RELEASE, RETENTION AND AMINO ACID INTERACTION OF SELENOMETHIONINE IN RECLAIMED COAL MINE ENVIRONMENT[1]

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Abstract: Selenomethionine (SeM), a toxic organo-selenium compound, was detected in coal mine soils and in plants used for mine reclamation. The release of SeM from soil and plant into the solution phase was mainly due to microbial degradation. Adsorption and clay-complexation were also responsible for SeM retention by soils. The adsorption isotherms followed a linear initial-mass model, and greater SeM retention capacity was observed for a clayey soil than for a sandy soil. Release or retention of SeM was also directly related to solution pH; greater solution SeM concentrations were detected at higher pH. In the soil-plant system, various amino acids were found to be related to changes in SeM concentrations.

Additional Key Words: Adsorption, Clay-Complexation, Degradation.
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Introduction

Selenium (Se), a potentially toxic element to some plants and animals (Rosenfeld and Beath, 1964), occurs naturally in several coal mine environments (Valkovic, 1983). Mining activities of seleniferous lands may enhance Se solubility and mobility in resaturated backfills (Boon, 1989). During mine reclamation, backfill spoil material is revegetated, afterwhich the land is commonly used for grazing. Many non-accumulator selenium-containing vegetation types are typically used for mine reclamation. During decomposition of such plant residues under natural field conditions, many amino acids, including selenomethionine (SeM), may be released into the soil solution. The SeM can accumulate in the soils and with time microbially mineralized to mobile inorganic Se phases. Plants and bacteria as natural source of SeM were reported by Ganther (1974), and soil as a source of SeM was described by Abrams et al. (1990). The phytotoxicity and animal-poisoning of SeM was described by Rosenthal (1982). Information on the mobility of this organo-seleno compound in coal mine environments is lacking. Therefore, the objectives of this study were: (1) evaluation of SeM release and retention with time in soil-only and soil-plant systems, and (2) examination of SeM interactions with other amino acids released from a soil-plant mixture.

Materials and Methods

Samples

Surface horizons (0-30 cm) of two coal mine soils (BR and WT, both typic torriorthent) were used for this study; general soil characteristics are shown in Table 1.

Table 1. General physico-chemical characteristics of the soil samples.

Soils	Texture	pH	EC dS m^{-1}	Organic Carbon %	Total Se mM kg^{-1}
BR	Sandy loam	8.3	0.7	0.8	0.025
WT	Clayey	8.0	1.3	0.8	0.028

Both soils have alkaline pHs, high electrical conductivities, low organic carbon, and comparable total Se contents. The soils have different textures: sandy loam (79% sand) and clayey (59% clay) for BR and WT,

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respectively. Thus, we were able to compare SeM mobility in soils having contrasting textures, but similar chemical characteristics. Eighteen different plant species collected from coal mine sites located at the Powder River Basin of Wyoming, were composited and used for our soil-plant study. The plant species used in this study included: *Grindelia squarrosa, Melilotus officinalis, Astragalus bisulcatus, Halogeton glomeratus, Artemisia tridentata, Agropyron intermedium, Cirsium canescens, Agropyron elongatum, Hordeum brachyantherum, Sphaeralcea coccinea, Chenopodium berlandieri, Bromus inermis, Ambrosia psilostachya, Medicago sativa, Elymus smithii, Chrysothamnus nauseosus, Artemisia frigida,* and *Elymus juncens*. These species are often used for mine reclamation or as forage for livestock. Soil and plant samples were air-dried, finely-ground, and sieved through 2 and 0.25 mm screen, respectively, and then used for the following laboratory studies.

