Chapter 23

Soil Methylation–Demethylation Pathways for Metabolism of Plant-Derived Selenoamino Acids

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There is conflicting field information about Se toxicity in waterfowl and fish, based on criteria of total Se concentration. At least part of this uncertainty is due to the difference in toxicity associated with various Se species. There is toxicity data on the selenoamino acid, selenomethionine (SeMet) to avian species, but little is known on the environmental transformations of SeMet and the possible intermediates of organic Se decomposition. To determine the potential decomposition of Se amino acids, methylation and demethylation pathway intermediates for the transformations of sulfur (S) amino acids, identified from aerobic marine sediments were compared to potential analog Se intermediates synthesized for this study. Two terrestrial soils with apparently different pathways for metabolizing SeMet were treated with 25 μg S intermediate-S g^{-1} soil and the soil headspace analyzed for the methylation pathway gas dimethylsulfide (DMS) or the demethylation pathway gas dimethyldisulfide (DMDS). Addition of S-methyl-methionine (MMet), and dimethylsulfoniopropionic acid (DMSP) to the Panhill and Panoche soils resulted in only DMS evolution; addition of 3-methiopropionic acid (MTP) resulted in DMDS in the soils

and 3-mercaptopropionic acid (MCP) addition was not volatized confirming that terrestrial soil S pathways are similar to documented marine pathways. The Panhill soil evolved only DMDS as a result of the methionine (Met) demethylation pathway and the Panoche soil evolved only DMS from the methylation of Met. The evolution of Se gases dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) from addition of SeMet, methyl-selenomethionine (MSeMet), dimethylselenopropionic acid (DMSeP) followed the same pattern as noted with the S products. DMSe evolved from a methylation pathway and DMDSe evolved from a demethylation metabolism. Selenocystine (SeCys) and a methylated selenocysteine (MSeCys) added to the two soils showed limited volatilization as DMSe. A large portion of the Se not volatilized from soil was found as a non amino acid organic selenide compound(s) and these unidentified intermediate compounds may be present in significant concentrations in some environments. The different metabolic pathways of Se in soils may explain why in certain waterfowl areas Se-induced problems have not been found where predicted based on total Se concentrations.

The geologic setting and climate of the west-central San Joaquin Valley of California has resulted in soil salinization of land used for agriculture. Agricultural engineering solutions to decrease naturally occurring salinity have in turn created problems with respect to disposal of the highly saline irrigation drainage waters. A major problem with disposal of return waters from the west-central San Joaquin Valley of California is the inadvertent cycling and concentration of Se in evaporation pond sediments. As plants and organisms in the evaporation ponds assimilated the dominant inorganic Se forms, selenate (Se+6) and selenite (Se+4) present in the waters into organic Se forms, the death and decomposition of the biomass released organic forms of Se back into the environment. Although the Se uptake by plants is competitively inhibited by the presence of sulfate this appears not to be the case for aquatic organisms (*1*).

Selenium toxicity results from the alteration of the three-dimensional structure of proteins and the impairment of enzymatic function by substitution of Se for sulfur (S) in S-amino acids (*2*). Of the naturally occurring Se compounds tested for toxicity, the S amino acid analog SeMet was the most toxic to

waterfowl (*3*). The formation of the toxic Se-amino acids in nature can be from plant or microbial sources, but the synthesis of SeMet by soil microorganisms has been reported to be low (*4*) and many plant species have been found to assimilate large amounts of inorganic Se into Se-amino acid analogs Met and cysteine (Cys)(*5*).

