Journal of Industrial Microbiology (1995) 14, 226–232
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Volatilization of selenium from a dewatered seleniferous sediment: a field study

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(Received 4 April 1994; accepted 16 August 1994)

Key words: Dimethylselenide; Fungi; Microbial transformations of trace elements; Selenium; Volatilization

SUMMARY

One of the major concerns in central California (San Joaquin Valley) is the level of selenium (Se) in evaporation ponds containing agricultural drainage water. The objective of this work was to determine if volatilization of Se could be used as a bioremediation program to detoxify a saline seleniferous sediment of a dewatered evaporation pond. The dewatered sediment was rototilled, divided into subplots, and amended with various organic materials including citrus (orange) peel, cattle manure, barley straw and grape pomace. Some of the subplots were fertilized with nitrogen [$(NH_4)_2SO_4$] and zinc ($ZnSO_4$). Selenium volatilization was monitored in the field with a flux chamber system utilizing alkaline peroxide to trap the gas. Overall, the greatest emission of gaseous Se was recorded in the summer months and the lowest emission during the winter months. The background emission of volatile Se averaged 3.0 μg Se h^{-1} m^{-2}. The most effective organic amendment was cattle manure with an avg. Se emission of 54 μg Se h^{-1} m^{-2}. Composite soil samples from each subplot (upper 15 cm) were analyzed for total Se on a monthly interval during the course of this field study. After 22 months, the application of water plus tillage alone removed 32.2% of the Se content while the cattle manure treatment removed 57.8%. Among the parameters which enhanced volatilization of Se were an available C source, aeration, moisture, and high temperatures. This field study indicates promising results in detoxifying seleniferous sediments via microbial volatilization once environmental conditions have been optimized.

INTRODUCTION

Biogenic Se volatilization is an important link in the global cycle of this element [7]. It is estimated that in the northern hemisphere alone, approximately 5000–10 000 metric tons of Se are emitted into the atmosphere annually, more than one-third of which originates from soils and plants [21]. Gaseous Se is recycled to the earth's surface by dry and wet deposition. Kinetics of the gas-phase reaction of dimethylselenide (DMSe) in the atmosphere were determined by Atkinson et al. [2]. The residence time of atmospheric Se sorbed to particulates is approximately 7–9 days [19]. Typical Se concentrations in rain water and snow range between 0.5 and 1.5 μg L^{-1} [21].

This study was initiated to determine if biomethylation and volatilization of selenium (Se) could detoxify a saline seleniferous sediment of a dewatered evaporation pond. Seleniferous salts from drainage waters are accumulating in sediments of evaporation ponds in California (San Joaquin Valley) being derived from soils of marine sedimentary parent materials. Specific soil microorganisms have been known for years to have the ability to convert soluble Se into a volatile gaseous form [1,3,5,8]. For comprehensive reviews of this microbial transformation see Doran [8], Frankenberger and Karlson [11], Thompson-Eagle and Frankenberger [22], and Karlson and Frankenberger [13]. The primary Se species evolved is dimethylselenide (DMSe, $[CH_3]_2Se$) with small quantities of dimethyldiselenide (DMDSe, $[CH_3]_2Se_2$) (<5%) and possibly dimethylselenone ($[CH_3]_2SeO_2$) also being released. The alkylselenides have high vapor pressures [18] and thus are readily diluted and dispersed into the atmosphere. In addition, inhaled gaseous DMSe is nontoxic to the rat [see Frankenberger, W.T., Jr, and Karlson, U. 1988, Microbial volatilization of selenium at Kesterson Reservoir, Final Report, December 1988. Prepared for the US Dept of Interior, Bureau of Reclamation, Contract No. 7-FC-20-05240], and in the dissolved form, DMSe toxicity is approximately 1000 times less than that of selenite [20,27].

