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## RAISING THE SELENIUM CONTENT OF SPRING WHEAT AND BARLEY USING SELENITE AND SELENATE

TOIVO YLÄRANTA

YLÄRANTA, T. 1984. Raising the selenium content of spring wheat and barley using selenite and selenate. *Ann. Agric. Fenn.* 23: 75—84. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

Field experiments were carried out to study ways of raising the selenium content of spring wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.). The methods used were foliar spraying with sodium selenite and selenate, application of compound fertilizer containing selenate, and seed treatment with aqueous solutions of sodium selenate.

On fine sandy soil 5—10 g/ha of selenium had to be applied as selenate in the fertilizer to raise the selenium contents of spring wheat and barley grain from the base level of 0,01 mg/kg dry matter to the target level of 0,1 mg/kg. On clay soil 10—20 g/ha of selenium applied in the fertilizer should be sufficient. On clay soil the application of selenate fertilizer proved slightly more effective than treating the seeds with selenate solution.

The plants grown on clay soil were sprayed with selenite and selenate during the final stage of tillering, those grown on fine sand were sprayed at the 3—4 leaf stage, while those grown on fine sand with a high humus content were sprayed at the start of tillering. Under these conditions application of selenate by foliar spraying and as fertilizer raised the selenium contents of spring wheat and barley by about the same amount. Foliar spraying of selenite was less effective.

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Index words: selenium fertilization, foliar spraying, seed treatment, selenite, selenate, selenium content, spring wheat, barley.

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### INTRODUCTION

The selenium content of cereal crops can be raised by means of selenium fertilization, foliar spraying of selenium, and seed treatment using aqueous solutions of selenium compounds. The most suitable selenium compounds for this

purpose are selenites and selenates (GISSEL-NIELSEN and BISBJERG 1970, GISSEL-NIELSEN 1977).

In both field and pot experiments carried out by YLÄRANTA (1983 b) selenate was much more effective than selenite in raising the selenium

content of barley grain, irrespective of whether the selenium was applied to the soil, the plants or the seeds. On clay soil, when NPK compound fertilizer containing selenate was placed close to the roots of barley, in accordance with Finnish practice, 4—10 % of the selenium in the fertilizer was incorporated into the grain.

The selenium content of Finnish grain is usually 0,010—0,015 mg/kg of dry matter. The aim is to raise this to 0,1 mg/kg. More extensive series of experiments were therefore necessary in order to find a suitable way of applying the

selenium. The use of selenite in the form of fertilizer and as an aqueous solution for seed treatment was not included, as these two methods have little effect on the selenium content of grain (cf. GISSEL-NIELSEN 1975, 1981 a, KORKMAN 1980, GUPTA and WINTER 1981, YLÄRANTA 1983 b); the main attention was focused on the use of selenate. The foliar spraying experiments were directed at finding the most suitable amounts of sodium selenite and selenate for different soils with a view to later experiments concerned with the time of spraying.

## MATERIAL AND METHODS

The field experiments were carried out at three locations in 1981. The plants used for the experiments on clay soil at the Institute of Soil Science, Jokioinen (JO) were spring wheat (*Triticum aestivum* L., variety Ruso) and barley (*Hordeum vulgare* L., variety Pomo). The other two fields were located at research stations belonging to the Agricultural Research Centre of Finland. The plants grown on fine sand at the Satakunta Research Station (SAT) were spring wheat and barley. At the South Ostrobothnia Research Station (EPO) the soil was fine sand with a high humus content, and the plant studied was barley. The residual effect of the selenium applications was studied in 1982. The experimental plots at JO measured 2 m × 12 m, those at SAT 2 m × 11 m, and at EPO 2,5 m × 10 m. The treatments with four replicates were carried out in the design forming four blocks.

The arrangement of the individual treatments within each block was random.

Measured according to the pipette method (ELONEN 1971), the plough layer (0—20 cm) of the experimental fields at JO contained 43 % and 45 % clay, those at SAT 12 % and 18 %, and the field at EPO 18 % (Table 1). The fine sandy soil at EPO had a high humus content, as it contained 9,0 % organic carbon. The pH(CaCl<sub>2</sub>) of the experimental fields varied from 4,6 for the barley field at EPO to 6,3 for the spring wheat field at JO. Chemical and physical characteristics of the deeper layer, 20—40 cm, were in each experimental field very similar to the plough layer.

The experimental fields at JO were next to each other. Thus the amounts of calcium (2880 mg/l soil), potassium (350 mg/l), magnesium (410 mg/l) and phosphorus (45 mg/l) extracted

Table 1. Chemical and physical characteristics of the plough layer (0—20 cm) and of the deeper layer (20—40 cm) of the experimental soils. The analytical figures of the deeper layer are shown in parentheses.

Experimental site and plant	Particle size composition (%)					Org. C (%)	pH (CaCl <sub>2</sub> )
	Ø < 0,002 mm	0,002—0,02 mm	0,02—0,06 mm	0,06—0,2 mm	0,2—2 mm		
<b>Spring wheat</b>							
Jokioinen	45 (49)	26 (26)	14 (13)	7 (6)	8 (6)	2,8 (1,7)	6,3 (6,1)
Satakunta							
Research Station	18 (25)	25 (33)	20 (19)	34 (22)	3 (1)	2,2 (1,3)	5,4 (5,5)
<b>Barley</b>							
Jokioinen	43 (51)	26 (24)	15 (14)	7 (6)	9 (5)	2,9 (1,9)	6,1 (6,0)
Satakunta							
Research Station	12 (14)	18 (20)	24 (28)	43 (36)	3 (2)	2,4 (1,2)	5,0 (5,2)
South Ostrobothnia							
Research Station	18 (17)	33 (30)	45 (51)	4 (2)	— (—)	9,0 (5,0)	4,6 (4,4)

from the plough layer into acid ammonium acetate solution (0,5 M  $\text{CH}_3\text{COONH}_4$ , 0,5 M  $\text{CH}_3\text{COOH}$ , pH 4,65; VUORINEN and MÄKITIE 1955) were, on average, about the same. The fertility of the clay soil at JO was considered good (KURKI et al. 1965). The fertility of the other experimental fields was fair. With the exception of the magnesium content, the fertility of the experimental fields at SAT was the same. An average of 1280 mg/l of calcium, 130 mg/l of potassium and 10 mg/l of phosphorus were extracted. On extraction, the spring wheat field yielded 290 mg/l of magnesium, while the barley field gave 130 mg/l. The figures for the high-humus fine sandy soil at EPO were: Ca 1250 mg/l, K 80 mg/l, Mg 150 mg/l and P 3,8 mg/l. The amount of selenium obtained from the plough layer of the experimental field after extraction for 30 min with boiling water (YLÄRANTA 1982) was 11  $\mu\text{g/l}$  at JO and 8  $\mu\text{g/l}$  of soil at SAT and EPO.

The following treatments were used in the spring wheat and barley experiments at JO:

- A. Foliar spraying with aqueous  $\text{Na}_2\text{SeO}_3$  solution  
Se 0, 5, 10, 50 g/ha
- AW. Foliar spraying with aqueous  $\text{Na}_2\text{SeO}_3$  solution, but with Citowett surfactant (Kemira Oy, Finland)  
Se 0, 5, 10, 50 g/ha
- B. Foliar spraying with aqueous  $\text{Na}_2\text{SeO}_4$  solution  
Se (0), 5, 10, 50 g/ha
- BW. Foliar spraying with aqueous  $\text{Na}_2\text{SeO}_4$  solution, but with surfactant  
Se (0), 5, 10, 50 g/ha
- C.  $\text{Na}_2\text{SeO}_4$  in NPK compound fertilizer  
Se 0, 9, 55 g/ha
- D. Seed treatment with aqueous  $\text{Na}_2\text{SeO}_4$  solution  
Se 0, 5, 10, 50 g/ha

In the experiments carried out at JO, groups A and B had the same control treatment. For determination of the base level selenium content, a common control was also taken as adequate for groups AW and BW. Treatments AW, BW and C were the only ones studied at

SAT and EPO. The fertilizer applied in all the experiments at the rate of 500 kg/ha was the NPK compound fertilizer normally used in Finland; it contains 16 % nitrogen, 7 % phosphorus, 13 % potassium and 2 % sulphur. The selenated fertilizers were prepared at an experimental factory of Kemira Oy by spraying uncoated NPK fertilizer grains with aqueous sodium selenate solution. The selenium fertilizers contained 0,000 015 %, 0,0018 % and 0,011 % selenium (YLÄRANTA 1983 b).

The experiments at JO also included seed treatment with aqueous sodium selenate solutions. The seeds were treated by spraying with hand sprayer the required amount of selenium onto the surface of the seeds. During spraying, the seeds were mixed carefully to make the treatment as uniform as possible. The volume of  $\text{Na}_2\text{SeO}_4$  solution used was 100 ml/20 kg seeds.

The seeds and the selenium fertilizers used in the group C experiments were all from the same production batch. The seeds contained 0,01 mg/kg of selenium; 160–220 kg were sown per hectare. The "selenium-free" NPK fertilizer used at each experiment was from the local commercially available batch and contained less than 0,000 08 % Se. The fertilizer was placed in every case slightly below the seeds in the soil as in the Jokioinen experiment of 1980 (YLÄRANTA 1983 b).

All spraying of spring wheat and barley was carried out using an AZO-propane experimental sprayer, which applies the solution evenly and reliably and also prevents the spray from affecting adjoining plots. At SAT the plants were sprayed at the 3–4 leaf stage. At EPO spraying was carried out when the plants were slightly less advanced, i.e. when the barley was just beginning to tiller. Spraying was latest at JO, i.e. at the end of tillering, 4–5 on the FEEKES development scale (LARGE 1954). On the experimental fields 400 l/ha of water was used. Citowett surfactant was used 0,4 l/ha. Some of the spraying treatments at JO were carried out without this agent. The aim of these treatments was to determine whether the agent increases the uptake of selenium from the spray by the plants. The plants were sprayed with selenium 3–8 days

after spraying with the herbicide.

The weather during the 1981 growing season was unfavourable, and for this reason the yields were rather small. The early part of the summer was dry, and the plants tended to be thinly spaced because of poor sprouting and growth of seedlings. The heavy rain which fell late in the summer delayed ripening of the crops and caused considerable lodging, particularly of the barley. Despite all this, the crops were cut according to plan using experimental harvesters with a cutting width of 1,5 m. The crops were cut to leave a stubble of about 10 cm. The yields of both grain and straw from each plot were weighed. During weighing a representative sample of about 1 kg was taken from the grain obtained from each plot for chemical analysis. The straw samples weighed about 300 g when freshly cut. All the plant samples were dried at 50 °C.

Autumn ploughing was carried out at a depth of 20–22 cm across the width of the plots. In 1982 sowing, cutting, sampling and sample

handling took place as in 1981. The weather during the 1982 season was generally good and, with the exception of SAT, the yields were far better than the previous year. At SAT the growing season was dry from spring onwards. The late sowing carried out on the rapidly drying fine sandy soil, combined with the dry summer, caused the plants to be short and thinly spaced.

The selenium content of plant samples and aqueous extracts was determined using the hydride method (YLÄRANTA 1983 a). The grain samples from the spring wheat experiment in 1981 at JO were also subjected to sulphur analysis using a LECO SC-132 sulphur analyser. The sulphur analyses were carried out in the Oulu Research Laboratory of Kemira Oy. The analysis methods used in this work are described in more detail in a previous publication (YLÄRANTA 1983 b). The dry matter contents of the grain and straw were determined by drying 10 g of ground grain and 2 g of ground straw overnight at 105 °C.

## RESULTS

In the spring wheat experiment at JO, spraying 5–10 g/ha of selenium in the form of either sodium selenite or selenate onto the plants was sufficient to raise the selenium content of the grain from 0,015 mg/kg dry matter of the untreated control crop to the target of 0,1 mg/kg (Table 2). The greatest foliar application of 50 g/ha raised the selenium content of the grain to 0,6–0,8 mg/kg. As the average grain yield was 3400 kg/ha dry weight, 5 % of the selenium sprayed onto the plants in the form of selenite and selenate had accumulated in the grain. On top of this, use of the Citowett surfactant raised the selenium content of the grain by 13–40 %. Seed treatments with selenate raised the selenium content of the wheat grain less than did selenite and selenate sprayings, but were about equally effective in raising the selenium content of the wheat and barley grain.

In the spring wheat and barley experiments at JO the plants were sprayed with selenium at the same stage of growth. Nevertheless, the selenium

content of the barley grain obtained from the selenite experiments was about 50 % of that found in the corresponding spring wheat experiments at the various selenium levels. The spring wheat field and barley field were adjacent to each other, so that the growing conditions were the same. The similarity in the composition of the growth media can be seen from the analysis of soil samples (Table 1).

Selenate spraying proved slightly more effective than selenite, and hence the selenium contents of the barley grain were almost exactly half those of the corresponding wheat grain contents. The surfactant had little effect in the selenate sprayings; in the barley experiments it raised the selenium content by only 12–16 %.

The application of selenate fertilizer was slightly more effective than selenate treatment of the seeds in raising the selenium content of the grain of both spring wheat and barley. The average yield of barley grain was 3000 kg/ha, which is slightly lower than that for wheat.

Table 2. Effect of foliar spraying of selenite, and selenate, selenate fertilization and seed treatment with selenate on the selenium content of spring wheat and barley grain grown on the clay soils of Institute of Soil Science (JO), the fine sandy soils of Satakunta Research Station (SAT) and the high-humus fine sandy soil of South Ostrobothnia Research Station (EPO) in 1981. Mean selenium content of the grain ( $\bar{x}$ ) and standard deviation (s).

	Se $\mu\text{g/kg}$ dry matter									
	JO wheat		JO barley		SAT wheat		SAT barley		EPO barley	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
<b>Foliar spraying</b>										
<b>A. Selenite</b>										
0	15	1,8	11	2,1						
5	87	5,1	43	3,7						
10	140	20	85	3,8						
50	595	76	286	21						
<b>AW. Selenite + Citowett</b>										
0	16	1,3	13	2,4	11	2,6	14	2,8	12	1,3
5	115	8,9	66	5,9	37	4,8	33	6,0	22	2,1
10	176	23	117	22	60	9,8	35	2,6	30	10
50	816	100	262	23	189	21	92	8,9	85	12
<b>B. Selenate</b>										
0*	(15)	(1,8)	(11)	(2,1)						
5	75	1,5	45	9,8						
10	140	14	69	6,7						
50	646	70	327	37						
<b>BW. Selenate + Citowett</b>										
0*	(16)	(1,3)	(13)	(2,4)	13	1,6	13	1,4	14	2,0
5	92	5,6	52	2,0	84	7,5	88	13	37	3,6
10	168	14	79	6,0	182	33	187	25	80	2,3
50	727	136	368	27	874	49	981	143	333	78
<b>Fertilization</b>										
<b>C. Selenate</b>										
0	14	2,7	12	2,3	11	3,7	14	2,9	13	4,4
9	77	6,8	60	5,6	219	19	132	13	83	7,8
55	527	37	648	67	1500	36	1053	112	381	59
<b>Seed treatment</b>										
<b>D. Selenate</b>										
0	16	0,9	10	3,1						
5	55	8,7	52	7,5						
10	90	2,8	87	14						
50	426	34	399	28						

\*) At JO the common control treatments A and B, AW and BW.

The spring wheat and barley grown on the fine sandy soil at SAT were at the 3—4 leaf stage at the time of spraying. The plants grown on the clay soil at JO were more advanced, as can also be seen from the higher selenium content of the grain in the selenite experiments on clay soil. At SAT the selenium content of barley grain rose from the base level of 0,014 mg/kg dry matter to 0,092 mg/kg as a result of spraying with the highest selenite amount of Se 50 g/ha. The same treatment caused the selenium content of spring wheat to double. Foliar application of selenate, however, was far more effective than that of selenite, as the selenium contents of both spring wheat and barley were as high as those from corresponding experiments with spring wheat on clay soil at JO.

The average dry weight yield of grain at SAT

was 3000 kg/ha for spring wheat and 2900 kg/ha for barley. When 55 g/ha of selenium was applied in the fertilizer the selenium content of spring wheat grain was 1,50 mg/kg dry matter and that of barley grain 1,05 mg/kg dry matter. Thus the spring wheat grain had accumulated 8 % of the selenium applied in the fertilizer, while the barley grain had accumulated just over 5 % (Table 3). The corresponding accumulations of selenium for the clay soil experiments at JO were only 3,1 % for spring wheat and 3,5 % for barley.

The plants grown on the high-humus fine sandy soil at EPO were sprayed at a slightly less advanced stage of growth than was the case on the fine sandy soil at SAT. The results obtained from the selenite experiments were equally poor. Even the highest amount of selenite, Se 50 g/ha,

Table 3. Selenium uptake of spring wheat and barley grain and straw as a proportion of the selenium applied as fertilizer at the three experimental sites. Selenium applied in fertilizer averaged 55 g/ha.

Experimental site and plant	Grain		Straw		Total Selenium uptake of added (%)
	Yield kg/ha	Selenium uptake of added (%)	Yield kg/ha	Selenium uptake of added (%)	
<b>Spring wheat</b>					
Jokioinen	3240	3,1	3740	2,6	5,7
Satakunta					
Research Station	2990	8,2	5230	10,6	18,8
<b>Barley</b>					
Jokioinen	2980	3,5	2550	1,9	5,4
Satakunta					
Research Station	2750	5,3	2550	3,2	8,5
South Ostrobothnia					
Research Station	3830	2,7	2150	2,2	4,9

raised the selenium content of the barley grain from the 0,012 mg/kg dry matter in the control plots to only 0,085 mg/kg (Table 2). Selenate was equally effective whether sprayed onto the plants or applied in the form of fertilizer: at all the amounts sprayed, selenate was four times more effective than selenite. The average dry weight yield of barley grain obtained at EPO was 3900 kg/ha.

The selenium contents of the straw from spring wheat grown in the selenium-treated plots at JO and SAT averaged 70–80 % of the selenium contents of the corresponding grain (Table 4). The corresponding selenium contents of barley straw at these two experimental sites were 90–100 % of the grain contents. The selenium contents of the barley straw from EPO were highest in relative terms, amounting to an average of 130 % of the selenium contents of the grain.

The average yield of spring wheat straw was 3600 kg/ha dry matter at JO and 5300 kg/ha at SAT. The corresponding yields for barley were 2500 kg/ha and 3600 kg/ha. The average yield of barley straw at EPO was 2300 kg/ha. The selenium treatments could not be shown to have statistically significantly ( $P = 0,05$ , DUNCAN 1955) affected grain and straw yields.

The straw and grain of the spring wheat and barley cut accumulated about the same amount of selenium applied as selenate in the fertilizer and in the foliar spray. The fertilizer containing 0,011 % Se was applied at the rate of 500 kg/ha. The barley cut at SAT accumulated 18,8 % of

the 55 g/ha of Se applied in this fertilizer (Table 3). Selenium uptake by spring wheat and barley at the other experimental sites ranged from 4,9 % to 8,5 %.

The sulphur content of the dry grain yield of spring wheat at JO varied throughout the material from 1,5 g/kg to 2,0 g/kg. The highest sulphur content of 1,86 g/kg of dry matter was found in the treatments in which the seeds had been treated with 5 g/ha of selenium in the form of selenate. The lowest average sulphur content of 1,70 g/kg was found in those treatments in which 10 g/ha of selenium had been sprayed on the plants in the form of selenite and in the control treatment of the same experimental group (A), and in the control treatment of group (D), in which the seeds were treated with selenate. No statistically significant differences ( $P = 0,05$ , DUNCAN 1955) were found in sulphur contents between the various treatments.

The residual effect of the 1981 selenium treatments was studied in 1982. The average selenium content of spring wheat and barley grain at JO and SAT ranged from 7  $\mu\text{g}/\text{kg}$  dry matter to 16  $\mu\text{g}/\text{kg}$ . There were no statistically significant differences ( $P = 0,05$ , DUNCAN 1955) in the selenium contents of the grain obtained from the treatments with or without selenium application in 1981. The same was true of the selenium contents of the straw in these experiments, which ranged from 8 to 15  $\mu\text{g}/\text{kg}$  of dry matter at JO and from 12 to 22  $\mu\text{g}/\text{kg}$  at SAT.

At EPO the selenium contents of barley grain and straw from the treatments given the highest

Table 4. Effect of foliar spraying of selenite and selenate, selenate fertilization and seed treatment with selenate on the selenium content of spring wheat and barley straw grown on the clay soils of Institute of Soil Science (JO), the fine sandy soils of Satakunta Research Station (SAT) and the high-humus fine sandy soil of South Ostrobothnia Research Station (EPO) in 1981. Mean selenium content of the straw ( $\bar{x}$ ) and standard deviation (s).

Se g/ha	Se $\mu\text{g/kg}$ dry matter									
	JO wheat		JO barley		SAT wheat		SAT barley		EPO barley	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
<b>Foliar spraying</b>										
<b>A. Selenite</b>										
0	14	1,8	15	1,3						
5	42	5,5	51	2,9						
10	88	17	71	9,9						
50	370	45	279	17						
<b>AW. Selenite + Citowett</b>										
0	16	0,9	15	1,1	13	2,7	16	1,9	11	1,7
5	73	15	65	6,4	31	3,6	30	3,3	28	12
10	116	7,8	100	7,9	37	1,9	31	4,4	35	3,4
50	514	42	396	46	129	18	87	22	95	14
<b>B. Selenate</b>										
0*	(14)	(1,8)	(15)	(1,3)						
5	43	2,0	44	1,9						
10	99	21	69	13						
50	540	144	411	86						
<b>BW. Selenate + Citowett</b>										
0*	(16)	(0,9)	(15)	(1,1)	16	2,0	14	0,8	11	1,7
5	58	9,3	43	3,8	60	7,6	91	11	57	12
10	107	9,8	81	15	134	4,6	188	20	108	14
50	579	5,0	434	65	733	81	1155	121	465	143
<b>Fertilization</b>										
<b>C. Selenate</b>										
0	15	2,3	14	2,9	14	0,6	16	2,2	13	2,2
9	63	18	56	2,2	181	25	106	13	117	13
55	382	92	416	27	1116	60	686	74	553	119
<b>Seed treatment</b>										
<b>D. Selenate</b>										
0	15	1,6	14	2,0						
5	41	4,1	47	4,0						
10	75	9,3	87	14						
50	388	78	436	105						

\*) At JO the common control treatments A and B, AW and BW.

amounts of selenium were statistically significantly higher (Table 5). The selenium content of

Table 5. Residual effect of foliar spraying of selenate (BW) and selenate fertilization (C) on the selenium content of barley grain and straw on high-humus fine sandy soil at South Ostrobothnia Research Station in 1982. In each selenium treatment group, grain and straw selenium contents not marked with the same letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Se g/ha. (1981)	Se $\mu\text{g/kg}$ dry matter	
	Grain	Straw
<b>BW. Foliar spraying</b>		
0	10 <sup>a</sup>	8 <sup>a</sup>
5	9 <sup>a</sup>	13 <sup>a</sup>
10	10 <sup>a</sup>	13 <sup>a</sup>
50	26 <sup>b</sup>	29 <sup>b</sup>
<b>C. Fertilization</b>		
0	10 <sup>k</sup>	10 <sup>k</sup>
9	13 <sup>k</sup>	13 <sup>k</sup>
55	35 <sup>l</sup>	38 <sup>l</sup>

grain from the 1981 experiment involving foliar application of Se 50 g/ha in the form of selenate was 26  $\mu\text{g/kg}$ , and that of the straw 29  $\mu\text{g/kg}$ . When about the same amount of selenium was applied in the fertilizer, the resulting grain had a selenium content of 35  $\mu\text{g/kg}$  and the straw a selenium content of 38  $\mu\text{g/kg}$ . The average selenium contents for the control plots ranged from 8 to 10  $\mu\text{g/kg}$  dry matter.

The yields of grain in 1982 were about 50 % higher than in 1981, with the exception of the spring wheat experiment at SAT, in which the grain yield was only 60 % of the previous year's yield. The yields of straw also showed an increase, with the exception of the spring wheat and barley experiments at SAT, although the increase was not as great as for the grain yields.

## DISCUSSION

Foliar spraying of sodium selenite solution in the experiments at both JO and SAT raised the selenium content of spring wheat grain considerably more than that of barley grain. The same trend was also seen in the selenium contents of the straw, although the difference in contents was smaller. The selenium content of spring wheat was also higher than that of barley on the clay soil at JO in those experiments involving foliar application of selenate. The results achieved by spraying depend on many factors, such as the growth stage of the plants, how great deal of soil area the plants are covered and the type of soil. At both JO and SAT the spring wheat and barley fields were adjacent to each other, so that the type of soil and growing conditions were the same. At each of these two locations the spring wheat and barley were sprayed at about the same stage of development. Because of the larger foliage on the barley than on the spring wheat it could be assumed that barley would have accumulated more of the selenium sprayed than the wheat, giving the barley a higher selenium content.

The selenium content of the crop normally falls as the dry weight yield increases (GISSEL-NIELSEN 1975). On the other hand only the yield of barley grain at JO was slightly higher (about 400 kg/ha) than the wheat grain yield. It would therefore appear from these experiments that the same amount of selenium sprayed over the same area raises the selenium content of wheat more than that of barley. In the pot experiment GISSEL-NIELSEN (1975) also found that foliar spraying of selenite raised the selenium content of wheat more than that of either barley or oats.

Selenates are usually more soluble in soil than the corresponding selenites. Thus selenate spray falling on the ground penetrates the soil more easily than selenite, and can be leached to within reach of the roots and hence be taken up by the plants. It would seem that some of the selenate sprayed to the crops grown on the fine sand at SAT and on the high-humus fine sand at EPO was taken up through the soil in this way. This means that the results obtained by spraying

cannot be compared directly with the selenite results or with the results on the clay soil at JO. The results of a previous experiment carried out at JO on a field adjacent to the fields used here showed that neither selenate or selenite applied as spray leaches through the plough layer of the clay soil (YLÄRANTA 1983 b).

