Selenium Content of Some Fertilizers and Their Influence on Uptake of Selenium in Plants

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The selenium and the sulfur contents of some fertilizers were measured. During the production of two compound fertilizers, samples were taken from the raw material and products for quantitative selenium determination to evaluate the contribution of the raw materials to the selenium content of the fertilizers. The uptake by plants of selenium from these fertilizers was about 1% of the total selenium uptake. Subsequently, ^{75}Se-selenite was incorporated in a PK and a NPK fertilizer used in a microplot experiment in order to measure their characteristics as carriers of added selenium. The uptake was, in all cases, highest when using the sulfur-poor NPK fertilizer.

Since selenium has been shown to be an essential element for livestock nutrition, it has also been shown that many areas produce crops low in selenium (Carter *et al.*, 1968; Gardiner *et al.*, 1962; Kubota *et al.*, 1967) and much effort has been spent on investigations into possible ways to increase the selenium content of crops from these areas (Cary *et al.*, 1967; Davies and Watkinson, 1966; Ehlig *et al.*, 1968; Gissel-Nielsen and Bisbjerg, 1970; Grant, 1965). One possible selenium source for plants is applied fertilizer and it is, therefore, of interest to know the selenium content of the fertilizers and the raw materials from which they are manufactured. Rader and Hill (1936) determined the selenium content of many different natural phosphates from all over the world, and recently Robbins and Carter (1970) published new results concerning selenium in phosphate rocks and superphosphates.

This paper deals with the selenium content of common fertilizers in Denmark and of raw materials for the manufacturing procedure of some compound fertilizers. It also describes the results from a microplot experiment where two different fertilizers were compared as carriers for addition of selenium to soils.

Selenium Content in Fertilizers and Raw Materials. A collection of fertilizers and fertilizer raw materials commonly used in Denmark was analyzed for selenium and sulfur.

The selenium contents were measured by neutron activation analysis, as described by Bowen and Cawse (1963) with some modifications. All samples except the heavy fuel oil were dried to constant weight at 55° C, the acids were first neutralized with NaOH, and then evaporated in vacuum to dryness. Three grams of all the samples were irradiated together with 5 μg of Se-standard in the Risø reactor DR 2 for about 40 hr in a neutron flux at 5–8 × 10^{12} n/cm^2 sec. The chemical treatment followed that described by Gregers-Hansen (1964), and the activity of ^{75}Se was measured on a 512-channel analyzer. The only exceptions in the treatment were that the sulfur and the heavy fuel oil were oxidized in a boiling mixture of concentrated HCl and HNO_3, a method described by Virgin (1924). The sulfur content was measured gravimetrically after oxidation and precipitation with $BaCl_2$.

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The selenium content of these materials is shown in Table I. The selenium concentration varied from 0.025 ppm in sulfur to 25 ppm in certain rock phosphates. With the exception of some of the rock phosphates, all materials contained at least 10,000 times as much sulfur as selenium. The selenium concentrations of the pyrites that were mixtures of different origin are within the range of those described by Williams and Byers (1934). The North African rock phosphates ranged from 3 to 25 ppm Se. This is in agreement with the data of Rader and Hill (1936). Most of the sulfur in the two NPK fertilizers is due to their contents of micronutrients, added as sulfates.

Losses of Selenium during Fertilizer Manufacturing. In order to measure the importance of the raw materials on the selenium content of a PK and a NPK fertilizer, samples from a whole manufacturing procedure were analyzed for selenium as described above, and the loss in every production step was calculated.

In the actual case investigated, about 90% of the sulfuric acid was produced from pyrites and the rest from raw sulfur (Table II). With 50% sulfur in the pyrites, it can be calculated that the selenium content of this mixed sulfuric acid should be 16.5 ppm, but an analysis showed only 8.6 ppm. It means that nearly 50% of the selenium has disappeared since the purple ore byproduct (Table II) only accounts for about 4%. This sulfuric acid was used together with Kourigha phosphate in the production of superphosphate and PK-fertilizer, and no further loss of selenium occurred in this process.