There is a similarity between the biogeochemistry of organic S compounds such as Met and cysteine and the Se analogs SeMet and SeCys (*6*). Both Met and SeMet decomposition in soil result in volatilization of the methylated compounds dimethylsulfide (DMS) and dimethylselenide (DMSe), respectively. The S cycle has received much attention because DMS accounts for nearly 50% of the global biogenic S entering the atmosphere and influences climate by promoting cloud formation (*7*). In the S cycle, Met is oxidized by several pathways resulting in DMS (methylation) or dimethyldisulfide (demethylation), promoted by both anaerobic and aerobic organisms (*8*). The vast majority of the S work has involved marine sediments with a very limited research effort occurring in terrestrial soils. Martens and Suarez (*6*) reported the occurrence of Se methylation and demethylation pathways in two terrestrial soils treated with Met and SeMet. The methylation pathway resulted in the majority of Se being evolved as DMSe and the demethylation pathway evolved DMDSe and resulted in the accumulation of an unidentified nonamino acid organic Se compound. They also detected MSeMet and DMSeP by hydroelimination analysis (*9*) as possible intermediates in the soil exhibiting the methylation pathway. Reamer and Zoller (*10*) speculated that different microorganisms are responsible for the formation of each volatile Se species and that shifts in volatile species composition may be due to the differing tolerances of microorganisms to environmental stress. Despite the intensive research efforts on Se cycling, little is known about the resulting speciation of Se with mineralization of organic Se compounds and no information is available for determining the importance of the different decomposition pathways for organic S and Se present in terrestrial soils.

Predicting Se-induced problems in waterfowl based only on Se concentration in the receiving waters and waterfowl have not proved to be a consistent for identifying areas likely to have Se problems (*11*). This study was conducted to determine the decomposition of S and Se pathway intermediates in soil and evolution of volatile S and Se species indicative of the metabolizing pathways. Speciation of nonvolatilized Se, following soil incubation with the Se pathways intermediates was also determined because the activity of methylation or demethylation pathways in soil may influence the accumulation of organic Se compounds.

Materials and Methods

Reagents and Standards

A description of the properties of the Panhill and Panoche soils used in this study was given by Martens and Suarez (*6*). The Met, SeMet, S-methyl-methionine (MMet), 3-mercaptopropionic acid (MPA), 3-bromopropionic acid and selenocystine (SeCys) were obtained from Sigma Chemical Company (St. Louis, MO); 3-methiolpropionic acid (MTP) was obtained by alkaline hydrolysis (*6*) of methyl-3-(methiol)propionic acid (Aldrich Chemical Company, Milwaukee, WI); dimethylsulfoniopropionic acid (DMSP) was obtained from Research Plus, Inc. (Bayonne, NJ) and dimethyl selenide (DMSe) was obtained from Strem Chemicals, Inc. (Newburyport, MA).

Synthesis of DMSeP, MSeMet, and Methylselenocysteine (MSeCys)

Dimethylselenopropionate was synthesized as proposed for synthesis of DMSP by Challenger and Simpson (*12*). Equimolar quantities (neat) of 3-bromopropionic acid and dimethyl selenide were refluxed together at 55°C for 6 h. The resulting gelatinous mass was thoroughly washed with successive 5 mL aliquots of ethyl ether to remove the unreacted substrates and then solubilized over night in absolute alcohol. A white precipitate remaining was separated from the ethanol, rinsed with ether, then alcohol and dried over sulfuric acid. This material was found to be the trimethylselenonium ion ($TMSe^+$) by C and Se content analysis. The remaining ethanol material was concentrated and washed with ethyl ether and separated from the formed white precipitate until no further white precipitation ($TMSe^+$) was noted with ether addition. The DMSeP was a viscous liquid, not a granular solid as reported for DMSP synthesis, dried over sulfuric acid and the stored at -25°C in a desiccator.

Methylselenomethionine was synthesized by the method proposed by Toennies and Kolb (*13*) for synthesis of MMet. Selenomethionine (0.1961 g) was mixed with 1.7 mL formic acid, 0.5 mL acetic acid, 0.3 mL deionized water, and 0.56 methyl iodide (Sigma Chemical Co.), and incubated in a Teflon stoppered round bottom flask for 5 days in the dark at ambient temperatures (22°C). The mixture was then reduced to one-fourth volume under reduced pressure and 10 mL of methanol was added. The resulting white precipitate was washed with methanol, dissolved in a minimum of 50% ethanol, and crystallized

with addition of 50 mL ethanol. The MSeMet was dried over sulfuric acid, weighed and stored at -25°C in a desiccator.

