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Abstract

Experiments in the field and greenhouse were conducted in the presence of coal fly ash to determine whether gypsum can reduce Se concentration in alfalfa (Medicago sativa L.). In the field experiment, gypsum was applied to soil as a top dressing in amounts of 0 and 11.2 t ha^{-1} each year over a two year period, to test the effect of gypsum in reducing selenium (Se) concentration in aboveground plant tissue. In 1990, each dose of gypsum (0, 11.2 t ha^{-1}) was applied to three plots of alfalfa, and in 1991, half of each plot received 0 and half received 11.2 t ha^{-1} gypsum; this resulted in four treatment combinations of gypsum over the two year period: (0, 0), (0, 11.2) (11.2, 0) and (11.2, 11.2). In 1991, the Se concentration was lower in alfalfa grown with gypsum applied in either or both years than in alfalfa grown without gypsum in both years, indicating that the effect of gypsum application in the previous year persisted into the current year. Since there was no increase in aboveground biomass with added gypsum, differences in Se concentration reflect a competitive interaction between S and Se, rather than a dilution of Se due to increased growth. In the greenhouse experiment, 12 soil treatments were tested: three levels of fly ash (0, 10 and 20 %) in combination with each of four levels of gypsum (0, 2.5, 5, and 7.5 %). The Se concentration in alfalfa grown in 10 % fly ash declined linearly with increasing gypsum dose, resulting in a reduction in Se concentration of 0.04 ± 0.02 $\mu g\ g^{-1}$ for each 1 % gypsum added for the first harvest and 0.06 ± 0.03 $\mu g\ g^{-1}$ for each 1 % gypsum added in the second harvest. However, the Se concentration in plants grown with 0 or 20 % fly ash did not change with increasing gypsum dose. Based on these results, gypsum may prove useful as a management tool to reduce the uptake of Se by plants growing on coal fly ash landfills.

Introduction

Up to 120 million tons of fly ash are produced annually as a byproduct of coal combustion for the generation of electric power in the United States (U.S. Environmental Protection Agency 1988). Of this, 75 to 80 percent is disposed in landfills (U.S. Department of Transportation 1986). These landfills normally are covered with about 0.5 to 1.0 m of soil and then seeded with a mix of forage species. Coal fly ash contains most naturally occurring elements (Page et al. 1978); the concentration of Se in fly ash ranges from 1.2 to 17 $\mu g\ g^{-1}$ (Furr et al. 1977). Some species of plants growing on fly ash landfills, especially those in the Fabaceae, can accumulate Se in concentrations that reach the range of chronic toxicity to mammals (Arthur et al. 1992a-c, Weinstein et al. 1989). As a result of this finding, research was initiated to determine whether gypsum ($CaSO_4{\cdot}2H_2O$) application to soil could mitigate Se uptake by plants.

The mitigation of Se uptake by plants from soils by the addition of sulfur (S) has been known for more than 50 years (Hurd-Karrer 1938). Sulfur can act as a competitive ion in Se uptake due to the similar chemical properties of S and Se and their interchangeability in some aspects of plant metabolism; in some cases, applications of S have reduced Se uptake (Hurd-Karrer 1938, Pratley and McFarlane 1974, Singh et al. 1980, Westerman and Robbins 1974). However, studies of the effects of S or SO_4 application on Se uptake have shown that other factors, such as initial soil S content and plant species, affect the response (Mikkelsen et al. 1988, Davies and Watkinson 1966). Reducing the uptake of Se by plants through surface applications of S can be delayed until the S moves through the soil into the rooting zone. Thus, short-term experiments may not detect effects of S on Se uptake. (Mikkelsen et al. 1988). Another complicating factor is that reduced Se concentration in foliage can result from dilution as well as decreased uptake. Such a dilution effect has been observed in alfalfa (Medicago sativa L.) following S application, either as SO_4 fertilizer or as gypsum ($CaSO_4{\cdot}2H_2O$), due to fertilized plants having increased shoot growth without a concomitant increases in Se uptake (Pratley and McFarlane 1974, Walker 1971, Westerman and

Robbins 1974). From an ecological perspective, total uptake of Se from a fly ash layer could be as important as Se concentrations in aboveground biomass.

Gypsum application to plots of alfalfa on a fly ash landfill in 1990 indicated that gypsum can reduce Se uptake (Arthur et al. 1992b). No change in Se concentration of alfalfa grown with added gypsum was detected in the first harvest, which occurred four weeks after gypsum application, but a significant linear decrease in Se concentration with increasing gypsum dose was detected in alfalfa harvested 7 weeks later, indicating a time lag in the response. In that study we did not measure productivity and, thus, could not evaluate whether the decrease in Se concentration in alfalfa was a dilution effect.