The effectiveness of selenium sprayed in the form of selenite can be as much as doubled by using surfactant or by combining herbicide spraying with selenite spraying (GISSEL-NIELSEN 1981 a, b). GISSEL-NIELSEN (1981 b) sprayed barley with Se 10 g/ha in the form of aqueous sodium selenite at growth stage 4 on the FEEKES scale. The experiment was carried out on five farms in Denmark, where the selenium content of untreated barley grain was 0,021—0,045 mg/kg dry matter, and the grain yield 2,57—5,78 t/ha. Use of a surfactant and application of Se 10 g/ha raised the selenium content of barley grain to an average 0,13 mg/kg dry matter.

In the experiment at JO the barley was at stage 4—5 on the FEEKES scale, and the selenium content of the grain following spraying with Se 10 g/ha in the form of selenite was 0,12 mg/kg, i.e. roughly the same as in the experiments conducted by GISSEL-NIELSEN (1981 b). At JO the use of a surfactant raised the selenium content of spring wheat grain by only 13—40 % above the results obtained by spraying with aqueous selenium salt alone. The average change in the selenium content of barley grain was not quite so clear: for the highest foliar application of selenium (Se 50 g/ha) there was no increase in the selenium content of barley grain, while inclusion of the surfactant, even with selenate spraying, raised the selenium content by a mere 12—16 %.

GISSEL-NIELSEN (1975) has shown that when the yield is constant, the selenium content of barley grain and straw rises linearly as the amount of selenium sprayed in the form of selenite is increased from 0,5 g/ha to 50 g/ha. This is also true, on average, of the selenium contents of the spring wheat and barley grain grown at all the experimental fields in this study.

In the experiments on clay soil the effect of seed treatment with selenium on the selenium content of spring wheat and barley grain was smaller than that achieved with selenate fertilizer. Careful and accurate seed treatment with concentrated and toxic solutions of selenium salts is far from easy, however, and seed treatment with selenium cannot be recommended for general use.

Comparison of selenate fertilizer with foliar application is difficult because the effectiveness of spraying, at least in the case of selenite, is greater the more advanced the stage of growth of the plants (GISSEL-NIELSEN 1981 a). In addition, the spring wheat and barley grown on fine sandy soil obviously took up some of the selenium contained in the selenate spray via the soil. The type of soil is also important when using selenate fertilizer. This is demonstrated by the fact that the selenium content of the spring wheat and barley grain grown on the fine sandy soil at SAT was much higher than that on the clay soil at JO. The selenium content of spring wheat grain from SAT was almost three times as high as that obtained at JO. It was surprising to find that on the high-humus fine sandy soil at EPO the effect of selenate, both as fertilizer and as a spray, was small. Unfortunately, the results obtained with selenate fertilization cannot be compared with international research results because virtually no corresponding fertilizer experiments have been carried out with small amounts of selenate.

The selenium uptake by plants is affected by the selenium content of the plant and by the size of the yield. The unfavourable weather in 1981 prevented peak yields. Despite this, the selenium content of the spring wheat grain and straw harvested at SAT, which represented almost 19 % of the selenium applied in the fertilizer, can be considered excellent. The results obtained by GISSEL-NIELSEN (1981 a) indicate that about 0,5 % of the selenite applied as PK fertilizer ac-

cumulated in the straw and grain of barley.

Application of 5—50 g/ha of selenium caused no changes in the sulphur contents of wheat grain, at least on clay soil. The sulphur content of barley grain remained unchanged by the application of 500 g/ha of selenium as selenite or selenate, even when the selenium content of the grain exceeded 7 mg/kg dry matter (YLÄRANTA 1983 b).

The residual effect of the selenium treatments on the selenium content of the following year's crops was small, as in an earlier field experiment with barley (YLÄRANTA 1983 b). The residual effect of treatment with selenite, in particular, disappears extremely rapidly. GUPTA et al. (1983) carried out field experiments in which barley plants were sprayed with up to 2 kg/ha of selenium in the form of selenite. The selenium content of barley grain grown on a fine sandy loam with pH 6,0 was more than 0,1 mg/kg dry matter in the treatment year and then only in the following year. Nevertheless, it appears that on certain soils, selenate applied to the soil may have a notable residual effect, even under Finnish growing conditions. This may explain why the selenium content of barley grain and straw grown on the high-humus fine sandy soil at EPO rose as a result of application of selenate in fertilizer and foliar spraying the previous year.

The selenium contents of the various parts of the grain and straw of spring wheat and barley were not studied in this work. KORKMAN (1980) has carried out several series of experiments with selenite fertilizers. In these experiments, in which the selenium contents of kernel, middle and husk of spring wheat grain varied from 0,040 to 1,80 mg/kg dry matter, the selenium content of the husk was only about 30 % higher than that of the kernel. Clearly, selenium is distributed fairly uniformly over all the different parts of the grain.

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## SELOSTUS

### Kevätvehnän ja ohran seleenipitoisuuden kohottaminen seleniitillä ja selenaatilla

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Viljojen seleenipitoisuutta voidaan kohottaa lisäämällä seleeniä lannoitteisiin, ruiskuttamalla seleeniä kasvustoon tai käsittelemällä kylvösiementä seleeniyhdisteiden vesiliuoksilla. Jokioisten savimaalla, Satakunnan tutkimusaseman karkealla hietamaalla ja Etelä-Pohjanmaan tutkimusaseman runsasmultaisella hienohietaisella maalla suoritettiin 1981 kenttäkokeita, joissa kevätvehnä- ja ohrakasvustoihin ruiskutettiin seleeniä 0, 5, 10 ja 50 g/ha natriumseleniitin ja -selenaatin vesiliuoksina. Jotta saataisiin käsitys erilaisten seleeniläysmenetelmien tehosta, oli Jokioisten kenttäkokeissa mukana kasvustoruiskutusten ja selenaattilannoituksen ohella kylvösiementen seleenikäsittelyjä natriumselenaatin vesiliuoksilla.

Selenaattimuotoinen seleeni kohotti seleniittiä tehokkaammin kevätvehnän ja ohran seleenipitoisuutta lisättiinpä se sitten kasvustoon ruiskuttamalla tai maahan lannoitteessa. Selenaattilannoitus seleenipitoisella Normaali Y-lannoksella kohotti puolestaan kevätvehnän ja ohran jyvien seleenipitoisuuden kylvösiementen seleenikäsittelyä eli merkäpeittäusta

tehokkaammin. Siementen käsitteleminen luotettavasti ja turvallisesti väkevillä, myrkyllisillä seleenin vesiliuoksilla ei ole helppoa, joten siementen seleenikäsittelyä ei voi suositella yleisesti käyttöön.

Hietamaassa tarvitaan selenaattiseleeniä lannoitteessa 5—10 g/ha kohottamaan kevätvehnän ja ohran jyvien seleenipitoisuus tavoitetasolle 0,1 mg/kg kuiva-ainetta. Savimaassa riittävä seleenimäärä olisi 10—20 g/ha.

Selenaatti ruiskutettiin viljakasvustoihin Jokioisissa pensomisen loppuvaiheessa, Satakunnan tutkimusasemalla 3—4-lehtiasteella ja Etelä-Pohjanmaan tutkimusasemalla pensomisen alussa. Näissä oloissa kohotti selenaattiruiskutus ja -lannoitus likimain yhtä paljon kevätvehnän ja ohran seleenipitoisuutta. Hietamaalla kevätvehnä ja ohra ottivat osan kasvustoon ruiskutetusta selenaattiseleenistä maan kautta. Selenaattilannoituksen vertailu seleniittiruiskutuksiin on vaikeata, koska ruiskutusten teho on ilmeisesti sitä suurempi mitä pidemmälle kasvusto on kehittynyt.

EFFECT OF SELENIUM FERTILIZATION AND FOLIAR SPRAYING AT DIFFERENT GROWTH STAGES ON THE SELENIUM CONTENT OF SPRING WHEAT AND BARLEY

TOIVO YLÄRANTA

YLÄRANTA, T. 1984. Effect of selenium fertilization and foliar spraying at different growth stages on the selenium content of spring wheat and barley. Ann. Agric. Fenn. 23: 85—95. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

Spring wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) were sprayed with aqueous solutions of sodium selenite and selenate at the rate of 50 g/ha of Se at the 2,5—3 leaf stage, at the start of stem extension and at the end of stem extension. The results of foliar spraying with selenium were compared with those obtained with NPK compound fertilizer containing selenate, giving a rate of application of 9 or 55 g/ha of selenium.

The effect of selenate spraying on the selenium content of the grain and the straw of spring wheat and barley was independent of the stage of growth of the plants at the time of spraying, while the effect of selenite spraying depended greatly on it. The selenium content of the grain of plants sprayed with selenite at the 2,5—3 leaf stage was only 15—25 % of that obtained with selenate spraying at the same stage. Spraying with selenite and selenate at the end of stem extension raised the selenium content of the spring wheat and barley grain by about the same amount.

The biggest increase in the selenium content of the grain was due to selenate fertilization. Selenate applied at the rate of 5—10 g/ha Se would be sufficient to raise the selenium content of spring wheat and barley grain from the normal level of 0,010—0,015 mg/kg of dry matter to 0,1 mg/kg on clay, loam and organogenic soils.

Index words: selenium fertilization, foliar spraying, selenite, selenate, selenium content, growth stage, spring wheat, barley.

INTRODUCTION

The selenium content of spring wheat and barley can be raised effectively by means of selenate fertilizer. Field experiments show that to raise the selenium content of spring wheat and barley grain from the normal level of 0,010—0,015

mg/kg of dry matter to 0,1 mg/kg requires application of selenium at the rate of 5—10 g/ha on fine sandy soil and 10—20 g/ha on clay soil (YLÄRANTA 1983 c, 1984 a).

The selenium contents of cereal grain and

straw can also be raised by foliar spraying of aqueous solutions of selenite and selenate to the plants themselves. The effectiveness of spraying depends on the chemical form of the selenium compound used, the type of soil and the growth stage of the plants at the time of spraying. Foliar spraying of selenate usually raises the selenium content of the crops more than selenite as some of the readily soluble selenate is probably taken up by the plants via the soil (YLÄRANTA 1984 a).

GISSEL-NIELSEN (1981 a) has compared the uptake of selenium by barley grain following foliar spraying of selenite at different growth stages. The barley was sprayed at growth stage 4 on the FEEKES scale (LARGE 1954), i.e. at the mid-tillering stage, at the end of tillering at growth stage 4—6, and at growth stage 6 at the start of stem extension. Spraying at stage 6 resulted in accumulation of almost twice as much selenium in the grain as spraying at stage 4.

In field experiments conducted by YLÄRANTA (1984 a) selenate fertilization and foliar spraying of selenate raised the selenium contents of spring

wheat and barley grain by about the same amount. The effect of foliar spraying of selenite was slightly smaller. However, the time of spraying varied from the start of tillering to the end at the different experimental sites, thus making it difficult to compare the effects of foliar application with those of fertilization. The information obtained from foliar application was however, necessary for investigation of the effect of the growth stage at spraying on the selenium contents of spring wheat and barley, and to compare the effectiveness of spraying with that of selenium fertilization.

The promising results obtained in field experiments with selenium fertilization of crops were sufficient grounds for the Finnish fertilizer producer Kemira Oy to produce a trial batch of NPK fertilizer containing selenium in the form of selenate. Farmers in different parts of Finland used this NPK fertilizer in normal cultivation of spring wheat and barley at experimental sites chosen for different soils.

## MATERIAL AND METHODS

### Field experiments

The selenium treatments were carried out in seven different field experiments in 1982. The plants tested were spring wheat (*Triticum aestivum* L., variety Ruso) and barley (*Hordeum vulgare* L., variety Pomo). Barley was cultivated in five experiments and spring wheat in two. The same crops were also cultivated on the same sites in 1983, when the residual effect of the previous year's selenium treatment was studied on the selenium content of both grain and straw.

The spring wheat field at the Institute of Soil Science, Jokioinen (JO) and one of the barley fields (JO I) were on clay soil adjacent to the fields used for experiments in 1980 and 1981 (YLÄRANTA 1983 c, 1984 a). The soil of the experimental fields had an average pH(CaCl<sub>2</sub>) of 6,2 (JO) and 6,3 (JO I) an average organic carbon content of 2,2 % (JO) and 2,6 % (JO I) (Table 1). Two of the barley fields at Jokioinen were

organogenic soils. The average pH(CaCl<sub>2</sub>) values of these mould soils were 4,8 (JO II) and 4,7 (JO III) and the organic carbon content of the plough layer (0 to about 20 cm) 17 %. The soil below the plough layer (20—40 cm) on JO II was peat, as it had an organic carbon content of 36 %. The lower organic carbon content of the plough layer was due to a previous addition of clay.

One of the two loam fields at the Satakunta Research Station (SAT) was used for growing spring wheat and the other for barley. The pH(CaCl<sub>2</sub>) of the plough layer of the fields averaged 5,2. The soil of the spring wheat field had an average organic carbon content of 2,3 % and that of the barley field 2,1 %. The crop cultivated on the high-humus fine sandy soil at the South Ostrobothnia Research Station (EPO) was barley. The soil on this field had a pH(CaCl<sub>2</sub>) of 4,8 and an organic carbon content

Table 1. Chemical and physical characteristics of the plough layer (0—20 cm) and of the deeper layer (20—40 cm) of the experimental soils. The analytical figures of the deeper layer are shown in parentheses.

Experimental site and plant	Particle size composition (%)					Org. C (%)	pH (CaCl <sub>2</sub> )
	Ø <0,002 mm	0,002—0,02 mm	0,02—0,06 mm	0,06—0,2 mm	0,2—2 mm		
<b>Spring wheat</b>							
Jokioinen	41 (48)	23 (22)	18 (16)	11 (9)	8 (5)	2,2 (1,2)	6,2 (6,1)
Satakunta							
Research Station	27 (35)	34 (35)	17 (16)	20 (13)	2 (1)	2,3 (0,9)	5,2 (5,6)
<b>Barley</b>							
Jokioinen I	38 (52)	24 (21)	16 (13)	10 (7)	13 (7)	2,6 (1,1)	6,3 (6,2)
" II	—	—	—	—	—	17 (36)	4,8 (4,4)
" III	—	—	—	—	—	17 (19)	4,7 (4,6)
Satakunta							
Research Station	29 (41)	34 (34)	15 (12)	16 (12)	3 (1)	2,1 (0,8)	5,2 (5,6)
South Ostrobothnia							
Research Station	21 (12)	33 (26)	43 (59)	3 (3)	— (—)	9,5 (3,1)	4,8 (4,6)

of 9,5 %.

In Finland, assessment of the fertility of soils used for cultivation takes into account in the soil groups clay soils, coarse mineral soils and organic soils the pH(H<sub>2</sub>O), as well as the Ca, K and P contents soluble in acid ammonium acetate solution (0,5 M CH<sub>3</sub>COONH<sub>4</sub>, 0,5 M CH<sub>3</sub>COOH, pH 4,65) according to the method of VUORINEN and MÄKITIE (1955). Analysis showed the fertility of the clay soils at JO to be good and that of the organogenic soils to be satisfactory (KURKI et al. 1965). The fertility of the wheat field at SAT was good, except for the pH(H<sub>2</sub>O) value 5,8 which was only satisfactory. The fertility of the barley fields at SAT and EPO was satisfactory.

The content of available selenium in the soil was determined by boiling a 25 ml soil sample in 100 ml of water 30 min (YLÄRANTA 1982). The selenium extracted from the soil in this way ranged from 7 to 13 µg/l of soil. The highest selenium value was obtained for the clay fields at JO and the lowest for the fields at SAT.

All experimental fields were subjected to the following treatments:

AW. Foliar spraying of aqueous Na<sub>2</sub>SeO<sub>3</sub> solution containing Citowett surfactant (Kemira Oy, Finland). Se 50 g/ha, spraying carried out at three growth stages.

BW. Foliar application of aqueous Na<sub>2</sub>SeO<sub>4</sub> solution, otherwise as in AW.

Treatments AW and BW each had one common control treatment.

Treatments AW and BW had the following three spraying times:

1. Selenium spraying at the 2,5—3 leaf stage
2. Selenium spraying at growth stage 5—6 on the FEEKES scale (LARGE 1954), i.e. at the end of tillering (5) or at the start of stem extension (6)
3. Selenium spraying at growth stage 9—10 on the FEEKES scale, i.e. the ligule of the last leaf is just visible (9) or the ear swollen but not yet visible (10).

C. Na<sub>2</sub>SeO<sub>4</sub> in NPK compound fertilizer  
Se 0, 9 or 55 g/ha.

There were four replicates for each treatment, totalling 44 plots per experiment. At JO the plots measured 2 m × 12 m, at SAT 2 m × 11 m, and at EPO 2,5 m × 10 m. To make the results of selenium spraying comparable with those obtained from selenium fertilization, the amount of selenium sprayed was chosen as 50 g/ha. This corresponds with the higher amount of selenium applied in the fertilizer.

Fertilizer application, sowing, selenium spraying, management and harvesting and sampling were carried out as in earlier field experiments (YLÄRANTA 1983 c, 1984 a). The NPK compound fertilizer contained 16 % nitrogen, 7 % phosphorus and 13 % potassium. The quantity used in all plots was 500 kg/ha. The seeds and the NPK fertilizer used in the AW and BW experiments contained very little selenium. The amount of selenium introduced through them

was only 400 mg/ha, with roughly 95 % of this coming from the fertilizer.

The first spraying was carried out at the 2,5—3 leaf stage, which is a suitable stage for spraying with most herbicides. This growth stage was selected for spraying in order to find out if selenium could be combined with herbicide spraying.

The weather during the 1982 growing season was favourable and the yield in general was extremely good. The yields of spring wheat and barley on the loam soil at SAT were exceptionally low. This was because the seeds were sown too late and because the weather was dry during the early part of the growing season.

The residual effect of the selenium treatments of 1982 was studied 1983 in the same way as in the earlier field experiments (YLÄRANTA 1983 c, 1984 a). The weather during the 1983 growing season was excellent, and good yields were obtained at all experimental sites.

### Selenate fertilization in practice

In 1983 field experiments with use of selenized fertilizer were started with spring wheat on four Finnish farms and barley on nine. The size of the fields treated with NPK fertilizer containing 0,004 % selenium in the form of selenate was about 2500 m<sup>2</sup>. Apart from its selenium content, the NPK fertilizer used had the same elemental composition as the selenated fertilizers used in this and previous studies (YLÄRANTA 1983 c, 1984 a). The adjoining field, which was cul-

tivated in the same way but using NPK fertilizer containing no selenium, served as a control. The crop varieties differed from farm to farm, though all were varieties commonly grown in Finland. The amount of fertilizer applied was 300—820 kg/ha, corresponding to 12—33 g/ha of selenium, averaging 25 g/ha for spring wheat and 19 g/ha for barley. During harvesting, a 2 kg representative grain sample was taken from each field.

### Methods of analysis

All the plant samples were dried at 50 °C. The dry matter contents of the grain and straw were determined at 105 °C. The selenium contents of the plant samples and aqueous extracts were determined using the hydride method followed by analysis on a Perkin-Elmer 5000 atomic absorption spectrophotometer (YLÄRANTA 1983 a). The grain samples obtained from the spring wheat experiment at JO following selenium treatment in 1982 were also subjected to sulphur content analysis using a LECO SC-132 sulphur analyser. The sulphur analyses were carried out in the Oulu Research Laboratory of Kemira Oy. The other analysis methods used in this work were same as described in a previous publication (YLÄRANTA 1983 c).

The significance of the results was statistically evaluated using analysis of variance with F test at the 0,05 probability level. For comparison of means DUNCAN's (1955) test was applied at the 1 % level of significance.

## RESULTS

At all experimental sites the lower selenium fertilizer application of 9 g/ha was sufficient to raise the selenium contents of spring wheat and barley grain from 10—20 µg/kg dry matter to above the target level of 100 µg/kg (Table 2). The highest grain selenium contents of 500—600 µg/kg were found in spring wheat and barley grown at the Satakunta Research Station. However, the average dry matter yield of spring wheat

grain from the selenium fertilizer treatments at this station was only 1060 kg/ha, while that for barley grain was 1620 kg/ha. The grain yields at the other stations were good, varying from 4000—6200 kg/ha. In these experiments the highest grain selenium contents, some exceeding 200 µg/kg dry matter, were found in barley grown on mould soil at JO. With the higher selenium fertilizer application (55 g/ha), the

Table 2. Effect of foliar spraying of selenite and selenate and selenate fertilization on the selenium content of spring wheat and barley grain grown on the clay soils and mould soils of the Institute of Soil Science (JO), the loam soils of Satakunta Research Station (SAT) and the high-humus fine sandy soil of South Ostrobothnia Research Station (EPO) in 1982. Foliar sprayings were carried out at growth stages on the FEEKES scale (LARGE 1954): 1. 2,5—3 leaf stage, 2. stage 5—6, 3. stage 9—10. Mean selenium content of the grain ( $\bar{x}$ ) and standard deviation (s).

Se g/ha	Se $\mu\text{g/kg}$ dry matter													
	JO wheat clay soil		JO barley I clay soil		JO barley II mould soil		JO barley III mould soil		SAT wheat loam soil		SAT barley loam soil		EPO barley fine sand	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
<b>Foliar spraying</b>														
<b>A. Selenite</b>														
0	19	7,4	14	0,7	9	1,1	19	3,4	19	8,8	16	3,7	11	3,1
1. 50	222	30	109	3,4	116	12	85	15	204	45	98	13	50	7,6
2. 50	1029	76	339	13	247	48	338	22	558	53	108	51	234	51
3. 50	1078	101	574	33	567	58	777	150	915	125	309	12	497	55
<b>B. Selenate</b>														
0	19	4,5	14	6,2	12	1,2	17	9,6	25	4,8	21	5,3	9	2,5
1. 50	1189	180	760	124	785	128	491	38	816	107	701	67	304	134
2. 50	1443	100	887	107	860	130	535	28	942	55	643	133	425	98
3. 50	1661	12	660	38	757	176	558	65	732	64	793	117	360	95
<b>Fertilization</b>														
<b>C. Selenate</b>														
0	20	4,0	18	2,5	10	1,3	18	3,1	17	8,4	18	8,2	11	3,0
9	157	19	133	18	172	9,8	255	13	617	36	529	83	137	16
55	1460	131	1204	60	1282	130	1175	43	2336	23	2012	129	1165	267

selenium contents of the grain varied from 1200  $\mu\text{g/kg}$  to 1500  $\mu\text{g/kg}$  when the crop was "normal". At SAT the grain of spring wheat and barley had a selenium content of over 2000  $\mu\text{g/kg}$ .

Foliar spraying of sodium selenate at the rate of Se 50 g/ha raised the selenium content of the grain of both spring wheat and barley to about the same level in all experiments, irrespective of the time of spraying. The highest selenium contents of 1200—1700  $\mu\text{g/kg}$  of dry matter were found in spring wheat grain grown at JO. In the other experiments the selenium content of spring wheat and barley grain varied from 600 to 900  $\mu\text{g/kg}$ , with the exception of the barley grown at EPO, where 300—400  $\mu\text{g/kg}$  was recorded, the lowest selenium content found for barley grain. Application of selenium fertilizer at the rate of 55 g/ha raised the selenium content of the grain more effectively than foliar spraying of the same amount of selenium. The only exception to this was the wheat grown on the clay soil at JO, where the selenium contents of the grain were the same with both techniques.

The selenium content of the grain of plants sprayed with selenite varied considerably with the stage at which the plants were sprayed. The

highest selenium contents found in wheat grain grown at JO and SAT when the plants were sprayed at the 2,5—3 leaf stage, the earliest stage of spraying, were about 200  $\mu\text{g/kg}$  of dry matter. The lowest selenium content of only 50  $\mu\text{g/kg}$  was found in barley grain grown at EPO. At the other experimental sites the grain had a selenium content of about 100  $\mu\text{g/kg}$ . Foliar spraying of the same amount of selenite (Se 50 g/ha) at the start of stem extension in most cases resulted in grain with selenium contents many times higher than those achieved with the first spraying. The highest selenium contents were found in spring wheat grain. Spring wheat grain grown at JO had an average selenium content of 1029  $\mu\text{g/kg}$ , and that grown at SAT 558  $\mu\text{g/kg}$ . The average selenium content of the grain grown at the other experimental sites ranged from 110  $\mu\text{g/kg}$  to 340  $\mu\text{g/kg}$ .

When the plants were sprayed with selenite at the end of stem extension, the selenium content of spring wheat grain grown at JO was the same as that for the previous stage of application, i.e. about 1100  $\mu\text{g/kg}$ . In the other experiments, though, the selenium content of the grain was found to be 2—3 times higher than for the previous stage of application, i.e. 300—900

Table 3. Selenium uptake of spring wheat and barley grain as a proportion of the selenium applied as fertilizer at the three experimental sites. Selenium applied in fertilizer averaged 9 g/ha (1) and 55 g/ha (2).

Experimental site and plant	Grain yield kg/ha	Grain selenium content mg/kg dry matter	Grain selenium uptake percentage of added selenium
<b>Spring wheat</b>			
Jokioinen 1.	4660	0,157 (0,020)*	7,1
„ 2.	4180	1,46 „	10,9
Satakunta }1.	1060	0,617 (0,017)	7,1
Research Station }2.	1190	2,34 „	5,0
<b>Barley</b>			
Jokioinen I 1.	5620	0,133 (0,018)	7,2
„ 2.	5610	1,20 „	12,1
„ II 1.	4030	0,172 (0,010)	7,3
„ 2.	3910	1,28 „	9,0
„ III 1.	5190	0,255 (0,018)	13,7
„ 2.	4920	1,18 „	10,4
Satakunta }1.	1620	0,529 (0,018)	9,2
Research Station }2.	1570	2,01 „	5,7
South Ostrobothnia }1.	6160	0,137 (0,011)	8,6
Research Station }2.	6450	1,17 „	13,6

\*) The selenium content of the control treatment.

µg/kg.

A significant finding from the foliar spraying of selenite is that at every experimental site, and hence on different types of soil, the selenium content of spring wheat and barley grain depended greatly on the growth stage of the plants at the time of spraying. Foliar spraying of selenite at the latest growth stage, i.e. at the end of stem extension, resulted in the greatest transfer of selenium to the grain of both spring wheat and barley. Even in this case, however, the average grain selenium content was lower than that obtained with selenate spraying.