Laboratory Studies

In 50 mL polypropylene tubes, 1 g soil and 10 mL of 0.00, 0.05 or 0.10 mM/L SeM were reacted for 4 to 112 days under laboratory conditions. At the end of each reaction period, solution pH was measured and the samples centrifuged and passed through 0.45 μm filters. The filtrates were analyzed by high performance liquid chromatography with fluorescence detection for SeM and other amino acids, and by ion chromatography for selenite and selenate. Fluorescence detection method has been reported to be sensitive for analyzing selenomethionine (Wolf et al., 1992) and other amino acids as well (Roth and Hampai, 1973). A second experiment was designed for the soil-plant composite system, where 1 g soil, 0.5 g plant material, and 10 mL distilled deionized water were reacted with time as described above. In another experiment, soils (soil:solution = 1:10) were reacted with 0.0025 to 0.1 mM/L SeM for 48 hours and also analyzed as described above. The solid residues obtained from the above experiments were cultured to isolate the microorganisms involved in the soil-plant study. The composite plant material was also digested by distilled deionized water (at 90 °C for 8 hrs.) and the aqueous extract was analyzed for various amino acids (Table 2).

Table 2. Amino acid distribution in an aqueous extract of the composite plant material.

Amino Acids	Structural Formula	Conc. mM kg^{-1}
Serine	$HOCH_2$-$CHNH_2$-COOH	3.94
Glycine	HOOC-CH_2-NH_2	2.34
Threonine	HOOC-$CH(NH_2)$-CHOH-CH_3	2.85
Histidine	HOOC-$CH(NH_2)$-CH_2-$C_3N_2H_3$	2.15
Glutamine	HOOC-$CH(NH_2)$-CH_2-CH_2-COOH	2.54
Alanine	HOOC-$CH(CH_3)$-NH_2	10.93
Methionine	HOOC-$CH(NH_2)$-CH_2-CH_2-S-CH_3	1.38
Selenomethionine	HOOC-$CH(NH_2)$-CH_2-CH_2-Se-CH_3	4.45

Results and Discussion

Studies with the plain aqueous system showed release of SeM from the soils, which indicated the presence of indigenous SeM in the mine soils (Fig. 1). The amount released was higher for the clayey soil (WT) at the beginning of the study (after 4 and 7 days); which could be attributed to the presence of SeM either sorbed onto or complexed with clay. The SeM concentrations decreased with time, and after 14 days the amount present was the same for both soils. After 84 days, SeM concentration in the WT sample was near zero, whereas SeM levels in BR (sandy soil) samples were considerably higher. The time-dependent decrease in the solution concentration of SeM

was probably due to microbial degradation. However, a faster removal rate in the clayey soil suggests SeM adsorption or clay-complexation, in addition to microbial degradation, may have occurred.

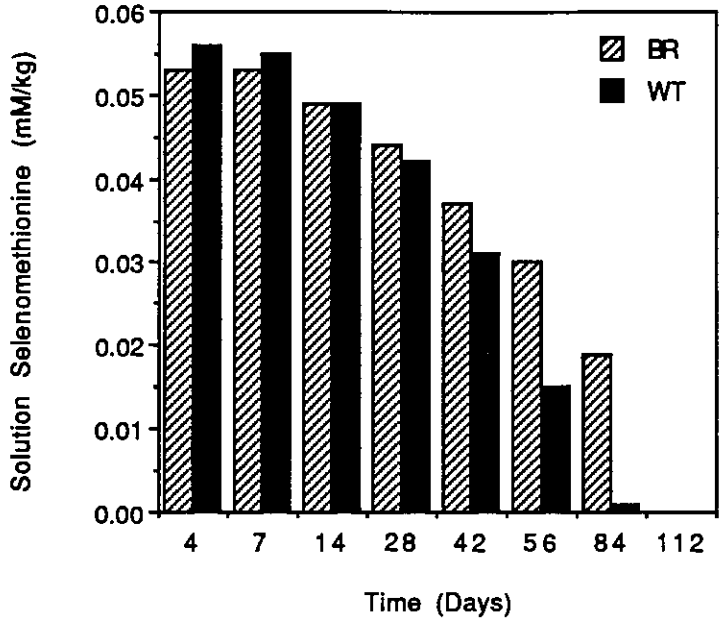

Figure 1. Time-dependent selenomethionine release from sandy (BR) and clayey (WT) soils into the aqueous phase.