We conducted two experiments in 1991 to examine more closely the potential mitigative effects of gypsum on Se uptake by plants. A field study was designed to determine whether (1) there are residual effects of gypsum treatment from the previous year, (2) the response changes with a second year of gypsum application, and (3) the decreased Se in alfalfa after gypsum application results from dilution or decreased Se uptake. The great spatial variability in the availability of Se on the landfill (Arthur et al. 1992b) prompted us also to investigate the mitigative role of gypsum applied to soil containing fly ash in a greenhouse setting, where the conditions could be more closely controlled. The objective of the greenhouse study was to assess the potential for decrease in Se uptake by alfalfa grown in homogeneous mixtures of soil with known amounts of gypsum and fly ash.

Materials and methods

Field study

Study site The field study was conducted at a coal fly ash landfill located in Lansing, N.Y., 22 km north of Ithaca, N.Y., and the details of the features of this site can be found in Arthur et al.

(1992a). Alfalfa was established in 1988 and all harvests reported here are from fourth year growth of the crop. The primary roots of alfalfa plants extended to the fly ash layer but did not penetrate more than 1 to 2 cm into it (personal observation, M. Arthur). During site preparation for establishing forage crops, care was taken to avoid penetration of the ash substratum to prevent contamination of the soil cap with fly ash. However, some contamination may have occurred 10 years previously when the landfill was closed.

Experimental design Alfalfa [Oneida VR (Agway, Syracuse, NY)] was established in 1988 on the landfill in three blocks. One plot of alfalfa (3.05 m x 6.10 m) occurred in each of the blocks. In 1990, as part of a previous study (Arthur et al. 1992b), each of the three alfalfa plots on the landfill were subdivided into four quadrants (subplots) with a 0.15 m border surrounding each subplot. Each of four gypsum doses (0, 5.6, 11.2, and 16.8 t ha^{-1}) was assigned at random to one of the four subplots of each 3.05 m x 6.10 m plot, resulting in a randomized complete block experimental design.

In the 1990 study, Se uptake by alfalfa was significantly lower when grown on plots treated with gypsum than on those without gypsum (Arthur et al. 1992b). However, no difference in response could be detected among the 5.6, 11.2, and 16.8 t ha^{-1} gypsum doses. Hence, in 1991, we limited gypsum applications to 0 and 11.2 t ha^{-1}, the dose recommended for commercial application to soils, usually to provide additional calcium. Using the plots from the 1990 study, we selected only those that had received 0 or 11.2 t ha^{-1} in 1990 and split them in half, producing 3.05 m x 3.05 m plots. In 1991, each 3.05 m x 3.05 m half-plot was selected at random to receive a dose of 0 or 11.2 t ha^{-1}, resulting in the following two-year treatment combinations: (1) 0 gypsum, 1990; 0 gypsum, 1991; (2) 0 gypsum, 1990; 11.2 t ha^{-1}, 1991; (3) 11.2 t ha^{-1}, 1990; 0 gypsum, 1991; (4) 11.2 t ha^{-1}, 1990; 11.2 t ha^{-1}, 1991 (Figure 1). Hence, the 1991 field study had a split unit experimental design, with the whole unit treatment factor the 1990 gypsum dose and the subunit treatment factor the 1991 gypsum dose. The experimental unit for the whole unit treatment factor was the 3.05 m x 6.10 m plot, and these were arranged in blocks, whereas that for the subunit treatment was each half plot (3.05 m x 3.05 m). In 1991, the gypsum was applied at the beginning of the growing season (April 12).

Sample treatment Harvest dates were tied to alfalfa phenology, and cuttings were timed to correspond with commercial alfalfa harvests. Samples were hand-clipped from three 0.1 m^2 areas that were selected at random from each plot. Then the plots were mown to a 10 cm stubble and allowed to regrow. The three cuttings of alfalfa occurred on June 3, July 16, and August 27, 1991.

Sampling and analysis

All plants were dried at 40° C to prevent loss of Se through volatilization (Fourie and Peisach 1977), weighed, and ground in a stainless steel mill to pass a 1 mm sieve. Plant tissues were analyzed for Se by the diaminonaphthalene fluorometric method (Olson 1969), and for Ca and S using a Jarrell Ash inductively-coupled argon plasma analyzer (ICP). For S and Ca analyses, samples were wet-ashed with HNO_3 and $HClO_4$ by heating to 200°C for two hours. After cooling, 37% HCl was added and the sample analyzed by ICP.

In each batch of 12 samples submitted for Se analysis, one or two samples of a standard tissue were submitted for analysis, for a total of 11% of all plant samples analyzed. Two standard tissues were used interchangeably, a mixture of clover and orchard grass harvested from the landfill in 1988 (0.53 ± 0.03 $\mu g\ g^{-1}$) and alfalfa harvested from the landfill in 1990 (2.92 ± 0.06 $\mu g\ g^{-1}$). In addition, samples of the National Institute of Standards and Technology rice flour standard reference material were analyzed periodically for Se, and the observed mean concentration was close to the certified value (observed: 0.36 ± 0.01 $\mu g\ g^{-1}$; certified: 0.38 ± 0.04 $\mu g\ g^{-1}$). Rice flour, citrus leaves, and pine needles standards from the National Institute of Standards and Technology also were analyzed for S or Ca. The observed mean S concentrations were (1) rice flour, 0.111 ± 0.002 % (certified: 0.120 ± 0.002 %), and (2) citrus leaves, 0.440 ± 0.004 %

(certified: 0.407 ±0.009 %). The observed mean Ca concentrations were (1) pine needles, 0.46 ± 0.02 % (certified: 0.41 ± 0.02 %) and (2) citrus leaves, 3.35 ± 0.02 % (certified: 3.15 ± 0.1 %).