The average yields of dry grain in the JO barley experiments were 5730 kg/ha (JO I), 4010 kg/ha (JO II) and 5040 kg/ha (JO III), and in the EPO barley experiment 6200 kg/ha. The average yield of wheat grain at JO was 4510 kg/ha. The grain yields obtained at SAT were exceptionally low, the wheat yield being only 1150 kg/ha and the barley yield 1640 kg/ha. The selenium treatments had no statistically significant effect on the differences in yields of any experiment.

Application of selenium fertilizer, which gave the highest average grain selenium contents, resulted in 7,1—13,7 % of the selenium in the fertilizer being transferred to the grain in the case of the low-selenium fertilizer (Table 3). In the case of the higher selenium fertilizer 5,0 %

and 10,9 % of the added selenium was transferred to the wheat grain and 5,7—13,6 % to the barley grain.

In the selenium fertilizer treatments, the selenium content of the straw was usually 50—70 % of that of the grain (Table 4). The exception was the barley experiment (JO III) on mould soil at JO, where the straw contained almost as much selenium as the grain.

In the experiments involving foliar spraying of selenate to barley, the straw was found to have about the same selenium content as the grain, with the exception of the results obtained from the final spraying. The selenium content of wheat straw was half that of the corresponding grain, again with the exception of the final spraying results. The selenium content of straw obtained from the final spraying treatments was closer to that of the grain than when the plants were sprayed at an earlier growth stage.

The yields of dry straw were 60—70 % of the corresponding grain yields, and at JO and EPO totalled 2500—3500 kg/ha. No statistically significant differences in yields that could be attributed to selenium treatments were observed.

In the wheat experiment at JO, the sulphur content of the grain obtained with the different treatments varied from 1,50 g/kg of dry matter to 1,66 g/kg. The differences in grain sulphur content between the different treatments were

Table 4. Effect of foliar spraying of selenite and selenate and selenate fertilization on the selenium content of spring wheat and barley straw grown on the clay soils and mould soils of the Institute of Soil Science (JO), the loam soils of Satakunta Research Station (SAT) and the high-humus fine sandy soil of South Ostrobothnia Research Station (EPO) in 1982. Foliar sprayings were carried out at growth stages on the FEEKES scale (LARGE 1954): 1. 2,5—3 leaf stage, 2. stage 5—6, 3. stage 9—10. Mean selenium content of the straw ( $\bar{x}$ ) and standard deviation (s).

Se g/ha	Se $\mu\text{g/kg}$ dry matter													
	JO wheat clay soil		JO barley I clay soil		JO barley II mould soil		JO barley III mould soil		SAT wheat loam soil		SAT barley loam soil		EPO barley fine sand	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
<b>Foliar spraying</b>														
<b>A. Selenite</b>														
0	20	6,2	10	1,9	10	0,8	19	6,1	25	4,2	25	6,7	11	2,1
1. 50	93	20	78	9,2	78	5,9	84	10	103	22	98	14	34	4,4
2. 50	448	45	296	61	189	53	423	46	269	75	108	28	207	21
3. 50	926	121	1120	53	885	62	1070	247	845	34	751	87	839	39
<b>B. Selenate</b>														
0	12	4,1	14	8,7	13	3,9	13	6,2	17	5,3	19	4,3	10	1,0
1. 50	446	87	593	165	492	44	480	21	327	57	534	63	309	100
2. 50	644	82	768	197	586	92	519	48	430	44	462	83	406	83
3. 50	1125	65	1002	20	1010	116	926	121	638	78	542	99	662	81
<b>Fertilization</b>														
<b>C. Selenate</b>														
0	16	12,6	14	4,7	11	1,8	20	2,0	22	3,1	21	6,0	9	2,2
9	80	11	99	17	119	5,1	199	19	271	31	416	82	100	11
55	605	81	785	179	695	103	1276	295	909	33	1246	132	733	139

not statistically significant.

Foliar spraying of selenite during 1982 was not found to affect the selenium contents of spring wheat and barley in 1983. The selenium contents of those crops treated with selenite in 1982 varied from 5  $\mu\text{g/kg}$  of dry matter to 17  $\mu\text{g/kg}$ . These figures did not differ statistically significantly from those obtained for the corresponding controls. Neither did the selenium contents of the crops treated with selenite in the JO spring wheat

experiment, barley experiments JO I and JO II or in the SAT experiments differ statistically significantly from the selenium contents of the corresponding crops sprayed with selenate.

Foliar spraying of selenate in the JO barley experiment (JO III) on mould soil and in the EPO barley experiment on fine sand with a high humus content produced a clear residual effect (Table 5). There were no statistically significant differences in selenium content between the

Table 5. Residual effect of foliar spraying of selenate (B) and selenate fertilization (C) on the selenium content of wheat and barley grain and straw at the three experimental sites in 1983. In each field experiment grain and straw selenium contents not marked with the same letter differ from each other at the 1 % level of significance (DUNCAN 1955). The mean dry matter yields are also presented.

Se g/ha (1982)	Se $\mu\text{g/kg}$ dry matter														
	JO								SAT				EPO		
	wheat grain straw		barley I grain straw		barley II grain straw		barley III grain straw		wheat grain straw		barley grain straw		barley grain straw		
<b>Foliar spraying</b>															
<b>B. Selenate</b>															
0	10 <sup>a</sup>	7 <sup>a</sup>	6 <sup>a</sup>	6 <sup>a</sup>	6 <sup>a</sup>	6 <sup>a</sup>	10 <sup>a</sup>	7 <sup>a</sup>	7 <sup>a</sup>	17 <sup>a</sup>	17 <sup>a</sup>	8 <sup>a</sup>	13 <sup>a</sup>	6 <sup>a</sup>	7 <sup>a</sup>
50	12 <sup>a</sup>	10 <sup>a</sup>	8 <sup>a</sup>	6 <sup>a</sup>	8 <sup>a</sup>	9 <sup>a</sup>	23 <sup>b</sup>	21 <sup>b</sup>	13 <sup>a</sup>	17 <sup>a</sup>	12 <sup>a</sup>	15 <sup>a</sup>	66 <sup>b</sup>	63 <sup>b</sup>	
<b>Fertilization</b>															
<b>C. Selenate</b>															
0	9 <sup>a</sup>	10 <sup>a</sup>	7 <sup>a</sup>	6 <sup>a</sup>	6 <sup>a</sup>	6 <sup>a</sup>	7 <sup>a</sup>	7 <sup>a</sup>	6 <sup>a</sup>	14 <sup>a</sup>	9 <sup>a</sup>	13 <sup>a</sup>	8 <sup>a</sup>	6 <sup>a</sup>	
9	8 <sup>a</sup>	8 <sup>a</sup>	8 <sup>a</sup>	7 <sup>a</sup>	8 <sup>a</sup>	8 <sup>a</sup>	10 <sup>a</sup>	9 <sup>a</sup>	14 <sup>a</sup>	17 <sup>a</sup>	9 <sup>a</sup>	16 <sup>a</sup>	8 <sup>a</sup>	7 <sup>a</sup>	
55	11 <sup>a</sup>	8 <sup>a</sup>	9 <sup>a</sup>	7 <sup>a</sup>	7 <sup>a</sup>	7 <sup>a</sup>	28 <sup>b</sup>	22 <sup>b</sup>	29 <sup>b</sup>	31 <sup>b</sup>	22 <sup>b</sup>	25 <sup>b</sup>	85 <sup>b</sup>	72 <sup>b</sup>	
<b>Yield kg/ha dry weight</b>	3790	4240	4630	2200	3230	3880	3860	3520	3490	2830	3880	3100	3550	3450	

Table 6. Effect of selenate fertilization on the selenium content of spring wheat and barley grain on the farms in 1983. NPK compound fertilizer contained 0,004 % selenium in the form of selenate.

Plant	Number of experimental sites	Selenate fertilization Se g/ha		Grain selenium content, Se mg/kg dry matter			
		Mean	Range	Selenium treatment		Control treatment	
				Mean	Range	Mean	Range
Spring wheat	4	25	20—33	0,70	0,65—0,75	0,013	0,007—0,025
Barley	9	19	12—32	0,43	0,16—0,82	0,014	0,006—0,029

crops sprayed at different stages of growth. For this reason the selenium contents of both the straw and the grain are presented as the mean values for the three growth stages. In the JO barley experiment the selenium content of the grain was 23  $\mu\text{g}/\text{kg}$ , compared with 10  $\mu\text{g}/\text{kg}$  for the control, while the straw contained 21  $\mu\text{g}/\text{kg}$  of selenium, as against 7  $\mu\text{g}/\text{kg}$  for the control. The residual effect of selenium treatment at EPO was much greater, the grain containing 66  $\mu\text{g}/\text{kg}$  of selenium compared with only 6  $\mu\text{g}/\text{kg}$  for the controls, and the straw 63  $\mu\text{g}/\text{kg}$  as against 7  $\mu\text{g}/\text{kg}$  for the controls.

When the higher selenium fertilizer was applied (Se 55 g/ha) the selenium contents of both grain and straw grown in the various experiments were statistically significantly higher ( $P=0,01$ , DUNCAN 1955) than those of the controls, with the exception of the spring wheat and barley grown on clay soil and the barley grown on mould soil at JO. In the experiments at JO (JO III) and SAT the selenium content of the grain and straw was 22—31  $\mu\text{g}/\text{kg}$  of dry matter,

compared with 6—14  $\mu\text{g}/\text{kg}$  for the controls. The greatest residual effect was seen in the experiment at EPO, in which the selenium content of barley grain was 85  $\mu\text{g}/\text{kg}$  compared with 8  $\mu\text{g}/\text{kg}$  for the control, and that of the straw 72  $\mu\text{g}/\text{kg}$  as against 6  $\mu\text{g}/\text{kg}$  for the control. Application of the lower selenium fertilizer (9 g/ha) had no measurable effect on the selenium content of the crops. The yield was good in all experiments.

Under practical cultivation conditions selenate from the fertilizer was taken up effectively by both spring wheat and barley. The selenium content of spring wheat grain showed little variation with experimental site, ranging from 0,65 mg/kg of dry matter to 0,75 mg/kg (Table 6). Barley grain showed a greater variation in selenium content ranging from 0,16 mg/kg of dry matter to 0,82 mg/kg. The yields were generally good. The effect of soil type on the selenium content of spring wheat and barley grain was not investigated because of the small number of experiments.

## DISCUSSION

Foliar spraying of selenate raised the selenium content of both the grain and the straw of spring wheat and barley to the same level, irrespective of the growth stage at the time of spraying. The effect of foliar spraying of selenite was initially small, as the grain of plants sprayed at the 2,5—3 leaf stage contained only 50—200  $\mu\text{g}$  of selenium per kg of dry matter, i.e. 15—25 % of the selenium content obtained with selenate. When the plants were sprayed at later stages of growth, the greater surface area of the foliage meant that selenite spraying had a greater effect on the selenium content of the grain. Thus foliar spraying of selenite and selenate at the end of

stem extension raised the selenium contents of spring wheat and barley grain by about the same amount.

The finding by GISSEL-NIELSEN (1981·a) that the effectiveness of selenite spraying depends on the growth stage of the plants at the time of spraying thus does not seem to apply to selenium applied in the form of selenate. It would therefore be better to spray with selenate than selenite in a situation where it is not possible to select the spraying time accurately and consistently. For the same reason, there would seem to be no point in combining selenite spraying with herbicide spraying, since most of the herbicide spraying is done

before the stem extension. In Finland it has not been considered necessary to study combined selenate and herbicide spraying since foliar spraying of selenium is unlikely to be adopted.

The results of earlier field experiments (YLÄRANTA 1984 a) suggested that the type of soil affected the effectiveness of spraying, particularly in the case of selenate. The selenium reaching the surface of the soil during spraying with the readily soluble selenate appears to be leached through coarse mineral soil more easily than through clay soil. It is therefore more accessible to the roots of spring wheat and barley, and hence is more readily taken up by the plants. The effect of the soil type in the present study was small, as the selenate was taken up by the plants in the same way, whether the soil was clay, loam or mould. The only exception to this was the barley experiment at EPO, which was conducted on fine sandy soil with a high humus content. For some unknown reason the selenium contents of the grain grown there were lower than those found at the other experimental sites. This series of experiments lacked a clearly coarse mineral soil.

In the final spraying with selenium carried out at the end of stem extension, both selenite and selenate raised the selenium contents of the crops by almost the same amount. It is thus clear that the selenate falling onto the soil surface has sufficient time to reach the roots and hence pass into the plants only when spraying is carried out at the earlier growth stages. Selenite is sorbed strongly onto the soil particles, and little leaching takes place even with large amounts of water (YLÄRANTA 1982). Thus in addition to depending on the growth stage of the plants at the time of spraying, the effect of foliar spraying of selenite on the selenium content of the crops is more dependent on the weather conditions than in the case of selenate. Rain falling immediately after spraying with selenite thus reduces the effectiveness of spraying by washing selenium off the plants and onto the soil. In this study, there was an interval of at least several hours between spraying and the onset of rain.

As in the pot experiments by GISSEL-NIELSEN (1975) and the field experiments by YLÄRANTA

(1984 a), foliar spraying of selenite raised the selenium content of wheat grain more effectively than that of barley grain.

Field experiments carried out in 1981 by YLÄRANTA (1984 a) showed that the fertilizer used on fine sandy soil should have a selenium content of 5–10 g/ha in the form of selenate if the selenium content of the spring wheat and barley grain cultivated on this soil is to reach the target of 100 µg/kg. On clay soil application of 10–20 g/ha of selenium in the fertilizer was calculated to be necessary. The results of the present field experiments gave a considerably more encouraging picture of the effect of selenium fertilization. The experiments carried out on clay soil, loam and organogenic soils show that 5–10 g/ha of selenium is sufficient to raise the selenium of spring wheat and barley grain to 100 µg/kg of dry matter.

In experiments with selenite fertilizer and foliar spraying with selenite GISSEL-NIELSEN (1981 b) found that the selenium content of the grain of wheat, barley and oats diminishes as the size of the dry yield increases. This would seem to be true in the case of selenate fertilization, though not, according to the present results, for the foliar spraying of selenite and selenate. The uptake of selenium by the crops was about the same, although application of selenate fertilizer containing the smaller amount of selenium (Se 9 g/ha) raised the selenium content of spring wheat and barley grain at SAT to a level 2–4 times higher than that obtained at the other experimental sites.

The results obtained with selenium fertilizer under practical cultivation conditions were good, as the spring wheat and barley grain were found to have selenium contents up to eight times the target level of 0,1 mg/kg dry matter.

In order to be able to control the effects of selenium applications a full scale follow-up program with increased number of long term trials has been established.

According to GISSEL-NIELSEN (1981 a) selenite fertilizer would have to be applied at the rate of 120 g/ha of selenium to raise the selenium content of barley grain from the base level of 0,02 mg/kg to 0,05–0,1 mg/kg dry matter.

However, it appears that even with such a large amount of selenium applied four years in succession at the same site, the residual effect would be insufficient if the target for the selenium content of the grain is 0,05 mg/kg dry matter.

In Finland, results on the residual effect of selenate application are available from only one year following the use of fertilizer (YLÄRANTA 1983 c, 1984 a). These results, together with those of the present study, show that the residual effect of selenate spraying and application of selenate fertilizer on the selenium content of the following year's cereal crop is small if the amount of selenium applied during the year is about 10 g/ha. The residual effect of a higher rate of selenium application (about 50 g/ha) is also small on clay soil. However, on the high-humus fine sandy soil at EPO the residual effect of selenate treatments was clearly seen in both the present and the previous series of experiments with barley (YLÄRANTA 1984 a). On peat soils, on the other hand, selenate may be leached away out of reach of the roots (YLÄRANTA 1982). This would explain why the selenium treatments of the barley grown on mould soil at JO II were not observed to have any effect on the 1983 barley crop. The field in question has a layer of peat extending from a depth of 20 cm down to 110 cm. The soil type of the plough layer of the other mould field used for barley cultivation (JO III) was the same, but below it was a layer of coarse mineral soil.

It is quite clear that the effectiveness of selenate fertilizer in raising the selenium content of spring wheat and barley is partly due to the practice of fertilizer placement, which is widely used in Finland. This involves placing the fertilizer between every second row of seeds at depth of about 8 cm, i.e. just below the seeds so

that the elements provided by the fertilizer are readily accessible to the roots of the growing crops. Soil preparation work carried out after harvesting and before sowing the seeds the following spring distributes the selenium remaining in the soil from the fertilizer throughout the entire plough layer, thus making it more difficult for the new plants to obtain.

GISSEL-NIELSEN (1977) expressed concern that sulphur in the form of sulphate reduced the uptake of selenium applied as selenate. However, neither these results nor earlier studies by YLÄRANTA (1983 b, c, 1984 a) provide proof that under normal cultivation conditions the effect of sulphur on the uptake of selenium by spring wheat, barley and rye grass represents any obstacle to the introduction of selenate fertilization.

In Finland experiments with selenium fertilizer have been carried out on plants other than cereal crops. The results of selenium fertilization experiments carried out by YLÄRANTA on grassland intended for silage will be published later. It is precisely cereal crops and grassland plants whose selenium contents should be raised first to improve the intake of selenium in Finland, which by international standards is currently low. Selenate selenium addition to the multinutrient fertilizers most commonly used on agricultural land has already decided in Finland. The fertilizers used on fields devoted to grain crops will initially contain 16 g/t of added selenium. As fertilizer is applied at the average rate of about 500 kg/ha, the fertilizer will provide about 8 g/ha of selenium. Annual selenium topdressing of pasture at the rate of 10 g/ha Se with prills containing 1 % selenium as sodium selenate is also permitted in New Zealand in preventing selenium deficiency in grazing animals (WATKINSON 1983).

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## SELOSTUS

### Seleenilannoituksen ja seleeniruiskutuksen vaikutus kevävehnän ja ohran seleenipitoisuuteen

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Seleenilannoituksen ohella voidaan viljojen seleenipitoisuutta kohottaa käytännössä ruiskuttamalla seleeniä kasvustoon. Viljakasvuston kehitysvaiheen ruiskutushetkellä on todettu vaikuttavan ruloiksiin. Tämän selvittämiseksi ruiskutettiin kahteen kevävehnäkavustoon ja viiteen ohrakasvustoon natriumseleniitin ja -seleniitin vesiliuoksia, Se 50 g/ha, 2,5—3-lehtiasteella, versonnan päättyessä ja juuri ennen tähkän tuloa näkyville. Ruiskutus tuloksia verrattiin lannoitukseen, jossa Normaali Y-lannoksessa annettiin seleeniä 9 ja 55 g/ha.

Selenaattilannoituksen vaikutusta kevävehnän ja ohran seleenipitoisuuteen tutkittiin myös viljelijöiden pelloilla eri puolilla Suomea. Koelohkoilla käytetty Normaali Y-lannos sisälsi seleeniä 0,004 % selenaattina.

Selenaattiruiskutuksen kevävehnän ja ohran jyvien ja olkien seleenipitoisuutta kohottava vaikutus ei riippunut ruiskutusajasta. Sen sijaan seleniittiruiskutuksen vaikutus riippui voimakkaasti kasvuston kehitysvaiheesta ruiskutushetkellä. Jyvien seleenipitoisuus oli 2,5—3-lehtiasteella suoritettussa ruiskutuksessa vain 15—25 % vastaavien selenaattikoekärsien seleenipitoisuudesta.

Myöhempiä ruiskutusaikoina lehvistön pinta-ala oli lisääntynyt ensimmäisestä ruiskutuksesta, joten suurempi osa

ruiskutteen seleenistä joutui kasviin myös seleniittiruiskutuksessa. Niinpä vähän ennen viljojen tähkälle tuloa suoritetuissa ruiskutuksissa seleniitti ja selenaatti kohottivat likimain saman verran kevävehnän ja ohran jyvien seleenipitoisuutta. Selenaattiruiskutus soveltuisi siten seleniittiruiskutusta paremmin käytäntöön, jossa tarkan ja yhdenmukaisen ruiskutusajan valinta on mahdotonta.

Kevävehnän ja ohran jyvien seleenipitoisuus kohosi kaikkein eniten selenaattilannoituksella. Sekä savimaassa, hiukkaassa että multamaassa riittäisi seleeniä 5—10 g/ha selenaattina kohottamaan kevävehnän ja ohran jyvien seleenipitoisuuden perustasolta 0,01—0,02 mg/kg kuiva-ainetta 0,1 mg/aan/kg.

Viljelijöiden pelloilla suoritettujen seleenilannoituskokeiden vahvistivat selenaattilannoituksen kohottavan tehokkaasti kevävehnän ja ohran jyvien seleenipitoisuutta myös käytännössä. Maa- ja metsätalousministeriö antoi luvan lisätä 1.7.1984 alkaen selenaattiseleeniä yleisimpiin pelto- ja puutarhaviiljelyssä käytettäviin moniravinnelannoitteisiin. Ensi sijassa viljanviljelyssä käytettäviin lannoitteisiin saa seleeniä lisätä 16 g lannoitetonnia kohti.

## EFFECT OF SELENITE AND SELENATE FERTILIZATION AND FOLIAR SPRAYING ON SELENIUM CONTENT OF TIMOTHY GRASS

TOIVO YLÄRANTA

YLÄRANTA, T. 1984. Effect of selenite and selenate fertilization and foliar spraying on selenium content of timothy grass. Ann. Agric. Fenn. 23: 96—108. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

Field experiments were conducted to study the effect of selenium fertilization and foliar spraying of aqueous solutions of sodium selenite and selenate on the selenium content of timothy grass (*Phleum pratense* L.).

NPK fertilizer containing 0—0,21 % added selenium in the form of either selenite or selenate was placed at the rate of 500 kg/ha into the soil immediately prior to sowing timothy grass. The selenium content of the grass intended for silage raised from the base level of 0,02 mg/kg of dry matter to 0,12 mg/kg applying 205 g/ha selenium in the form of selenite and to 0,09 mg/kg applying 9 g/ha selenium in the form of selenate. The residual effect of the selenium treatments diminished rapidly. Two cropping seasons after applying the selenium fertilizer the target selenium content of 0,1 mg/kg of dry matter was not reached at all.

In another experiment serie one week before cutting the timothy grass at the heads-emerging stage, the three experimental fields were sprayed with 0, 1, 3 and 10 g/ha of selenium in the form of aqueous solutions of either sodium selenite or selenate. Some plots were treated with NPK fertilizer containing 0,0018 % or 0,011 % selenate selenium. As much as 70 % of the selenium sprayed onto the crops accumulated in the grass; a selenium content of 0,08—0,20 mg/kg of dry matter was achieved in the first crop using 1 g/ha of selenium in the form of selenite or selenate. The grass selenium content raised respectively to 0,6—1,7 mg/kg dry matter spraying 10 g/ha of selenium. The selenium fertilization was less effective. Applying 11 g/ha selenate selenium in the fertilizer it was attained the selenium content of 0,6 mg/kg of dry matter.

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Index words: selenium fertilization, foliar spraying, selenite, selenate, timothy selenium content.

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### INTRODUCTION

The minimum requirement for the selenium content of animal fodder is considered to be 0,1 mg/kg of dry matter (AMMERMAN and MILLER 1975). In Finland, the average selenium content

of pasture crops as timothy and clover is 0,01 mg/kg of dry matter (OKSANEN and SANDHOLM 1970, SIPPOLA 1979).

As in the case of grain crops, attempts to raise

the selenium content of pastures have centred on the use of selenite. Spraying the first grass crop with 10–20 g/ha of selenium in the form of selenite has been reported to raise the selenium content of the grass for the entire growing season to around 0,1 mg/kg of dry matter (GISSEL-NIELSEN 1981). MORÉ and COPPENET (1980) sprayed Italian rye grass with 70 g/ha of selenium in the form of sodium selenite. The first crop from one field experiment had a selenium content of 0,76 mg/kg and the first crop from the other experiment a selenium content of 2,7 mg/kg of dry matter. In both experiments even the fourth crop had a selenium content above 0,1 mg/kg. GUPTA et al. (1983) mixed one kilogram of selenium in the form of aqueous sodium selenite solution into the plough layer. The selenium content of the timothy grass, which was 1,58 mg/kg of dry matter during the year of selenium application,

was still 0,1 mg/kg three further cropping seasons.

NPK fertilizers containing various amounts of selenite and selenate were being produced in Finland back in the late 1970s. These fertilizers have been used in a number of field experiments aimed at raising the selenium contents of grain crops and potatoes (KORKMAN 1980, YLÄRANTA 1983 d, 1984 a, b). Selenium fertilization experiments with timothy grass (*Phleum pratense* L.) intended for silage were started alongside similar experiments involving grain crops, and hence NPK fertilizer containing both selenite and selenate was in use right from the start. As foliar spraying experiments carried out in different countries have involved most commonly selenite, both selenite and selenate were chosen for the spraying experiments discussed here.

## MATERIAL AND METHODS

### I Comparison of selenite and selenate fertilization

A selenium fertilization experiment without a nurse crop was started in spring 1981 at the North Savo Research Station (PSA) of the Agricultural Research Centre of Finland. The topsoil (0–25 cm) of the experimental field was high-humus silt with 21,5 % clay and 44,1 % silt (Table 1). The organic carbon content of the soil averaged 9,7 % and the pH(CaCl<sub>2</sub>) 4,6. The subsoil (25–60 cm) contained 21 % organic carbon and had a pH(CaCl<sub>2</sub>) of 4,7. The amount of selenium extractable from the topsoil into boiling water was 8,9 µg/l of soil. The macronutrient status (Ca, K, P) of the soil fell into the class "fair" in the Finnish soil testing method (KURKI et al. 1965).

The experimental field was treated with NPK compound fertilizer (N 16 %, P 7 %, K 13 %) to which selenium had been added in the form of either sodium selenite or sodium selenate. The field experiment was divided into the following seven treatments:

1. No Se addition, Se 0,000 07 % in fertilizer
2. Se 0,0096 % as selenite
3. Se 0,041 % as selenite
4. Se 0,21 % as selenite
5. Se 0,0018 % as selenate
6. Se 0,011 % as selenate
7. Se 0,10 % as selenate

The randomized plots, 2,5 m x 11 m, with four replicates were fertilized 500 kg/ha to a depth of 8 cm using fertilizer drill. The selenium fertilizers were from the same production batch as those used in the 1980 barley experiment (YLÄRANTA 1983 d). On May 28, immediately after applying the fertilizer, the timothy grass seeds (*Phleum pratense* L., variety Tarmo) were sown and the soil rolled. At the time of harvesting, September 10, 1981, the timothy grass was at the silage stage, i.e. at the heads-emerging stage.