Support for the above mentioned hypothesis is exhibited by the greater retention of added SeM by the clayey soil (Fig. 2). The isotherms for both soils followed a linear initial-mass pattern. The adsorption phenomenon of SeM was also predicted by Alemi et al. (1991) with their studies in a different soil environment.

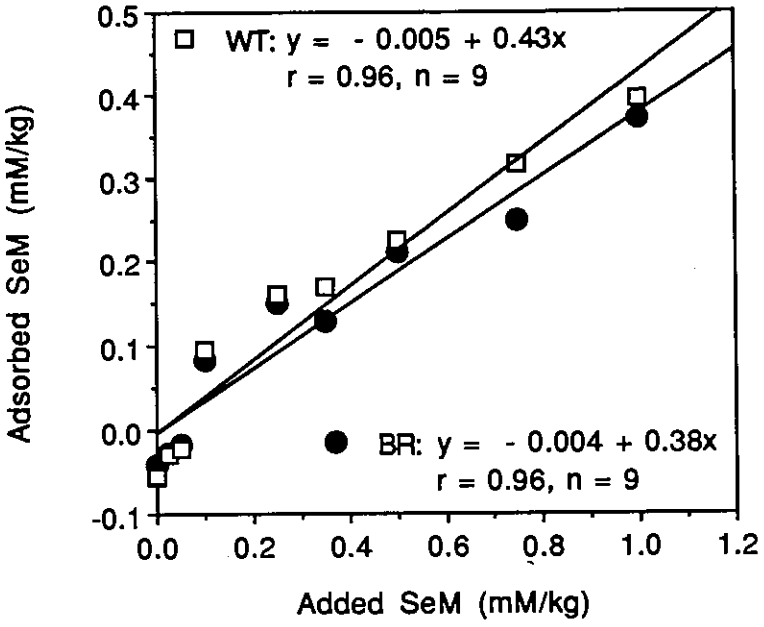

Figure 2. Adsorption isotherms for selenomethionine retention by sandy (BR) and clayey (WT) soils.

A kinetic study, using 0.05 and 0.10 mM/L SeM, indicated there was rapid removal of SeM by the WT soil in comparison to the BR soil (Fig. 3a and 3b), which was probably due to the greater retention capacity of the clayey soil. After nearly 40 and 30 days, the sandy soil retained greater amounts of SeM for 0.05 and 0.1 mM/L SeM treatments, respectively. This would suggest adsorption was the dominant process at the initial stage of SeM removal, although degradation and transformation processes could also be involved. Removal was also dependent on SeM treatment levels. Initial SeM removal was much greater in the WT soil at the 0.05 mM/L treatment level. Thus, the clayey soil had higher SeM adsorption at lower SeM concentrations. Participation of clay in organic Se fixation was also observed by Hamdy and Gissel-Nielsen (1976). However, for BR, where adsorption was relatively lower, the removal pattern was almost similar for both treatment levels.

