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Leaching of Added Selenium From Alkaline Soils as Influenced by Sulfate[1]

M. J. BROWN AND D. L. CARTER[2]

ABSTRACT

A $BaSO_4$-$BaSeO_4$ mixture (S:Se = 10) and $BaSeO_4$ alone were applied at 1.60 and 3.20 mg Se per column to two soils and leached with water or gypsum solution. Eight hundred milliliters (10-cm depth) of leaching solution were added to columns containing 2,100 g of Portneuf silt loam and 2,500 g of Gooding loamy sand at 4-week intervals for 20 weeks. More Se was leached by gypsum solution than by water from all columns. Where 1.60 mg Se per column was applied, more Se was leached from Gooding loamy sand than from Portneuf silt loam soil with both water and gypsum solution. Where 3.20 mg Se per column was applied, more Se was leached by water from Gooding than from Portneuf soil, but the reverse was true with gypsum solution. The Se leached from the Portneuf soil treated with the $BaSO_4$-$BaSeO_4$ mixture ranged from 0.34 mg, where 1.60 mg Se per column was applied and soils leached with water, to 2.32 mg, where 3.20 mg Se per column was applied and soils leached with gypsum solution.

Much less Se was leached where only $BaSeO_4$ was applied to Portneuf soil. The amount leached ranged from 0.07 mg, where 1.60 mg Se was applied and water used for leaching, to 0.64 mg Se, where 3.20 mg Se was applied and gypsum used for leaching. The Se recovery from the Gooding soil was within these ranges for the same treatments. The Se leached increased with application rate, but not proportionately. The data indicate that addition of SO_4^{2-} increases the solubility of $BaSeO_4$ in these soils.

Additional Key Words for Indexing: **white muscle disease, soil columns, barium-selenate, barium-sulfate.**

SMALL amounts of Se in the animal diet are required for normal organ function and for prevention of WMD (white muscle disease) (3, 8, 13, 14, 16). Animals eating feeds containing less than about 0.03 to 0.1 ppm Se are subject to WMD (11, 12, 13). In contrast, more than 5 ppm Se in the animal diet is toxic (5).

A material is needed that can feasibly and economically be applied to increase plant uptake of Se from soils now providing too little available selenium. The criterion for such a material is that it provide Se to plants in quantities sufficient to prevent WMD in animals but low enough to be nontoxic. A material that will meet the criterion for alkaline soils may be difficult to find because selenate is theoretically the stable form of Se in alkaline soils, and selenates are generally quite soluble. Nevertheless such a compound applied to soil could greatly reduce livestock losses from WMD and save millions of dollars annually.

Adding barium chloride to some alkaline seleniferous soils reduced Se uptake by plants. Presumably $BaSeO_4$ was formed, and the level of available Se in the soil solution was reduced (15). Based on this report $BaSeO_4$ is quite insoluble in some alkaline soils. Therefore, it may be a slowly available Se source in alkaline soils low in Se.

Applying S compounds to soils also influences Se uptake. Uptake of Se applied as $Na_2SeO_4 \cdot 10H_2O$ to field plots of winter wheat was decreased from 110 to 2 ppm by applying gypsum and elemental S (9, 10). Selenium taken up by *chlorella vulgaris* cells in nutrient solutions decreased with increased external S concentrations (17).

Studies have been conducted to determine the movement of Se in the soil-plant-animal cycle (4), but information is lacking on the actual Se movement from its placement source in the soil-water system. The availability of Se in soil to plants is determined by measuring the amount of Se taken up by plants. There is no accurate soil test to determine the availability of Se in soil to plants. However, it has been determined that the amount of water-soluble Se leached from soil approximates the amount plants will absorb (6).

This paper reports results of a study conducted to determine the effects of sulfate on the solubility of $BaSeO_4$ applied to two alkaline soils and subsequent leaching of selenium.

