{75}Se gas produced in the

Table 4
Recovery of DMSe (13 μg Se) and DMDSe (8 μg Se) as soil Se or volatile Se after passing Se gas through soil layers, B, bottom closest to gas entrance and T, top layer and incubating for 7 days 25°C

Soil	μg Se recovered							
	Phosphate buffer			Volatile Se[a]				
	SeO_3	SeO_4	Se-II	$K_2S_2O_8$	HNO_3	6 h	7 d	Sum
DMSe								
Traver 1 B	0.94	0.42	0.36	0.51	0.91	6.22	0.76	13.24 (1.05)
Traver 1 T	1.00	0.33	0.20	0.59	1.00			
Traver 2 B	0.17	0.13	0.34	0.22	0.48	8.09	0.88	12.42 (1.56)
Traver 2 T	0.52	0.23	0.00	0.09	0.46			
Panoche B	0.25	0.05	0.21	1.37	0.69	7.05	1.06	12.77 (0.85)
Panoche T	0.18	0.07	0.22	0.75	0.87			
Panhill B	0.58	0.43	0.18	0.00	0.79	8.60	1.05	12.86 (0.56)
Panhill T	0.23	0.64	0.05	0.00	0.31			
DMDSe								
Traver 1 B	0.15	0.15	0.37	1.79	1.97	1.31	0.66	7.97 (0.35)
Traver 1 T	0.08	0.09	0.3	0.78	0.22			
Traver 2 B	0.00	0.10	0.13	2.31	1.28	1.43	1.09	8.03 (0.45)
Traver 2 T	0.00	0.09	0.11	0.28	1.21			
Panoche B	0.09	0.11	0.53	3.16	1.21	0.84	1.17	7.30 (1.07)
Panoche T	0.00	0.00	0.00	0.19	0.00			
Panhill B	0.20	0.13	0.47	1.94	0.78	1.55	1.32	8.13 (0.23)
Panhill T	0.08	0.17	0.30	1.10	0.09			

[a] Recovery of Se gas during 6 h gas addition before incubation and recovery of Se gas after the 7 day incubation. Value in parentheses indicate standard deviation of the mean.

work of Zieve and Peterson (1985) included DMDSe as well as DMSe.

Most of Se volatilized from soils is expected to originate from the biologically-active top 4 or 5 cm of soil. If Se volatilization is to be considered as a remediation pathway, DMSe and DMDSe must volatilize from depths deeper than just the soil surface. Table 4 shows that most of the DMSe passed through the two layers of soil (3 cm soil depth) and was trapped by the charcoal at the outlet. The results show that if DMSe was sorbed, the DMSe-Se would be mineralized during the 7 day experiment. Extracted Se ranged from 26% in the Panhill soil to 47% in the Traver 1 soil indicating that a significant portion of the sorbed Se was mineralized by the microorganisms as DMSe passed through the soil matrix.

In contrast to the results with DMSe, the majority of DMDSe in contact with the soil was not captured on the charcoal trap, but was sorbed by the first layer of soil (44 to 64% of DMDSe-Se added) and determined as insoluble forms of Se (Table 4). The findings that little oxidized Se was measured and the short duration (24 h) of the experiments suggests that microbial mineralization was not a dominant factor in DMDSe sorption. This rapid sorption and instability of DMDSe may help explain why researchers have noted

Table 5
Speciation of soil Se after treatment of a Panoche soil with 129.5 μg SeMet and incubation for 7 days 25°C as a static or with an airflow system[a]

Se species	μg Se recovered	
	Static	Airflow
P-buffer extract		
Selenite	4.15 (0.37)	2.47 (0.79)
Selenate	8.45 (1.35)	3.87 (1.56)
Selenide	10.25 (4.19)	3.03 (0.59)
$K_2S_2O_8$ extract	30.51 (2.80)	16.92 (0.44)
HNO_3 extract	11.68 (2.40)	5.25 (0.44)
Volatile Se[b]	62.30 (5.32)	95.47 (3.69)
Total Se	127.34	127.01

[a] The values in parentheses indicate standard deviation of the mean.

[b] Volatile Se was measured by gas chromatographic analysis of the headspace in the static system and volatile Se was measured in the airflow system by use of charcoal traps and HGAAS analysis.

that DMSe is the prominent volatile species noted in soil incubations (Doran and Alexander, 1977; Karlson and Frankenberger, 1988) and environmental water samples (Cooke and Bruland, 1987).

Martens and Suarez (1997a) reported that low concentrations of inorganic Se were detected in the Panoche and Panhill soils during incubation of SeMet–Se. The origin of the inorganic Se, either from mineralization of SeMet–Se or from sorption and mineralization of the released Se gases, could not be determined. The results from these experiments suggest that the measured inorganic forms of Se originated from the adsorption and mineralization of the volatilized Se gases.

If the inorganic Se measured during the incubation of SeMet (Martens and Suarez, 1997a) was due to Se gas sorption, then incubation of soil treated with SeMet in a static environment that increased contact of the Se gases with the soil would result in a larger proportion of inorganic Se forms than SeMet amended soils incubated in a flow-through environment that limits the residence time of the Se gases in the soil. Selenium speciation as a result of this experiment with the Panoche soil is shown in Table 5. Incubation of SeMet in a system designed to minimize contact of the Se gases with the soil resulted in a 40% decrease in phosphate-soluble Se, a 45% decrease in persulfate-extractable Se and a 55% decrease in nitric acid-extractable Se, when compared to the static system. The flow-through system resulted in a 35% increase in volatilized Se compared to the Se concentrations from the static system. The results show that even with a flow-through system designed to minimize the residence time of Se gases released from SeMet mineralization, 25% of the SeMet–Se remained in the soil. The

static incubation system resulted 51% of the SeMet–Se remaining in the soil. The concentration of Se in the persulfate and nitric extracts compared to the total soil Se remaining was 65% for the static system and 70% for the flow-through system suggesting that most of the Se recovered in the two systems was due to the instability of DMDSe.

Our results indicate that although both DMSe and DMDSe may be volatilized under field conditions, most of the Se gas reaching the atmosphere will be DMSe. Even employing conditions to maximize volatilization of Se as a remediation technique, such as weekly tilling of soil for aeration, addition of carbon sources and optimum moisture for microbial volatilization, the instability of DMDSe will result in a portion of volatilized Se being sorbed by the soil.

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