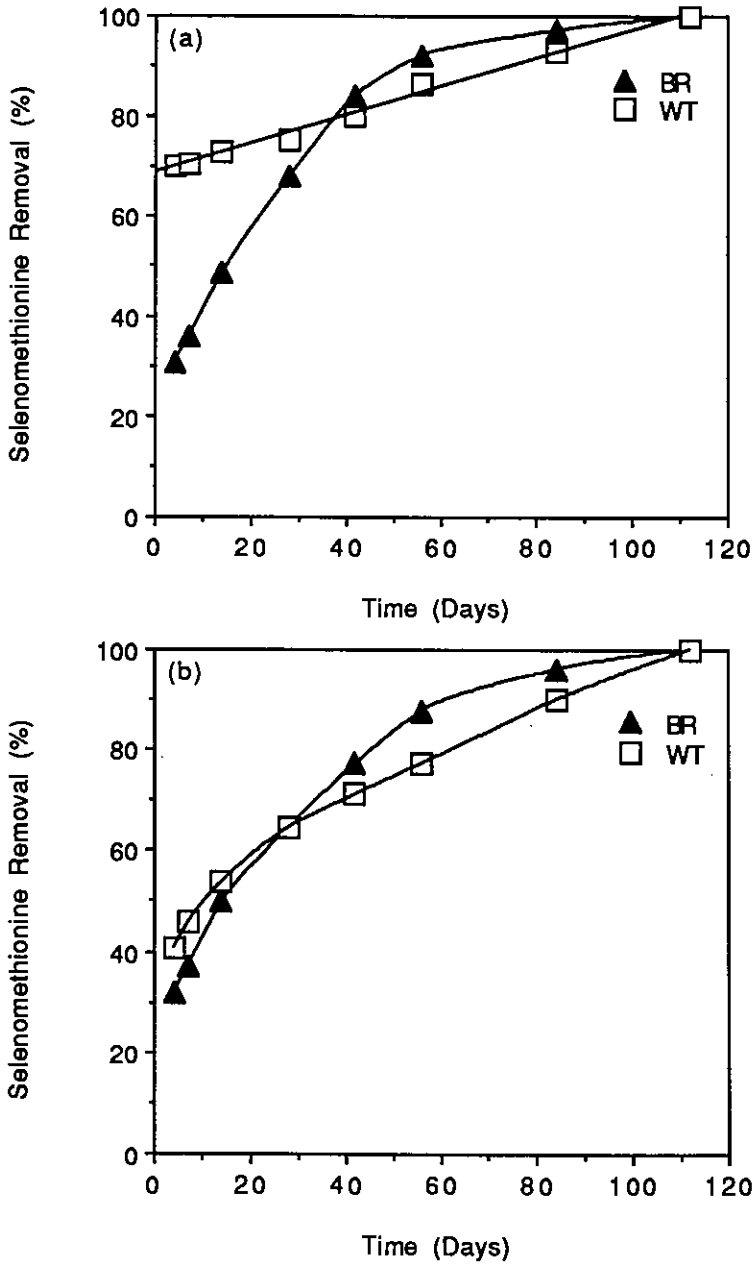

Figure 3. Removal of selenomethionine by sandy (BR) and clayey (WT) soils at (a) 0.05 and (b) 0.1 mM/L treatment levels.

Solution pH in the kinetic study also changed with time. The equilibrium SeM level increased with increasing pH for the two SeM treatment levels and both WT and BR soils (Fig. 4a and 4b). This would suggest there was greater SeM availability at higher pH; however, it should be noted that in this case the range of pH change was rather narrow (7.6 to 8.4).