MATERIALS AND METHODS

Bulk supplies of Portneuf silt loam and Gooding loamy sand (Table 1) were taken from the surface 20 cm of the two soils, air dried, passed through a 2-mm sieve, and packed into columns at densities of 1.32 and 1.57 g/cm^3, respectively. The columns were 10 cm in diameter and 30 cm high, and the soils were packed 20 cm deep in the columns as described by Hannapel et al. (7). The soils were leached with 1,500 ml of deionized water over a 6-day period to obtain more uniform compaction in the columns. After drying for 8 weeks, 300 ml of water were added to each soil column, and draining was allowed for 3 days before treating with Se compounds.

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[1] Contribution from the Northwest Branch, Soil & Water Conservation Research Division, ARS, USDA. Idaho Agr. Exp. Sta., cooperating. Received Feb. 24, 1969. Approved April 10, 1969.

[2] Soil Scientist and Research Soil Scientist, Kimberly, Idaho.

Table 1—Cation exchange capacity, pH and particle size distribution of Portneuf and Gooding soil

Soil description	Portneuf Silt loam	Gooding loamy sand
Cation exchange capacity* (meq/100)	23.9	9.05
pH (1:25 soil: water soln)	7.8	7.7
Particle size distribution		
% sand	25	85
% silt	54	11
% clay	21	4

* Determined by sodium acetate method.

$BaSeO_4$ and a $BaSO_4$-$BaSeO_4$ mixture (S:Se = 10) were applied in suspension at 1.6 and 3.2 mg Se per column. The materials were reagent grade chemicals, and the mixture was obtained by mechanically mixing appropriate amounts of the two salts. Four columns of each soil were treated with 1.6 mg Se as $BaSeO_4$. Another group of four columns of each soil received 3.2 mg Se as $BaSeO_4$. A third group was treated with the $BaSO_4$-$BaSeO_4$ mixture to give 1.6 mg Se per column, and a fourth group received the mixture at 3.2 mg Se per column. Eight columns of each soil received no Se. The materials were applied by using a cork borer to remove a core of moist soil 1.8 cm in diameter and 2.5 cm deep from the center of the surface of each column. The Se compounds were placed into the hole and the soil core was replaced.

Duplicate columns of the treated and control soils were leached with 800-ml portions of deionized water at 4-week intervals to displace the soil solution. Another group of duplicate columns were similarly leached with a saturated gypsum solution. After five leachings the soil was removed from the columns, cut into 5-cm sections, and prepared for Se analyses. Each soil section was thoroughly mixed and a 1-g sample was placed in a 250-ml beaker and predigested overnight with 5 ml HNO_3. Four milliliters of 1:1 HNO_3 and H_2SO_4 were added and the samples were further digested without boiling until nearly dry. The sample was removed from the hotplate, cooled, and washed through a no. 1 Whatman filter paper. The filtrate was made to a 50-ml volume and analyzed for Se (1). The Se leached by water and saturated gypsum solution was determined fluorometrically (1). The quantities of Se leached from treated soils were corrected for the Se leached from untreated soils.

RESULTS AND DISCUSSION

The Se leached from Portneuf silt loam treated with the $BaSO_4$-$BaSeO_4$ mixture ranged from 0.34 mg, where 1.60 mg Se per column was applied and water used for leaching, to 2.32 mg, where 3.20 mg Se per column was applied and gypsum solution used for leaching (Table 2). Much less Se was leached where only $BaSeO_4$ was applied. The amount leached ranged from 0.07 mg, where 1.60 mg Se was applied and water used for leaching, to 0.64 mg Se, where 3.20 mg Se was applied and gypsum solution used for leaching. The Se recovered from the Gooding loamy sand was within these ranges for the same treatments (Table 2).