The method of Foster and Ganther (*14*) was used to synthesize MSeCys. Selenocystine (20.3 mg) was dissolved in 2 mL of 0.1 M NaOH in a round bottom flask under a nitrogen purge and treated with 2.5 mg sodium borohydride and stirred 0.5 h to form selenocysteine. Three additions of 0.2 mL methyl iodide were added over one h with stirring and subsequent acidification to pH 1.5 with 6 M HCl, and the volume reduced under reduced pressure (37°C). The MSeCys was purified by ion-exchange chromatography on SP-Sephadex (Sigma Chemical Co.) by applying the sample in water to a 1.5 x 17.5 cm column equilibrated with 50 mL of 0.05M formic acid, pH 2.5. The column was then washed with 75 mL 0.05M ammonium formate, pH 4.0 and the MSeCys was eluted with 150 mL 0.1M ammonium formate. The sample was lyophilized at ambient temperatures to remove water and then at 30°C to remove the remaining buffer and the MSeCys was dried over sulfuric acid, weighed and stored in a desiccator at -25°C.

Compound identity and purity were confirmed by C and Se content analysis, electron impact and thermospray mass spectrometry, NMR and hydroelimination as described by Fan et al. (*15*).

Aerobic Soil S and Se Pathway

Organic S and Se mineralization experiments were conducted with 5 g of air-dry soil added to duplicate 125 mL screwtop Erlenmeyers equipped with a Mininert™ gas sampling valves and incubated for up to 7 d at –34 kPa moisture tension after addition of specified amount of organic S-S or Se-Se compound flask^{-1}. Volatile Se and S evolution as DMSe, DMS, DMDS or DMDSe was determined by gas chromatography as described by Martens and Suarez (*16*) and measured daily. Selenium speciation following decomposition was determined by sequential extraction as outlined by Martens and Suarez (*16*). Briefly, DI water was used to wash the soil quantitatively into 40 mL Teflon™ centrifuge tubes, shaken and centrifuged to remove water-soluble Se compounds. The samples were then treated with a 0.1 M phosphate buffer (pH 7.0) and centrifuged to determine adsorbed Se, followed by a 0.1 M NaOH extraction for organic Se and tightly-held Se+4. The samples were then extracted with 17 M nitric acid for determination of elemental Se (Se°). Hydride generation atomic absorption spectrometry was conducted with a Perkin Elmer 3030B instrument under conditions given by Martens and Suarez (*16*).

Results and Discussion

Synthesis of DMSeP, MSeMet, and MSeCys

Challenger and Simpson (*12*) reported that the bromide salt of DMSP was a granular white solid, which was confirmed by synthesis in our laboratory. However using the same method for DMSeP resulted in formation of a white $TMSe^+$ precipitate and a very viscous DMSeP liquid. Elemental analysis of the final DMSeP product yielded values in good agreement with theoretical: C content 21.3 measured vs. 22.9% expected, Se content 29.1% measured vs. 30.1% expected. Both $TMSe^+$and DMSeP were highly resistant to hydrolysis by concentrated HNO_3 (16 h; 130°C). Extended (3 h; 130°C) oxidization by H_2O_2 (30%) and potassium persulfate (0.1 M) were necessary for Se analysis.

A theoretical yield of 75% S-methyl methionine was reported by Toennies and Kolb (13) for the outlined synthesis pathway. However we obtained a yield of only 10% for the synthesis of MSeMet using the published S method. The resulting white granular precipitate was resistant to HNO_3 oxidation, but was oxidized by the peroxide and persulfate treatment, which yielded 23.0% Se and 21.7% C, again in good agreement with the theoretical values (23.1% Se and 21.3% C).

A 90% recovery of MSeCys was determined using the method described by Foster and Ganther (*14*). The MSeCys was found to be very hydroscopic and sensitive to elevated temperatures, and following peroxide and persulfate oxidation resulted in 42.2 vs. 43.4% Se; C analysis found 23.9 vs. 26.4% C. The hydroscopic nature of this product may account for the slight deviation from theoretical values.