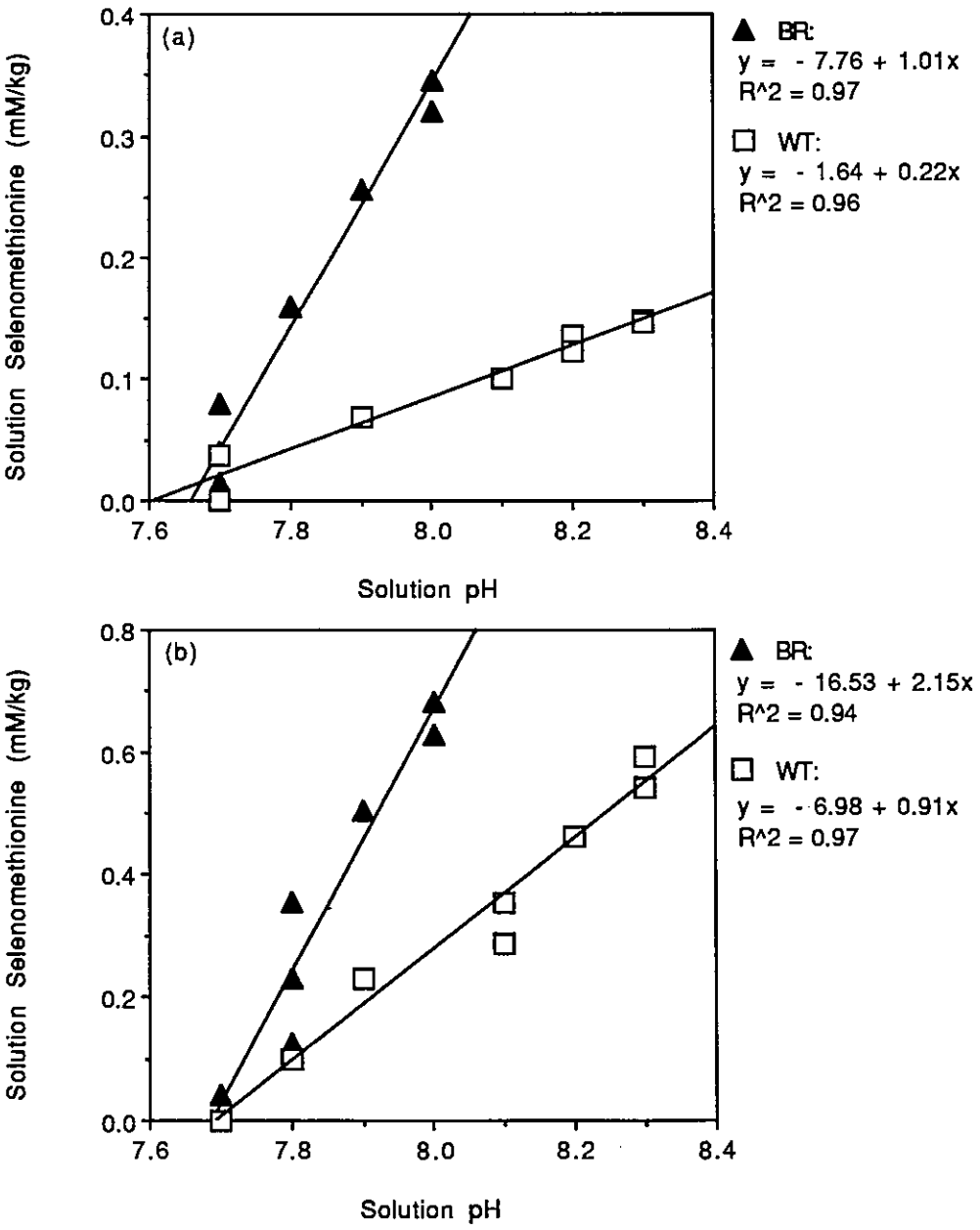

Figure 4. Variation of solution selenomethionine concentrations with equilibrium pH for sandy (BR) and clayey (WT) soils at (a) 0.05 and (b) 0.1 mM/L treatment levels.

A broader pH range (5.4 to 7.8) occurred over time in the soil-plant mixture kinetic study (Fig. 5). For both soils, the pH increased with time in a curvilinear manner. The drop in pH from the original soil pH (8.0 and 8.3 for WT and BR, respectively) at the beginning of the experiment indicated there was an initial release of acidic compounds from the added plant materials. The gradual increase in pH indicated time dependent disappearance of released H^+ from the soil-plant-water mixture, which could be due to degradation of the compounds or their transformation into other derivatives. Transformation of organic Se has also been reported by Doran and Alexander (1977).

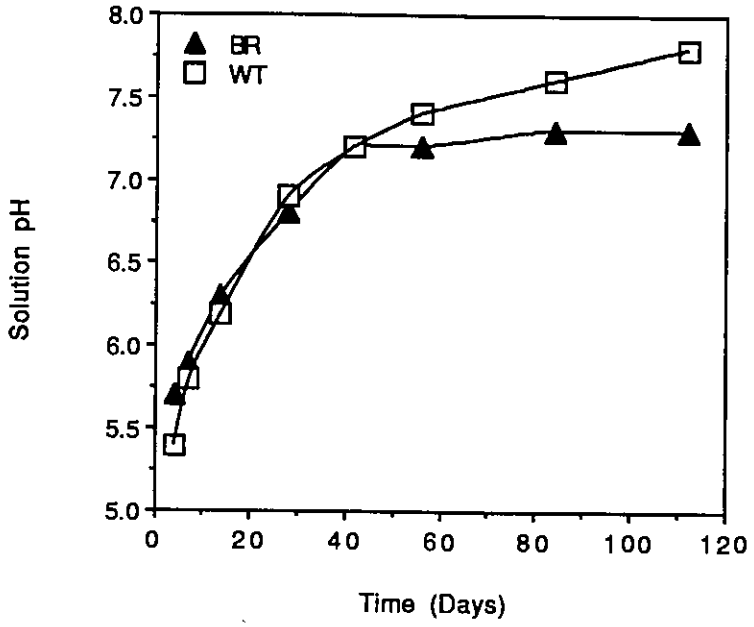

Figure 5. Time-dependent variation of pH in the soil-plant-water mixture for sandy (BR) and clayey (WT) soils.