More Se was leached from all columns by saturated gypsum solution than by water (Table 2). Differences between the amounts leached by the two solutions were more pronounced at the highest application rate. Furthermore, the amount leached from the $BaSO_4$-$BaSeO_4$ mixture was greater than that from $BaSeO_4$ alone. These results show that adding SO_4^{2-} to the system increased $BaSeO_4$ solubility. This results because $BaSO_4$ is less soluble than $BaSeO_4$ (18). Different sources of SO_4^{2-} were additive in this effect on $BaSeO_4$ solubility as evidenced by greater Se leaching where the mixture was applied and gypsum solution used for leaching than where $BaSeO_4$ alone was applied and gypsum solution used. Greater $BaSeO_4$ solubility should mean greater Se availability to plants in contrast to reports that applying elemental S and gypsum reduces Se uptake (9, 10). Results from a field study verified that SO_4^{2-} applied to the Portneuf soil increases Se uptake by alfalfa [D. L. Carter, M. J. Brown, and C. W. Robbins. 1969. Selenium concentrations in alfalfa from several sources applied to a low selenium, alkaline soil. Soil Sci. Soc. Amer. Proc. Vol. 33 (in press).]. For example, when $BaSeO_4$ was applied at 2 kg Se/ha (approximately equivalent to 1.6 mg Se/column) to Portneuf soil in the field, the resulting Se concentration in alfalfa was 6.05 ppm. When the same amount of Se was applied as a $BaSO_4$-$BaSeO_4$ mixture, the resulting plant concentration was 33.80 ppm. Adding the $BaSO_4$ caused a fivefold increase in Se uptake. Adding $BaSO_4$ to the soil columns receiving 1.60 mg Se resulted in a fivefold increase in the quantity of Se leached by water from the Portneuf soil (Table 2). Thus, in the Portneuf soil, Se availability is controlled by $BaSeO_4$ solubility.

Table 2—Selenium leached with water or gypsum solution from Portneuf and Gooding soils treated with $BaSeO_4$ and a $BaSO_4$-$BaSeO_4$ mixture

Material	Amount applied	Leaching solution	Se leached* Portneuf	Se leached* Gooding
	mg		mg	mg
$BaSO_4$-$BaSeO_4$	1.60	Water	0.34 cd	0.49 bcd
	1.60	Gypsum	0.51 bcd	0.76 bcd
	3.20	Water	0.88 bcd	1.23 abc
	3.20	Gypsum	2.32 a	1.55 ab
$BaSeO_4$	1.60	Water	0.07 d	0.15 cd
	1.60	Gypsum	0.17 cd	0.28 cd
	3.20	Water	0.09 cd	0.19 cd
	3.20	Gypsum	0.64 bcd	0.31 cd
		Averages		
$BaSO_4$-$BaSeO_4$			1.02	1.01
$BaSeO_4$			0.24	0.24
		Water	0.34	0.52
		Gypsum	0.91	0.73

Statistical significance of comparisons at the 1% probability level:

Water vs gypsum solution	S	Soil × material	NS
$BaSEO_4$ vs. $BaSO_4$-$BaSeO_4$	S	Soil × rate	S
1.60 vs 3.20 mg Se per column	S	Solution × material	S
Gooding vs. Portneuf soil	NS	Solution × rate	S
Soil × solution	S	Material × rate	S

* Values followed by the same letter do not differ significantly.

The effects of SO_4^{2-} on $BaSeO_4$ solubility or Se availability became more pronounced with time (Fig. 1 and 2). Evidently more $BaSeO_4$ is dissolved as the reaction time is increased, and the overall effects are accumulative. The effects of SO_4^{2-} differed with the soil where 3.20 mg Se was applied. At this rate the SO_4^{2-} had a much greater effect in the Portneuf soil than in the sandy Gooding soil (Fig. 1 and 2). The reason for this difference is not known, but is must be associated with differences in soil properties. The difference between soils was not so evident at the low Se application rate (Table 2).