Greenhouse study

Experimental design The greenhouse experiment had a factorial treatment design, with each of 3 levels of fly ash (0, 10, and 20 %) in combination with each of 4 levels of gypsum (0, 2.5, 5, and 7.5 %). Three pots of each of the 12 soil treatments were arranged in a completely randomized experimental design.

Sample treatment The soil for this experiment, a Hapludalf (association Lima-Honeoye), was collected from the Cornell University farm in Aurora, NY. Soil was sieved through a 12 mm mesh and mixed with fly ash and gypsum on a dry weight/dry weight basis to produce the 12 treatment combinations. The soil mixture was separately weighed and thoroughly mixed for each pot. The soil was well-watered so that all subsidence within the pots would occur prior to seeding. Pots were seeded with Oneida VR (Agway, Syracuse, NY) alfalfa and all pots were watered equally and as needed throughout the experiment. Alfalfa was thinned to 16 plants per pot by 40 days after germination.

Alfalfa plants were harvested when approximately 20 % of the pots had flowering plants, at 74 days and 118 days after planting. The plants were cut to approximately 8 cm above the soil surface. There were two harvests of alfalfa; in the second harvest, the treatments with 2.5, 5 and 7.5 % gypsum with 0 % fly ash were omitted due to cost constraints. These treatments had no bearing on the ability to test the hypothesis that gypsum would reduce Se uptake by plants growing in contact with fly ash. Samples were dried, ground, weighed, and chemically analyzed as described for the field experiment.

Statistical analyses

Statistical analysis of the data from each experiment was performed using the General Linear Models procedure in SAS (SAS Institute Inc. 1985) with a model statement appropriate to the experimental design. F-tests for a split-unit design (field experiment), or those for a factorial design (greenhouse experiment), were used to test for differences in Se concentration in alfalfa among gypsum treatments.

Results

Field experiment

For all harvests, higher mean concentrations of Se were found in alfalfa growing with no gypsum application (0 gypsum in both 1990 and 1991) than in plots treated with gypsum at some time in the 2 seasons (Table 1). However, differences among the four treatment combinations were statistically significant in the second harvest only. For harvests 1 and 3, there was no significant interaction ($p>0.1$) between the 1990 and 1991 gypsum treatments, indicating that any additional reduction in Se concentration with the 1991 gypsum application was similar for alfalfa grown with and without gypsum in 1990. However, for harvest 2 there was some evidence of an interaction between the gypsum doses in the two years ($p=0.1006$, Se concentration; $p=0.0400$, Se content). The large standard errors for Se concentration are similar to those for alfalfa grown in these plots in the three previous years (Arthur et al. 1992b).

There was a strong indication of a residual effect from application of gypsum in one year into the next year, resulting in reduced Se concentration in alfalfa grown with gypsum ($p=0.0764$ and 0.0930 for content and concentration, respectively, second harvest). Because of the split unit experimental design, to test for an overall effect of the 1990 application of gypsum, the average Se concentration must be compared across treatments applied in 1991. The overall effect of the 1990 treatment alone was to reduce Se concentration in alfalfa in 1991, regardless of the 1991 treatment (Table 2). This result is further supported by analyzing the difference in Se concentration or content of alfalfa, grown without gypsum and with gypsum added in 1991, for each whole plot (3.05m x 6.10m) of each level of gypsum application in 1990 (Table 3). The difference in Se between alfalfa grown with no gypsum and with 11.2 t ha^{-1} in 1991 was much greater when no gypsum had been added in the previous year ($p=0.0230$ and 0.0860 for content and concentration, respectively), again suggesting a strong carryover effect of gypsum added in the previous year.

The reductions in Se concentration in plants treated with gypsum were not the result of a dilution effect caused by increased growth, but by an actual decrease in Se uptake. There was no increase in aboveground biomass in plots that received gypsum.