For both soils, the solution SeM concentrations increased gradually with increasing pH, reaching a maximum at pH values 6.2 and 6.3 for WT and BR, respectively, and finally diminished gradually as pH approached 7.8 (Fig. 6). It is also of interest to note that the maximum SeM concentrations for both soils were reached at the same pH, indicating that the solution dynamics were probably being governed predominantly by the plant-decomposition compounds. Also the shorter peak height for the WT curve indicated greater SeM removal by the clayey soil.

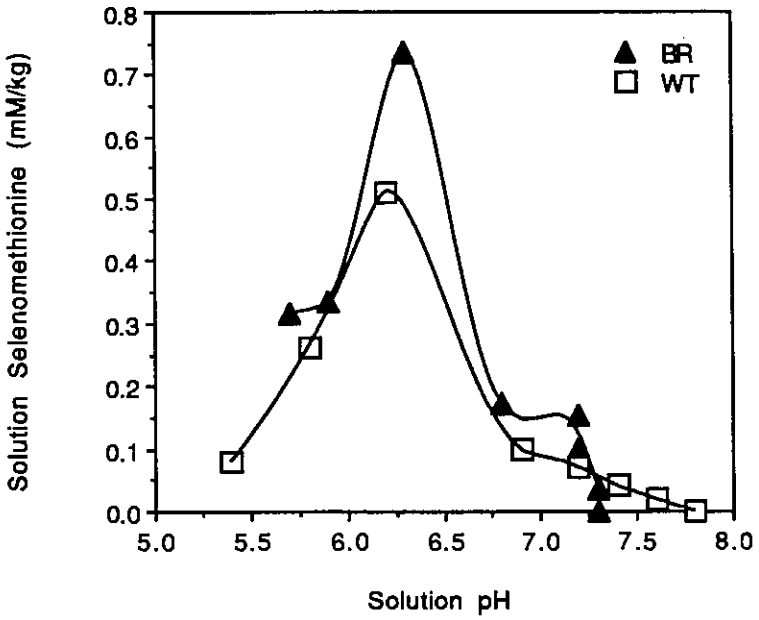

Figure 6. Variation of solution selenomethionine concentrations with equilibrium pH in the soil-plant-water mixture for sandy (BR) and clayey (WT) soils.

This can also be observed in Fig. 7, where the solution SeM concentration at different time intervals was found to be higher for the BR soil. The solution SeM concentration increased with time for both soils, reaching a maximum after 14 days, and then decreased with time. The solution SeM concentration was much higher for the soil-plant mixture than for soil only. This suggests that plants are a major source of this organo-selenium, whereas soils act as a sink.