Only recently has a thorough investigation been made of the factors affecting alkylselenide production from soil and sediment [4,14,15,17]. Karlson and Frankenberger [16] developed an effective method to monitor volatile Se as a microbial metabolite when soils were exposed to labeled inorganic Se (^{75}Se). Some of the factors affecting volatilization included organic carbon (C) sources, metallic activators, temperature, moisture, and aeration [4,12,15,17]. Marked acceleration of this process was observed upon the addition of specific C sources in short-term experiments with ^{75}Se-labeled Se(IV) and Se(VI). Among the C compounds tested (cellobiose, cellulose, galacturonic acid, glucose, glucuronic acid, pectin, and starch), pectin stimulated the reaction more than any other treatment. Volatilization rates tended to decrease as C became depleted in soil, but increased again upon C reload [17]. Stimulation of Se volatilization was also observed upon the addition of plant residues. As much as 9% of the added Se

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was recovered in the volatile form in only 13 days of incubation upon treatment with pectin. The stimulatory effects of the C amendments are dependent upon the specific matrices (e.g. sand vs clay or water) [23,24,26]. In soils, the greatest evolution of volatile Se occurs under aerobic conditions, with the soil water content at field capacity [12].

The primary organisms involved in volatilization of Se from dewatered sediments are fungi. *Scopulariopsis brevicaulis* was the first organism reported to convert Se(IV) and Se(VI) into an alkylselenide [6]. Since then, a number of other fungi (*Fusarium, Acremonium, Alternaria, Penicillium, Ulocladium*) have been reported to form DMSe from inorganic Se [15,25]. It is believed that this transformation is a detoxification mechanism enabling these organisms to tolerate high levels of Se. Both inorganic and organic Se compounds can be methylated into gaseous Se.

The primary objective of this study was to conduct a pilot-scale project in the field assessing the feasibility of volatilization as a bioremedial approach to remove Se from a dewatered evaporation pond sediment. Supporting objectives included identification of the optimal soil management conditions to promote Se volatilization, such as tillage for soil aeration, irrigation to sustain biological activity, and incorporating organic amendments to stimulate the activity of Se-methylating microorganisms.

MATERIALS AND METHODS

Experimental design

Field experiments were conducted at the Sumner Peck Ranch (Fresno County, CA, USA) in a dewatered evaporation pond (cell 4). Approximately 0.10 ha (0.28 acre) was required for this project with 30 subplots. The site was first rototilled 10–15 cm deep to loosen the soil. The subplots were then staked out with dimensions of 3.7 × 3.7 m with borders of 2.4 m between the subplots. This experiment consisted of a complete random block design. For all treatments, there were three replications.

Soil management

Because of the heavy soil texture (high in clay), all subplots, except for the amendment-free treatments received wheat straw applied at 20.4 kg (45 lb) subplot^{-1} (equivalent to 1.53 kg m^{-2} or 6.8 tons acre^{-1}). Table 1 provides information on the type and amount of organic amendments applied to each of the subplots. All plots were rototilled to approximately 15 cm in depth within 24 h after application of amendments. In addition, all plots were rototilled every 2–3 weeks if weather permitted. Amendments were first applied in October 1987, and repeated (except for $ZnSO_4$) in March 1988 and July 1988.

The irrigation system consisted of commercial sprinkler irrigation equipment. The experimental plots were irrigated every other day during the summer season for approximately 10 min. Water application rates were reviewed and altered periodically. The surface soil was moist but not saturated to minimize leaching of the soil constituents below the 15 cm depth. Irrigation water was tailwater with the following water quality parameters: EC, 0.70 dS m^{-1}; Ca, 35.1 mg L^{-1}; Mg, 11.9 mg L^{-1}; Na, 96.4 mg L^{-1}; Si, 9.2 mg L^{-1}; Fe, 0.26 mg L^{-1}; B, 0.20 mg L^{-1}; Ba, 0.10 mg L^{-1}; Sr, 0.30 mg L^{-1}; Al, 0.03 mg L^{-1}; and non-detectable levels ($<$0.001 mg L^{-1}) of Mn, Cu, Zn, Cd, Pb, Ag, V, Mo, Ni, Co, Cr, Li, Ti, Be, Tl, Ga, Au, U, Sc, Hg, Se, As, Sb, Bi, Te, Ge, and Sn.

Soil sampling

All plots were sampled with a 2.5-cm diameter probe in a five-point pattern at the 0–15 cm depth at monthly intervals. In addition, an initial inventory of the Se distribution vs soil depth was taken along 60-cm profiles at 10–15 cm intervals. Profile samples were taken from randomly assigned subplots.