As expected, the effect of gypsum application on concentration of S in alfalfa was the inverse of that on concentration of Se: S concentration was lowest when no gypsum was added in 1990 or 1991 (cf. Tables 2 and 4). In the first harvest, this was due both to an increase in S concentration caused by the 1990 application of gypsum (Table 2; $p=0.0283$) and to an effect of additional application of gypsum in 1991 (Table 4; $p=0.0094$), indicating both a carryover effect of gypsum applied in the previous year and an additional incremental increase in S associated with application in the current year. In the second harvest, differences among treatments were due to the 1990 application only (Table 2; $p=0.0201$); thus the carryover effect dominated the concentrations of S in alfalfa from the second harvest of 1991. In the third harvest, there was a significant interaction between the gypsum doses in the two years ($p=0.0578$). There was an overall effect of 1990 application of gypsum with average S concentration higher for the 11.2 t ha^{-1} treatment ($p=0.0081$; Table 2).

For both the first and second harvests, the differences in S concentration between 0 and 11.2 t ha^{-1} gypsum added in 1991 for each level in 1990 were greater when no gypsum had been added in the previous year (Table 3); however, the differences were similar for the third harvest. In the first harvest there was a strong inverse relationship between S and Se (partial correlation coefficient -0.94, p=0.0166). In the second harvest the relationship was weaker (partial correlation coefficient -0.64, p=0.2352). In the third harvest, the relationship between S and Se was not significant (p=0.7981). Thus, the inverse relationship between S and Se concentration in alfalfa disappeared as the growing season progressed.

There was no seasonal trend in Se concentration of alfalfa treated with gypsum, but for alfalfa that did not receive gypsum in either year, there was a trend for the concentration of Se to increase with successive cutting through the season (Table 1; p=0.0496). There was a weak seasonal trend toward higher S concentration with successive cutting for all treatment combinations (p=0.0980). The lack of a strong inverse relationship between S and Se concentrations in alfalfa tissue in the second and third harvests can be explained by the slight increase in S with successive cuttings (or time) without a similar decrease in Se. The significant increase in Se with time for alfalfa not treated with gypsum also weakens the inverse relationship between S and Se concentrations as the season progresses.

As observed in the 1990 experiments, gypsum treatments did not affect Ca concentration (Table 4). Hence, gypsum application appears to affect S and Se uptake by alfalfa without affecting Ca concentrations in alfalfa. Our concern was that the Ca level should not be elevated in plants when gypsum, a Ca salt, was applied, and that was not the case.

Greenhouse experiment

The primary objective of the greenhouse experiment was to quantify the Se concentration in alfalfa as a function of gypsum dose in the soil for each of the three fly ash treatments. This approach reflects a management perspective: the soil in a field (or landfill) will contain a given amount of fly ash; to reduce the impact of fly ash on uptake of Se by plants, one can amend the soil by adding gypsum. Thus, the focus of this research was to obtain and compare the dose-response relationships for different levels of fly ash (or Se) in the soil in which alfalfa is grown, and the statistical analysis reflects this objective.. Another objective was to verify, under controlled conditions, the field observation that the Se concentration in alfalfa increased when grown in soil containing fly ash.

The concentration of Se in alfalfa was significantly greater in the second harvest than in the first ($p=0.0151$). For the first harvest, Se concentration in alfalfa increased linearly with increased doses of fly ash when grown without gypsum amendment ($p=0.0001$; see column 1 of Table 5). Increasing concentrations of Se in alfalfa with increasing amounts of fly ash was expected, and supports our field observations that alfalfa accumulates much more Se when grown on a fly ash landfill than on a control site (Arthur et al. 1992a-c, Weinstein et al. 1989). Plant concentration of Se was not affected by gypsum when fly ash was not present (see row 1 of Table 5). No effect of gypsum on Se concentrations was expected when Se is present in low concentrations in the soil. There was a significant reduction in plant Se concentration with gypsum amendment only for soil containing 10 % fly ash (Table 5). For the treatments with 10 % fly ash there was a significant negative linear response to added gypsum, with a reduction in Se concentration of 0.04 ± 0.02 $\mu g\ g^{-1}$ per 1 % gypsum added ($p=0.0286$; Figure 2). There was no significance to anything other than a linear dose response, despite similar Se concentrations in both the 5 and 7.5 % gypsum doses ($p=0.8760$ for the quadratic). For the treatments with 20 % fly ash, there was no significant reduction in plant concentration of Se with added gypsum (Table 5).

Similar results were obtained for the second harvest. Selenium concentration in alfalfa declined linearly with increasing levels of gypsum amendment only for soil with 10 % fly ash ($p=0.0375$; Table 5, Figure 2). A reduction of 0.06 ± 0.03 $\mu g\ g^{-1}$ Se per 1 % added gypsum was found. Again, there was no significance for any curvature ($p=0.2026$). There was no significant reduction in Se concentration of alfalfa grown with gypsum added to soil with 20 % fly ash (Table 5). Although there was no statistically significant curvilinearity in the dose-response for 10% fly ash in either harvest, the data indicate a tapering off of the decline in the concentration of Se at the highest level of gypsum.

As in the field experiment, we compared total aboveground biomass in each of the treatments to determine whether the presence of gypsum resulted in a fertilizer effect of increased biomass. There was no effect of gypsum addition on aboveground biomass for either harvest (data not shown). Thus, a dilution effect was not the cause of reduced Se concentration with added gypsum in the treatments with 10 % fly ash.