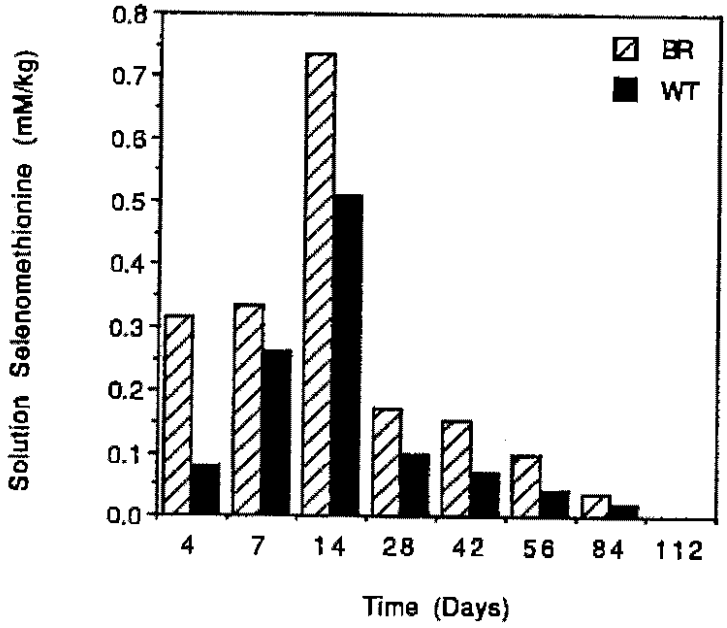

Figure 7. Time-dependent selenomethionine release from the soil-plant-water mixture for sandy (BR) and clayey (WT) soils.

In the soil-plant system other amino acids, such as serine, glycine, threonine, histidine, glutamic acid, methionine and alanine, were detected. These amino acids were not detected in the soil-only system, thus indicating plants are major source of these amino acids. Amino acids in solution followed trends that related to changes in SeM concentrations (Fig. 8a and 8b). For BR, concentrations of serine, glycine, histidine, and methionine increased initially with increasing SeM; after reaching maximum concentrations, these amino acids decreased in an approximately asymptotic fashion. The initial synergistic effect was probably due to release of amino acids along with SeM mainly from plant-decomposition. However, decreasing concentrations at later stages would be suggestive of antagonistic interactions of these amino acids with SeM. Threonine, glutamic acid and alanine did not show any initial synergism, but an antagonistic affect was noted with increasing SeM concentrations. For WT, only serine and methionine increased with increasing SeM, while the other amino acids followed an inverse pattern. Some minor discrepancies in the pattern of the amino acids for the two soils were probably due to the difference in their clay content and adsorption capacities. However, in general, at relatively high Se concentrations the antagonistic trend with the other amino acids was noted.

Antagonism with methionine through S substitution by Se was also reported by Rosenthal (1982), and participation of glutamine, serine and other organic compounds in Se metabolism cycle was described by Whanger (1989). Thus transformation of SeM to other organic derivatives or amino acids would be likely. Figure 8 also indicated an approximate concentration pattern for some amino acids. For example, in the BR soil the trend was, serine > glycine > histidine > methionine > alanine; the WT soil pattern was serine > glycine > threonine > histidine > alanine. Finally it should be noted that, the other amino acids, like SeM, also would probably undergo adsorption or degradation process; however, from their inverse trend with SeM we infer that SeM would probably compete with them for the sorption sites.

Isolation of microbial cultures indicated the presence of various fungi, bacteria, and actinomycetes in the soil-plant mixture, which suggested SeM was probably degraded along with being adsorbed or complexed by clay. In fact, an apparent white microbial growth and musty smell were observed in samples of the longer time periods. The relative population of these microorganisms followed the order of: fungi > bacteria >> actinomycetes. Thus, predominantly fungi and bacteria (and to some extent actinomycetes) would be responsible for SeM degradation. Participation of microorganisms in organic Se mineralization was also observed by Doran and Alexander (1977); and such a process would be mostly effected by fungi (Abu-Erreish et al., 1968), and also bacteria (Zeive and Peterson, 1981).