Decomposition Met and Pathway Intermediates

Table I shows the amount of volatile S and the species evolved from aerobic soils treated with Met, MMet, DMSP, MTP and MCP. A low percentage of the Met added to the Panhill (24% as DMDS) or Panoche (34% as DMS) soil was volatilized during the 4 d incubation suggesting that soil microorganisms initially conserved Met and was not utilized as an energy source. Hadas et al. (*17*) found that ^{14}C-alanine was rapidly assimilated during short-term incubations with increased ^{14}C mineralization only after alanine was no longer present in solution. Martens and Suarez (*6*) reported more extensive volatilization of DMS from Met additions to the Panhill and Panoche and ion chromatography analysis detected very low levels of SO_4 with incubations longer than 10 d. The Panhill soil

evolved exclusively DMDS indicating that the organisms with a demethylation metabolism pathway dominated (Figure 1). Taylor and Gilchrist (*7*) reported that DMDS evolution in aerobic marine sediments was via demethylation of MTP and resulted in methane thiol, which was in turn oxidized to DMDS. Met addition to the Panoche soil resulted in only DMS. Taylor and Gilchrist (*7*) reported that MMet is formed from the methylation of Met before volatilization of DMS occurred. Addition of MMet to the Panhill and Panoche soils resulted in near quantitative DMS evolution suggesting that methylation of Met is the rate limiting step in the volatilization of S from aerobic soils tested (Table I). It is apparent from the results that both soils have the enzyme(s) required to convert MMet to DMS. An isolated soil bacteria using MMet as a C source was found to express the enzyme Met sulfonium lyase, which when purified, converted MMet to DMS (*18*). Dimethylsulfoniopropionic acid also resulted in nearly quantitative evolution of DMS from the Panoche soil, but a limited volatilization of DMS from DMSP additions was noted with the Panhill soil, suggesting organisms using the demethylation pathway do not express enzyme systems for synthesis of MMet or DMSP.

Table I. Cumulative evolution of volatile S species after addition of 25 μg organic compound-S g^{-1} soil to a Panhill and Panoche soil in a sealed screw-top Erlenmeyer for various times.

		Sulfur Species									
Soil	*Time*	*Met*		*MMet*		*DMSP*		*MTP*		*MCP*	
	(h)	*DMS*[a]	*DMD*	*DMS*	*DMD*	*DMS*	*DMD*	*DMS*	*DMD*	*DMS*	*DMD*
		---------- μg S evolved g^{-1} soil ----------									
Panhill	12	0.0	0.0	5.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0
	24	0.0	0.0	10.5	0.0	2.8	0.0	0.0	0.0	0.0	0.0
	48	0.0	2.6	18.6	0.0	4.6	0.0	0.0	3.2	0.0	0.0
	108	0.5	6.0	23.0	0.0	5.0	0.0	0.0	4.8	0.0	0.0
Panoche	12	0.8	0.2	4.3	0.0	4.1	0.0	0.3	0.7	0.0	0.0
	24	1.6	0.3	7.6	0.0	7.8	0.0	0.4	1.2	0.0	0.0
	48	2.6	0.1	15.3	0.0	16.4	0.0	0.4	2.3	0.0	0.0
	108	8.6	0.0	22.0	0.0	23.5	0.0	0.3	4.6	0.0	0.0

[a]DMS, dimethylsulfide; DMD, dimethyldisulfide.