When no gypsum was present, the S concentration in alfalfa increased slightly with increased fly ash ($p=0.02058$; see column one of Table 6). For the first harvest, there was no significant effect of gypsum treatment on S concentration in alfalfa grown in soil with 10 % or 20 % fly ash ($p=0.1308$ and 0.9351, respectively). However, for alfalfa grown in soil without fly ash, the S concentration was significantly greater in plants grown with added gypsum than without ($p=0.0001$; see row one Table 6). In the second harvest, there was a significant increase in S concentration of alfalfa grown with increasing gypsum addition to the soil containing 10 % fly ash ($p=0.0010$), but no increase when grown with 20 % fly ash ($p=0.7546$; Table 6).

Gypsum affected the concentration of Ca in alfalfa in the first harvest, but not in the second, and its effects in the first harvest occurred in treatments with 0 and 10 % fly ash but not in those with 20 % fly ash. In the first harvest, concentration of Ca in alfalfa declined linearly with increasing levels of gypsum added to soil for the 0 and 10 % fly ash treatments ($p=0.0037$ and 0.0074, respectively). A similar decline of 0.05 ± 0.02 % per 1 % gypsum added was found for both 0 and 10 % fly ash. No significant decrease in the concentration of Ca was found with increasing gypsum for alfalfa grown in soil with 20 % fly ash ($p=0.2654$; Table 7). The decline in Ca concentration in alfalfa with increasing gypsum dose found in the first harvest for 0 and 10 % fly ash are small and may not be of biological significance.

Discussion

In the greenhouse experiment, the presence of a significant negative linear response to added gypsum for the treatments with 10 % fly ash demonstrates that amending soils with gypsum can be an effective method of reducing Se uptake by alfalfa. The lack of a response for the treatments with 20 % fly ash may be due to insufficient S addition to the soil. We have noted previously (Arthur et al. 1992b) that in field experiments, additional increments of gypsum may not significantly reduce Se concentration below some (unknown) threshold. From this experiment it is impossible to know whether a higher percentage of added gypsum could have further reduced the concentration of Se in alfalfa grown with 10 % fly ash, or would have resulted in lower Se concentration in the 20 % fly ash treatment. The amount of gypsum added (up to 7.5 %) may not provide enough S to effectively compete in plant uptake with the Se in the treatments with 20 % fly ash. Nevertheless, it is possible to demonstrate a clear linear response of Se concentration to gypsum in the controlled environment of the greenhouse, working with known combinations of fly ash and gypsum, with little variation in Se concentration for each treatment. Further experimentation could focus profitably on estimating the appropriate gypsum dose to achieve the desired reduction in Se concentration. However, actual recommendations should be based on field trials, and not on greenhouse experiments, because of the much greater array of factors influencing the interaction between S and Se in a field.

The field experiment demonstrated that gypsum can be used to reduce Se concentration in alfalfa growing on a fly ash landfill. However, great local variation in the concentration of Se in both the soil and alfalfa in adjacent loci (Arthur et al. 1992) resulted in difficulty in declaring treatment differences statistically significant although the mean Se concentration of plants grown with gypsum added were 3- to 6-fold lower than those in plants grown without added gypsum. Such large variation could be due to the accidental mixing of fly ash with the soil during the capping process, differences in soil characteristics on the landfill resulting in differential uptake by plant roots, or a non-uniform capping layer. The difficulties of spreading gypsum evenly in the field also may have contributed to the large variation within treatments.

Despite the large local variation in Se concentration of alfalfa grown on the landfill, there was a strong indication that the reduction in Se concentration in alfalfa that results from the application of

11.2 t ha^{-1} gypsum persists into the second year, rendering appplication of gypsum in two consecutive years unnecessary to achieve an ecologically meaningful reduction in Se concentration. Selenium concentrations were reduced to levels well below the concentrations considered toxic to mammals when ingested in the diet (5 to 15 ug g^{-1}; Mayland et al. 1989).

Apparently we achieved the maximum reduction in Se concentration possible through the application of gypsum, because additional gypsum in the second year did not result in significantly lower Se concentrations in alfalfa. In addition, the lack of a decline through the season in Se concentration of alfalfa treated with gypsum, despite an increase in S concentration, indicated that the competitive interaction between S and Se possible occurs at a lower level of soil S concentration. Other researchers have noted that additional S is most effective in reducing Se concentration in plants when S availability is initally low (Davies and Watkinson 1966). Thus, adding S to soil that contains adequate S for plant nutrition may not reduce uptake of Se, despite increased plant concentrations of S with subsequent addition of S to the soil. In addition, a decrease in plant Se concentration with S addition to the soil typically is detected only with high Se concentrations in the soil (Milchunas et al. 1983, Spencer 1982). Thus, additional increments of S may not reduce Se concentrations below a given level, which probably varies among crops, soils, and Se source.

