DIVISION S-8—FERTILIZER TECHNOLOGY AND USE

Selenium Concentrations in Phosphorus Fertilizer Materials and Associated Uptake by Plants[1]

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ABSTRACT

The Se concentration of seven Florida Land Pebble deposit phosphate rocks ranged from 0.7–7.0 ppm. The range was 1.4–178 ppm Se in seven samples from the western phosphate field. The Meade Peak phosphatic shale member of the Phosphoria formation contains more Se than rock from other phosphatic formations. Normal and concentrated superphosphates made from phosphatic rocks containing 100 ppm Se can be expected to contain about 60 and 40 ppm Se, respectively. Laboratory-prepared concentrated superphosphate containing 23 ppm Se applied to an alkaline soil that normally produced alfalfa (*Medicago sativa* L.) low in Se at a rate of 156 ppm P increased Se concentration in alfalfa above the minimal requirements to protect livestock from white muscle disease. Concentrated superphosphate and single superphosphate prepared from phosphate rock containing 178 ppm Se and applied at a rate of 80 ppm P increased the Se concentration in alfalfa compared to the same amount of P applied as Se free concentrated superphosphate. Normal phosphate fertilizer practices can provide required Se for livestock provided the fertilizer is prepared from phosphate rock containing sufficient Se.

Additional Key Words for Indexing: **white muscle disease, phosphate rock, Meade Peak phosphatic shale, Florida Land Pebble deposits.**

SINCE THE discovery that small amounts of Se are required for normal animal nutrition and to prevent white muscle disease (WMD) (12), some research effort has been directed towards developing a convenient, economical method of providing livestock with adequate Se (2, 5, 8). The minimal Se requirement for livestock ranges from 0.03–0.10 ppm in the diet depending upon the vitamin E level and possibly other factors (2). Maintaining minimal Se levels in livestock feed is complicated because present regulations do not permit the addition of Se to feed, and concentrations above 3–5 ppm are toxic to livestock (2). Applying commercially available Se sources to soil has resulted in toxic Se concentrations in forage and hay (2, 5, 7, 8), but some laboratory-prepared Se compounds and some selenites applied to the soil provide slowly avail-

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Table 1—Selenium concentration in phosphate rock, phosphoric acid, and concentrated superphosphate

	Phosphate rock	Phosphoric acid	Concentrated superphosphate	Concentrated superphosphate predicted value
	ppm			
		Western Field		
TRC Trail, B.C. (Canada)	5.98	0.15		
Pocatello, Idaho (J.R. Simplot Co.)	7.50	0.02	2.78	2.87
Vernal, Utah	1.42	0.06	0.57	0.58
Leefe, Wyoming (open pit mine)	1.76			
Leefe, Wyoming (underground mine)*	50.0			
Conda, Idaho	6.77	0.06	3.53	3.13
Georgetrown, Idaho*	178.0			
Pocatello, Idaho (furnace acid) (FMC Corp)	3.36	<0.01		
		Florida Land Pebble		
Swannee River Mine, Hamilton Co., Florida	0.77	0.09	0.41	0.39
Sidney Mines, Brewseter, Polk Co., Florida	0.71	0.18	0.43	0.39
Tenoroc, Polk Co., Florida	1.51	0.19	0.58	0.69
Bartow, Polk Co., Florida	7.00	0.40	3.88	3.66
Bartow, Polk Co., Florida	3.35	0.02	1.61	†
South Pierce Mine, Polk Co., Florida	2.10	0.04	0.43	†
Silver City Mine, Polk Co., Florida	0.90	0.04	0.54	0.50

* Samples taken from the Meade Peak phosphatic shale. † No calculated value due to lack of information.

able Se from which plants absorb adequate but nontoxic concentrations for livestock (3, 5, 6).

A regularly applied fertilizer that would supply adequate but nontoxic Se levels in plants would be useful in preventing WMD. For example, if a phosphate fertilizer that contained the appropriate Se concentration were available, it could be applied to satisfy P needs, and at the same time satisfy Se needs at no additional cost. Geological data indicate that there are naturally occurring phosphate sources that contain up to 150 ppm Se (9). In 1936, Rader and Hill (13) were concerned that plants grown on soils treated with fertilizers made from some of these phosphate rock materials would contain sufficient Se to be toxic to livestock.

This paper reports Se concentrations in phosphate rocks and fertilizers from 15 sources in the United States and Canada. The availability of the Se in three concentrated superphosphates and a single superphosphate prepared in the laboratory from some of the phosphate rocks is also reported.