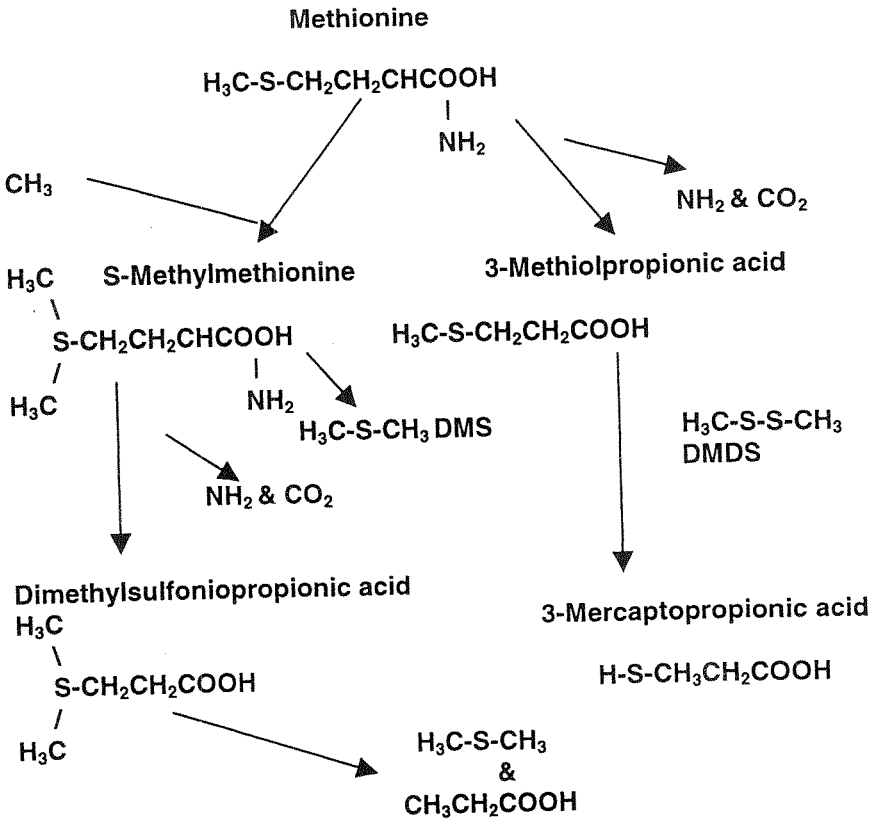

Figure 1. Methylation (MMet) and demethylation (MTP) pathways for Met as suggested by Visscher and Taylor (8).

Decomposition SeMet and Pathway Intermediates

When samples of the Panoche and Panhill soil were steam sterilized (2 h, 120°C, 104 kPa) on two consecutive days and sterilized solutions of S and Se intermediates were added, no volatilization was noted for the tested intermediates for up to four d (data not presented), confirming the biological nature of the two pathways. The speciation results for nonsterile Panoche and Panhill soils incubated with SeMet and SeCys for 2 and 7 d are presented in Table II. Approximately 80% of the SeMet-Se added to the Panoche soil was evolved as DMSe confirming the findings of Martens and Suarez (6). Only 4.6%

of the added Se remained in a Se(-2) state at the end of 7 d, suggesting that the methylation pathway limits accumulation of Se organic compounds in the Panoche soil. In contrast, the Panhill soil evolved about half of the added Se (44%) as a DMDSe volatile form compared to the Panoche soil and the majority of the remaining Se (41.5%) was found as a nonamino acid Se(-2) form (Table II). Martens and Suarez (*6*) first identified the compounds DMSeP and MSeMet by hydroelimination analysis (*9*) in the Panoche soil treated with SeMet indicating that SeMet followed pathways similar to the S methylation pathway identified in marine sediments, but the same Se intermediates were not noted in the Panhill soil. In contrast to the Se volatilization pattern noted for SeMet, after 2 d SeCys-Se incubation, no or low levels of volatile Se were noted and 44% (Panoche) and 28% (Panhill) of the remaining Se was present as nonamino acid Se(-2) as shown by Martens and Suarez (*6*), suggesting that the majority of the Se volatilization from the environment results from the methylation pathways of SeMet. Figure 2 suggests that the failure to identify

Table II. Selenium recovery and speciation after incubation of 50 μg SeMet-Se g^{-1} soil and 25 μg SeCys-Se g^{-1} soil in a Panhill and Panoche soil for various times (average ± standard deviation).

Soil	*Se Form*	*Day*	*Se(+6)*	*Se(+4)*	*Se(-2)*	*Volatile Se*[a]		*Total Se*
			---------- μg Se g^{-1} soil ----------					
Panoche	SeMet	2	2.3	6.5	15.3	0.8	27.3	52.2±1.3
Panoche	SeMet	7	2.2	5.3	2.3	0.9	40.3	51.0±0.4
Panhill	SeMet	2	3.2	1.3	30.1	0.5	14.5	49.6±1.2
Panhill	SeMet	7	2.7	4.2	21.3	0.6	22.5	51.3±0.5
Panoche	SeCys	0.25	0.4	6.1	15.1	1.8	1.9	25.3±0.1
Panoche	SeCys	2	1.1	7.5	11.3	3.1	2.8	25.8±0.4
Panhill	SeCys	0.25	0.4	3.1	19.2	2.1	0.0	24.8±0.6
Panhill	SeCys	2	0.9	13.5	7.1	3.7	0.0	25.2±0.2

[a]Panoche soil evolved dimethylselenide; Panhill soil evolved dimethyldiselenide.