TABLE 1

Amendments applied to subplots to promote volatilization of Se from a dewatered evaporation pond sediment. All subplots, except 2, 10 and 30 (moist, tilled) received 1.53 kg straw m^{-2} (6.8 tons acre^{-1})

Subplot	Amendment	Application rate
2,10,30	Moist, tilled	N/A
1,7,9	$(NH_4)_2SO_4$	0.29 kg m^{-2} (1.29 tons acre^{-1}), i.e. 190 g kg^{-1} straw (for a C/N = 10)
13,22,28	Orange peel	6.73 kg m^{-2} (30 tons acre^{-1})
15,17,31	Orange peel plus $(NH_4)_2SO_4$	as for subplots 13, 22 and 28, plus 8.6 g $(NH_4)_2SO_4)$ kg^{-1} orange peel
14,27,29	Orange peel, $(NH_4)_2SO_4$ plus $ZnSO_4$	as for subplots 15, 17 and 31, plus 2.8 g $ZnSO_4$ kg^{-1} orange peel
18,23,25	Grape pulp	6.73 kg m^{-2} (30 tons acres^{-1})
12,19,32	Grape pulp plus $(NH_4)_2SO_4$	as for subplots 18, 23 and 25, plus 8.6 g $(NH_4)_2SO_4$ kg^{-1} grape pulp
16,21,24	Grape pulp plus $(NH_4)_2SO_4$ plus $ZnSO_4$	as for subplots 12, 19 and 32, plus 2.8 g $ZnSO_4$ kg^{-1} grape pulp
4,5,11	Cattle manure	1.57 kg m^{-2} (70 tons acre^{-1})
3,6,8	Cattle manure plus $ZnSO_4$	as for subplots 4, 5 and 11, plus 1.2 g $ZnSO_4$ kg^{-1} cattle manure

Upon collection, each soil sample was passed through a 2-mm sieve and ground to 100 mesh (0.15 mm). All samples were kept refrigerated at 4 °C during storage. Samples were extracted with the digestion procedure of EPA Method 3050 and analyzed by atomic absorption spectrometry (AAS/hydride generation) (EPA Method 270.3) for determination of Se [9] and reported on a dry-weight basis.

Monitoring selenium volatilization in the field

The apparatus used for in-field measurements of volatile alkylselenide production was originally designed by O. Weres (Lawrence Berkeley Laboratory, Berkeley, CA, USA). Inverted aluminum boxes (56 × 56 × 10 cm) with a brass tube connector at the top center were used as flux chambers. Additional equipment consisted of a vacuum pump (Fisher, Tustin, CA, USA), 250-ml gas wash bottle (40–60 μm porosity) (Fisher), 6-place manifold, 0.6-cm i.d. vinyl tubing, and surgical tubing. Reagents used for the trapping solution were hydrogen peroxide (H_2O_2) (30%) and 0.05 M sodium hydroxide (NaOH). The purpose of the peroxide was to oxidize the volatile Se to the Se(VI) species.

The flux chambers were placed in the center of each subplot to be sampled and pushed approximately 2.5 cm into the soil. The vacuum pump was connected to an electrical supply. The manifold was then connected to the pump with vinyl tubing. A trap was inserted between the manifold and pump to prevent the scrubbing solution from being drawn into the pump in case the gas wash bottle was tipped or blown over by the wind. From the manifold, 0.5–6 m sections of vinyl tubing were connected to the gas wash bottles and from these to the sampling boxes. The trapping solution consisted of 80 ml 0.05 M NaOH (premeasured) plus 20 ml of H_2O_2 (final concentration, 6%) which was kept cold in an ice chest until used. Because vinyl tubing binds to glass, which makes it difficult to attach and remove it from the wash bottle, a small piece of surgical tubing was placed on the end of the vinyl tubing to alleviate this problem. When the trapping solution had been added and all the tubing was connected, the pump was started. The flow rate of the manifold was adjusted at the port of each chamber with a flow gauge to 2 L min^{-1} and checked repeatedly. The duration of the measurements was 1 h, with the starting and finishing times being recorded. In most cases, measurements were made at mid-day. At the end of sampling, the pump was turned off, the wash bottle was opened, and the alkali-peroxide solution was poured directly into a 125-ml polyethylene bottle and placed into an ice chest packed with blue ice. The wash bottles were then rinsed twice with deionized water and filled with 80 ml of 0.05 N NaOH to be used for the next sampling.