Alternatively, it is possible that alfalfa roots, which we know extend 1 to 2 cm into the fly ash, continue to access Se directly from the fly ash, and that gypsum additions at the surface cannot compete with Se uptake by those roots. The effect of S additions on Se uptake at this site may be limited by the depth of the roots and the ability of the gypsum to penetrate the full depth of the soil cap.

Based on these results and our previous investigations (Arthur et al. 1992b, c) gypsum might prove useful as a management tool to reduce the uptake of Se by plants growing on coal fly ash landfills. The results from the field experiment demonstrate that surface application of gypsum can mitigate Se uptake. If gypsum were applied before seeding, and the land tilled after application, the mitigation of Se uptake might occur sooner. Selenium uptake also could be mitigated by identifying and planting only those plant species that do not (1) root as deeply as alfalfa, thus limiting root-fly ash contact, and (2) take up Se as readily as alfalfa. For example, concentrations of Se in brome grass (Bromus inermis Leyss) and fescue (Festuca pratensis Huds.) on four fly ash landfills did not exceed 0.50 ug g^{-1} (Weinstein et al. 1989). A predominance of those species as cover on fly ash landfills could greatly reduce Se uptake from the fly ash.

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Table 1: The effect of two year's gypsum treatments on Se concentration and content of alfalfa harvested in 1991. Mean Se concentration ($\mu g\ g^{-1}$) and content ($mg\ m^{-2}$) in alfalfa harvested in 1991 from plots with 0 and 11.2 t ha^{-1} gypsum applied in 1990 and 1991. Standard errors are given in parentheses and are based on n=3 half plots.

		Gypsum levels			
	1990	0	0	11.2	11.2
Harvest	1991	0	11.2	0	11.2
June 1991					
Concentration		3.42	1.03	0.72	0.62
		(0.97)	(0.97)	(0.97)	(0.97)
Content		2.13	0.52	0.43	0.39
		(0.63)	(0.63)	(0.63)	(0.63)
July 1991					
Concentration		5.22	2.39	0.91	1.12
		(0.72)	(0.72)	(0.72)	(0.72)
Content		1.29	0.70	0.33	0.40
		(0.11)	(0.11)	(0.11)	(0.11)
August 1991					
Concentration		5.22	1.42	0.58	0.70
		(1.59)	(1.59)	(1.59)	(1.59)
Content		1.80	0.41	1.67	0.19
		(0.61)	(0.61)	(0.61)	(0.61)

Table 2: The effect of the 1990 gypsum treatment alone on Se concentration and content and S concentration of alfalfa harvested in 1991. Mean Se concentration ($\mu g\ g^{-1}$) or content ($mg\ m^{-2}$) and S concentration (%) in alfalfa growing in 1991 on plots with 0 and 11.2 t ha^{-1} gypsum applied in 1990. Standard errors are given in parentheses and are based on n=6 half plots.

	Harvest					
	June 1991		July 1991		August 1991	
	Gypsum levels (t ha^{-1}) in 1990					
	0	11.2	0	11.2	0	11.2
Se concentration	2.23	0.67	3.80	1.01	3.32	0.64
	(0.67)	(0.67)	(0.99)	(0.99)	(1.46)	(1.46)
Se content	1.33	0.41	1.00	0.37	1.10	0.18
	(0.43)	(0.43)	(0.20)	(0.20)	(0.54)	(0.54)
S concentration	0.35	0.39	0.48	0.51	0.52	0.61
	(0.01)	(0.01)	(0.00)	(0.00)	(0.01)	(0.01)

Table 3: The mean differences in Se concentration ($\mu g\ g^{-1}$), Se content ($mg\ m^{-2}$) and S concentration (%) between alfalfa growing in 1991 on adjacent half plots (receiving 0 and 11.2 $t\ ha^{-1}$ gypsum in 1991) for the different 1990 gypsum treatments (0 and 11.2 $t\ ha^{-1}$). Standard errors are given in parentheses and are based on n=3 whole plots (3.05 m x 6.10 m).

	Harvest					
	June 1991		July 1991		August 1991	
	Gypsum levels ($t\ ha^{-1}$) in 1990					
	0	11.2	0	11.2	0	11.2
Se concentration	2.40	0.10	2.90	-0.21	3.79	-0.09
	(1.26)	(1.26)	(1.33)	(1.33)	(2.38)	(2.38)
Se content	1.63	0.04	0.59	-0.07	1.40	-0.02
	(0.89)	(0.89)	(0.22)	(0.22)	(0.89)	(0.89)
S concentration	-0.10	-0.03	-0.07	0.01	-0.14	-0.19
	(0.03)	(0.03)	(0.03)	(0.03)	(0.10)	(0.10)

Table 4: The effect of gypsum applications on S and Ca concentration in alfalfa harvested in 1991. Mean S and Ca concentrations (%) in alfalfa harvested in 1991 from plots with 0 and 11.2 t ha^{-1} gypsum applied in 1990 and 1991. Standard errors are given in parentheses and are based on n=3 half plots.