In 1982 and 1983 three silage grass crops were cut from plots to which selenium-free NPK fertilizer (N 16 %, P 7 %, K 13 %) had been

Table 1. Chemical and physical characteristics of the plough layer (0—20 cm) and of the deeper layer (20—40 cm) of the experimental soils. The analytical figures of the deeper layer are shown in parentheses.

Experimental site	Particle size composition (%)					Org. C (%)	pH (CaCl <sub>2</sub> )
	Ø <0,002 mm	0,002—0,02 mm	0,02—0,06 mm	0,06—0,2 mm	0,2—2 mm		
North Savo Research Station 0—25 cm, (25—60 cm)	21,5 (—)	44,1 (—)	18,3 (—)	11,1 (—)	5,0 (—)	9,7 (21)	4,6 (4,7)
Sata-Häme Research Station	20,1 (18,6)	42,6 (43,6)	26,9 (29,1)	7,5 (6,4)	3,0 (2,4)	2,9 (1,4)	4,8 (5,0)
Central Ostrobothnia Research Station	7,4 (7,3)	34,4 (35,8)	45,9 (46,9)	9,1 (8,4)	3,3 (2,2)	2,4 (0,86)	4,7 (4,8)
North Ostrobothnia Research Station 0—25 cm, (25—45 cm)	— (6,5)	— (11,0)	— (50,1)	— (30,2)	— (2,3)	21,0 (2,4)	4,6 (3,7)

applied immediately after cutting the previous crop. The first crop was given 600 kg/ha of fertilizer, the second 500 kg/ha the third 400 kg/ha.

## II Foliar spraying of selenite and selenate compared with selenate fertilizer

The selenium treatments were carried out in 1982 at research stations Sata-Häme (SAH), North Ostrobothnia (PPO) and Central Ostrobothnia (KPO) belonging to the Agricultural Research Centre. The residual effect of the selenium treatments was then investigated a year later, in 1983. The experimental plots, measured 1,5 m x 10 m, were bordered by healthy first-year timothy grass. The plough layer (0—20 cm) at SAH was silt and at KPO fine sand. The topsoil (0—25 cm) at PPO was mould containing 21 % organic carbon. The pH(CaCl<sub>2</sub>) was in the range 4,6—4,8 for all three topsoils. The main characteristics of the experimental soils are given more detailed in Table 1.

The amount of selenium extracted from the plough layer into boiling water was 13 µg/l of soil at SAH, 8,0 µg/l of soil at KPO and 2,9 µg/l of soil at PPO. The general fertility of the soils corresponded to fair — satisfactory level (KURKI et al. 1965).

The field experiments were divided into selenium treatments, each of which had four randomized replicates.

A. Spraying the plants with aqueous solutions of either sodium selenite or sodium selenate.

Fertilizing with NPK (N 16 %, P 7 %, K 13 %) compound fertilizer with no added selenium.

1. No selenium spraying
2. Se 1 g/hä as selenite
3. Se 3 g/ha as selenite
4. Se 10 g/ha as selenite
5. Se 1 g/ha as selenate
6. Se 3 g/ha as selenate
7. Se 10 g/ha as selenate

B. Fertilizing with NPK (N 16 %, P 7 %, K 13 %) compound fertilizer containing added sodium selenate (YLÄRANTA 1983 d).

1. No Se addition, Se 0,000 03—0,000 11 % in fertilizer
2. Se 0,0018 % as selenate
3. Se 0,011 % as selenate. This treatment was only conducted at PPO.

600 kg/ha of NPK fertilizer were applied to the first crop, 500 kg/ha to the second and 400 kg/ha to the third. Fertilizer was applied to the second and third crops immediately after cutting the previous crop. Spraying was carried out one week before the grass was cut at the silage stage using an experimental AZO-propane sprayer. Consumption of water was 400 l/ha and of Citowett surfactant (Kemira Oy, Finland) 0,4 l/ha.

In 1982, the year of the selenium treatments, three crops were harvested at SAH and PPO, and two crops at KPO. The residual effect of the selenium treatments was studied in 1983 at SAH and PPO, at both of which three crops were harvested.

### III Application of selenium fertilizer in practice

Application of fertilizer containing selenate was studied on farmers' fields in different parts of Finland in 1983 (YLÄRANTA 1984 a). The series of experiments included application of NPK fertilizer (N 16 %, P 7 %, K 13 %) containing 0,004 % selenium as selenate to timothy grass-dominated leys intended for both silage and hay. Each experimental site had two fields of around 2500 m<sup>2</sup> cultivated using the farmers' normal methods. The only difference between the fields was that one was treated with selenium fertilizer, while the other was treated with fertilizer containing no added selenium. In six experiments the grass was grown for silage, and in a further six experiments for hay. Two crops were cut from the grassland intended for silage. The yields were good.

#### Methods of analysis

The crops of the field experiments were cut using a Hege or a Haldrup harvester, and the yield from each plot weighed. A fresh, representative

sample of about 1 kg was taken from each crop for chemical analysis at the time of weighing. The samples were dried at 50 °C. The dry matter yields were determined at 105 °C. The selenium contents of all plant samples and soil extracts were determined using the hydride method (YLÄRANTA 1983 a). In addition, the sulphur contents of the first crop during the selenium treatment year at SAH and of the third crop at PPO were determined using a LECO SC-132 sulphur analyser. The sulphur analyses were carried out in the Oulu Research Laboratory of Kemira Oy.

The particle size composition of the soils was determined using the pipette method of ELONEN (1971). Organic carbon was determined using LECO CR-12 carbon analyser (SIPPOLA 1982). The pH(CaCl<sub>2</sub>) values were measured in soil suspensions made by mixing 25 ml of soil with 62,5 ml of 0,01 M CaCl<sub>2</sub> solution. The selenium was extracted from the soil samples into hot water using the method described by YLÄRANTA (1982).

For comparison of means DUNCAN's (1955) test was applied at the 1 % level of significance.

## RESULTS

### I Comparison of selenite and selenate fertilization

The highest selenium content, 8,3 mg/kg of dry matter, was found in the selenate treatment in which 500 g/ha of selenium were applied in the fertilizer. To achieve the target selenium content of 0,1 mg/kg of dry matter required almost 200 g/ha of selenium as selenite, but only about 10 g/ha as selenate (Table 2). The lowest addition of selenite, Se 48 g/ha, raised the selenium content of the grass from the 0,02 mg/kg of the control to 0,05 mg/kg of dry matter. The slightly higher selenate addition, Se 55 g/ha, raised the selenium content of the grass to 1,2 mg/kg. The effectiveness of selenite in raising the selenium content of the grass diminished as the amount of

selenium applied increased. The lowest addition of selenite raised the selenium content of the grass by 0,0007 mg/kg of dry matter for each one gram of selenium applied per hectare. The highest addition of selenite, Se 1050 g/ha, raised the selenium content of the grass to 0,322 mg/kg of dry matter, the increase per gram of selenium added per hectare being only 0,0003 mg/kg.

In the case of selenate fertilizer the uptake of selenium was proportionally about the same, irrespective of whether the selenium application was 55 g/ha or 500 g/ha, the increases in the selenium content of the grass being 0,021 and 0,017 mg/kg for every gram of selenium applied per hectare. The effect of the lowest selenate addition on the selenium content of the grass was smaller.

Table 2. Effect of selenite and selenate fertilization on the selenium content of timothy grass grown on high-humus silt soil of North Savo Research Station in 1981. Residual effect of selenium treatments in 1982 and 1983.

Se g/ha	Se mg/kg dry matter						
	1981	1982			1983		
		I cut	II cut	III cut	I cut	II cut	III cut
0	0,020	0,009	0,008	0,009	0,011	0,007	0,005
<b>Selenite</b>							
48	0,052	0,020	0,011	0,010	0,012	0,008	0,006
205	0,124	0,036	0,030	0,021	0,011	0,009	0,006
1050	0,322	0,132	0,113	0,078	0,039	0,051	0,035
<b>Selenate</b>							
9	0,094	0,017	0,009	0,010	0,013	0,008	0,005
55	1,16	0,131	0,045	0,022	0,015	0,011	0,006
500	8,32	0,766	0,329	0,227	0,036	0,029	0,035

The average dry matter yield of silage grass was 5600 kg/ha. Application of selenium fertilizer did not produce any statistically significant differences in yield between the different treatments. The grass took up 0,15—12,0 % of the selenium applied in the fertilizer. The smallest selenium uptake in percentages was found in the plots with the highest addition of selenite. The highest selenium uptake resulted from addition of Se 55 g/ha as selenate.

In 1982, the year following the selenium treatments, the selenium content of the first crop cut from the plots treated with selenate had fallen to one tenth of the previous year's level, while that of the crop from the selenite treatments had fallen to only one third (Table 2). In the first cut the target selenium content of 0,1 mg/kg of dry matter was exceeded only in the treatment with the highest selenite addition and in the selenate treatments in which the selenium additions were 55 and 500 g/ha. In the second and third cuts the selenium content of the grass fell faster in the selenate treatments than in the selenite treatments. The highest selenium contents in the second crop, 0,113 and 0,329 mg/kg, were found in plots given the highest amounts of selenite and selenate in the fertilizer. In the third crop only the treatment with the highest selenate addition produced grass with a selenium content in excess of the target 0,1 mg/kg.

In 1983, two years after selenium application, the selenium contents of the crops differed with statistical significance from that of the control

only in the case of the highest selenite and selenate additions. The selenium contents on the three crops from these treatments were all about the same, averaging 0,029—0,051 mg/kg of dry matter.

The average dry matter yields obtained in the two years following selenium treatment were (kg/ha):

	Cut I	Cut II	Cut III
1982	2800	4300	2100
1983	4500	2800	2200

The variation in selenium content of silage grass within the different selenium treatments was small in all three years. In 1981, the year the selenium fertilizer was applied, the coefficient of variation ranged from 4,7 % to 19 % for the different treatments. The variation during 1982 was from 2,8 % to 28 %, and in 1983 from 1,4 % to 24 %.

## II Foliar spraying of selenite and selenate compared with selenate fertilizer

Solutions of sodium selenite and sodium selenate sprayed onto the grass one week before cutting raised the selenium content of the first grass crop by the highest amount at SAH and PPO (Table 3). The selenium content of the first crop exceeded 0,1 mg/kg of dry matter following application of only Se 1 g/ha. Spraying was slightly more effective at SAH, where one gram of selenium per hectare raised the selenium content of the

Table 3. Effect of foliar spraying of selenite and selenate and selenate fertilization on the selenium content of timothy grass at Sata-Häme Research Station (SAH), Central Ostrobothnia Research Station (KPO) and North Ostrobothnia Research Station (PPO) in 1982. Mean selenium content of the grass ( $\bar{x}$ ) and standard deviation (s).

Se g/ha	Se $\mu\text{g/kg}$ dry matter													
	SAH				KPO				PPO					
	I cut		III cut		I cut		II cut		I cut		II cut		III cut	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
<b>Foliar spraying</b>														
0	21	1,5	20	1,9	21	5,2	25	7,6	27	9,4	27	8,8	24	2,8
<b>Selenite</b>														
1	197	16	178	22	76	22	130	21	153	26	166	12	482	25
3	468	44	309	22	193	27	272	18	405	41	398	26	1042	162
10	1450	130	982	47	624	89	1022	182	1172	116	1217	224	3379	180
<b>Selenate</b>														
1	162	19	240	24	82	17	167	33	135	14	152	14	419	44
3	443	28	374	27	223	74	348	21	379	6,8	385	18	1076	202
10	1731	213	1066	56	640	53	1052	56	1091	21	1221	125	3187	115
<b>Fertilization</b>														
<b>Selenate</b>														
0	20	2,7	21	2,9	21	7,7	24	4,6	19	4,4	26	4,2	24	2,1
11*	564	95	598	49	552	86	523	139	639	29	516	64	581	18
66**	—	—	—	—	—	—	—	—	2992	185	1844	240	2196	48

\* for second crop 9 g/ha, for third crop 7 g/ha

\*\* for second crop 55 g/ha, for third crop 44 g/ha

grass from the 0,021 mg/kg of the control to 0,162 mg/kg in the selenate treatment and to 0,197 mg/kg in the selenite treatment. The selenium content of the grass cut at KPO was only half that obtained at SAH, irrespective of the amount of selenium applied. The highest amount of selenium applied by spraying was 10 g/ha, and this raised the selenium content of the grass to ten times the figure obtained by spraying Se 1 g/ha. The highest selenium contents were thus 1,5—1,7 mg/kg of dry matter at SAH.

Selenium fertilization at the rate of Se 11 g/ha raised the selenium content of the first silage grass crop at all stations to about the same level, i.e. to 0,55—0,64 mg/kg of dry matter. The selenium content of the first silage grass crop at KPO was 0,55 mg/kg, which is almost as high as that obtained by spraying with Se 10 g/ha. At SAH, application of selenate fertilizer gave a selenium content only one third of that achieved with the highest foliar spraying of selenium, while at PPO it was just over half.

Both spraying with selenium and application of selenate fertilizer were carried out for every crop. No analysis results are given for the second crop at SAH because the SAH samples were destroyed in an accident. In the spraying treat-

ments at KPO the selenium contents of the second crop were about 50 % higher than those of the first crop but at PPO these were about equal.

Third crops were harvested only at SAH and PPO. Following the highest foliar applications of selenium, the selenium content of the third crop at SAH was almost 50 % lower than that of the first crop. In the other spraying treatments at SAH the differences were not so clear between the selenium contents of the first and third crops. At PPO, however, the selenium contents of the third crop were almost three times as high as those of the first and second crops.

In the selenate fertilizer treatment in which the first crop was given Se 11 g/ha, the second crop Se 9 g/ha and the third crop 7 g/ha, the selenium content of each crop was about the same at all three stations, i.e. 0,52—0,64 mg/kg of dry matter. The experiments at PPO included one treatment in which the crop was given six times the amount of selenium, i.e. 66 g/ha, 55 g/ha and 44 g/ha for the first, second and third crops, respectively. The selenium content of the first crop in this treatment was 3,0 mg/kg of dry matter, falling to 1,8 and 2,2 mg/kg in the second and third crops, respectively.

Table 4. Selenium uptake of first timothy grass crop as a proportion of the selenium applied as foliar spray and as fertilizer at Sata-Häme Research Station (SAH) and North Ostrobothnia Research Station (PPO) in 1982.

Se g/ha	SAH			PPO		
	Yield kg/ha dry matter	Se mg/kg dry matter	Selenium uptake of added (%)	Yield kg/ha dry matter	Se mg/kg dry matter	Selenium uptake of added (%)
<b>Foliar spraying</b>						
<b>Selenite</b>						
1	4020	0,197 (0,021)*	70,8	4160	0,153 (0,027)*	52,4
3	3950	0,468	58,9	4340	0,405	54,7
10	4050	1,450	57,9	4350	1,172	49,8
<b>Selenate</b>						
1	3960	0,162	55,8	3980	0,135	43,0
3	4230	0,443	59,5	4250	0,379	49,9
10	4060	1,731	69,4	4280	1,091	45,5
<b>Fertilization</b>						
<b>Selenate</b>						
11	4050	0,564 (0,020)*	20,0	4270	0,639 (0,019)*	24,1
66	—	—	—	4030	2,992	18,2

\*The selenium content of the control treatment (mg/kg dry matter).

The average dry matter yields (kg/ha) were:

Cut	SAH	KPO	PPO
I	4000	2900	4200
II	2800	3600	4200
III	900	—	1500

Some random, statistically significant differences in yield were found between the different treatments, though there was no evidence that these were linked with the selenium treatments.

The highest yields and selenium contents of the first crop were found at SAH and PPO, so that selenium uptake by the grass was also highest at these two stations (Table 4). In these experiments 43—71 % of the selenium sprayed onto the grass was removed along with the crop. The corresponding figure for the selenium fertilizer treatments was "only" 18—24 %.

The average sulphur content of the first crop at SAH was 1,7 g/kg of dry matter and that of the third crop at PPO was 2,7 g/kg. There were no statistically significant differences in sulphur content between the different treatments at the 1 % level of significance.

The residual effect of the 1982 selenium treatments was studied in 1983 in the three crops at SAH and PPO. The average dry matter yields (kg/ha) were as follows:

	Cut I	Cut II	Cut III
SAH	6500	1700	1600
PPO	6200	3200	200

In the treatments given the highest amounts of selenium at SAH the selenium content of the first and second crops differed from the 0,011—0,015 mg/kg of dry matter of the control at the 1 % level of significance (Table 5). The greatest residual effect of selenium treatment in the first crop, namely selenium contents of 0,045 mg/kg and 0,048 mg/kg of dry matter, was found in the selenate fertilizer treatment and in the spraying treatment with the highest amount of selenate. The selenium content of the second crop in these treatments was lower, 0,021—0,030 mg/kg of dry matter. The selenium contents of the third crop were roughly the same in all treatments, i.e. 0,012—0,019 mg/kg of dry matter.

The selenium content of the grass grown at PPO was also higher than that of the control in those plots given the highest amounts of selenium. The highest selenium contents at PPO were found in crops treated in 1982 with a total of Se 165 g/ha in the fertilizer. The following year, the first crop had a selenium content of 0,263 mg/kg, the second crop 0,123 mg/kg and the third crop 0,159 mg/kg of dry matter.

### III Application of selenium fertilizer in practice

Selenium contained in fertilizer was taken up

Table 5. Residual effect of foliar spraying of selenite and selenate and selenate fertilization on the selenium content of timothy grass at the Sata-Häme Research Station (SAH) and North Ostrobothnia Research Station (PPO) in 1983. Mean selenium contents of each cuts not marked with the same letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Se g/ha (1982)	Se mg/kg dry matter					
	SAH			PPO		
	I cut	II cut	III cut	I cut	II cut	III cut
<b>Foliar spraying</b>						
0	14 <sup>a</sup>	11 <sup>a</sup>	14 <sup>a</sup>	8 <sup>a</sup>	8 <sup>a</sup>	15 <sup>a</sup>
<b>Selenite</b>						
1	15 <sup>a</sup>	14 <sup>a</sup>	12 <sup>a</sup>	10 <sup>a</sup>	8 <sup>a</sup>	16 <sup>a</sup>
3	14 <sup>a</sup>	14 <sup>a</sup>	13 <sup>a</sup>	13 <sup>ab</sup>	8 <sup>a</sup>	18 <sup>a</sup>
10	26 <sup>b</sup>	21 <sup>b</sup>	19 <sup>b</sup>	23 <sup>b</sup>	12 <sup>a</sup>	22 <sup>a</sup>
<b>Selenate</b>						
1	17 <sup>a</sup>	13 <sup>a</sup>	14 <sup>a</sup>	11 <sup>a</sup>	10 <sup>a</sup>	16 <sup>a</sup>
3	14 <sup>a</sup>	15 <sup>a</sup>	14 <sup>a</sup>	17 <sup>ab</sup>	10 <sup>a</sup>	18 <sup>a</sup>
10	45 <sup>c</sup>	30 <sup>c</sup>	16 <sup>ab</sup>	41 <sup>c</sup>	19 <sup>b</sup>	27 <sup>b</sup>
<b>Fertilization</b>						
<b>Selenate</b>						
0	11 <sup>a</sup>	15 <sup>a</sup>	14 <sup>a</sup>	10 <sup>a</sup>	8 <sup>a</sup>	14 <sup>a</sup>
11*	48 <sup>c</sup>	28 <sup>c</sup>	19 <sup>b</sup>	54 <sup>d</sup>	35 <sup>c</sup>	48 <sup>c</sup>

\* for second crop 9 g/ha, for third crop 7 g/ha

fairly easily by the silage grass, as shown by the fact that the selenium content of the first crop rose to an average of 1,33 mg/kg of dry matter, range 0,84—2,06 mg/kg (Table 6). Application of selenium averaged 25 g/ha. The selenium content of the hay crop was considerably lower, 0,87 mg/kg of dry matter, following the same

selenium fertilization. The average amount of selenium applied to the second silage grass crop in the fertilizer was smaller than the first crop, namely 19 g/ha. The average selenium content of the second crop was 1,47 mg/kg of dry matter.

Table 6. Effect of selenate fertilization on the selenium content of timothy grass-dominated leys intended for both silage and hay on the farms in 1983. NPK compound fertilizer contained 0,004 % selenium in the form of selenate.

Plant stand	Number of experimental sites	Selenate fertilization		Grass selenium content		Se mg/kg dry matter	
		Sc g/ha		Selenium treatment		Control treatment	
		Mean	Range	Mean	Range	Mean	Range
<b>Silage grass</b>							
I cut	6	25	20—28	1,33	0,84—2,06	0,013	0,006—0,020
II cut	6	19	12—27	1,47	0,57—2,13	0,011	0,007—0,016
<b>Hay</b>	6	25	24—28	0,87	0,27—1,28	0,007	0,005—0,009

## DISCUSSION

### Selenium placement

Selenate applied in the fertilizer to the soil within reach of the roots raised in the experiment at PSA the selenium content of timothy grass to the same level as that of barley grain following corresponding selenium treatments on clay soil (YLÄRANTA 1983 d). Selenite fertilizer, on the

other hand, had a smaller effect on the selenium content of the grass than on the selenium content of barley grain.

The highest amounts of selenite and selenate applied in 1981 had a marked residual effect on the selenium content of the grass crops in 1982. This may be partly due to the selenium accumulated in the roots and other uncut parts of

the plant in the year of selenium application.

Only some thousandth of the selenium applied in the selenite fertilizer had been removed along with the crops. On the other hand, very little selenite is leached or volatilized from the soil (YLÄRANTA 1982), so that the low selenium content of the grass was due to the fact that selenite is not easily taken up by the timothy grass.

Not enough is known of the rate at which selenate is reduced in the soil under different conditions. In an incubation experiment selenate was found to remain readily soluble for at least three months (YLÄRANTA 1983 b). The low selenium content of the crops grown in the field experiment in the years following selenate treatment is thus explained either by the reduction of selenate into a form that is less readily taken up by the plants, or else by leaching away from the roots of the timothy grass.

Application of selenium fertilizer using the placement method has been studied rather little. Most field experiments with selenium have involved adding aqueous solutions of selenite or selenate on the soil surface, sometimes followed by light preparation of the soil (CARY and ALLAWAY 1973, GUPTA and WINTER 1981, GUPTA et al. 1982, GUPTA et al. 1983). Prior to sowing timothy grass, GUPTA and WINTER (1981) sprayed two acid fine sandy loam experimental fields with aqueous sodium selenite at the rate of 0, 1, 12 and 2, 24 kg Se/ha. The pH of one of the fields was raised from 6,0 to 6,6 by liming. The amounts of selenium used in these experiments must be considered very high. Nevertheless, even such a high amount of selenium raised the selenium content of timothy grass cut when timothy heads were fully emerged to only 0,96 or 1,18 mg/kg of dry matter. The selenium content of grass still reached 0,1 mg/kg of dry matter from the 0,02 mg/kg of the control even four years after application of selenium fertilizer. However, compared with the result obtained in the present study, in which the highest amount of selenium placed in the soil (Se 1050 g/ha) gave the silage grass a selenium content of 0,3 mg/kg of dry matter during the year the fertilizer was applied, the selenium content of

timothy grass obtained by GUPTA and WINTER (1981) is high.

### Selenium spraying and topdressing

Foliar spraying of selenite or selenate and application of selenate fertilizer have a greater effect on the selenium content of grass grown for silage than on the selenium content of grain crops. Under favourable conditions spraying 0,5—1 g of selenium per hectare is sufficient to raise the selenium content of grass intended for silage from the base level of 0,02 mg/kg to 0,1 mg/kg of dry matter. Foliar spraying of selenite or selenate one week before cutting grass grown for silage is more effective than applying selenate fertilizer.

Between five and twenty per cent of the selenium applied in the form of selenate fertilizer accumulates in the parts of cereals above the ground (YLÄRANTA 1983 d, 1984 a, b). In the present study 13—24 % of the selenium topdressed accumulated in the first crop of silage grass. The amount of selenium that raised the selenium content of spring wheat and barley grain to 0,1—0,2 mg/kg of dry matter raised the selenium content of grass to three times this figure. This requires that the selenium fertilizer be spread on the surface in grassland cultivation, but placed about 3 cm below the seeds between every second row for cereal cultivation, as is the practice in Finland. The dry matter yield from one cut of silage grass is often smaller than that for the grain and straw yield of a cereal crop, and so the uptake of selenium by the grass may appear rather small. According to the field experiments carried out here spreading selenium on the grassland at the rate of 2 g/ha is sufficient to raise the selenium content of silage grass to the target level of 0,1 mg/kg of dry matter.

The proportion of selenium taken up by spring wheat and barley grain following foliar spraying of selenite is greater the more advanced the stage of growth of the plants at the time of spraying (YLÄRANTA 1984 b). The main reason for this is that very little of the selenite that falls to the soil

surface ever reaches the plants. In the case of readily soluble selenate, however, some of the selenium falling on the soil is taken up by the plants via the roots. Both selenite and selenate sprayed onto grass intended for silage one week before cutting raised the selenium content of the grass by about the same amount. Grasses cover the soil surface very effectively, and so most of the selenium sprayed onto the crop settles on the surface of the plants and is taken up. The dense network of roots in the case of grass means that most of the selenium reaching the soil is close to the roots. In view of the fact that grass is not cut with any great precision, the 50—70 % removal of selenium along with the grass following spraying is high. In field experiments with cereal crops, about 10 % of the selenium applied in the form of spray accumulates in the parts of the plants above the ground (YLÄRANTA 1983 d, 1984 a, b).

It is not clear what proportion of the selenium in the grass has become part of the plants' selenium compounds within the space of a week. According to GISSEL-NIELSEN (1979), selenate is converted into an organic form much more slowly than selenite. Preliminary studies show that selenite sprayed onto grass is retained well, since the juice pressed from silage has been found to contain only 6—7 % of the selenium originally present in the grass.