The alkali-peroxide sample was boiled to drive off the residual H_2O_2, using a hot plate. Each sample was boiled for 15 min, allowed to cool, brought up to volume (100 ml) and stored in 125-ml polyethylene bottles. The samples were treated with conc. HCl to give a sample acidity of 6 N HCl and boiled for 1 h immediately before analysis. Analyses were carried out with atomic absorption spectrometry–hydride generation (EPA Method 270.3) for determination of Se [9].

Air and soil temperatures were recorded at the onset and end of sampling. Likewise, the temperature and relative humidity inside the flux chambers were recorded. Soil temperature was measured in randomly assigned plots. A thermometer was inserted into the soil bermed up against the chamber approximately 2–4 cm below the surface.

Quality control

Quality control was maintained in both soil and gaseous Se analyses through the use of matrix spikes, matrix spike duplicates and a National Institute of Standards and Tables standard reference material (SRM). Recovery of analytical spikes was monitored at two levels including both ‘low’ (100 μg L^{-1}) and ‘high’ level (500 μg L^{-1}) spikes. Average percent recoveries for analytical spikes were well within the 80 to 110% range and reference sample recoveries averaged 95.8%.

Modelling

Soil Se depletion was modelled assuming that Se methylation follows first-order reaction kinetics, expressed by

$$v = -\frac{d[\mathrm{Se}]}{dt} = k[\mathrm{Se}] \tag{1}$$

where v is the methylation rate and [Se] is the residual soil Se concentration at any given time. After integration, Eqn 1 can be rewritten as

$$\log\,[\mathrm{Se}] = \log\,[\mathrm{Se}_0] - \frac{k}{2.303}\,t \tag{2}$$

where t is the time since the start of the experiment, and [Se_0] is the soil Se concentration at $t = 0$. Soil Se data (63 observations per treatment) were fitted to Eqn 2, the coefficient of determination (r^2) and the rate constant (k) were calculated. The time required to reach the clean-up goal of 4 mg kg^{-1} was calculated by rearranging Eqn 2 to

$$t = \frac{2.303}{k}\,(\log[\mathrm{Se}_0] - \log[\mathrm{Se}]) \tag{3}$$

inserting 4 mg kg^{-1} for [Se], and the Y-intercept at $t = 0$ from the fit to Eqn 2 for log[Se_0].

RESULTS AND DISCUSSION

Selenium distribution in soil profiles

Most of the Se (approx. 58%) was found within the upper 15 cm of the soil profile. The Se content below 15 cm of depth never exceeded 4 mg kg^{-1}. In the soil surface (upper 15 cm), the Se content was somewhat uniform, ranging in concentration from 7.1 mg kg^{-1} (subplot 33) to 18.1 mg kg^{-1} (subplot 15), with a median of 11.9 mg kg^{-1} and a mean of 11.4 mg kg^{-1}. The distribution frequency of the pooled Se levels and the range in Se concentrations is illustrated in Fig. 1.

Gaseous emission of selenium

Background emission, measured on non-rototilled, non-treated sites adjacent to the plots, averaged 3.0 μg Se h^{-1} m^{-2}.