Harvest		Gypsum levels			
	1990	0	0	11.2	11.2
	1991	0	11.2	0	11.2
June 1991					
Sulfur		0.30	0.40	0.38	0.41
		(0.02)	(0.02)	(0.02)	(0.02)
Calcium		1.91	2.05	2.09	1.99
		(0.10)	(0.10)	(0.10)	(0.10)
July 1991					
Sulfur		0.45	0.52	0.52	0.51
		(0.03)	(0.03)	(0.03)	(0.03)
Calcium		2.48	2.41	2.46	2.40
		(0.05)	(0.05)	(0.05)	(0.05)
August 1991					
Sulfur		0.45	0.60	0.58	0.64
		(0.02)	(0.02)	(0.02)	(0.02)
Calcium		1.85	2.02	2.07	1.94
		(0.03)	(0.03)	(0.03)	(0.03)

Table 5: Mean Se concentrations ($\mu g\ g^{-1}$) in alfalfa, grown with 12 treatment combinations of fly ash and gypsum amendments to soil. n=3 pots per treatment combination.

	Harvest									
	74 days					118 days				
	Gypsum (%)					Gypsum (%)				
Fly ash (%)	**0**	**2.5**	**5**	**7.5**	**SE**	**0**	**2.5**	**5**	**7.5**	**SE**
0	0.07	0.05	0.04	0.05	0.01	0:06	*	*	*	0.01
10	0.96	0.90	0.68	0.70	0.33	1.05	0.70	0.61	0.62	0.14
20	2.31	2.37	1.97	2.23	0.33	2.34	1.72	2.22	2.09	0.14

* Not measured at harvest 2.

Table 6: Mean S concentration (%) in alfalfa, grown with 12 treatment combinations of fly ash and gypsum amendments to soil. n=3 pots per treatment combination.

	Harvest									
	74 days					118 days				
	Gypsum (%)					Gypsum (%)				
Fly ash (%)	**0**	**2.5**	**5**	**7.5**	**SE**	**0**	**2.5**	**5**	**7.5**	**SE**
0	0.41	0.54	0.51	0.51	0.03	0.29	*	*	*	0.06
10	0.48	0.48	0.44	0.45	0.01	0.33	0.34	0.45	0.46	0.02
20	0.48	0.46	0.48	0.48	0.01	0.47	0.50	0.46	0.49	0.02

* Not measured at harvest 2.

Table 7: Mean Ca concentration (%) in alfalfa, grown with 12 treatment combinations of fly ash and gypsum amendments to soil. n=3 pots per treatment combination.

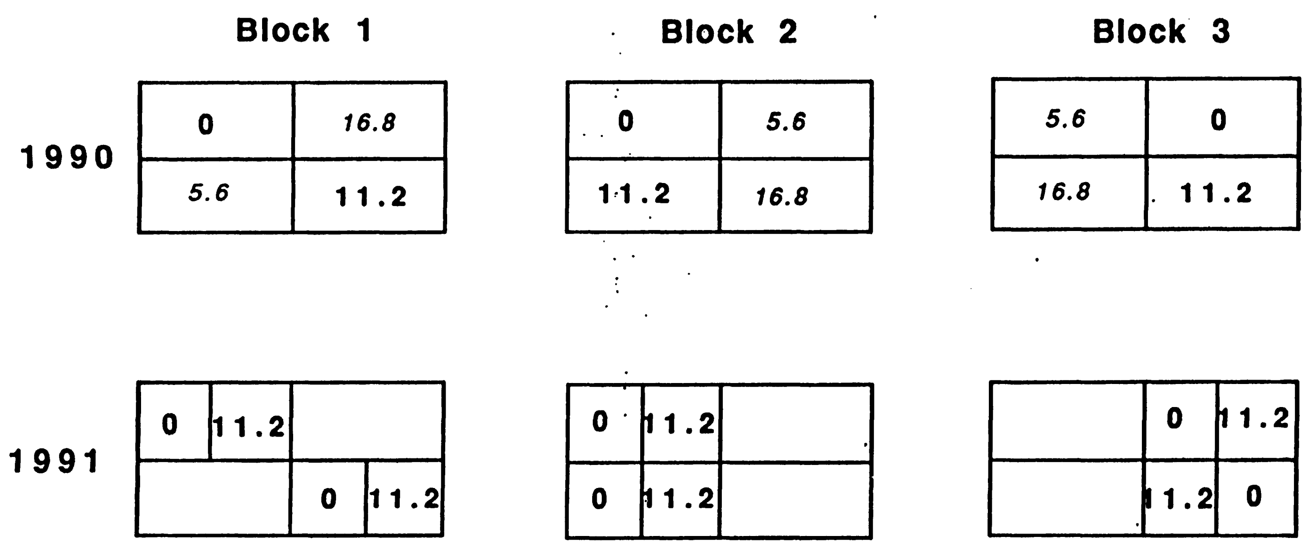
	Harvest									
	74 days					118 days				
	Gypsum (%)					Gypsum (%)				
Fly ash (%)	0	2.5	5	7.5	SE	0	2.5	5	7.5	SE
0	2.44	2.57	2.21	2.15	0.08	2.31	*	*	*	0.07
10	2.42	2.18	2.11	2.06	0.06	2.58	2.60	2.33	2.58	0.10
20	2.28	2.15	2.13	2.14	0.06	2.42	2.58	2.36	2.49	0.10

* Not measured at harvest 2.