Since more than half of the selenium sprayed onto the plants may be removed from the field along with the first crop, it is understandable that application of selenium has only a small residual effect on the selenium contents of subsequent crops. Only about 20 % of the selenium topdressed in selenate fertilizer was removed along with the first crop. Since every crop was treated with selenium fertilizer, it might be expected that the selenium contents of the second and third crops would exceed that of the first crop. This was not usually the case, however, which makes the application of selenium fertilizers easier. Since selenium fertilizers can be applied to every crop without raising the selenium content to an unnecessarily high figure, selenium-free fertilizers are not required at all. In Finland two or three crops are cut each

growing season from grass intended for silage. The amount of compound fertilizer given to the first crop is greater than that given to subsequent crops. This evens out the amounts of selenium available to successive crops. The first crop usually gives the highest yield. The third grass crop is often very small in Finland. This was the case at PPO, where the selenium content of the third crop was three times higher than that of the first. The dry matter yield from the third crop at PPO was 1500 kg/ha, which is only just over one third of the yields of 4200 kg/ha obtained for the first and second crops. At SAH, the yield from the third crop was proportionally even smaller than those from the first and second crops. In contrast to the results from PPO, the selenium content of the third crop was smaller on average, than that of the first crop. The growing conditions, particularly the chemical and physical characteristics of the growing site, may affect the uptake of selenium by the grass. No conclusion can be drawn here, however, because of the small number of experiments.

The highest additions of selenium had a quite clear residual effect on the selenium content of the following year's grass crop at both SAH and PPO. Spraying every crop with Se 10 g/ha, the highest amount of selenium used, is out of the question if the target selenium content for the grass is 0,1 mg/kg of dry matter. The amount of selenium suitable for achieving this selenium content by spraying, i.e. 1—2 g/ha, does not seem likely to cause insurmountable problems in practice, and will under no circumstances produce selenium contents that would be toxic to animals. Fodder is toxic if its selenium content exceeds 3 mg/kg of dry matter (AMMERMAN and MILLER 1975).

In theory, spraying every silage grass crop with selenium is a suitable way of raising the selenium content of the grass. In Finland, grassland intended for silage is not usually subjected to any spraying with which selenium treatment could be combined, and so spraying with selenium could involve additional expenditure. GISSEL-NIELSEN (1981) stress that spraying the pastures in spring with selenite at the rate of Se 10—20 g/ha is sufficient to maintain the selenium content of

the grass at 0,1 mg/kg of dry matter throughout the growing season. This method would cause the selenium content of the grass to vary greatly, however. The fodder available early in the growing season would have a selenium content of up to 2 mg/kg of dry matter, while the last cut would contain only fraction of this.

The foliar spraying of selenium to timothy grass reported by GUPTA et al. (1983), which involved spraying a 10—15 cm high stand with aqueous sodium selenite at the rate of Se 1, 2 and 4 kg/ha, would seem even more alarming. The first timothy crop, which was cut at the heads-emerging stage, had a selenium content of 42—140 mg/kg of dry matter, although the treatment was sufficient to keep the selenium content of the crops at the 0,1 mg/kg level for only 2—4 cropping seasons. It is quite clear that, in practice, spraying grass crops with selenium at the rate of several kilograms per hectare is not an acceptable way of raising their selenium content.

#### Fertilization with selenate in practice

Finland has begun to add selenate to the NPK, NP and PK fertilizers used in both agriculture and horticulture as a means of raising the selenium contents of plants to the desired level of 0,1 mg/kg of dry matter. Fertilizers containing selenium have been in general use from 1.7.1984. Selenium at the rate of 16 g/1000 kg is added to the fertilizers used mainly for cereal production, while the addition in the case of fertilizers used for grassland cultivation is 6 g/1000 kg. The selenium is incorporated into the fertilizer by treating the uncoated granules with aqueous sodium selenate. In Finland fertilizer is applied to each crop at the rate of 500 kg/ha. The selenium applied in this way would then be 8 g/ha for cereal and 3 g/ha for grass crops.

Intensive studies with selenium fertilizers have been going on in New Zealand since the 1960s. The work has been aimed mainly at raising the low selenium content of pastures (GRANT 1965, DAVIES and WATKINSON 1966 a, b, WATKINSON and DAVIES 1967 a, b).

New Zealand has finally decided to use

selenate topdressing of pasture. WATKINSON (1983): "The maximum approved rate of 1 kg/ha of prills containing 1 % selenium as sodium selenate (i.e. 10 g/ha Se) is designed for annual application to the whole farm. Prills are permitted to be applied either mixed in with fertilizer, or alone".

In Finland, the target selenium content for both cereal grain and grass grown for fodder is 0,1 mg/kg of dry matter, which is roughly ten times the present selenium content. Field experiments and selenium fertilizer experiments started on farms in 1983 show that the selenium content of grass intended for silage increases, on average, to 0,1 mg/kg following application of Se 2—3 g/ha. Slightly more selenium has to be applied in the case of hay crops, possibly because hay gives a higher dry matter yield and also contains a higher proportion of fibre than grass grown for silage.

As the experiment carried out at PSA showed, a little of the selenate placed in the soil at the time of sowing is taken up by timothy grass. In Finland, some grasslands are sown without a nurse crop, in which case selenium fertilizer is also naturally placed in the soil. A grass fields sown early in spring will produce a crop the same year, though its selenium content may be less than 0,1 mg/kg of dry matter.

Selenate ions and sulphate ions exhibit very similar behaviour. Thus a high sulphate content in the soil may reduce the uptake of selenium by the plants from selenate. Correspondingly, selenate probably interferes with the sulphur economy of plants (GISSEL-NIELSEN 1982). In pot experiments carried out by YLÄRANTA (1983 c) the uptake of selenate by Italian rye grass (*Lolium multiflorum* Lam.) was reduced on Carex peat but not on clay or fine sand by the addition of calcium sulphate to the soil at the rate of S 400 mg/l of soil. In Finland, sulphur fertilizer is not normally applied separately to either cereal or grass crops, as the NPK fertilizers in general use contain 2—11 % sulphur, which is quite sufficient. The NPK fertilizer used in the field experiments contained 2 % sulphur. Neither selenium fertilizer nor spraying with selenium affected the sulphur content of the

grass. Earlier studies have shown that under normal cultivation conditions the application of selenate does not affect the sulphur content of cereal grain, either (YLÄRANTA 1983 d, 1984 a, b). According to SPENCER (1982) the negative

interaction between sulphate and selenate is of no practical significance when both are applied to pastures in the appropriate quantities for remedying sulphur deficiency or raising the selenium content of pastures to the desired level.

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## SELOSTUS

### Timoteinurmirehun seleenipitoisuuden kohottaminen

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Eläinrehun seleenipitoisuuden vähimmäisvaatimuksena pidetään 0,1 mg/kg kuiva-ainetta. Suomessa nurmirehun seleenipitoisuus on kuitenkin vain kymmenesosa tästä pitoisuudesta. Rehun seleenipitoisuutta voidaan kohottaa helpoimmin ruiskuttamalla kasvustoon seleniitti- tai selenaatiseleenin vesiliuosta tai lannoittamalla nurmi seleenipitoisella lannoitteella.

Maatalouden tutkimuskeskuksen Pohjois-Savon tutkimusasemalla perustettiin timoteisäilörehunurmi erittäin runsasmultaiselle hiesumaalle. Lannoitukseen käytettiin Normaali Y-lannosta, johon oli lisätty seleeniä 0—0,21 % natriumseleniittinä tai -selenaattina. Säilörehunurmisadon seleenipitoisuuden tavoitetaso 0,1 mg/kg kuiva-ainetta saavuttamiseksi tarvittiin seleeniä noin 200 g/ha seleniittinä ja 10 g/ha selenaattina. Seleeniä sisältävien jälkivaikutus laski nopeasti, vaikka satojen kohonnut seleenipitoisuus näkyikin suurimmat seleenimäärät, 1050 g/ha seleniittinä ja 500 g/ha selenaattina saaneissa koejäsenissä, kahden seuraavan satokauden ajan. Toisena seleeniä sisältävien jälkivaikutusvuotena ei kuiva-ainesadon seleenipitoisuus ylittänyt 0,1 mg/kg missään koejäsenessä. Ensimmäisenä jälkivaikutusvuotena tämä raja ylittyi kaikissa kolmessa sadossa vain suurimman seleenimäärän selenaattina saaneissa koejäsenissä.

Sata-Hämeen (SAH), Keski-Pohjanmaan (KPO) ja Pohjois-Pohjanmaan (PPO) tutkimusaseman koekentälle ruiskutettiin viikkoa ennen timoteisäilörehunurmen korjuuta seleeniä 0, 1, 3 ja 10 g/ha natriumseleniittinä tai -selenaatin vesiliuoksina. Kokeissa oli myös koejäseniä, joita lannoitettiin selenaattise-

leenipitoisella Normaali Y-lannoksella. Jopa 70 % kasvustoon ruiskutetusta seleenistä kertyi nurmirehuun ja ensimmäisen kuiva-ainesadon seleenipitoisuus 0,1—0,2 mg/kg saavutettiin seleenimäärällä 1 g/ha. Seleeniä lannoitus oli tehottomampi, sillä seleenipitoisuuden 0,1 mg/kg kuiva-ainetta saavuttamiseksi arvioitiin tarvittavan seleeniä 2 g/ha.

Suurin ruiskutettu seleenimäärä oli kolmelle sadolle yhteensä 30 g/ha. Lannoitteesta annettiin seleeniä kolmelle sadolle yhteensä 27 g/ha ja 165 g/ha. Näiden seleeniläysysten jälkivaikutus seuraavan vuoden säilörehunurmisatojen seleenipitoisuuteen oli varsin selvä. Siitä huolimatta, että seleeniä ruiskutettiin ja annettiin lannoitteesta jokaiselle sadolle, vain SAH:n tutkimusaseman toisen nurmisadon ja PPO:n tutkimusaseman kolmannen nurmisadon seleenipitoisuus oli käsitelyvuonna kohonnut ruiskutusten vaikutuksesta ensimmäisen sadon seleenipitoisuudesta. Tämä osoittaa, että muuttamalla seleenigrammalla voitaneen ongelmitta tuottaa nurmirehua, jonka seleenipitoisuus on 0,1 mg/kg kuiva-ainetta. Tavoitteeseen päästään joko ruiskuttamalla seleeniä jokaiselle sadolle viikkoa ennen säilörehunurmen korjuuta tai lannoittamalla nurmi selenaattiseleenipitoisella lannoitteella. Käytännön viljelyksillä suoritettujen lannoituskokeiden mukaan säilörehunurmen ja kuivaheinänurmen sopiva seleeniä lannoitus lienee noin 3 g/ha. Maa- ja metsätalousministeriö antoi luvan lisätä 1.7.1984 alkaen valmistettaviin, lähinnä nurmenviljelyssä käytettäviin, moniravinne-lannoitteisiin selenaattimuotoista seleeniä 6 g lannoitetonnia kohti.

THE EFFECT OF TIME ON THE AVAILABILITY OF  $^{90}\text{Sr}$  AND  $^{137}\text{Cs}$  TO PLANTS FROM FINNISH SOILS

ARJA PAASIKALLIO

PAASIKALLIO, A. 1984. The effect of time on the availability of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  to plants from Finnish soils. *Ann. Agric. Fenn.* 23: 109—120. (Agric. Res. Centre, Central Lab., SF-31600 Jokioinen, Finland.)

The long-term availability of strontium-90 and cesium-137 from seven different Finnish soil types was studied. Extractions of the radioisotopes from the contaminated soils were conducted over a period of six years using acid ammonium acetate. The same soil types were used in pot experiments for studying the content and uptake of the radioisotopes by ryegrass during four growing seasons.

After about half a year the total extractability of  $^{90}\text{Sr}$  began to increase and four years after the contamination it had decreased to its initial level, at which it remained. The mean extracted amount of  $^{137}\text{Cs}$  decreased slightly with time; after six years it was 3/4 of the amount in the first year.

The content of  $^{90}\text{Sr}$  in ryegrass was generally highest in the first year after contamination of the soil, followed by a significant decrease in the second year. In the following years the plant content of  $^{90}\text{Sr}$  again increased on some of the soils. The plant content of  $^{137}\text{Cs}$  increased on the mineral soils and the clayey mull soil, while it decreased on the other organic soils as a function of time.

Over a period of four years ryegrass removed approximately 7 % of the  $^{90}\text{Sr}$  and 4 % of the  $^{137}\text{Cs}$  applied to the soils. The mean annual uptake of  $^{90}\text{Sr}$  by ryegrass ranged from 0,5 % (compost) to 2,9 % (Sphagnum peat) and that of  $^{137}\text{Cs}$  from 0,07 % (compost) to 3,6 % (Sphagnum peat) according to soil type.  $^{137}\text{Cs}/^{90}\text{Sr}$  ratios in plant samples varied markedly with years and soil types.

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Index words:  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  long-term availability,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  aging, fallout nuclides,  $^{137}\text{Cs}/^{90}\text{Sr}$  ratios.

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## INTRODUCTION

Strontium-90 and cesium-137 are characteristic of the radioactive fallout from the testing of nuclear weapons. They are also released into the environment from nuclear power plants and from storage of atomic waste. Because of their long effective half-life and high radiation energy they are dangerous to man.  $^{90}\text{Sr}$  is a bone-seeking nuclide that causes bone sarcoma and leukaemia,

while  $^{137}\text{Cs}$  circulates throughout the body and causes genetic and somatic injury. In the course of a few months or a year after a radioactive deposition the importance of the radioactive surface contamination of vegetation decreases and the transfer of the radionuclides from soil to plants and further to food chains becomes more important.

Physical, chemical and biological factors are responsible for the retention of radionuclides in soils and their availability to plants. There are many studies on the short-term effects of these factors on the behaviour of radionuclides in soil-plant systems, but few studies concerning their long-term effects. With regard to Finnish soils, in particular, the effects of aging of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in soils on their availability to plants have not been studied earlier.

The fixation of  $^{90}\text{Sr}$  in soils after aging periods of 2,5 and 3,5 years has been studied using an extraction procedure (SCHULZ and RIEDEL 1961). The absorption of  $^{90}\text{Sr}$  by ryegrass was used to evaluate the availability of  $^{90}\text{Sr}$  in soil over periods of 3,5 and eight years (SQUIRE 1960, 1966) and that of  $^{137}\text{Cs}$  over six years (SQUIRE and

MIDDLETON 1966). The uptake of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  by crop plants and weeds was studied in soil in which the radioisotopes had been present for 16 and eight years, respectively (CLINE and RICKARD 1972). The same contaminated soil was used nine years later to study the uptake of the radioisotopes by barley and to compare it to the uptake of freshly added radioisotopes (CLINE 1981).

This work describes the extraction of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from seven Finnish soil types and the content and uptake of these radioisotopes by ryegrass grown on these soils. Soil extractions were conducted over a period of six years using acid ammonium acetate as extractant; pot experiments were carried out during four growing seasons.

## MATERIAL AND METHODS

### Soil extractions

The six-year extraction experiment was conducted with seven different soil types in order to study the effect of time on the behaviour of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in the soils.  $^{90}\text{Sr}$  as  $\text{Sr}(\text{NO}_3)_2$  and  $^{137}\text{Cs}$  as  $\text{CsCl}$  were mixed with the soils as a neutral aqueous solution. The radioisotopes of high specific activity were added 1,85 MBq per five litres of soil.  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  were added to the separate pots. The soils were kept in the pots at constant moisture (60 % of the water holding capacity) and at room temperature of about 21 °C. Soil samples (eight replicates per pot) were taken for extraction of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , air-dried, and amounts corresponding to 10 ml of soil weighed and extracted with acid ammonium acetate (pH = 4,65) in a volumetric ratio of 1:5 for one hour and centrifuged. Acid ammonium acetate is used in Finland in routine soil tests for Ca, Mg, K and P (VUORINEN and MÄKITIE 1955). The activity of 5 ml of the supernatant was counted using a two channel gamma spectrometer with a NaI (Tl) well crystal (2 x 2''). The extracts of  $^{90}\text{Sr}$  were allowed to stand for about 18 days before counting to

permit secular equilibrium of  $^{90}\text{Sr}$  ( $^{90}\text{Y}$ ) to be attained. The percentage of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  extracted from the soils was calculated by comparison with standard solutions. The first soil samples were extracted about five days after mixing the radioisotopes with the soils.

Some properties of the soils are given in Table 1; most of the soils were the same arable soils as those reported by PAASIKALLIO (1981). The Finnish clay minerals are mostly of illitic type. The soils are named according to the soil classification used by Finnish agricultural scientists (AALTONEN et al. 1949). The air-dried soil samples were ground to pass through a 2 mm sieve. Particle size distribution (in Table 1 only percentage clay) was determined by the sieving and pipette method (ELONEN 1971), soil pH was determined from a soil-water suspension (1:2,5), and the cation exchange capacity (CEC) by the ammonium acetate method (MÄKITIE and VIRRI 1965). The organic matter content was determined colorimetrically after sulphuric acid/potassium dichromate wet digestion (O.M. = 1,73 x org. carbon) (GRAHAM 1948) and total nitrogen using the Kjeldahl method. Extractable cations were determined using atomic absorption

Table 1. Some properties of the soils before the experiment.

Soil type	Clay %	Bulk density g/cm <sup>3</sup>	Conductivity mho/cm × 10 <sup>4</sup>	CEC me/100 g	C %	N %	Acid NH <sub>4</sub> -acet. extractable					
							Ca	K	Mg	P	Fe	Mn
Medium sand	4,8	1,21	0,48	8,9	2,4	0,15	804	127	44	17	1	6
Silt	18,1	0,99	0,51	15,4	2,2	0,22	1856	253	130	28	1	7
Sandy clay	35,6	0,97	0,25	15,2	1,8	0,17	1347	116	238	<1	5	10
Clayey mull	60,8	0,53	1,45	23,7	12,3	0,91	859	114	151	<1	28	6
Carex peat	—	0,36	0,60	29,6	30,3	1,65	897	43	78	1	28	14
Sphagnum peat	—	0,11	3,10	58,3	40,7	1,25	926	48	144	67	1	26
Compost	8,6	0,50	9,00	71,7	10,9	0,94	3489	1477	455	170	2	18

spectrometry and P colorimetrically using the molybdenum blue method from the same extracts as the radioisotopes.

### Pot experiments

The uptake of <sup>90</sup>Sr and <sup>137</sup>Cs from the contaminated soils by ryegrass was studied in pot experiments over a period of four years in Tikkurila, Vantaa. The soils (five litres per pot)

and the quantity of radioisotopes were the same as those used in the extraction experiments. Each year, 50 seeds of Italian ryegrass (*Lolium multiflorum* Lam., var. Samo) were sown per pot with four replicates and the plants were thinned to 40 specimens. The experiments were conducted in the open and the pots were sheltered from rain with transparent plastic sheets. The soils were kept at constant moisture (about 60 % of the water holding capacity). Some climatological data are given in Table 2. Three cuts were made

Table 2. Some meteorological data of four growing seasons of ryegrass.

Growing season	Temperature, °C			Mean temperature for a 30 year period	Total solar radiation MJ/m <sup>2</sup>	Sunshine hours	Precipitation, mm	
	mean	max	min				Total	Mean for a 30 year period
<b>1975</b>								
May	11,6	25,6	-2,1	9,0	604	289,7	40	41
June	13,6	25,6	-0,6	14,3	683	329,5	15	50
July	17,8	28,2	3,9	17,1	701	349,1	80	73
Aug.	16,3	30,7	5,1	15,6	474	253,7	49	71
Sept.	12,9	22,0	0,4	10,4	273	167,0	50	67
<b>1976</b>								
May	10,9	24,3	-5,0	9,0	649	333,4	27	41
June	12,8	26,0	3,7	14,3	570	239,7	40	50
July	15,5	24,8	5,0	17,1	538	231,4	50	73
Aug.	15,1	24,6	3,4	15,6	522	285,0	44	71
Sept.	8,0	18,8	-6,1	10,4	286	162,5	58	67
<b>1979</b>								
May	10,8	25,9	-2,5	9,0	602	270,1	31	41
June	16,0	29,7	3,8	14,3	724	325,5	46	50
July	14,7	23,0	4,6	17,1	489	164,3	111	73
Aug.	16,0	25,1	6,3	15,6	485	237,3	61	71
Sept.	9,7	16,9	-3,9	10,4	268	157,0	69	67
<b>1980</b>								
May	7,2	22,2	-2,9	9,0	530	245,7	66	41
June	16,9	26,9	3,9	14,3	672	298,5	24	50
July	16,8	29,1	6,6	17,1	609	284,7	48	73
Aug.	14,8	29,1	3,0	15,6	435	199,8	105	71
Sept.	10,9	20,7	0,3	10,4	229	107,0	65	67

Data taken from the monthly reports of Finland's Meteorological Institute; the observation points were in Vantaa airport.

Table 3. Dates of sowing and cuttings of ryegrass in pot experiments conducted during four years.

	1st year		2nd year		3rd year		4th year	
Date of sowing	May	16, 1975	May	18, 1976	June	1, 1979	June	4, 1980
„ „ 1st cut	July	3, „	July	7 „	July	17, „	July	16, „
„ „ 2nd „	Aug.	6, „	Aug.	3, „	Aug.	14, „	Aug.	12, „
„ „ 3rd „	Sept.	3, „	Sept.	3, „	Sept.	14, „	Sept.	16, „

during the growing season (Table 3). The ryegrass was cut 2 cm above the soil surface. After the last annual cut the soils were mixed; apart from the root system in the compost soil the plant roots were left in the soils. The soils were stored at room temperature and kept moist during storage. The extraction and the pot experiments were started in the same year. However, after two years the pot experiments were stopped for two years; the soils were allowed to dry during this time.

In the first year no fertilizers were added the soils. In the following years fertilizers were applied for proper growth of the plants. After each growing season, the soil pH values were determined, the soils were tested for nutrient elements and fertilizers were applied accordingly. In the second year, fertilization was the same as reported by PAASIKALLIO (1981), except that Ca was applied at 0,8 g/l and Fe 40 mg/l of soil. Mg, K and P were not added to the compost soil. In the third year, N, K and trace element supplements were applied to all the soils, P only

to the sandy clay, clayey mull and Carex peat soils. In the fourth year N and P were applied to all the soils except the medium sand soil and P to all except the medium sand and silt soils. A half dose of K was applied to all the soils. Calcium was not applied and the compost soil was not fertilized during the third and fourth years.

The plant cuts were dried and the activity of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was determined in ground and weighed plant material as in the case of soil extracts. The contents of Ca, Mg, K, Na, Mn, Fe and Zn of the plant were determined using atomic absorption spectrometry and P colorimetrically using the vanado-molybdate method.

The activities of the samples were corrected for radioactive decay. The differences between years in the radioisotope contents and their ratios in the soil extracts and the plant material were determined by analysis of variance and Tukey's studentized range test. The dependence of the content of radioisotopes on both the yield and the nutrient element contents of plants was computed by linear correlation analysis.

Table 4. The extractability of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  (%) with acid ammonium acetate from various soils during six years. The means in each column not followed by the same index letter differ significantly at the 95 % level.

Year	n	Extractability of the radioisotopes, %							Total
		Medium sand	Silt	Sandy clay	Clayey mull	Carex peat	Sphagnum peat	Compost	
$^{90}\text{Sr}$									
1st	72	55,2 <sup>a</sup>	58,5 <sup>b</sup>	75,5 <sup>a</sup>	64,4 <sup>a</sup>	49,7 <sup>a</sup>	67,3 <sup>a</sup>	51,2 <sup>a</sup>	60,3 <sup>a</sup>
2nd	24	59,1 <sup>bc</sup>	60,8 <sup>c</sup>	80,5 <sup>b</sup>	71,4 <sup>c</sup>	55,3 <sup>c</sup>	73,5 <sup>c</sup>	55,5 <sup>b</sup>	65,2 <sup>b</sup>
3rd	„	61,7 <sup>c</sup>	61,1 <sup>c</sup>	83,7 <sup>c</sup>	70,1 <sup>bc</sup>	55,6 <sup>c</sup>	72,6 <sup>c</sup>	54,7 <sup>b</sup>	65,6 <sup>b</sup>
4th	„	57,6 <sup>b</sup>	58,6 <sup>b</sup>	79,9 <sup>b</sup>	67,4 <sup>b</sup>	54,7 <sup>bc</sup>	71,5 <sup>bc</sup>	54,1 <sup>b</sup>	63,4 <sup>bc</sup>
5th	„	53,5 <sup>a</sup>	55,7 <sup>a</sup>	76,9 <sup>a</sup>	63,4 <sup>a</sup>	50,9 <sup>a</sup>	69,8 <sup>b</sup>	50,7 <sup>a</sup>	60,1 <sup>a</sup>
6th	32	55,6 <sup>a</sup>	54,9 <sup>a</sup>	76,0 <sup>a</sup>	62,5 <sup>a</sup>	52,9 <sup>b</sup>	72,1 <sup>bc</sup>	51,5 <sup>a</sup>	60,8 <sup>ac</sup>
Total	200	56,6	58,2	77,9	65,9	52,3	70,3	52,5	61,9
$^{137}\text{Cs}$									
1st	72	16,1 <sup>c</sup>	8,1 <sup>c</sup>	6,4 <sup>a</sup>	20,7 <sup>c</sup>	10,6 <sup>d</sup>	19,6 <sup>d</sup>	19,4 <sup>d</sup>	14,4 <sup>c</sup>
2nd	24	14,0 <sup>ab</sup>	7,7 <sup>bc</sup>	6,0 <sup>a</sup>	23,3 <sup>d</sup>	5,1 <sup>c</sup>	18,5 <sup>c</sup>	17,5 <sup>c</sup>	13,2 <sup>bc</sup>
3rd	„	13,3 <sup>a</sup>	7,4 <sup>ab</sup>	5,9 <sup>a</sup>	21,4 <sup>c</sup>	2,0 <sup>b</sup>	17,5 <sup>bc</sup>	16,6 <sup>bc</sup>	12,0 <sup>ab</sup>
4th	„	14,9 <sup>b</sup>	6,8 <sup>a</sup>	6,3 <sup>a</sup>	19,0 <sup>b</sup>	1,0 <sup>a</sup>	16,8 <sup>ab</sup>	15,8 <sup>ab</sup>	11,5 <sup>ab</sup>
5th	„	13,8 <sup>ab</sup>	7,0 <sup>ab</sup>	6,0 <sup>a</sup>	16,5 <sup>a</sup>	1,1 <sup>a</sup>	16,4 <sup>ab</sup>	15,5 <sup>ab</sup>	10,9 <sup>a</sup>
6th	32	13,8 <sup>ab</sup>	6,9 <sup>a</sup>	6,5 <sup>a</sup>	16,2 <sup>a</sup>	1,6 <sup>ab</sup>	15,8 <sup>a</sup>	15,0 <sup>a</sup>	10,8 <sup>a</sup>
Total	200	14,7	7,5	6,3	19,7	5,2	17,9	17,2	12,6

## RESULTS

### Soil extractions

The extractability of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  is presented for each soil type separately during the first two years of the experiment (Figs. 1 and 2) and during six years (Table 4). During the first months after radioactive contamination of the soils the extractability of the radioisotopes de-

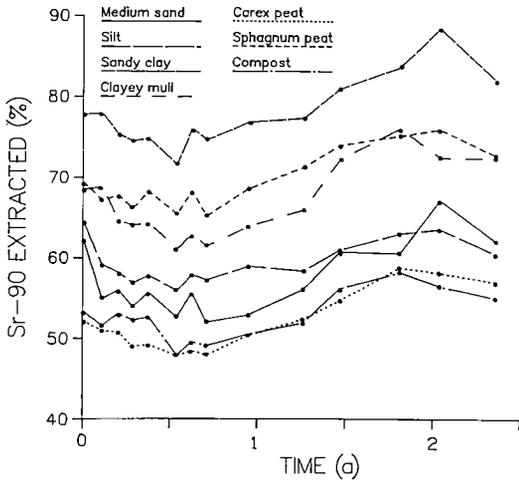


Fig. 1. The extractability of  $^{90}\text{Sr}$  (%) from seven soil types during the first two years after contamination of the soils.