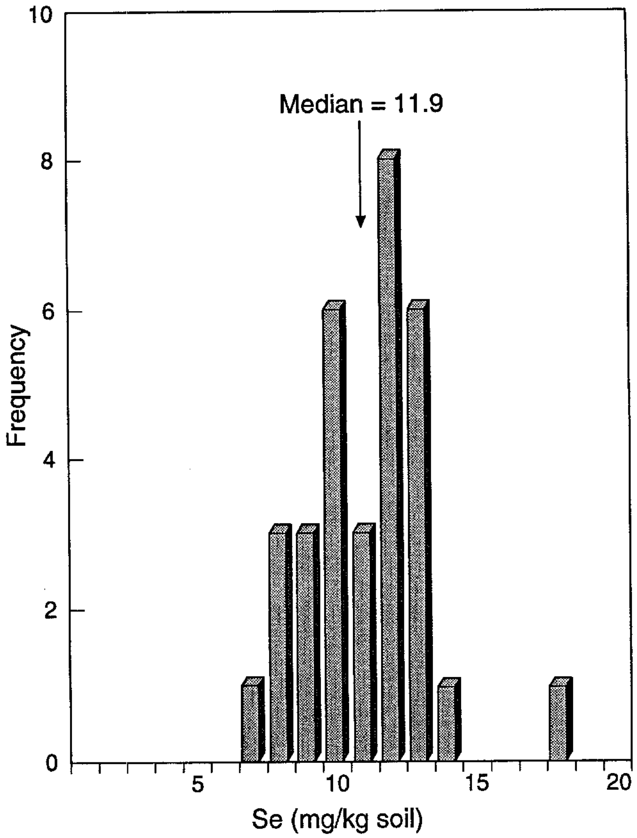

Fig. 1. Frequency distribution of the Se inventory in the upper 15 cm of the experimental subplots.

Seasonal variation of gaseous Se emission was evident with the greatest emission recorded in the late spring and summer months during the course of this study (Fig. 2). Soil temperatures ranged from 4 °C to 53 °C. In laboratory studies it was demonstrated that Se volatilization is highly temperature-dependent with an average Q_{10} calculated at 1.71. That is, for every rise in temperature of 10 °C, the rate of volatilization was increased 1.7-fold. The high temporal variability in gaseous Se evolution was most likely attributed to variations in daily temperatures, moisture content, availability of organic matter, and Se content.

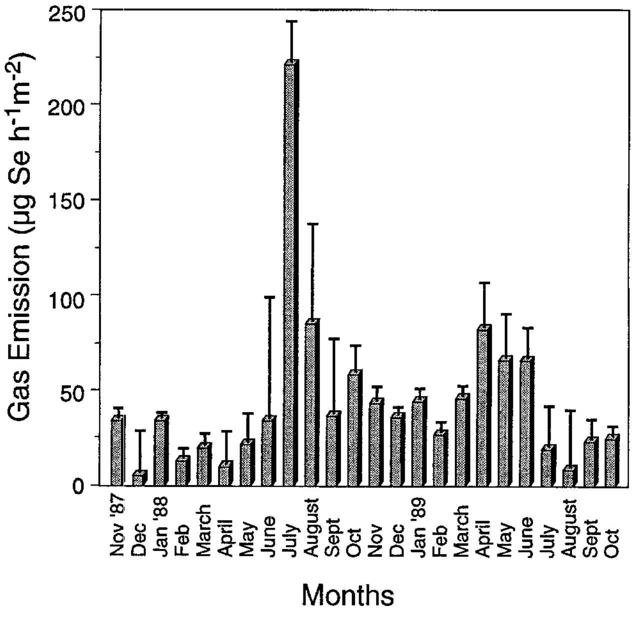

Fig. 2. Seasonal flux of volatile Se gas upon treatment of cattle manure plus $ZnSO_4$.

Table 2 shows the average and highest emission of alkylselenides produced upon the application of various treatments. The highest emission of gaseous Se was recorded on July 8, 1988 at 457 μg Se h^{-1} m^{-2} and involved the application of cattle manure. The average emission of volatile Se with this treatment was 54 μg Se h^{-1} m^{-2} enhancing Se volatilization 18-fold over the background level and three-fold over the moist-only subplot (without a C amendment). Cattle manure plus $ZnSO_4$, added as a trace supplement, enhanced volatilization with an average reading of 45 μg Se h^{-1} m^{-2}. Incorporation of cattle manure to these subplots not only promoted Se volatilization, but also enhanced the organic matter content. The subplots treated with cattle manure were considerably darker in color, which likely enhanced heat absorption and thus promoted Se volatilization. The Se content of the added manure was below detection level (<0.1 mg kg^{-1}).

Effect of temperature

A linear regression analysis was performed on the volatile alkylselenide gas being released in the field upon treatment with cattle manure vs soil temperature. A significant correlation between soil temperature and volatile Se released (r = 0.75*, significant at the 95% level) was found. Between 8 °C and 18 °C, there was a linear increase of Se volatilization with temperature, and volatilization rates approximately doubled. Volatile Se produced from the seleniferous sediments was related to the diurnal and seasonal variation of temperature. The diurnal peak of volatile Se was often detected in mid-afternoon, and over the year Se emission rates were optimum in the spring and summer months (Fig. 2).