the Se compounds DMSeP and MSeMet in the Panhill soil was due to the presence of a demethylation pathway. The evolution of DMDSe (from the oxidation of methaneselenol) from the Panhill soil reported here confirms the work of Martens and Suarez (*6*) providing further evidence that different Se metabolizing pathways can be present in the different soils. Studies to determine

the amount of organic Se assimilated in alfalfa grown in the presence of selenate (a model non-Se accumulating plant) found that the majority (75%) of the soluble organic Se was present as SeCys and MSeCys with lower levels of SeMet (*19*). Following residue microbial decomposition, Se speciation of the seleniferous alfalfa (*19*) reflected the speciation pattern noted for SeCys additions to soil (Table II). The presence of SeCys and SeMet in the plant biomass is no doubt the dominant source of the organic Se compounds to the environment, but virtually no information is available on the decomposition pathways of the organic forms of Se. This information is essential to understanding the toxicity potentials in evaporation ponds as up to 60% of the total dissolved Se in aquatic systems may be present as these organic forms (*20*).

To determine the importance of the methylation-demethylation pathways shown in Figure 3 for Se speciation, the Panoche and Panhill soils were incubated for up to 7 d after addition of 10 μg g^{-1} soil of each intermediate (Table III). Since no commercial sources of the Se pathway compounds were available, the Se compounds had to be synthesized for these mineralization studies. Results show that both soils tested were as efficient for removal of the MSeMet additions as SeMet additions (Table II), but were less efficient for volatilization of DMSeP. The Panoche soil evolved 95% of the sulfur analog DMSP addition as DMS confirming DMSP as the next proposed step in the S volatilization pathway (Table I), but the Se data suggested that volatilization of Se occurred following the methylation of SeMet (Table II, Figure 2). Lewis et al. (*21*) reported that an enzymatic fraction isolated from cabbage (*Brassica oleracea*) was active for catalyzing the release of DMSe from MSeMet and DMS from MMet suggesting the importance of the formation of MSeMet in Se volatilization. This is divergent from the evidence presented for the S pathway (Table I) (*7*) and suggests that conversion of MSeMet to DMSeP limits loss of Se from the soil. Even the Panhill soil, which did not volatilize DMSe from SeMet additions (Table III) evolved nearly all of the MSeMet-Se added as DMSe. This level of volatilization was not found when Se was added as DMSeP, suggesting that the pathways for methylation of SeMet was limited in the Panhill soil, but the enzyme(s) are still present for volatilizing MSeMet. The additional data supports the findings of Martens and Suarez (*6*) that the demethylation pathway results in accumulation of nonamino acid Se(-2) species and the volatile Se species will be DMDSe. Table III also shows the Panoche and Panhill soil Se speciation data when exposed to the $TMSe^+$ ion. That data shows that extensive volatilization of $TMSe^+$ (45%) can occur under soils exhibiting the methylation pathway as in the Panoche, but the Panhill soil treated with $TMSe^+$ accumulated organic Se (74%) as measured after 7d incubation. Cooke and Bruland (*20*) reported the identification of organic Se compounds MSeMet and $TMSe^+$ in ground water from beneath the Kesterson Wildlife Refuge and the Salton Sea in California. The identification of the organic Se compounds suggests that production and persistence of organic Se metabolites occurs in soil systems contaminated by inorganic Se.