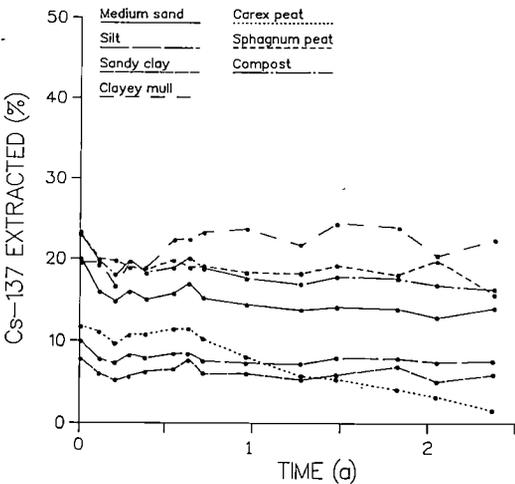


Fig. 2. The extractability of  $^{137}\text{Cs}$  (%) from seven soil types during the first two years after contamination of the soils.

creased in all the soils. In  $^{90}\text{Sr}$  the decrease took place over a period of half a year or more, in  $^{137}\text{Cs}$  over a couple of months. After the initial decrease the extractability of  $^{90}\text{Sr}$  began to increase and about two years after the contamination  $^{90}\text{Sr}$  had reached its initial level and even surpassed it. Thereafter the extractability decreased slowly to the level of that of the first year. The extraction of  $^{137}\text{Cs}$  did not reach the initial values in most cases although a slight increase was found in the activity after three months. The mean percentage extraction of  $^{90}\text{Sr}$  was highest in the sandy clay soil and lowest in the Carex peat and the compost soils, that of  $^{137}\text{Cs}$  was highest in the clayey mull and lowest in the Carex peat soils. The extractability of  $^{137}\text{Cs}$  in the Carex peat soil decreased most clearly with time; in four years it had decreased from 10 % to 1 %. In general, a slight decrease in the extractability of  $^{137}\text{Cs}$  with time was found after the first year.

The average decrease in the soil pH values over six years was about one pH unit and the greatest change was found during the first years. The change was most pronounced in the Carex peat soil (Table 5). The six-year storage period in-

Table 5. The initial pH values of the soils (1st) and the average pH values of the incubating soils in the third and sixth experimental years.

Soil type	Soil pH		
	1st	3rd	6th
Medium sand	5,72	4,85	4,65
Silt	6,74	5,83	5,73
Sandy clay	5,61	4,86	4,77
Clayey mull	5,11	4,15	4,01
Carex peat	5,03	4,05	3,83
Sphagnum peat	4,47	4,20	4,11
Compost	7,12	6,32	6,05
Total	5,69	4,89	4,74

creased to some extent the extractable amounts of Ca and Fe and decreased that of Mn. In the Carex peat soils the extractability of Mn increased slightly while that of K remained approximately constant.

Table 6. The content of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  of the plants grown on various soils during four years. The means in each column not followed by the same index letter differ significantly at the 95 % level.

Year	n	Radioisotope content of plant, Bq/g d.m.							Total
		Medium sand	Silt	Sandy clay	Clayey mull	Carex peat	Sphagnum peat	Compost	
$^{90}\text{Sr}$									
1st	12	1730 <sup>b</sup>	910 <sup>c</sup>	1246 <sup>c</sup>	2123 <sup>b</sup>	2730 <sup>b</sup>	4224 <sup>b</sup>	461 <sup>a</sup>	1917 <sup>b</sup>
2nd	"	1252 <sup>a</sup>	532 <sup>a</sup>	689 <sup>ab</sup>	1211 <sup>a</sup>	1294 <sup>a</sup>	2369 <sup>a</sup>	669 <sup>b</sup>	1145 <sup>a</sup>
3rd	"	1410 <sup>ab</sup>	607 <sup>a</sup>	641 <sup>a</sup>	1095 <sup>a</sup>	1334 <sup>a</sup>	2650 <sup>a</sup>	985 <sup>c</sup>	1246 <sup>a</sup>
4th	"	1434 <sup>ab</sup>	774 <sup>b</sup>	884 <sup>b</sup>	1446 <sup>a</sup>	1541 <sup>a</sup>	2931 <sup>ab</sup>	659 <sup>b</sup>	1381 <sup>a</sup>
Total	48	1456	706	865	1469	1724	3043	693	1422
$^{137}\text{Cs}$									
1st	12	67 <sup>a</sup>	5 <sup>a</sup>	32 <sup>a</sup>	273 <sup>a</sup>	1457 <sup>c</sup>	14011 <sup>b</sup>	118 <sup>b</sup>	2280 <sup>b</sup>
2nd	"	96 <sup>a</sup>	25 <sup>a</sup>	69 <sup>a</sup>	492 <sup>a</sup>	870 <sup>b</sup>	2961 <sup>a</sup>	55 <sup>a</sup>	652 <sup>a</sup>
3rd	"	159 <sup>a</sup>	64 <sup>b</sup>	259 <sup>b</sup>	1249 <sup>b</sup>	405 <sup>a</sup>	2269 <sup>a</sup>	42 <sup>a</sup>	636 <sup>a</sup>
4th	"	583 <sup>b</sup>	139 <sup>c</sup>	201 <sup>b</sup>	1130 <sup>b</sup>	202 <sup>a</sup>	1996 <sup>a</sup>	31 <sup>a</sup>	612 <sup>a</sup>
Total	48	226	58	140	786	733	5309	62	1045

## Pot experiments

### $^{90}\text{Sr}$ and $^{137}\text{Cs}$ contents of plants

The mean contents of the radioisotopes in the plants were significantly higher in the first year than in the following years (Table 6). However, with regard to the different soil types, in some cases there was a significant increase in the  $^{90}\text{Sr}$  content of the plant in the third and/or fourth year. The plant content of  $^{137}\text{Cs}$ , on the other hand, increased with time on mineral soils and the clayey mull soil while it decreased on other organic soils. The Ca and Mg content of the plant also increased and that of K decreased with

time on most of the soils. Yearly changes in the pH values of the soils were slight. The first cut yielded the lowest total contents of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  and they differed significantly from those of the second and third cuts (Table 8).

The  $^{90}\text{Sr}/\text{Ca}$  and  $^{137}\text{Cs}/\text{K}$  ratios were significantly higher in the first than in the following years but no significant differences were found in the  $^{90}\text{Sr}/\text{Ca}$  ratios between the different cuts (Fig. 3). The  $^{137}\text{Cs}/\text{K}$  ratio was significantly lower in the first cut than in the two later cuts (Fig. 4).

In general, the  $^{90}\text{Sr}$  content of plants seemed to correlate more closely with the contents of the macronutrients (Ca, Mg, K, P) in the plants

Table 7. The uptake of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  by plants (%) from various soils during four years. The means in each column not followed by the same index letter differ significantly at the 95 % level. The figures in parentheses indicate the sum of the uptake percentages of four years.

Year	n	Plant uptake of radioisotopes, %							Total
		Medium sand	Silt	Sandy clay	Clayey mull	Carex peat	Sphagnum peat	Compost	
$^{90}\text{Sr}$									
1st	12	0,82 <sup>a</sup>	0,87 <sup>a</sup>	0,43 <sup>a</sup>	2,05 <sup>b</sup>	1,97 <sup>b</sup>	1,92 <sup>a</sup>	0,68 <sup>b</sup>	1,25 <sup>a</sup>
2nd	"	2,52 <sup>b</sup>	1,42 <sup>b</sup>	1,07 <sup>a</sup>	2,77 <sup>c</sup>	2,89 <sup>d</sup>	3,72 <sup>b</sup>	0,62 <sup>b</sup>	2,14 <sup>b</sup>
3rd	"	1,20 <sup>a</sup>	1,36 <sup>b</sup>	0,97 <sup>a</sup>	1,82 <sup>ab</sup>	2,52 <sup>c</sup>	4,08 <sup>b</sup>	0,38 <sup>a</sup>	1,76 <sup>ab</sup>
4th	"	1,11 <sup>a</sup>	1,65 <sup>c</sup>	1,97 <sup>b</sup>	1,68 <sup>a</sup>	1,38 <sup>a</sup>	2,10 <sup>a</sup>	0,58 <sup>b</sup>	1,49 <sup>a</sup>
Total	48	1,41 (5,66)	1,33 (5,30)	1,11 (4,44)	2,08 (8,32)	2,19 (8,76)	2,96 (11,82)	0,56 (2,25)	1,66 (6,65)
$^{137}\text{Cs}$									
1st	12	0,03 <sup>a</sup>	0,01 <sup>a</sup>	0,01 <sup>a</sup>	0,32 <sup>a</sup>	1,19 <sup>c</sup>	5,67 <sup>d</sup>	0,17 <sup>c</sup>	1,06 <sup>a</sup>
2nd	"	0,28 <sup>b</sup>	0,08 <sup>b</sup>	0,15 <sup>ab</sup>	1,16 <sup>b</sup>	1,95 <sup>b</sup>	4,19 <sup>c</sup>	0,07 <sup>b</sup>	1,12 <sup>a</sup>
3rd	"	0,24 <sup>b</sup>	0,17 <sup>c</sup>	0,45 <sup>bc</sup>	2,19 <sup>d</sup>	0,75 <sup>b</sup>	3,28 <sup>b</sup>	0,01 <sup>a</sup>	1,01 <sup>a</sup>
4th	"	0,27 <sup>b</sup>	0,31 <sup>d</sup>	0,49 <sup>c</sup>	1,45 <sup>c</sup>	0,19 <sup>a</sup>	1,35 <sup>a</sup>	0,03 <sup>a</sup>	0,58 <sup>a</sup>
Total	48	0,21 (0,83)	0,14 (0,56)	0,27 (1,10)	1,28 (5,13)	1,02 (4,09)	3,62 (14,50)	0,07 (0,28)	0,95 (3,78)

Table 8. The content and uptake of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in three successive cuts by years. The totals of three cuts in each column not followed by the same index letter differ significantly at the 95 % level.

Year	Cut	n	$^{90}\text{Sr}$		$^{137}\text{Cs}$	
			Content Bq/g d.m.	Uptake %	Content Bq/g d.m.	Uptake %
1st	1st	28	1387	0,37	951	0,41
2nd	„	„	917	0,47	178	0,15
3rd	„	„	973	0,54	269	0,23
4th	„	„	951	0,39	287	0,12
Total		112	1057 <sup>a</sup>	0,44 <sup>a</sup>	421 <sup>a</sup>	0,23 <sup>a</sup>
1st	2nd	28	2158	0,63	3099	0,49
2nd	„	„	1083	0,88	724	0,62
3rd	„	„	1255	0,70	779	0,49
4th	„	„	1547	0,70	814	0,33
Total		112	1511 <sup>b</sup>	0,73 <sup>b</sup>	1354 <sup>b</sup>	0,48 <sup>b</sup>
1st	3rd	28	2207	0,25	2790	0,16
2nd	„	„	1434	0,79	1055	0,36
3rd	„	„	1509	0,52	859	0,29
4th	„	„	1646	0,40	734	0,14
Total		112	1699 <sup>b</sup>	0,49 <sup>a</sup>	1360 <sup>b</sup>	0,24 <sup>a</sup>

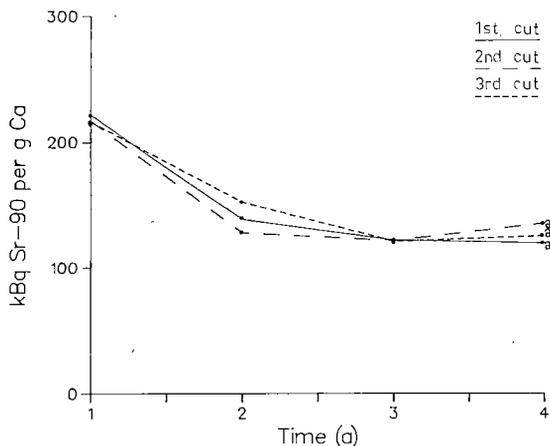


Fig. 3. The  $^{90}\text{Sr}/\text{Ca}$  ratios of the plants in three successive cuts as a function of time. The curves not marked by the same letter differ significantly at least at the 95 % level.

grown on the organic soils; the  $^{137}\text{Cs}$  content of plants correlated with both the macronutrients and micronutrients (Na, Mn, Fe, Zn) in the plants grown on the mineral soils, including the clayey mull soil (Table 9).

### Plant uptake of $^{90}\text{Sr}$ and $^{137}\text{Cs}$

The plant uptake of the radioisotopes (= plant radioisotope content times plant yield) refers to the amounts of the radioisotopes removed from the soil by the plant expressed as percentages of

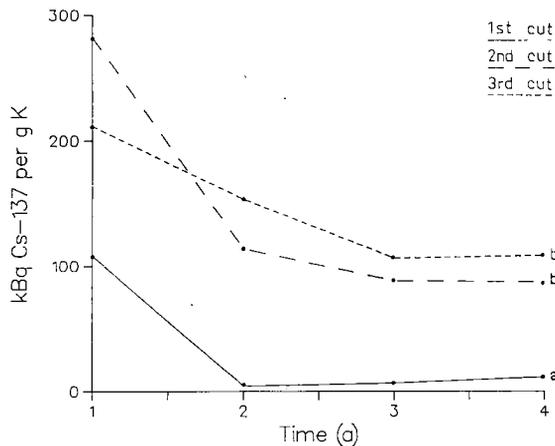


Fig. 4. The  $^{137}\text{Cs}/\text{K}$  ratios of the plants in three successive cuts as a function of time. The curves not marked by the same letter differ significantly at least at the 95 % level.

the amount of the radioisotopes originally applied to the soil. In Table 7 each figure represents the sum of three successive cuts. For example, during four years the plant had removed 11,8 % of the  $^{90}\text{Sr}$  originally added to the Sphagnum peat soil and 2,3 % of the  $^{90}\text{Sr}$  added to the compost soil; the corresponding figures for  $^{137}\text{Cs}$  were 14,5 and 0,3 %, respectively. The total uptake of both radioisotopes was greatest in the second cut. The maximum uptake of both radioisotopes occurred in the second and third cuts of the second year (Table 8). In general, the second cut gave the highest yield in all the soils

Table 9. Correlation coefficients between the contents of the radioisotopes and of some nutrient elements of the plants grown on different soil types (n = 48).

	Ca	Mg	K	P	Na	Mn	Fe	Zn
<b>Plant <sup>90</sup>Sr</b>								
Medium sand	0,47***	-0,18	-0,07	-0,17	-0,40***	0,53***	0,28*	0,44***
Silt	0,44***	-0,19	-0,19	0,22	-0,34**	0,10	0,43***	-0,03
Sandy clay	-0,18	-0,25*	-0,36**	-0,01	-0,19	0,29*	0,46***	0,08
Clayey mull	0,41**	0,25*	-0,51***	-0,33**	-0,00	0,24	0,13	-0,15
Carex peat	0,67***	0,22	-0,68***	0,54***	0,26*	0,35**	0,57***	0,50***
Sphagnum peat	0,87***	0,46***	-0,47***	0,76***	-0,48***	0,48***	0,19	0,18
Compost	0,97***	0,94***	0,00	0,46***	-0,06	-0,31*	0,41**	0,14
<b>Plant <sup>137</sup>Cs</b>								
Medium sand	0,43***	0,27*	-0,36**	0,54***	0,46***	0,24*	0,17	-0,42***
Silt	0,51***	0,49***	-0,56***	-0,11	0,32*	0,61***	-0,41**	-0,31*
Sandy clay	0,68***	0,76***	-0,36**	-0,35**	0,68***	0,41**	-0,44***	-0,17
Clayey mull	0,49***	0,52***	-0,45***	0,04	0,22	0,60***	-0,28*	0,57***
Carex peat	0,03	0,38**	-0,68***	0,05	0,37**	-0,05	0,35**	0,53***
Sphagnum peat	0,46***	-0,11	-0,15	0,94***	-0,19	0,85***	0,13	0,03
Compost	-0,30*	-0,13	0,12	-0,27*	-0,38**	0,73***	-0,03	0,27*

\*\*\* P < 0,001  
 \*\* P < 0,01  
 \* P < 0,05

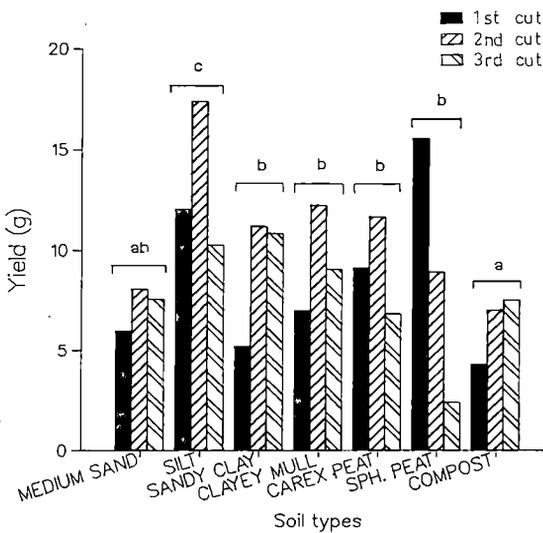


Fig. 5. The yields of the plants grown on different soil types in three successive cuts. The means of the yields of each soil type not marked by the same letter differ significantly at least at the 95 % level.

except the Sphagnum peat soil, where the yield was highest in the first cut. In the whole material the highest yield was obtained from the silt soil and the lowest from the compost soil (Fig. 5). The plant yield had a significant negative correlation with the <sup>90</sup>Sr content of the plant within a particular soil type (Table 10).

<sup>137</sup>Cs/<sup>90</sup>Sr ratios of the plant showed considerable differences between years and between soil types whereas the ratio of the soil extracts did not change much during six years (Table 11). In the whole material the plant accumulated about twice as much <sup>90</sup>Sr as <sup>137</sup>Cs, while nearly five times more <sup>90</sup>Sr than <sup>137</sup>Cs was extracted from the soils. The <sup>90</sup>Sr content of the plants grown on the different soil types was about two to twelve times higher than the corresponding contents of <sup>137</sup>Cs; an exception was the Sphagnum peat soil where the total <sup>137</sup>Cs content of the plant was higher than that of <sup>90</sup>Sr.

## DISCUSSION

The availability of <sup>90</sup>Sr to the plant is supposed to decrease due to physico-chemical changes in the soil during the first years after contamination and then remain at a rather constant level

(SQUIRE 1960, 1966, SCHULZ and RIEDEL 1961, CLINE 1981). In the extraction experiments, a temporary increase was observed in the first years, supposedly due to the fact that the equili-

Table 10. Correlation coefficients between the plant contents of the radioisotopes and the yield by soil types and by successive cuts.

	n	Yield		n	Yield
<b>Plant <sup>90</sup>Sr</b>			<b>Plant <sup>137</sup>Cs</b>		
Medium sand	48	-0,50***		48	-0,30*
Silt	„	-0,72***		„	0,23
Sandy clay	„	-0,36**		„	0,57***
Clayey mull	„	-0,30*		„	0,28
Carex peat	„	-0,56***		„	-0,15
Sphagnum peat	„	-0,85***		„	-0,58***
Compost	„	-0,71***		„	0,17
1st cut	112	-0,04		112	-0,10
2nd „	„	-0,39***		„	-0,28***
3rd „	„	-0,56***		„	-0,31***

\*\*\* P < 0,001

\*\* P < 0,01

\* P < 0,05

rium of <sup>90</sup>Sr in the soil had not yet been attained. In the pot experiments the availability of <sup>90</sup>Sr from some soils increased slightly in the third and/or fourth year after an initial decrease. The slowly advancing sorption of <sup>137</sup>Cs in the soil with time, which was observed in the extraction experiments, is explained as partly due to its slow diffusion into the mineral matrix. The clay minerals, and especially illite, exhibit a considerable capacity for retention of <sup>137</sup>Cs and the sorption is dependent on time (e.g. TAMURA and JACOBS 1960, LOMENICK and TAMURA 1965, KLOBE and GAST 1970, SHALHEVET 1973, FRANCIS and BRINKLEY 1976). As far as changes in the content of <sup>137</sup>Cs in the plant were concerned, the results were partly different from those reported

earlier (SQUIRE and MIDDLETON 1966, CLINE and RICKARD 1972, DAHLMAN and VAN VORIS 1976, CLINE 1981). Instead of an overall decrease in the <sup>137</sup>Cs content, plants grown on the mineral soils and the clayey mull soil showed an increasing trend in <sup>137</sup>Cs with time (cf. NISHITA et al. 1958).

The soil pH is an important factor in the retention of <sup>90</sup>Sr and <sup>137</sup>Cs in the soil (e.g. RHODES 1957, ROMNEY et al. 1957, JUO and BARBER 1970). The ways of storing soils, in either a dry or moist state, affect soil pH values and the solubility of some nutrients (SILLANPÄÄ 1977). Thus, a decrease in the soil pH during the six-year moist incubation period might have affected the fall in the <sup>137</sup>Cs extracted from the

Table 11. The <sup>137</sup>Cs/<sup>90</sup>Sr ratios of the soil extracts and the plants by years. The means in each column not followed by the same index letter differ significantly at the 95 % level.

Year	n	<sup>137</sup> Cs/ <sup>90</sup> Sr ratio of soil extracts						
		Medium sand	Silt	Sandy clay	Clayey mull	Carex peat	Sphagnum peat	Compost
1st	72	0,292 <sup>c</sup>	0,139 <sup>b</sup>	0,085 <sup>bc</sup>	0,322 <sup>c</sup>	0,214 <sup>c</sup>	0,292 <sup>d</sup>	0,379 <sup>b</sup>
2nd	24	0,237 <sup>ab</sup>	0,126 <sup>a</sup>	0,075 <sup>a</sup>	0,327 <sup>c</sup>	0,093 <sup>d</sup>	0,252 <sup>c</sup>	0,316 <sup>a</sup>
3rd	„	0,217 <sup>a</sup>	0,121 <sup>a</sup>	0,071 <sup>a</sup>	0,306 <sup>bc</sup>	0,035 <sup>bc</sup>	0,241 <sup>bc</sup>	0,305 <sup>a</sup>
4th	„	0,263 <sup>b</sup>	0,117 <sup>a</sup>	0,079 <sup>acd</sup>	0,288 <sup>ab</sup>	0,018 <sup>a</sup>	0,235 <sup>b</sup>	0,293 <sup>a</sup>
5th	„	0,258 <sup>b</sup>	0,126 <sup>a</sup>	0,078 <sup>ab</sup>	0,260 <sup>a</sup>	0,022 <sup>ab</sup>	0,235 <sup>b</sup>	0,305 <sup>a</sup>
6th	32	0,248 <sup>b</sup>	0,126 <sup>a</sup>	0,086 <sup>bd</sup>	0,259 <sup>a</sup>	0,030 <sup>ac</sup>	0,219 <sup>a</sup>	0,292 <sup>a</sup>
Total	200	0,262	0,129	0,081	0,299	0,102	0,256	0,329

<sup>137</sup> Cs/ <sup>90</sup> Sr ratio of plants								
1st	12	0,038 <sup>a</sup>	0,006 <sup>a</sup>	0,028 <sup>a</sup>	0,126 <sup>a</sup>	0,573 <sup>c</sup>	3,187 <sup>c</sup>	0,264 <sup>b</sup>
2nd	„	0,086 <sup>a</sup>	0,055 <sup>b</sup>	0,108 <sup>ab</sup>	0,414 <sup>b</sup>	0,640 <sup>c</sup>	1,188 <sup>b</sup>	0,085 <sup>a</sup>
3rd	„	0,131 <sup>a</sup>	0,111 <sup>c</sup>	0,421 <sup>c</sup>	1,165 <sup>d</sup>	0,293 <sup>b</sup>	0,848 <sup>ab</sup>	0,045 <sup>a</sup>
4th	„	0,424 <sup>b</sup>	0,178 <sup>d</sup>	0,279 <sup>bc</sup>	0,872 <sup>c</sup>	0,125 <sup>a</sup>	0,603 <sup>a</sup>	0,048 <sup>a</sup>
Total	48	0,170	0,087	0,209	0,644	0,408	1,456	0,111

Carex peat soil, while in the pot experiments, where the soil pH did not vary much, such a decrease in the availability of  $^{137}\text{Cs}$  was not found.