Phosphoric acid was made from sulfuric acid and the selenium-poor Kola phosphate. The amount of selenium involved in this process should give a concentration of 16.6 ppm Se in the phosphoric acid, but only 9.3 ppm was found. So the loss of selenium in this case was 44%. Since the gypsum was responsible for only about 1%, most of the selenium may have volatilized.

The NPK fertilizer was made from materials as shown in Table II plus ammonia, and the slurry was dried and granulated in a hot air stream directly from burning heavy fuel oil. As far as it is possible to calculate the amount of selenium involved in this process, no selenium was lost.

The oxidation state of the selenium in the PK- and the NPK-fertilizers was not determined directly because of the low concentrations, but the solubility of the native selenium in the fertilizers were compared with that of small amounts of added selenate and selenite labeled with ^{75}Se. Such in-

Table I. Selenium and Sulfur Content of Some Fertilizers and Raw Materials

	Number of samples	ppm Se	% S *ca.*	Se/S × 10^4
Pyrites	3	25–30	48	0.6
Sulfur (oil industry)	3	0.025–0.073	99.9	0.0005
Apatite, Kola	3	0.03–0.05	0.1	0.4
Rock phosphates, North Africa	8	3.1–25.0	0.2–1	20
Thomas phosphate	3	0.10–0.11	0.1	1
Superphosphate	8	4.2–8.0	12	0.5
PK	12	3.6–5.5	8	0.5
NPK (based on sulfuric acid)	7	1.1–4.0	2	1
NPK (based on nitric acid)	8	0.021–0.19	2	0.01–0.1
Potassium fertilizer (KCl)	6	0.04–0.09	0.02	0.3
Lime	3	0.033–0.037	trace	...

Table II. Selenium Content of Samples from the Different Production Stages of a PK and a NPK Fertilizer

Raw Materials	ppm Se	Inter-mediates	ppm Se	Products and byproducts	ppm Se
		PK			
Pyrites	41.6	Sulfuric acid	10.1	Purple ore	2.1
Raw sulfur	0.065	Sulfuric acid	0.25		
				Super-phosphate	7.0
Kourigha phosphate	3.1			PK (0-15-13)	5.4
Potassium chloride	0.03				
		NPK			
Sulfuric acid	8.6				
		Phosphoric acid	9.3	Gypsum	0.95
Kola phosphate	0.05				
Kourigha phosphate	3.1	Nitric acid	0.17		
				NPK (16-5-12)	4.0
Potassium chloride	0.03				
Kieserite	0.007				
Heavy fuel oil	0.03				

vestigations seem to prove that the selenium in the PK was selenite only, and the selenium in the NPK (based on sulfuric acid) was partly selenite and partly a less soluble form, probably elemental Se. These results are in accordance with the redox conditions during the manufacturing procedure.

Uptake of Selenium Contained in Fertilizers. In order to determine the uptake by plants of the selenium contained in fertilizers, a sample of a PK fertilizer containing 5.4 ppm Se and a sample of a NPK fertilizer containing 0.10 ppm Se was tagged with high specific activity ^{75}Se. The tagging was done by adding the ^{75}Se as Na_2SeO_3 in solution to a water slurry of the powdered fertilizers. After mixing, the slurry was dried, crushed, and screened. This procedure should effectively tag the soluble and adsorbed selenites, but it may not tag any elemental Se or heavy metal selenides present. Thus, the form of selenium most likely to be taken up by plants would have been tagged, and the uptake of ^{75}Se under these conditions should represent the maximum uptake of the selenium contained in fertilizers. When the tagged fertilizers were added to pots of soil, less than 1% of the activity added was found in the tops of barley plants harvested at maturity. It would therefore appear that the selenium that is native in fertilizers as the result of using selenium-bearing raw materials is not likely to have an important effect upon the selenium concentration in plants, when these fertilizers are used at practical rates. This is in agreement with the work of Robbins and Carter (1970) who found that highly seleniferous phosphate rocks were needed to produce superphosphates that would significantly increase selenium concentrations in plants.

Uptake of Selenium Added to Fertilizers. Because of the low uptake of the native fertilizer selenium, an experiment was designed to evaluate different fertilizers as carriers for added selenium. The reason for conducting this experiment was the probability that if soil additions of selenium are considered for prevention of selenium deficiency in animals, the use of fertilizers as carriers of the added selenium may minimize hazards in the handling of selenium, or dangers from overapplication of selenium.