METHODS AND MATERIALS

Phosphate rock and fertilizer samples were obtained from the more important sources in the United States and Canada (Table 1). Dry samples were ground to pass a 145μ (100 mesh) sieve. One-gram samples of each material were treated with 5 ml of concentrated HCl and 5 ml of concentrated HNO_3 for 1 hour. They were then washed through no. 42 Whatman filter paper and diluted to a 100-ml volume with distilled water (Trade names are for the benefit of the reader and do not represent endorsement by the USDA). The excess HNO_3 was removed from an aliquot containing less then 0.5μ g Se by a reducing solution composed of two parts concentrated HCl and one part 30% hypophosphorus acid. From this point, duplicate samples were analyzed according to the method of Allaway and Cary (1).

The Se recovered by the method outlined was determined by adding Na_2SeO_3 to rock samples or filter paper, drying at room temperature, and then treating the material as outlined for the dry samples. Recovery of the added Se was complete (Table 2).

Three superphosphate fertilizers were prepared in the laboratory from phosphate rocks of known Se concentration by treating the ground rock with H_3PO_4. The treated materials were allowed to stand for 2 hours to allow a minimum of 90% reac-

Table 2—Recovery of Se added as Na_2SeO_3 to filter paper and to phosphate rock

Material	Calculated Se content	Recovered Se,
	μg	μg
Na_2SeO_3	0.200	0.210 ±0.010
Na_2SeO_3	0.300	0.306 ±0.008
0.5 g phosphate rock no. 43 + 0.5 g Se*	0.940	0.938 ±0.034
0.5 g phosphate rock no. 43 + 0.4 g Se*	0.840	0.844 ±0.045
1 g phosphate rock no. 43		0.880

* Added as Na_2SeO_3.

tion between the rock and the acid (10). The finished phosphate fertilizers contained 0.0, 11.5, and 23.0 ppm Se.

Pots containing 3 kg Portneuf silt loam were treated with the laboratory-prepared concentrated superphosphates. The three treatments were 0, 23.5, and 47.0 μg Se and 156 ppm P per pot. The pots were placed in a randomized complete block design with three replications. Alfalfa shoots (*Medicago sativa* L. 'Ranger') from a mother plant were rooted in a misting table and transplanted, four plants to each pot. Five cuttings at approximately 1/10 bloom were taken. The plant material was dried at 55C, ground, and analyzed for Se (1).

The soil used in the greenhouse pots was taken from the surface 15 cm of Portneuf silt loam. It is a calcareous soil (pH 7.8) with a cation exchange capacity of 24 meq/100 g and a partical size distribution of 25, 54, and 21% sand, silt, and clay, respectively. The surface soil used in this study contained 7.2 ppm bicarbonate soluble P.

After the above described greenhouse study was nearly completed, we obtained some phosphate rock from Georgetown, Idaho that contained more Se than our other samples. Therefore we decided to conduct a second greenouse study utilizing the high Se phosphate rock to prepare fertilizers of higher Se content than those used in the first study.

Soil used in the second study was obtained from the surface of a Portneuf silt loam, but it was from a site where the surface soil was deeper and the cropping history different than that used in the first study. This soil contained 7.5 ppm bicarbonate soluble P. Each pot contained 3 kg of the soil.

A concentrated superphosphate and a single superphosphate were prepared from the high Se phosphate rock by treating with H_3PO_4 and H_2SO_4, respectively. The resulting concentrated superphosphate contained 70 ppm Se and the single superphosphate contained 105 ppm Se. The phosphate fertilizers were applied at rates to give 80 ppm added P per pot. The quantities of Se added were 108 and 216 μg per pot, respectively. The 0 Se level was obtained by applying a concentrated superphosphate containing no Se. Again, a randomized complete block design with three replications was used. Alfalfa shoots from a mother plant were rooted and planted, three plants per pot. Three cuttings at approximately 1/10 bloom were taken, and the plants were dried and analyzed as previously described.

RESULTS AND DISCUSSION

Seven samples from the Florida Land Pebble deposits located in North Carolina, South Carolina, and Florida contained from 0.7–7.0 ppm Se (Table 1). Nearly all of the phosphate rock from these deposits is mined in Florida at the present time (11).

No samples were obtained from the Arkansas, Kentucky, and Tennessee phosphate deposits. These deposits have produced less than 2% of the United States phosphate fertilizer since 1956.