In the pot experiments in the second year when the soils were fertilized for the first time, the fertilization might have affected the radioisotope content of plants in some cases. The high content of  $^{137}\text{Cs}$  in the plants grown on acid peat soils in the first year was assumed to be partly due to the low exchangeable K in the peat soils (cf. NISHITA et al. 1960, GISSEL-NIELSEN and ANDERSEN 1967, WALLACE et al. 1983). In the second year the addition of K might have caused the dilution of the exchangeable  $^{137}\text{Cs}$  in the soil solution and thus decreased the  $^{137}\text{Cs}$  uptake by the plants. On the other hand, on the mineral soils the  $^{137}\text{Cs}$  content of ryegrass increased with time in spite of the additions of K, which was probably due to the replacement of  $^{137}\text{Cs}$  fixed in the soil by the fertilizer K. The simultaneous decrease in the K content of the soil solution and plants might have had an effect on this increase. It is known that when soils are depleted of exchangeable K by cropping the  $^{137}\text{Cs}$  uptake by plants increases (NISHITA et al. 1958, 1960). The relatively low content of the radioisotopes in the plants grown on the compost, silt and sandy clay soils was probably caused by the rather high content of clay in the case of  $^{137}\text{Cs}$  and of exchangeable soil macronutrients, especially Ca, in the case of  $^{90}\text{Sr}$  (cf. EVANS and DEKKER 1963, ANDERSEN 1963, 1971).

The amounts of radiostrontium taken up by the plant were mostly less than 2 % per year, the mean uptake of four years ranging from 0,5 to 2,9 % per year, which correspond with the earlier findings (MILBOURN 1960, SQUIRE 1960, 1966, ROMNEY et al. 1963, van der STRICHT et al. 1971). The uptake of  $^{137}\text{Cs}$  (from 0,07 to 3,6 % per year) also complied with earlier results (NISHITA et al. 1958, EVANS and DEKKER 1966, SQUIRE and MIDDLETON 1966, CLINE and RICKARD 1972) with one difference: the  $^{137}\text{Cs}$  uptake from the Sphagnum peat soil in the first year was higher than reported in the literature.

An increasing trend in the radioisotope contents was observed with consecutive cuts; according to many earlier studies, the reverse should have been expected (e.g. NISHITA et al. 1958, EVANS and DEKKER 1966, KRIEGER et al. 1967). The opposing results may be due to differences in methods of radioisotope application, number of cuts, growth conditions, properties of the soils, plant species etc.

The  $^{137}\text{Cs}/^{90}\text{Sr}$  ratios in the plant samples varied markedly with year and soil type, which complies with the results reported by THOMAS et al. (1975). Constant ratios have also been observed (AARKROG 1975). The plant content of  $^{90}\text{Sr}$  was mostly higher than that of  $^{137}\text{Cs}$ ; this has been confirmed by several other investigators (e.g. SQUIRE and MIDDLETON 1966, CLINE and RICKARD 1972.)

The results of the present extraction and pot experiments assist in predicting the long-term availability of the radioisotopes from soils to plants, which is the first link in the food chains leading to man. However, in the pot experiments it was not possible to evaluate which portion of the available amounts of the radioisotopes was due to the fertilization and which to aging. The effect of time on the availability of the radioisotopes varied with soil type, and slight changes in the availability probably still continue beyond the years under study, at least in some soils. The amounts of the radioisotopes taken up per season by the plants were in general at such a moderate level that decontamination of the soils with the aid of successive harvests would be out of question. The  $^{137}\text{Cs}/^{90}\text{Sr}$  ratios in plant samples also varied significantly with years and soil types, and so it is not possible to estimate the content of one radioisotope on the basis of the content of the other. Finnish soils are acid and naturally poor in nutrients; consequently, they are expected to be prone to relatively high amounts of soluble  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in the soil.

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## SELOSTUS

### Ajan vaikutus kasvin strontium-90:n ja cesium-137:n ottoon suomalaisesta peltomaasta.

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Maatalouden tutkimuskeskus

Radiostrontium ( $^{90}\text{Sr}$ ) ja -cesium ( $^{137}\text{Cs}$ ) kuuluvat ydinräjäytyksissä syntyviin ja ydinreaktorien jätteissä esiintyviin radionuklideihin. Pitkä tehollinen puoliintumisaika, korkea-energinen säteily sekä strontiumin luu- ja cesiumin lihaskudoksisuus tekevät ne vaarallisiksi ihmiselle. Maahan joutuneista radionuklideista suurin osa kulkeutuu ravintoketjuihin kasvien juuriston kautta. On tärkeää tuntea ne tekijät, jotka vaikuttavat kasvien radionuklidien ottoon maasta, jotta voitaisiin keksiä keinoja ihmisen säteilyrasituksen pienentämiseksi.

Radionuklidien pidätykseen maahan vaikuttavat fyysiset, kemialliset ja biologiset tekijät, joiden lyhytaikaisia vaikutuksia radioisotooppien käyttäytymiseen maa-kasvi systeemissä on paljon tutkittu, sen sijaan on vähemmän kiinnitetty huomiota siihen, miten nämä tekijät vaikuttavat pitkän ajan kuluessa. Happamilla suomalaisilla peltomailla on myös erikoispiirteitä, joiden vaikutuksia radioisotooppien liukoisuuteen pitkällä aikavälillä ei ole aikaisemmin selvitetty.

Tässä tutkimuksessa selvitettiin maahan lisätyn radiostrontiumin ja -cesiumin uuttumista seitsemästä maalajista ja näillä maalajeilla kasvaneen raiheinän radioisotooppien pitoisuuksia ja ottoa. Maauuttoja suoritettiin kuuden vuoden ajan, uuttoliuoksena käytettiin hapanta ammoniumasettaattia. Samoja maalajeja käytettiin myös astiakokeissa, joita suoritettiin neljänä kasvukautena.

Heti radioisotooppien maahan lisäämisen jälkeen radio-

strontiumin uuttuminen pieniä jonkin verran. Puolen vuoden kuluttua lisäyksestä sen uuttuminen alkoi kasvaa saavuttaen lähtötason ja ylittäen sen. Noin neljän vuoden kuluttua radiostrontiumin uuttuminen oli jälleen alkuperäisellä tasolla, jossa se pysyi. Radiocesiumin keskimääräinen puuttuminen pieniä vähitellen, niin että se kuuden vuoden kuluttua oli 3/4 alkuperäisestä määrästä.

Neljän kasvukauden aikana raiheinä otti yhteensä noin 7 % maahan alunperin lisätystä radiostrontiumista ja noin 4 % lisätystä radiocesiumista. Kasvin ottamat vuotuiset aktiivisuusmäärät eri maalajeilla vaihtelivat radiostrontiumilla 0,5 %:sta 2,9 %:iin ja radiocesiumilla 0,07 %:sta 3,6 %:iin. Kasvin  $^{90}\text{Sr}$ -pitoisuus oli yleensä ensimmäisenä kasvukautena korkeampi kuin sitä seuraavina vuosina. Kasvin  $^{137}\text{Cs}$ -pitoisuus sensijaan kasvoi kivennäismailla ja savimultamailla mutta pieniä muilla orgaanisilla mailla ajan kuluessa. Kasvin satomäärä oli kääntäen verrannollinen kasvin  $^{90}\text{Sr}$ -pitoisuuteen saman maalajin puitteissa. Radiocesiumin kohdalla tämä riippuvuus oli havaittavissa vain rahkaturvemailla.

Kasvien vuosittain maasta ottamat radioisotooppimäärät olivat yleensä melko pieniä, niin ettei esim. saastuneen peltomaan puhdistaminen ole mahdollista useankaan peräkkäisen sadonkorjuun avulla. Radioisotooppien keskinäinen suhde kasvissa vaihteli huomattavasti eri maalajien ja vuosien välillä. Yhden radioisotooppilajin määrä ei ole laskettavissa toisen määrän perusteella, vaikka niiden alkuperäinen suhde olisikin tiedossa.

## MACRONUTRIENT AND MICRONUTRIENT STATUS OF CULTIVATED ACID SULPHATE SOILS AT TUPOS, FINLAND

RAIMO ERVIÖ and JUKKA PALKO

ERVIÖ, R. and PALKO, J. 1984. *Macronutrient and micronutrient status of cultivated acid sulphate soils at Tupos, Finland*. *Ann. Agric. Fenn.* 23: 121—134. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

Data on the soluble macronutrient and micronutrient status of cultivated acid sulphate soils at the village of Tupos are compared with data on ordinary Finnish cultivated soils.

Low pH and high ion content are the most typical features of the acid sulphate soils. Ca, K, and P do not differ to any great extent from the average for Finland, but Mg and S are present in larger amounts. Compared with Finnish cultivated soils in general, acidic cations (Fe, Mn, Cu, Zn, Cr, and Co) are much more abundant, but Al less so. The acid sulphate soils are typically rich in Na and B.

In general, organic soils are much richer in soluble nutrients than mineral soils, the poorest of which are the coarse mineral soils. K, P, Na, Cu, and Cr are exceptions to this rule. P, Cu, and Cr are most abundant in coarse mineral soils and Na in fine mineral soils. There are no marked differences in the concentration of K by soil type.

Subsoil nutrient concentrations were considerably lower than those in the topsoil, except for K, Na and Cu, which were at similar concentrations in both the topsoil and subsoil, and sulphate -S and Cr, which considerably exceeded the topsoil concentrations.

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Index words: acid sulphate soils, acid cultivated soils, soil nutrient status, sulphur status.

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## INTRODUCTION

There are more than 15 million hectares of potentially and actually cultivated acid sulphate soils in the tropics, and their existence has also been reported in New Zealand, Australia, Japan, Korea, Vietnam, Malaysia, India, Pakistan, Africa and N. and S. America, with smaller areas in the Netherlands, Sweden, the UK, Finland, and elsewhere (DOST 1972). Finland has about 55 000 hectares in the coastal regions along the Gulf of Bothnia, of which about 45 000 hectares are under cultivation (PUROKOSKI 1959). This estimate is probably too low, since as much as

26 000 hectares has been mapped in the drainage basin of the River Kyrönjoki alone (ERVIÖ 1975).

The Finnish acid sulphate soils were formed by sedimentation during the Litorina phase in the history of the Baltic basin (about 5 000 years B.C.). The sulphur in these sediments is derived from seawater sulphates and plant and animal residues. Under anaerobic conditions below the groundwater table it takes the form of sulphides, mostly pyrite, FeS<sub>2</sub>, and monosulphide, FeS (GEORGALA 1982).

Due to drainage and land uplift, the sulphides

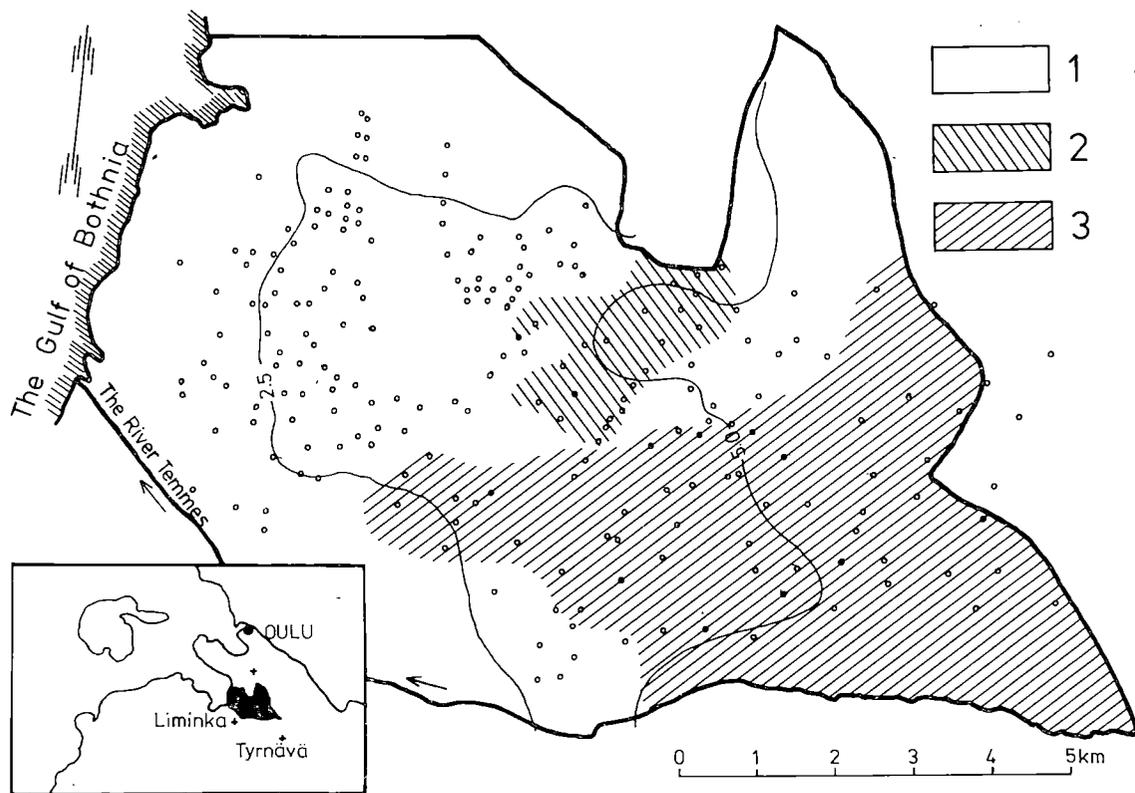
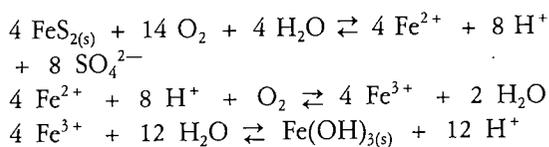


Fig. 1. The area investigated at Tupos village. Soil sample sites are marked with dots, height above sea level with countour lines of 2,5 and 5 meters. Areas of soil groups are: 1 = fine mineral soils, 2 = coarse mineral soils, 3 = organic soils.

are oxidised through elemental sulphur to sulphates, which are transported upwards by capillary water together with the acidic counterion ( $\text{Fe}^{3+}$ ). The free acidic metal ions hydrolyse to form hydroxyl ions and protons and acidification occurs.

The classical stoichiometric portrayal of acid mine drainage is:



Soil acidity leads to an acceleration of the weathering of the soil silicate structure, liberating

large amounts of aluminium ions, which are leached out into the watercourses. This in turn leads to highly acidic conditions in the rivers, especially during flood periods.

Acid sulphate soils therefore pose a great problem for water management (acidic drainage and destruction of fish stocks) and for agriculture (poor growth rate and macronutrient and micronutrient imbalance). For this reason a research project has been commenced in Finland in order to examine these problems and evolve useful measures for preventing them. The first stage is to examine the chemical character and nutrient status of the area (Fig. 1), and the second one will be to determine the macronutrients and micronutrients in cereals grown in the soils concerned.

## MATERIAL AND METHODS

Sampling was carried out at 212 sites in April, 1983. Two samples were taken from each site, one from the cultivated topsoil (0–20 cm) and the other from the subsoil (50–70 cm). The samples were then put into labelled plastic bags and transported immediately to the Water Laboratory of Oulu University, where they were frozen for storage.

The frozen samples were thawed, air-dried at 25–30 C° and then passed through a 2 mm sieve. The electrical conductivity and pH were measured from a soil–water suspension (1:2,5), and the pH also from a 0,01 M CaCl<sub>2</sub> solution. Bulk density was determined by weighing 25 ml of soil. Organic carbon content was determined by the dry combustion method using a LECO CR-12 CO<sub>2</sub> autoanalyser (SIPPOLA 1982).

Calcium, potassium, sodium, magnesium, phosphorus, and sulphate sulphur were extracted with a 0,5 N ammonium acetate–0,5 N acetic acid solution (pH 4,65), the extraction ratio being 1:10 (V/V), the extraction time 1 h and the shaking speed 27 rotations per minute (VUORINEN and MÄKITIE 1955).

Copper, zinc, manganese, iron, aluminium, cobalt, and chromium were extracted using a solution of 0,5 N ammonium acetate, 0,5 N acetic acid and 0,02 M EDTA (LAKANEN and ERVIÖ 1971), with the same extraction time and ratio as above.

Potassium and calcium were determined with a flame photometer and sodium, magnesium, copper, zinc, manganese, and iron with an atomic absorption spectrophotometer (Perkin Elmer 5000) using an air–acetylene flame, and for aluminium a nitrous oxide–acetylene flame. Cobalt and chromium were determined by electrothermal atomic absorption spectrometry (Perkin Elmer 3820 AAS, equipped with an HGA-400 graphite furnace and autosampler AS-40). Phosphorus was determined colorimetrically using the molybdenum blue method, and sulphate sulphur by measuring the turbidity of a barium sulphate precipitate using an AKEA autoanalyser.

The indirect atomic absorption method was used for the determination of total soil sulphur. All the sulphur was first oxidised to sulphate with conc. HNO<sub>3</sub> and HCO<sub>4</sub>, and the sulphate ions then precipitated from an acid solution as BaSO<sub>4</sub> and dissolved in ammoniacal EDTA-solution. Barium ions were determined with an AAS using an air–acetylene flame (ØIEN 1979).

Boron was extracted from the soil with boiling water (1:2) and determined from the extract using the Azomethine -H method (SIPPOLA and ERVIÖ 1977).

All the nutrient concentrations are given in mg per litre of dry soil.

## RESULTS AND DISCUSSION

### 1. The study area

The typical acid sulphate soil area, the village of Tupos (about 40 km<sup>2</sup>), is located on a flat coastal plain about 20 km south of Oulu. The sampling sites, contours and soil types are depicted in Fig. 1.

Most of the sites are situated at heights of between 2,5 and 10 metres a.s.l. The most common soil type is silt (main soil fraction  $\varnothing$  2–20  $\mu$ ), with organic soil types becoming more common further inland. The organic soil extends beyond the topsoil (0–20 cm) on only very few

occasions. The middle of the area contains a sand formation. Of the 212 topsoil samples 147 represent fine mineral soils, 20 coarse mineral soils and 45 organic soils (more than 20 % humus). The classification system introduced by ERVIÖ (1975) categorizes 128 of the 212 samples as acid sulphate soils.

### 2. Chemical properties and soluble macronutrients and micronutrients

The soil properties are compared with the data of

SIPPOLA and TARES (1978), who used exactly the same extraction methods for soil samples gathered from cultivated soils all over Finland. KURKI (1982) reports average properties for 508 000 samples of Finnish cultivated soils. ERVIÖ (1975) has mapped the cultivated acid sulphate soils in the drainage basin of the river Kyrönjoki (220 sites), and KORKMAN (1973) reports on the sulphur status of Finnish cultivated soils.

The mean  $\text{pH}(\text{H}_2\text{O})$  value for the Tupos samples, (5,27) is clearly lower than the figures for the whole country: 5,70 reported by KURKI (1982) and 5,55 by SIPPOLA and TARES (1978). The  $\text{pH}(\text{H}_2\text{O})$  distribution of the Tupos samples is also much broader, and there is another peak around  $\text{pH}$  4,5 (Fig. 2a). There are also some samples in the  $\text{pH}$  6,5—7,5 range, but these differ from the others in having a very high alkaline rare earth content and a typical red-brown colour. These soil samples are classified under the Muhos formation (PUROKOSKI 1958). ERVIÖ (1975) reports  $\text{pH}(\text{H}_2\text{O})$  values of 5,5 for coarse mineral soils and 5,2 for fine mineral and organic soils of acid sulphate soil areas in the drainage basin of river Kyrönjoki.

The mean  $\text{pH}(\text{CaCl}_2)$  value for the Tupos cultivated soils is 4,76, which is 0,5 pH units lower than the mean  $\text{pH}(\text{H}_2\text{O})$  value that usually characterizes Finnish soils (TARES 1979). SILLANPÄÄ (1982) reports a mean  $\text{pH}(\text{CaCl}_2)$  value of 5,21 and a mean  $\text{pH}(\text{H}_2\text{O})$  value of 5,73 for 94 Finnish cultivated soil samples.

The distribution of electrical conductivity values in the Tupos samples is very wide (range  $0,5\text{--}11,0 \text{ Scm}^{-1} \times 10^{-4}$ ), with the main peak around 2,0 (mean 3,57). The usual value in Finnish cultivated soils is only 0,6—0,7 (Fig. 2a). This shows best the enormous excess of ions in the Tupos soils.

The distributions of extractable calcium (Fig. 2a) and soluble phosphorus (Fig. 2b) are close to those given by SIPPOLA and TARES (1978). The main peak in the distribution of extractable potassium in the Tupos cultivated soils lies in a concentration range a little lower than the Finnish average. The magnesium content of the tilled soils at Tupos on its part is much higher,

with a peak at about 200 mg/l, whereas the data of SIPPOLA and TARES (1978) suggest a value of 70 mg/l (Fig. 2a and Fig. 2b). ERVIÖ (1975) observes that the calcium, potassium, and magnesium status of the acid sulphate soils in the Kyrönjoki drainage basin is satisfactory.

Their distributions of boron and sodium differ greatly from the Finnish averages. Their mean values in the Tupos samples are 1,47 and 113 mg/l, and the Finnish averages are 0,38 and 17,8 mg/l, respectively (Fig. 2a). These two elements are typical of young marine deposits such as Litorina sediments. The distribution peaks for exchangeable manganese, copper, and iron are higher in the topsoil at Tupos than in Finland generally but that of zinc is closer (Fig. 2b). The exchangeable copper and iron are more than twice as high as normal. ERVIÖ (1975) obtained a similar difference with a different extraction method when comparing his data with the Finnish average (SILLANPÄÄ and LAKANEN 1968). The high iron content arises from oxidation of the iron sulphides in the Litorina sediments.

The most surprising fact is that the exchangeable aluminium content in Tupos cultivated acid sulphate soils is much lower than the Finnish average (means 328 mg/l and 484 mg/l in Fig. 2c). ERVIÖ (1975) gives a mean of 196 mg/l for acid sulphate soils with a different extraction method (acid ammonium acetate solution). This value is greater than MÄKITIE (1966) gives (158 mg/l soil) for 30 samples gathered from all over Finland and extracted with the same extraction method. We extracted 50 random Tupos soil samples with this same extraction method and obtained a mean of 126 mg/l soil. This data shows that there is no excess of extractable aluminium in Tupos acid sulphate cultivated soils such as previously proposed. The seasonal variation in the aluminium content of cultivated soils has not been investigated.

The distribution range of cobalt is markedly broad. The distribution maximum value is about 1,0 mg/l (mean 1,21 mg/l). According to the data of SIPPOLA and TARES (1978) the value is 0,3 mg/l (mean 0,52 mg/l, Fig. 2b). SILLANPÄÄ et al. (1975) give a mean value of 0,3 mg/l, for more than 400 samples collected from the exper-

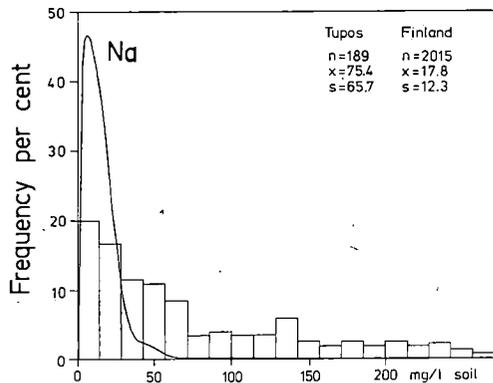
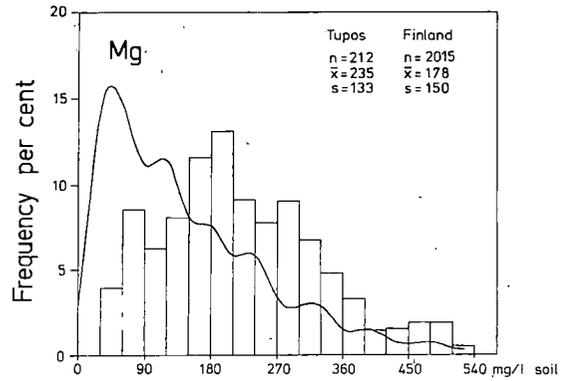
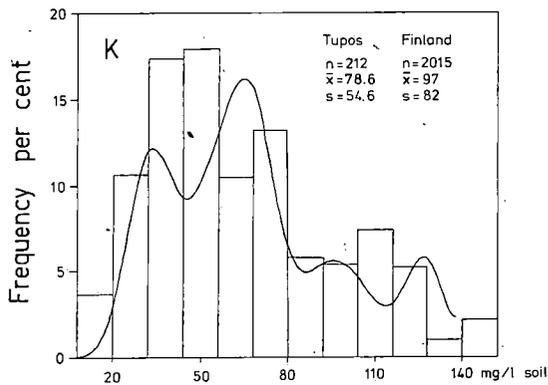
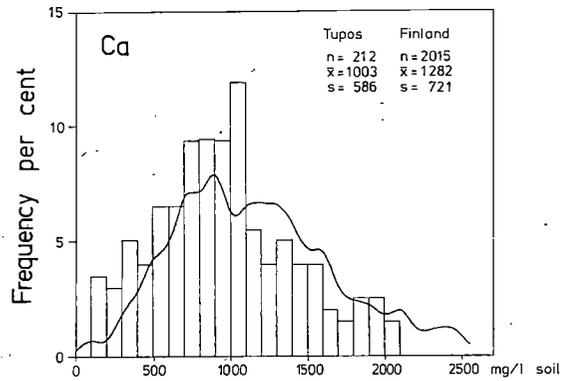
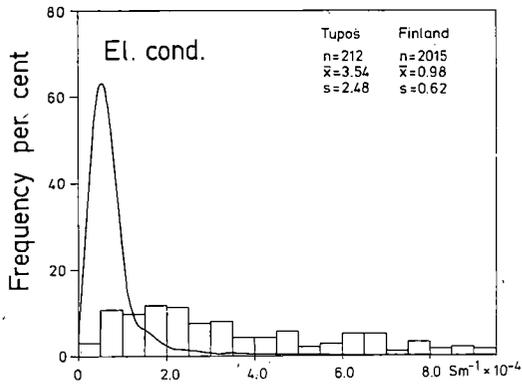
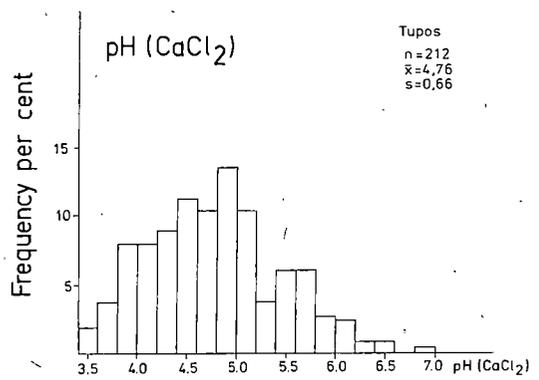
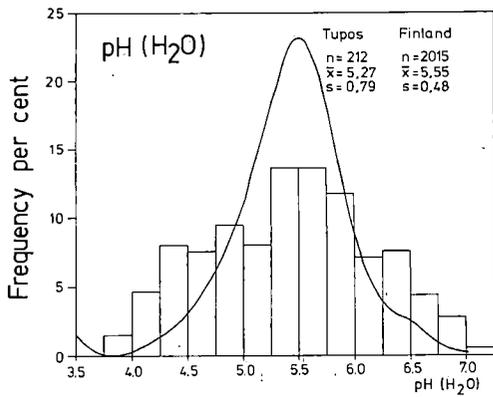


Fig. 2a. The main parts of the frequency distributions of pH(H<sub>2</sub>O), pH(CaCl<sub>2</sub>), electrical conductivity, extractable calcium, potassium, magnesium, and sodium in the cultivated topsoils of Tupos (bars). The curves show the average frequency of the same characters in Finland according to SIPPOLA and TARES (1978). n = number of samples,  $\bar{x}$  = mean value, s = standard deviation.