In this experiment the selenium was added in solution as $Na_2{}^{75}SeO_3$ to slurries of the fertilizers as before. The rates of fertilizer added and also the rate of addition of selenium carried by the fertilizers are shown in Table III. The fertilizers used were a NPK 16-5-12 (15.9-11.4-14.5) 1.6% S and a PK 0-5-13 (0-11.6-15.5) 9.0% S plus calcium ammonium nitrate.

Table III. Native Selenium Content[a] of Crops and Additional Uptake of Applied ^{75}Se-Selenite[b] Carried by a PK and a NPK Fertilizer

Microplot Experiment

Application to soil: Fertilizer per ha	Se per ha	Barley: Grain	Barley: Straw	Wheat: Grain	Wheat: Straw	Grass	Fodder beet: Top	Fodder beet: Root	Average
		ppb Se in dry matter							
400 kg NPK	0	68	72	71	46	85	69	12	59
400 kg NPK	50 g	37	22	19	8	39	12	5	21
	100 g	90	53	67	27	122	36	14	60
360 kg PK	50 g	18	11	11	5	39	8	2	15
300 kg $CaNH_4(NO_3)_3$	100 g	25	18	16	8	52	16	4	22

[a] The native selenium content was measured by neutron activation analysis on plants from the border areas. [b] The additional selenium uptake was determined by radioactivity measurements.

The experiment was set up in outdoor microplots of 0.5 m^2 with wood borders extended into the soil to a depth of 25 cm. The fertilizers were added to the surface of the soil, lightly tilled by hand, and then seeded to the crops shown. The area between microplots of each crop was fertilized with the NPK fertilizer with no selenium added. The plants grown were spring barley (var. Carlsberg II), spring wheat (var. Alma), perennial ryegrass (var. Øtofte Dux III), and fodder beet (var. Rød Øtofte S65).

The cereals were harvested at maturity, air-dried, and threshed. The straw and the grain were dried for 20 hr at 55° C, and milled into powder. The ryegrass was harvested twice, and a 200-g subsample of chopped fresh material was dried and treated like the cereals. The fodder beets were harvested in October, divided into top and root, and treated like the grass.

The uptake of native selenium from soil and fertilizer was measured in plants from the border areas around the microplots in all five crops by neutron activation analysis.

The uptake of added selenium was determined by radioactivity measurements. One gram pellets of the powdered plant material were counted using a NaI-well-crystal. One gram cellulose pellets containing aliquots of the ^{75}Se solution from the start of the experiment served as references. Since the difference in selenium content between the two cuts of ryegrass was insignificant, only the average values are given in Table III.

The results in Table III illustrate a significant difference between the influence of the PK and of the NPK fertilizer on the uptake of added selenite by plants. The uptake of selenium varied between the different crops and between the two amounts of added selenite, but in all cases the uptake was highest when the NPK fertilizer was used. The most plausible explanation of this seems to be a depressive effect from the higher content of sulfur in the PK than in the NPK. The same influence of PK and NPK fertilizer on the uptake of native selenium was seen (even though not statistically significant) in a pot and a field experiment (Gissel-Nielsen, 1967).

CONCLUSION

The selenium content of fertilizers differs a great deal, and the choice of raw materials and manufacturing procedures influence the selenium content of the compound fertilizers, but the contribution to the total selenium content of the plants from the selenium in the fertilizers is negligible, unless highly seleniferous raw materials are used as done by Robbins and Carter (1970).

However, fertilizers can be used as carriers for added selenite, though sulfur-rich fertilizers as superphosphates may be less effective as such than fertilizers low in sulfur content.

It appears that during the first year of cropping, plants may take up no more than a few percent of any selenium that is naturally present in fertilizers or that is deliberately added to fertilizers. These results are consistent with those of Cary *et al.* (1967) who used selenized triple superphosphate in a greenhouse experiment.

Effect of the fertilizer on availability of native selenium in the soil was not measured. However, when the NPK fertilizer was added without supplemental selenium, the selenium concentration in plants was in the low to marginal range for animal nutrition.

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