TABLE 2

Gas emission of volatile alkylselenides upon incorporation of organic amendments

Amendment	Subplots	Average emission	Highest emission
		μg Se h^{-1} m^{-2}	
Moist, tilled	2,10,30	18.4	239
$(NH_4)_2SO_4$ (N)	1,7,9	30.8	168
Orange peel	13,22,28	18.3	120
Orange peel + N*	15,17,31	24.2	179
Orange peel + N + Zn	14,27,29	15.7	114
Grape pulp	18,23,25	10.2	51
Grape pulp + N	12,19,32	9.3	81
Grape pulp + N + Zn	16,21,24	6.3	42
Cattle manure	4,5,11	54.2	457
Cattle manure + Zn	3,6,8	45.0	374

*N = $(NH_4)_2SO_4$.

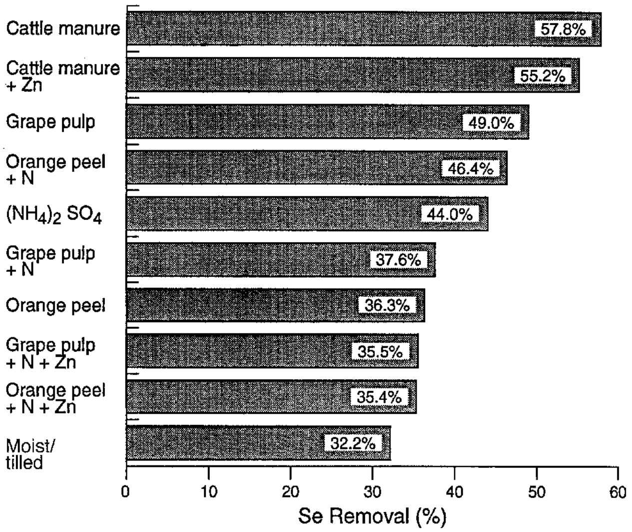

Fig. 3. Influence of organic amendments on the percentage of Se removed in the dewatered sediment after 22 months of study.

This bioremediation approach relies on gas exchange with the net release of DMSe from soil pores to the atmosphere. Two important factors affecting volatilization of Se include temperature and wind velocity. The thermal differentiation permits gaseous exchange of DMSe between the atmosphere and soil air at the immediate soil surface. The optimum temperature for DMSe production occurs at 35–40 °C [12]. The vapor pressure of DMSe increases with temperature. Raising the temperature from 10–25 °C doubles the vapor pressure of DMSe, while raising it from 25–40 °C doubles it again [18]. At temperatures above the optimum for microbial activity, the increased vapor pressure may more than compensate for the reduced production, thus explaining the highest emission rates at the extreme summer temperatures.

The pressure and suction effects of high wind result in renewal of soil air, particularly with barren soils. The effect of air turbulence on the transfer of vapor in soil suggests that mass air flow should be high. A wind speed of 25–50 miles per hour can penetrate several centimeters into soil [10]. Even without mass flow, fluctuations in air pressure at the soil surface result in considerable mixing, affecting gas fluxes higher than due to diffusion. Because of the structure of the soil, it was difficult to obtain a good seal with the flux chamber. Therefore, measurements of volatile Se in the field are most likely an underestimate of the actual gas released into the atmosphere.

Soil selenium removal

The influence of several treatments on the percentage of soil Se removed in the surface soil after 22 months of study are shown in Fig. 3. The soil data confirm the gaseous emission data, with the cattle manure treatments being the most effective amendment to dissipate Se from the dewatered sediment. There was an apparent logarithmic decrease in the Se inventory over time. Table 3 provides a summary of the soil Se removal rates and indicates how well the logarithmic regression analysis fits the data. Figure 4 shows the percentage of Se remaining in the Ap horizon over time upon treatment with grape pulp plus nitrogen. All treatments, except for the N amendment (without added C), significantly fit Eqn 2 describing Se dissipation in the Ap horizon. Thus, the soil data suggest that the conversion of the residual fraction of Se to DMSe follows first-order reaction kinetics.