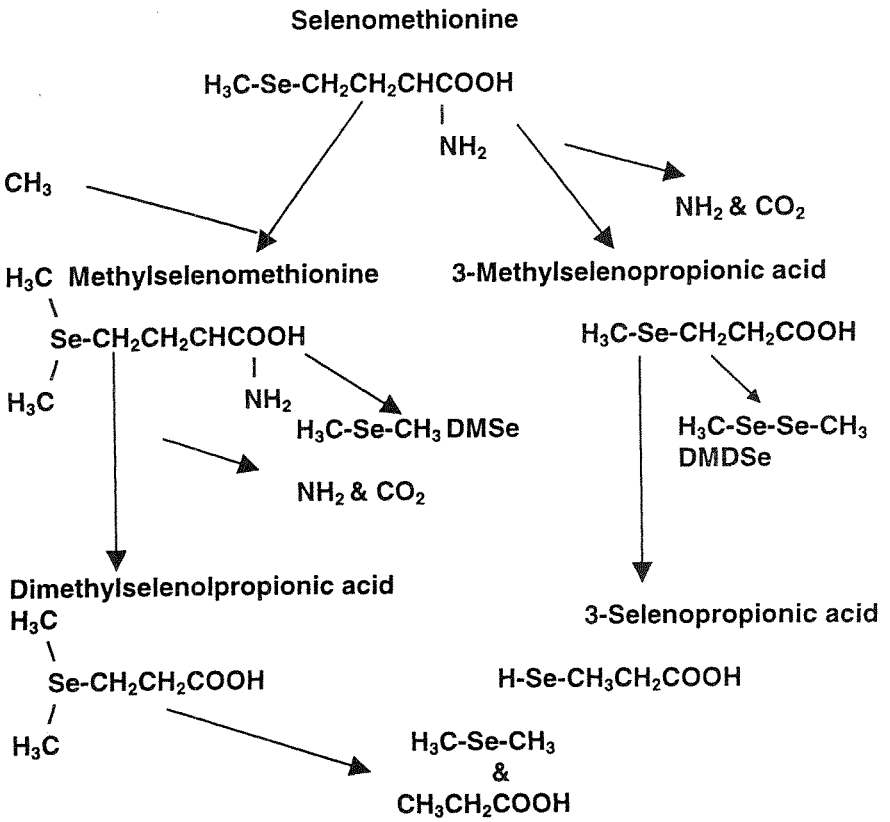

Figure 2. Methylation (MSeMet) and demethylation (3-methylselenopropionic acid) pathways for SeMet as suggested for Met (8).

Table III. Selenium recovery and speciation (average ± standard deviation) after incubation of 10 μg Se g^{-1} soil as MSeMet, DMSeP, MSeCys and $TMSe^+$ (50 μg Se total) in the Panhill and Panoche soils for up to 7 d.

Soil	*Se Form*	*Day*	*Se(+6)*	*Se(+4)*	*Se(-2)*	*Se^o*	*Volatile Se^a*	*Total Se*
			----------		μg Se Recovered		----------	
Panoche	MSeMet	2	1.1	9.2	13.0	0.6	27.2	51.1± 1.2
Panoche	MSeMet	7	0.0	7.5	6.2	1.8	37.5	52.9± 0.9
Panhill	MSeMet	2	1.5	3.3	27.4	0.6	17.3	50.1± 0.7
Panhill	MSeMet	7	1.9	5.6	17.1	0.6	26.4	51.5± 1.3
Panoche	DMSeP	2	2.1	8.5	32.9	1.1	7.6	52.2± 1.4
Panoche	DMSeP	7	0.0	7.0	19.4	4.2	21.0	51.6± 0.8
Panhill	DMSeP	2	3.8	3.6	40.3	0.7	1.8	50.2± 1.2
Panhill	DMSeP	7	1.4	6.2	35.2	1.1	5.5	49.4± 0.9
Panoche	MSeCys	2	0.7	15.6	27.1	2.0	5.0	48.4± 1.1
Panoche	MSeCys	7	0.3	15.8	20.9	5.6	8.4	51.0± 1.0
Panhill	MSeCys	2	6.4	6.4	37.2	1.6	0.0	51.6± 1.5
Panhill	MSeCys	7	2.7	18.8	20.3	2.0	5.9	49.7± 1.6
Panoche	$TMSe^+$	2	0.3	8.5	35.6	1.3	2.6	48.4± 0.6
Panoche	$TMSe^+$	7	0.6	8.7	14.5	2.4	23.1	51.0± 1.2
Panhill	$TMSe^+$	2	0.5	12.8	34.8	0.6	0.0	51.6±.09
Panhill	$TMSe^+$	7	0.0	6.8	36.7	1.3	2.8	49.7± 1.5

[a]The volatile Se was recovered as dimethylselenide from both soils.