Seven phosphate rock samples from the western phosphate field, which extends over western Wyoming, northern Utah, northeastern Nevada, southeastern and south-central Idaho, and southwestern Montana, contained from 1.4–178 ppm Se (Table 1). The Meade Peak phosphatic shale member of the Phosphoria formation of this field contains a significant amount of Se. Samples taken at Leefe, Wyo., and Georgetown, Idaho, from this shale contained 50 ppm and 178 ppm Se, respectively. Nine samples taken by Gulbrandsen (9) from this formation at Coal Canyon, Wyo., contained from 10–150 ppm Se, and five of them contained more than 90 ppm. The phosphate rock sample from T.R.C. Trail, B.C., Canada, contained 6.0 ppm Se.

Normal superphosphate can be expected to contain about 60% and concentrated superphosphate about 40% as much Se as the phosphate rock from which it is made. These figures represent the approximate rock content of the finished products. Using this information, Selenium concentrations in concentrated superphosphate were predicted (Table 1, column 4) for materials known to be prepared from specific rock and acid. Samples of the concentrated superphosphate were analyzed and the results are given (Table 1, column 3). The predicted and measured values are essentially identical.

The highly pure phosphoric acid produced by electric furnace distillation is selenium free. The wet process acid samples contained less than 0.2 ppm Se, probably because calcium selenates and selenites were removed during precipitation and filtering to remove the gypsum.

The ammonium phosphate products produced by neutralizing phosphoric acid with ammonia were below 0.2 ppm Se, as would be expected from low Se concentrations in the phosphoric acid.

The Se concentration in alfalfa for all five cuttings grown on soil treated with concentrated superphosphate containing 23 ppm Se in the first greenhouse study was above the minimal requirements for livestock (Table 3). In all cuttings but the second, treatment with this material significantly increased the Se concentration in alfalfa over that

Table 3—Selenium concentration in alfalfa from three concentrated superphosphate fertilizers applied to Portneuf silt loam

Se in fertilizer	Se added per pot	P added	Cuttings 1st	2nd	3rd	4th	5th
ppm	μg	ppm	Se concentration, ppm*				
0.0	0.0	156	0.062 a	0.109 a	0.108 a	0.075 a	0.068 a
11.5	23.5	168	0.098 b	0.103 a	0.117 a	0.097 b	0.081 b
23.0	47.5	166	0.101 b	0.111 a	0.147 b	0.130 c	0.115 c

* Means in the same columns followed by the same letter are not significantly different at the 5% level.

Table 4—Selenium concentrations in alfalfa from concentrated superphosphate and single superphosphate applied to Portneuf silt loam

Material	Se in fertilizer	Se added per pot	P added per pot	Cuttings 1st	2nd	3rd
	ppm	μg	ppm	Se concentration, ppm*		
Concentrated superphosphate	0	0	80	0.244 a	0.230 a	0.142 a
Concentrated superphosphate	70	108	80	0.368 b	0.292 b	0.183 b
Single superphosphate	105	216	80	0.455 c	0.315 b	0.212 c

* Means in the same column followed by the same letter are not significantly different at the 5% level.

where concentrated superphosphate containing no Se was applied. Applying concentrated superphosphate containing 11.5 ppm Se significantly increased Se uptake in three of five alfalfa cuttings. In three of five cuttings, the Se concentration in alfalfa grown on soil receiving the same amount of concentrated superphosphate without Se was too low to protect livestock from WMD when vitamin E is low.

Applying concentrated superphosphate contianing 70 and single superphosphate 105 ppm Se significantly increased the Se concentration in all three alfalfa cuttings in the second study (Table 4). Thus results from the second study varify results from the first study. The increase in Se concentration in the first cuttings for both studies approximated 0.001 ppm per 1 μg Se applied. The concentration increase was smaller for subsequent cuttings in the second study.

The Se concentration in all alfalfa cuttings from the second greenhouse study was above minimal requirements for livestock. Evidently the soil used had a higher level of available Se then that used in the first study. This may have resulted from previous fertilizer practices, and is typical of the field-to-field variation reported by Carter et al (4).

This study has shown that proper selection of phosphorus fertilizer may be doubly important for soils that produce low Se forage. Applying phosphorus fertilizers that contain 20 or more ppm Se may provide sufficient Se to the plants to protect livestock from WMD at no additional cost.

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