More Se was leached from the high application rate on both soils (Table 2). Here again differences between the amounts leached from low and high application rates were greater on the Portneuf soil. More Se was leached from the Gooding than the Portneuf soil for all treatments except where 3.20 mg Se were applied and saturated gypsum solution was used for leaching.

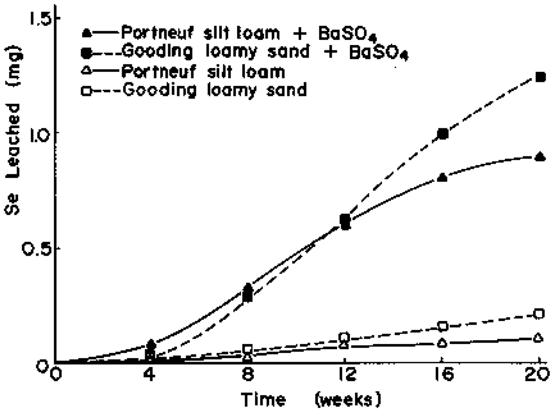

Fig. 1—Selenium leached with water from two soils containing 3.2 mg Se per column.

Se that leached through the soil columns moved readily from the point of application into the leachate. Small amounts of Se were found within each 5-cm increment of soil, but there was no consistent distribution of Se as a function of depth in the leached soils. Total Se recovery was good. Essentially all the Se applied was accounted for in the leachate and remaining in the soil.

The results obtained in this investigation are associated with the relative solubilities of several compounds in the system. These compounds and their solubilities in water at 25C in moles/liter are: $BaSeO_4$ at 4.21×10^{-4}; $BaSO_4$ at 9.51×10^{-6}; $CaSO_4$ at 1.53×10^{-2}; and $CaSeO_4$ at .431 (19). The least soluble of these compounds is $BaSO_4$. Therefore, as excess SO_4^{2-} is added to the system from the saturated gypsum solution or from $BaSO_4$ in combination with $BaSeO_4$, the Ba^{2+} is removed from the solution by the excess SO_4^{2-} to form $BaSO_4$. As the Ba^{2+} is removed, more $BaSeO_4$ dissolves. In the calcareous soils used in this study, this process would leave SeO_4^{2-} in solution probably associated with Ca^{2+}, and readily available to plants.

Based on the work of Ravikovitch and Margolin (15), Allaway et al. (2) and the authors have suggested that $BaSeO_4$ may have possibilities as a slowly available Se source for alkaline soils. The results reported here do not support that possibility.

In conclusion, the quantity of Se leached depended upon SO_4^{2-} concentration, soil, leaching solution, and application rate interactions. The primary factor controlling $BaSeO_4$ solubility and resultant Se leachability was SO_4^{2-} concentration.

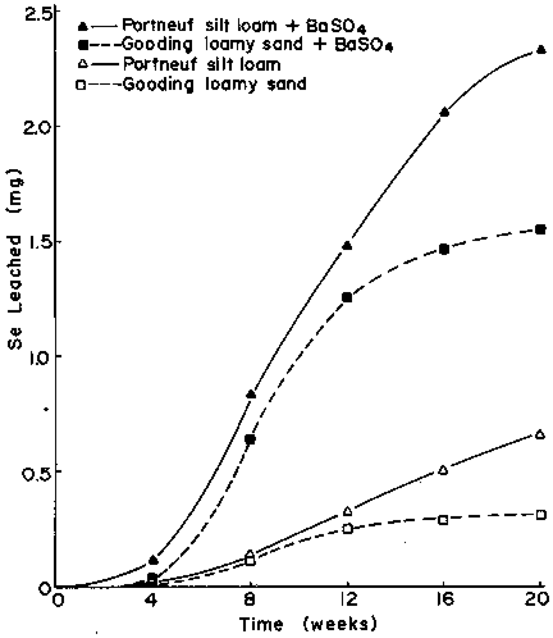

Fig. 2—Selenium leached with gypsum solution from two soils containing 3.2 mg Se per column.

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