The pathway for metabolism of SeCys is less complicated for SeMet (Figure 3). Addition of MSeCys determined that the soils were not efficient for Se volatilization from MSeCys additions and as noted with SeCys additions (Table II), the majority of the Se remaining was present in the Se(-2) species. The soil Se speciation pattern noted for SeCys and MSeCys (Tables II and III) is nearly identical to the soil Se speciation in the Panhill and Panoche following addition of seleniferous alfalfa (*19*), which contained the majority of extractable Se amino acids as SeCys and MSeCys. The formation and persistence of nonamino acid organic Se with SeMet additions to soils exhibiting a demethylation population and from SeCys or MSeCys suggest that certain soils may have a potential to accumulate organic Se compounds that have not been tested for toxicity to avian species. Future research needs to address the possible formation in soils and

sediments of nonamino acid Se with special attention to the toxicity of the organic Se compounds 3-methylselenopropionic or 3-selenopropionic acid to avian species.

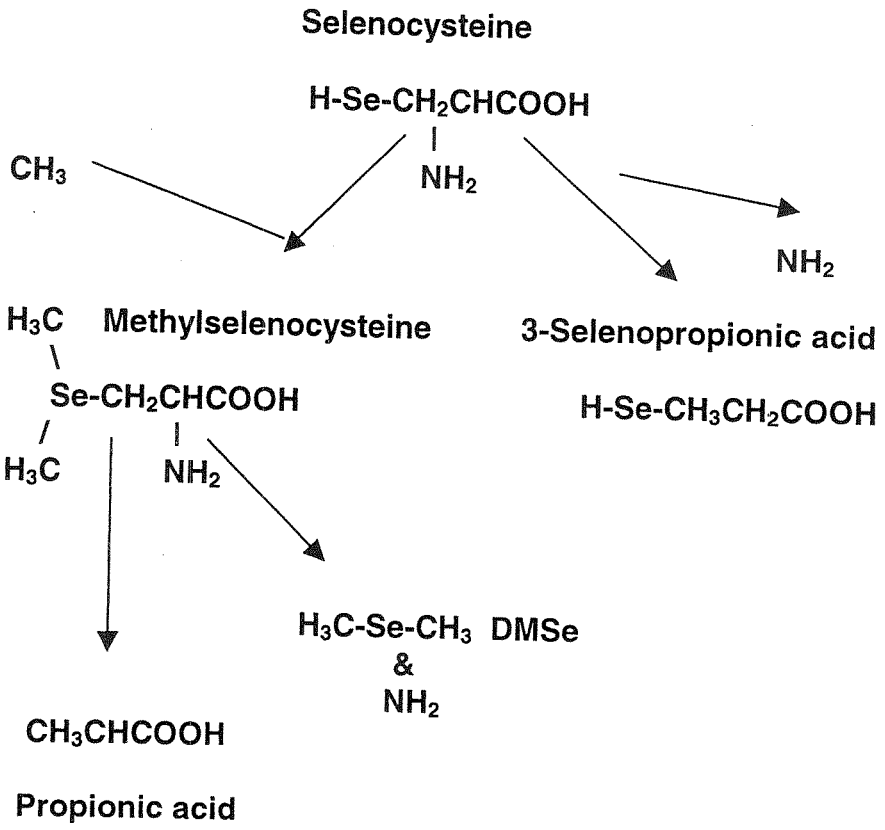

Figure 3. Methylation (MSeCys) and demethylation (3-selenopropionic acid) pathways for SeCys as suggested for Met (8).

Soils metabolizing SeMet via the methylation pathway will result in loss of Se from the system with lower Se(-2) accumulation, but the demethylation pathway will result in potential SeMet accumulation as 3-methylselenopropionic or 3-selenopropionic acid as noted by Martens and Suarez (*6*). A simple deamination of SeCys forming 3-selenopropionic acid may also result in an accumulation of organic Se compounds (Figure 3) and may explain why Martens and Suarez (*6*) found a rapid loss of SeCys from the soil system when analyzed

for the amino acid, and a comcomitant accumulation of a nonamino acid organic Se.

The toxicological significance of these proposed intermediates is not known as the only organic Se compound tested for toxicity is SeMet. While low levels of the organic Se forms accumulate with SeMet, elevated levels of persistent organic Se accumulate with MSeCys or SeCys additions. The organic Se compounds are important because under field conditions, MSeCys and SeCys are the major organic Se compounds present in plant residues and available for decomposition. The different pathways for metabolism of organic Se compounds in some instances result in formation of significant quantities of intermediates. The differences may explain why Se-induced problems with waterfowl have not been detected in wildlife refuges that had been predicted to be problem spots based on total Se concentrations (*11*).

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