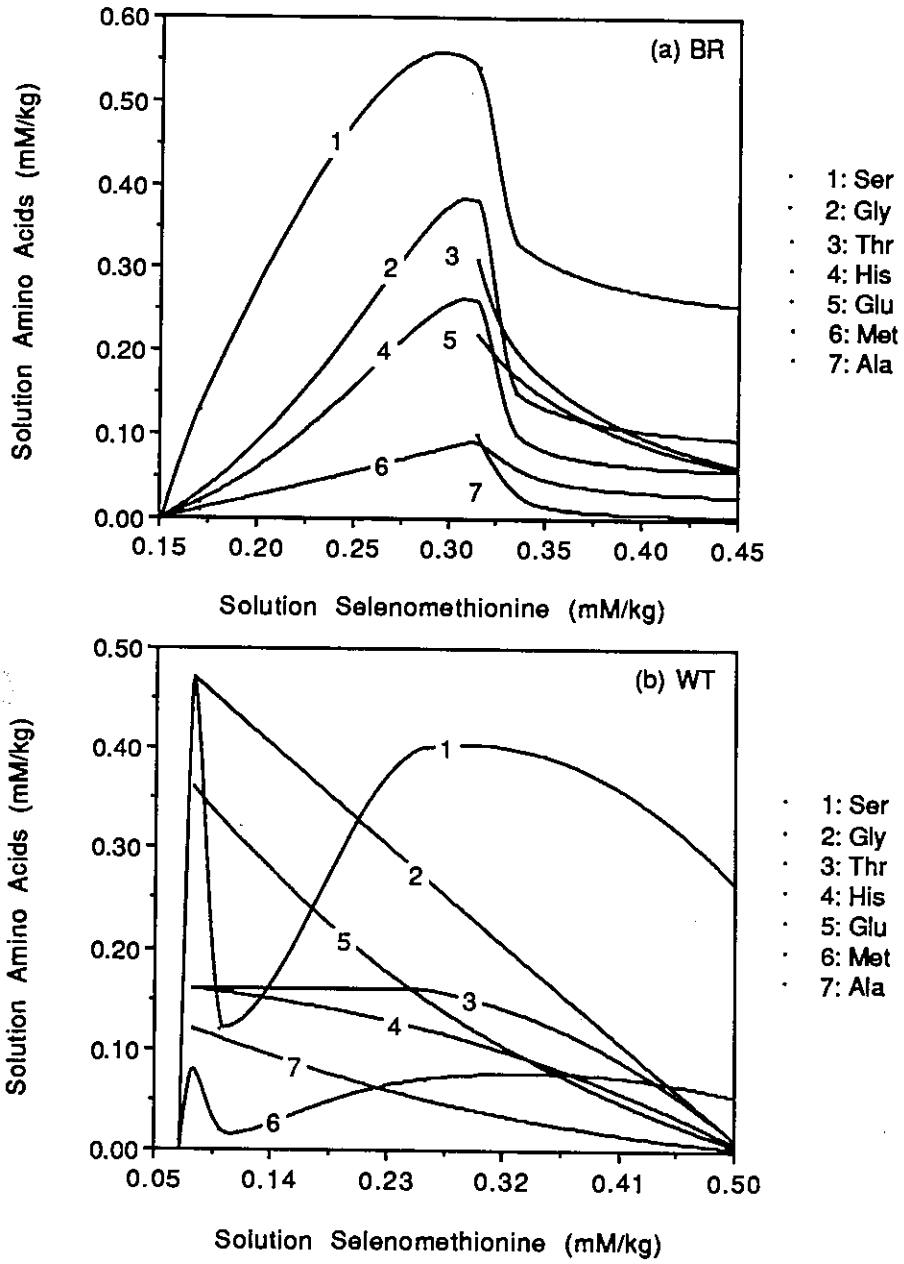

Figure 8. Variation of solution amino acid concentrations with changing selenomethionine levels in the soil-plant-water mixture for (a) sandy (BR) and (b) clayey (WT) soils. The amino acids are serine (ser), glycine (gly), threonine (thr), histidine (his), glutamic acid (glu), methionine (met) and alanine (ala).

Summary and Conclusions

The coal mine soils, particularly the clayey soil, was found to contain indigenous SeM. Time-dependent removal of SeM from the soil solution indicated microbial degradation. In our samples, several types of microorganisms were isolated; fungi were found to be most abundant. Adsorption or clay-complexation were estimated to be other mechanisms for SeM removal, in addition to microbial degradation. The adsorption isotherms followed a linear initial-mass model. Greater SeM retention capacity was observed for the clayey soils. SeM release or retention was also found to be directly related to solution pH, indicating greater SeM concentration at higher pH. Higher level of solution SeM for the soil-plant mixture than for soil-only suggested plants as a major source of this organo-selenium, rather than the soils. Various amino acids usually detected in the natural system, were found to be related to changes in SeM concentrations in our soil-plant system.

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