Figure Legends:

Figure 1: Layout for gypsum applications (t ha^{-1}) to alfalfa plots on a fly ash landfill in 1990 and 1991. The italicized numbers represent gypsum doses used in 1990 that were not continued in the 1991 experiment. Blank areas in the 1991 layout correspond to those plots.

Figure 2: Decrease in Se concentration in alfalfa as a function of gypsum dose for soil containing 10 % fly ash in the first (A) and second (B) harvests.


Block 1
Block 2
Block 3
1990
0
16.8
5.6
11.2
0
5.6
11.2
16.8
5.6
0
16.8
11.2
1991
0
11.2
0
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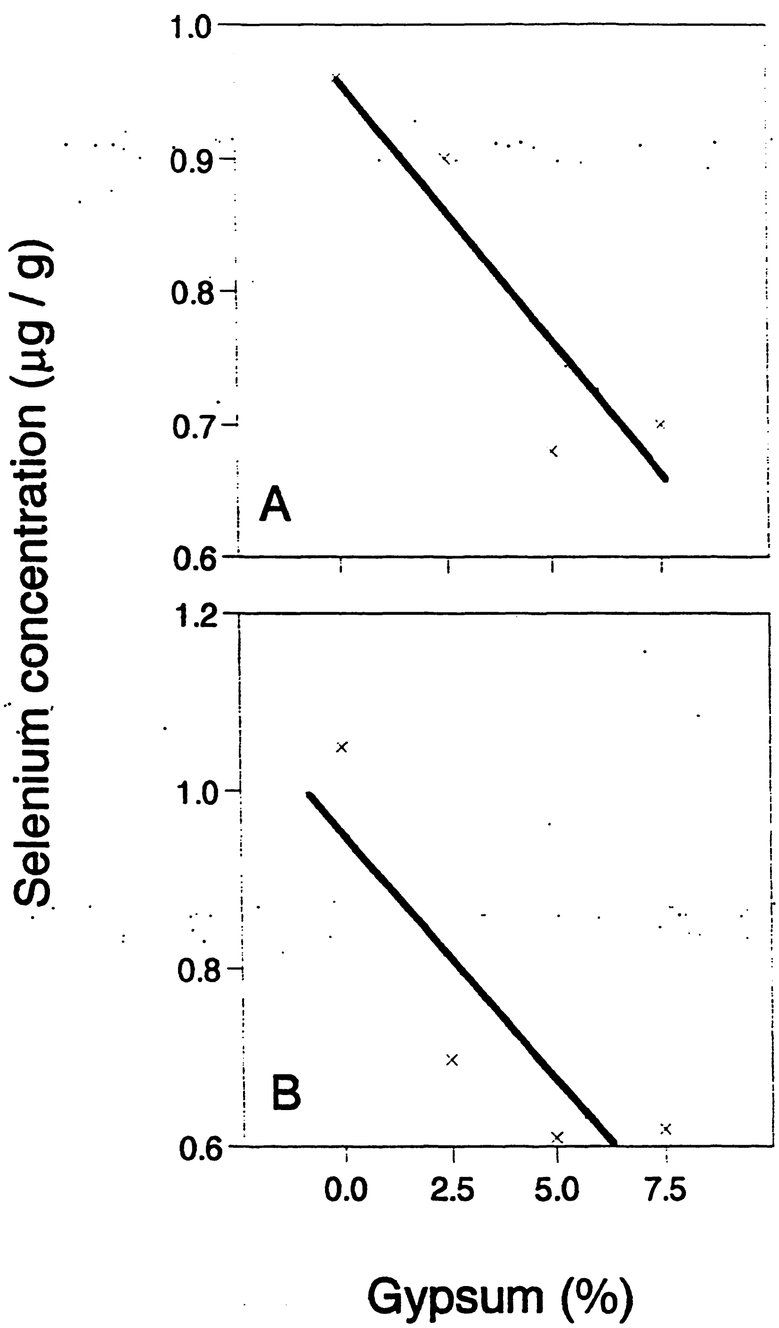
11.2
0
11.2
11.2
0



Selenium concentration (µg / g)
1.0
0.9
0.8
0.7
0.6
A
1.2
1.0
0.8
0.6
B
0.0
2.5
5.0
7.5
Gypsum (%)