The least effective treatment in promoting volatilization was the moist and aerated (tilled) amendment with 32% Se removal in 22 months. The addition of C promoted volatilization, with cattle manure being the most effective. Approximately 58% and 55% of the initial Se inventory was removed in the Ap horizon, with the treatments of cattle manure alone

TABLE 3

Soil selenium removal in response to organic amendments added to the dewatered sediment, based on soil analyses

Amendment	Coefficient of determination (r^2)	Rate constant, k, (fraction of residual Se removed per month)	Time required to reach clean-up goal of 4 mg kg^{-1} (years)
Moist, tilled	0.058	0.0073 ± 0.0037	7.8 ± 2.7
$(NH_4)_2SO_4$	0.156	0.0112 ± 0.0033	5.3 ± 1.2
Orange peel	0.340**	0.0149 ± 0.0027	3.4 ± 0.5
Orange peel + N†	0.331**	0.0209 ± 0.0038	2.9 ± 0.5
Orange peel + N + Zn	0.413***	0.0159 ± 0.0024	3.3 ± 0.4
Grape pulp	0.622***	0.0262 ± 0.0026	2.6 ± 0.2
Grape pulp + N	0.430***	0.0195 ± 0.0029	3.2 ± 0.4
Grape pulp + N + Zn	0.490***	0.0200 ± 0.0026	3.1 ± 0.4
Cattle manure	0.532***	0.0223 ± 0.0027	2.7 ± 0.3
Cattle manure + Zn	0.551***	0.0250 ± 0.0029	2.6 ± 0.3

,* indicate significance at the 99% and 99.9% level, respectively.
†N = $(NH_4)_2SO_4$.

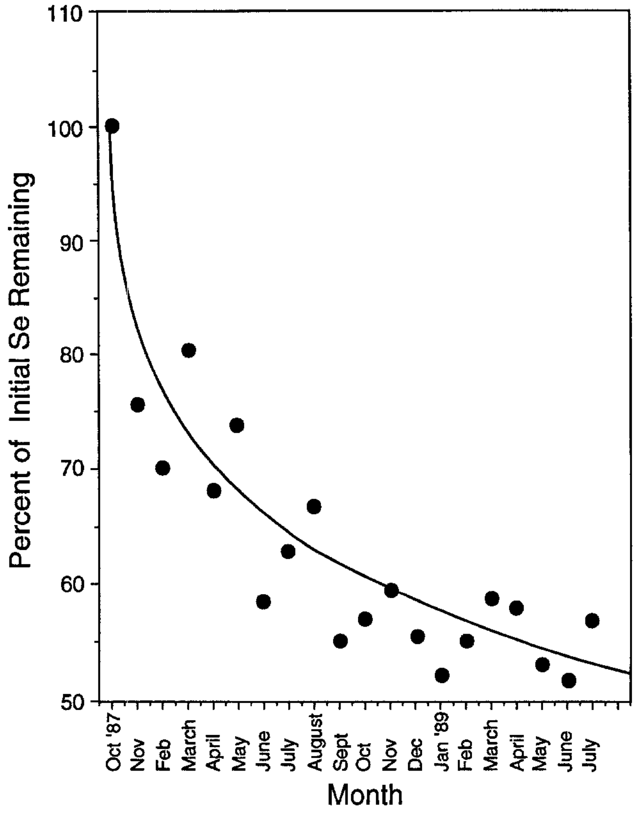

Fig. 4. First-order relationship between the percentage of Se remaining in the dewatered sediment and time upon treatment with grape pulp plus $(NH_4)_2SO_4$.

and cattle manure plus Zn added as a trace element, respectively.

CONCLUSIONS

Among the parameters which enhanced the dissipation of Se were an available C source, aeration, moisture and high temperatures. Rototilling promoted volatilization as long as the soil was kept moist. Frequent tillage, breaking the crust that may form as a result of sprinkler irrigation, can be used to maintain an aerobic environment and to facilitate diffusion of the volatile alkylselenide gas. Irrigation water should be applied to moisten the upper few cm of soil, otherwise water-soluble Se may be transported out of the surface layer making it unavailable for volatilization. Amendments with cattle manure can increase the removal of Se considerably. The results of this study indicate the feasibility of this bioremediation technology; however, more information is needed to determine the success of this approach at other seleniferous sites and the cost involved.

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