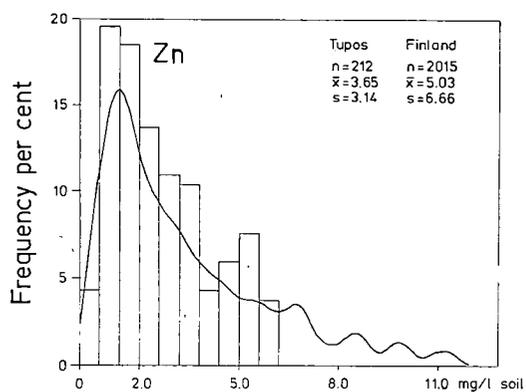
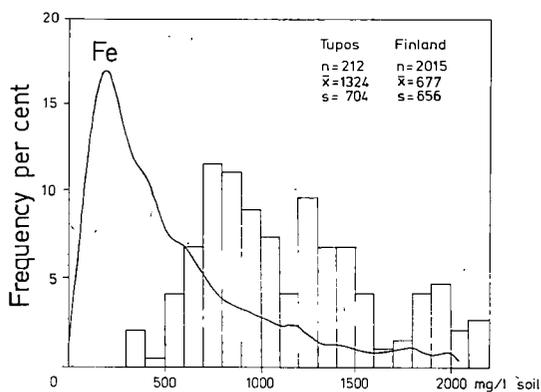
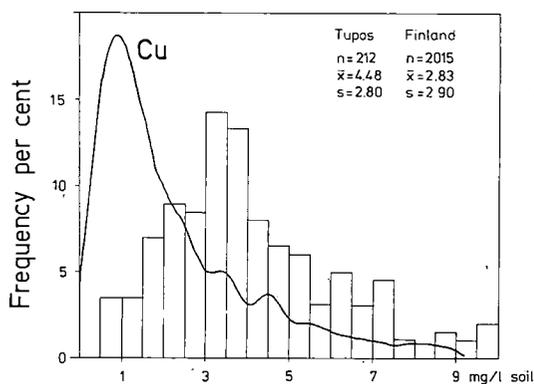
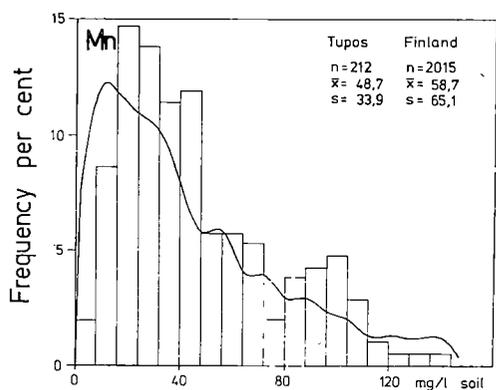
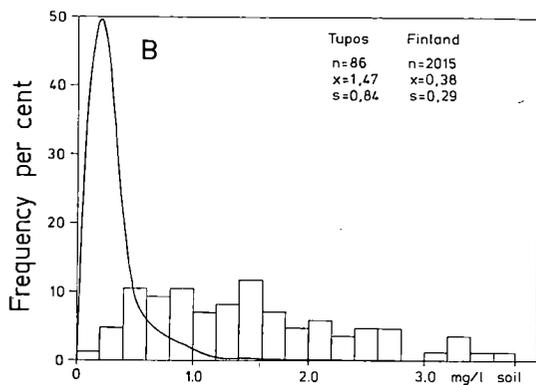
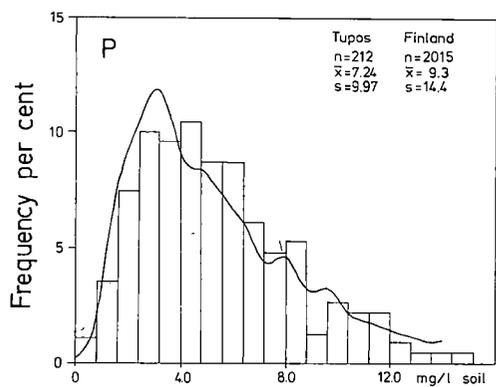


Fig. 2b. The main parts of the frequency distributions of extractable phosphorus, boron, manganese, copper, iron, and zinc in the cultivated topsoils of Tupos (bars). The curves

show the average frequency of the same characters in Finland according to SIPPOLA and TARES (1978).  $n$  = number of samples,  $\bar{x}$  = mean value,  $s$  = standard deviation.

imental stations of the Agricultural Research Centre.

The variation range for chromium (Fig. 2c) is almost the same as reported by SIPPOLA and TARES (1978) (0,1—0,8 mg/l); the mean value of Tupos samples (0,38 mg/l) is somewhat higher than the Finnish average (0,28 mg/l soil).

The sulphate sulphur content of acid sulphate soils is typically high; of 212 soil samples 128 contained more than 100 mg/l soil sulphate sulphur. The mean value of 232 mg/l soil is much greater than those obtained by ERVIÖ (1975) (37 mg/l for silts and 55 mg/l soil for organic soils). The mean value of ordinary Finnish cultivated soils is 8 mg/l soil according to KORKMAN (1973).

Total sulphur (Fig. 2c), which also includes elemental and organic sulphur, varies between 85—4800 mg/kg soil (mean 1580 mg/kg). According to KORKMAN (1973) the corresponding figures for the whole country are considerably smaller, range 130—1810 mg/kg, the mean values being 520 mg/kg for silts and 1130 mg/kg for organic soils.

### 3. Macronutrients and micronutrients by soil type

The topsoil samples (212) were divided into three soil type groups: coarse mineral soils (20), fine mineral soils (147) and organic soils (45). Coarse mineral soils include sand and finesand, fine mineral soils include, silt and clay, and organic soils are classed as samples with over 20 per cent humus (= 11,56 % org. C). The properties investigated differ markedly between these groups (Table 1).

The mean pH(H<sub>2</sub>O) values for the fine and coarse mineral soils were 5,37 and 5,64, and for the organic soils considerably lower (4,85). The mean pH(CaCl<sub>2</sub>) values in the mineral soils are about 0,6 pH units lower than the pH(H<sub>2</sub>O) values, while in the organic soils the difference is only 0,3 units (Table 1).

The mean electrical conductivity of fine mineral soils is twice as high as that of the coarse mineral soils. The organic soils exceed coarse mineral soils by a factor of three.

Table 1. Topsoil properties and extractable macronutrients and micronutrients (mg/l soil) by soil type.  $\bar{x}$  = mean, s = standard deviation and n = number of samples.

		Coarse mineral soils n = 20	Fine mineral soils n = 147	Organic soils n = 45
pH(H <sub>2</sub> O)	$\bar{x}$	5,64	5,37	4,83
	s	0,58	0,78	0,71
pH(CaCl <sub>2</sub> )	$\bar{x}$	5,00	4,85	4,55
	s	0,57	0,37	0,65
El. cond.	$\bar{x}$	2,02	4,39	6,29
	s	2,51	3,83	4,04
Ca	$\bar{x}$	802	991	1130
	s	294	499	866
Mg	$\bar{x}$	142	237	269
	s	85,0	117	173
K	$\bar{x}$	86,3	76,1	83,7
	s	50,8	51,9	64,6
B	$\bar{x}$	0,48	1,39	1,88
	s	0,17	0,88	0,52
P	$\bar{x}$	17,3	6,19	6,19
	s	25,7	5,54	6,19
Al	$\bar{x}$	242	279	526
	s	123	222	346
Fe	$\bar{x}$	991	1124	2130
	s	420	457	869
Mn	$\bar{x}$	36,0	46,7	60,5
	s	22,5	31,7	41,8
Zn	$\bar{x}$	3,66	2,95	5,94
	s	3,19	2,48	3,93
Co	$\bar{x}$	0,41	1,08	1,86
	s	0,28	0,57	0,87
Cu	$\bar{x}$	2,25	5,02	3,68
	s	2,00	2,83	2,31
Cr	$\bar{x}$	0,48	0,41	0,28
	s	0,20	0,17	0,10
Na	$\bar{x}$	31,8	128	98,0
	s	59,1	146	102
SO <sub>4</sub> -S	$\bar{x}$	78,4	206	383
	s	162	278	389
Tot-S	$\bar{x}$	398	1356	2570
	s	139	1413	1835

Organic soils are richer in extractable calcium, magnesium and boron than the fine mineral soils, the coarse mineral soils being the poorest in these elements.

Soluble phosphorus exists most abundantly in the coarse mineral soils. Phosphorus is firmly bound to the mineral matter of the soil, its fixation increasing with decreasing particle size. There is no marked difference in potassium between these soil groups, but sodium is most abundant in the fine mineral soils (Table 1).

The contents of the most acidic cations (aluminium, iron, manganese, zinc, and cobalt) are almost twice as high in the organic soils as in the fine mineral soils, and the lowest mean values for

all of these elements are always found in the coarse mineral soils (Table 1). This is mainly due to the greater cation exchange capacity (CEC) of organic matter and clay material. Copper and

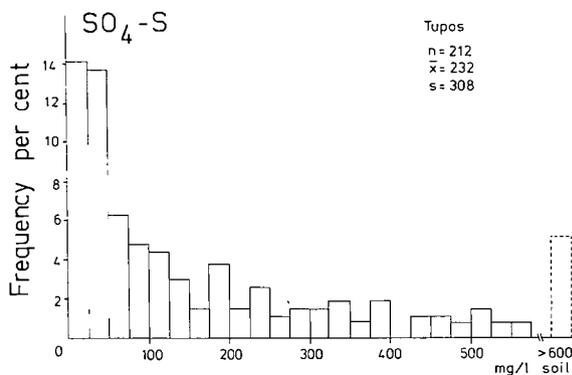
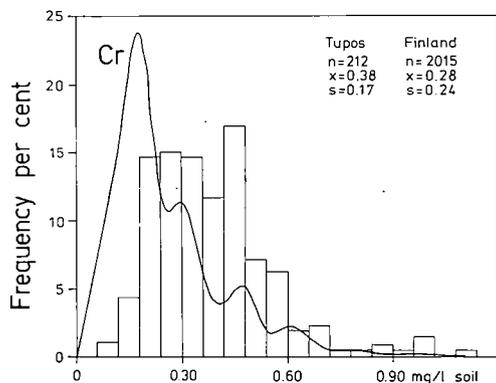
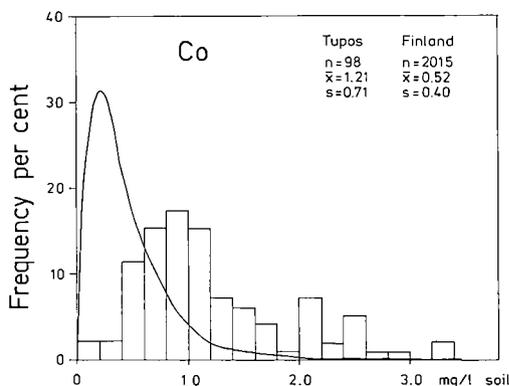
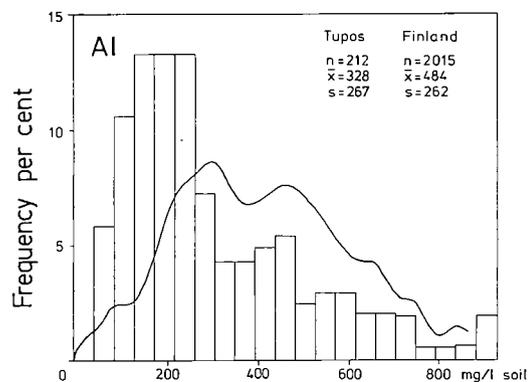


Fig. 2c. The main parts of the frequency distributions of extractable aluminium, cobalt, chromium, and sulphate sulphur in the cultivated topsoils of Tupos (bars). The curves

show the average frequency of the same characters in Finland according to SIPPOLA and TARES (1978). n = number of samples,  $\bar{x}$  = mean value, s = standard deviation.

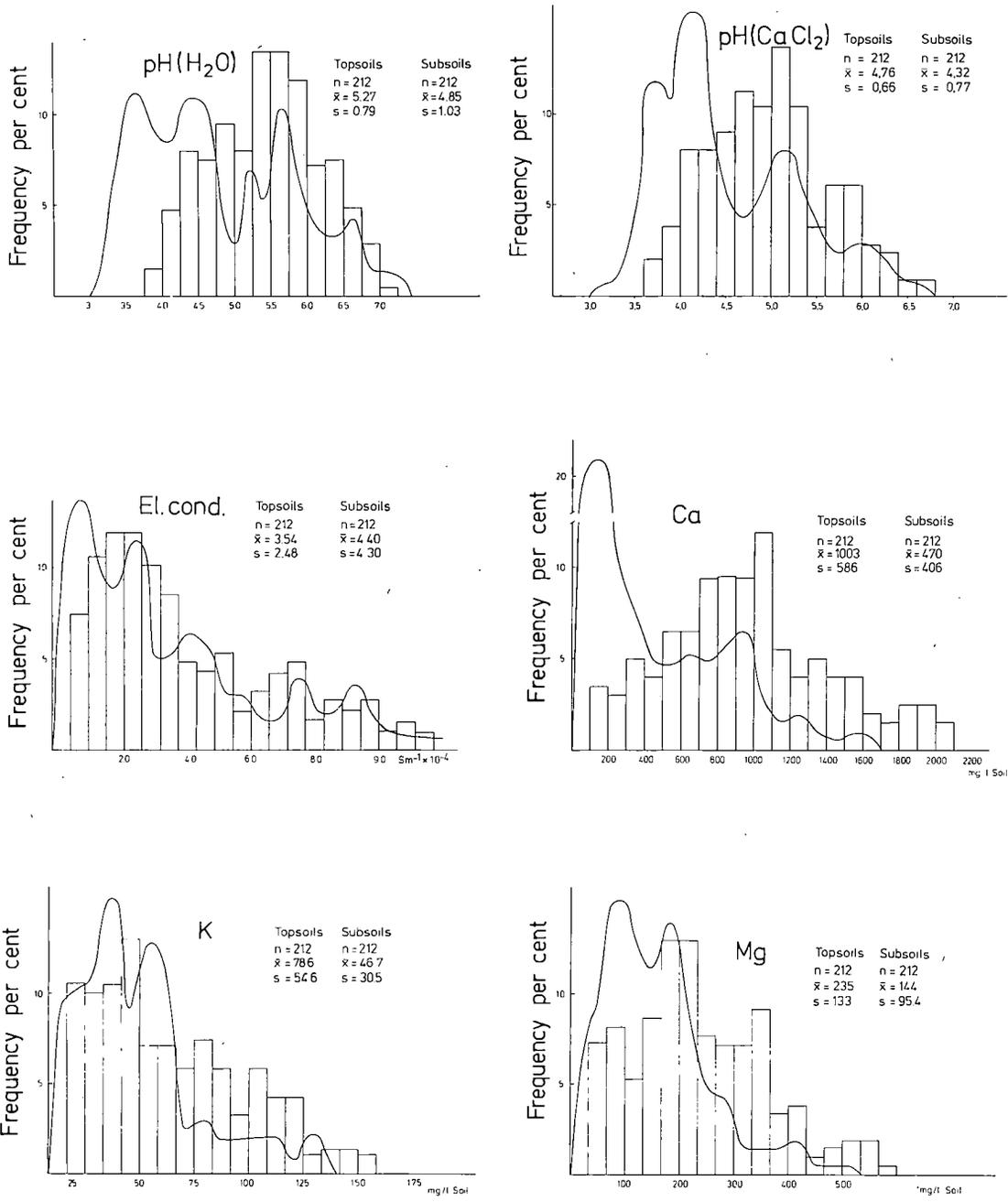


Fig. 3a. The main parts of the frequency distributions of pH(H<sub>2</sub>O), pH(CaCl<sub>2</sub>), electrical conductivity, extractable calcium, potassium, and magnesium in the cultivated topsoils

of Tupos (bars). The curves show the respective distributions in the subsoils. n = number of samples,  $\bar{x}$  = mean value, s = standard deviation.

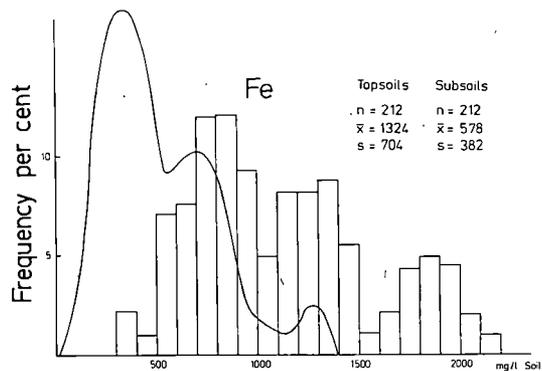
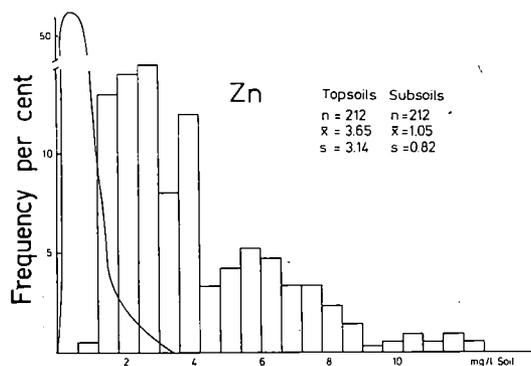
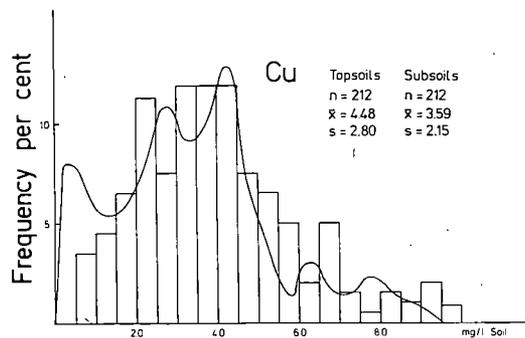
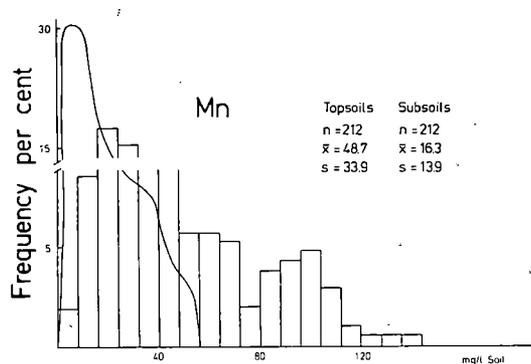
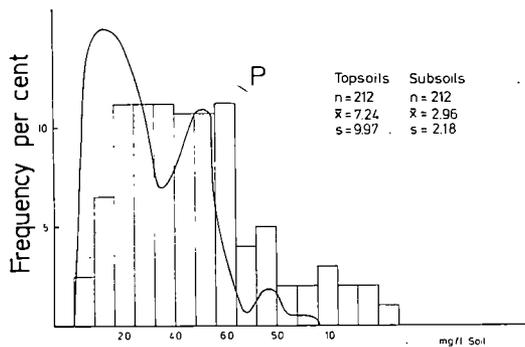
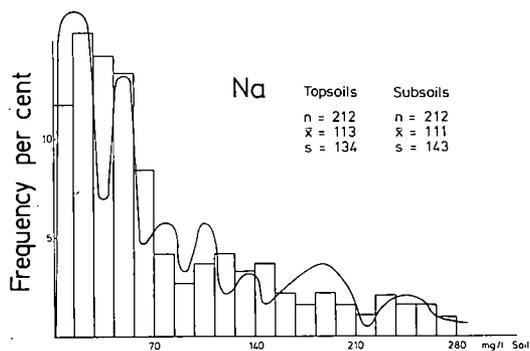


Fig. 3b. The main parts of the frequency distributions of extractable sodium, phosphorus, manganese, copper, zinc, and iron in the cultivated topsoils of Tupos (bars). The curves

show the respective distributions in the subsoils. n = number of samples,  $\bar{x}$  = mean value, s = standard deviation.

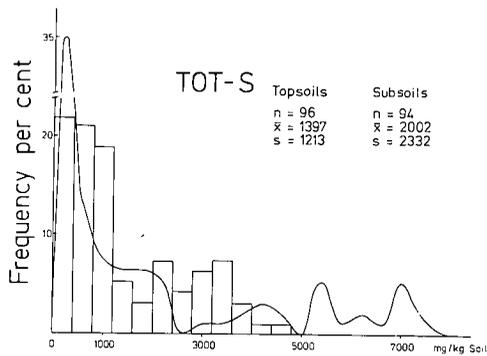
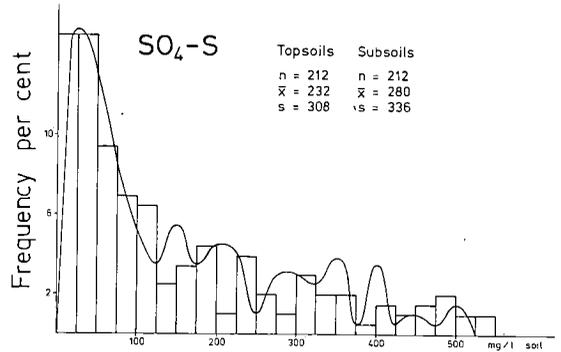
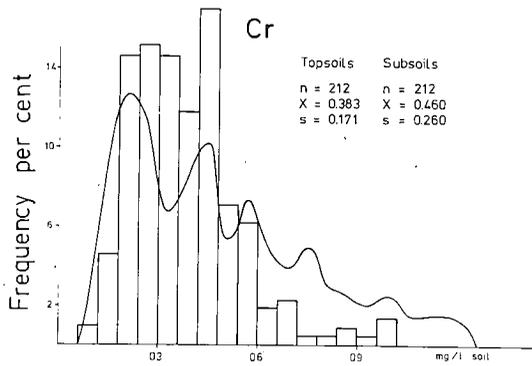
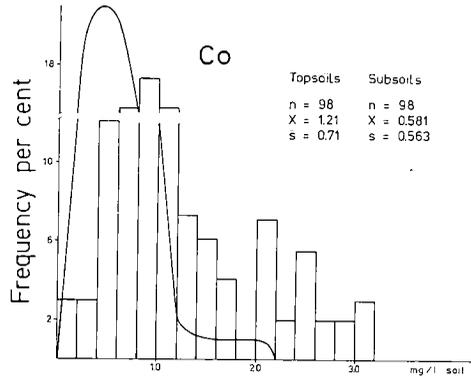
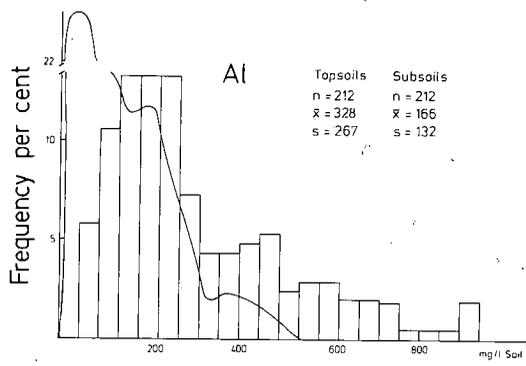


Fig. 3c. The main parts of the frequency distributions of extractable aluminium, cobalt, chromium, and sulphate sulphur and total sulphur in the cultivated topsoils of Tupos (bars). The curves show the respective distributions in the subsoils.  $n$  = number of samples,  $\bar{x}$  = mean value,  $s$  = standard deviation.

chromium are more abundant in the fine mineral soils than in the organic soils, and the highest chromium content is found in the coarse mineral soils.

The variations in sulphate sulphur and total sulphur content by soil type are quite similar, the lowest amounts occurring in the coarse mineral soils (78 mg/l and 139 mg/kg). The mean values for the fine mineral soils (206 mg/l and 1356 mg/kg) are about a half of those for the organic soils (383 mg/l and 2570 mg/kg).

#### 4. Comparison between topsoils and subsoils

All the subsoil samples represented mineral soils, 169 of which were fine soils and 43 coarse soils.

According to ERVIÖ (1975), acid sulphate soils are those in which the  $\text{pH}(\text{H}_2\text{O})$  value in the subsoil is less than 5,0 and/or the sulphate sulphur concentration is more than 100 mg/l. This classification divides the Tupos soil samples into two groups (Fig. 3a), 128 of the 212 samples representing acid sulphate soils. The main  $\text{pH}(\text{H}_2\text{O})$  peak for the non-acid sulphate soil samples is about 5,7. The topsoil and subsoil samples,  $\text{pH}(\text{H}_2\text{O})$  6,5, were distinguished on account of their red-brown colour as belonging to the Muhos formation (PUROKOSKI 1958).

There is no major  $\text{pH}(\text{H}_2\text{O})$  difference between different soil horizons at the non-acid sulphate soil sites, whereas there is a large difference, about one pH unit, at the acid sulphate soil sites.

The mean  $\text{pH}(\text{CaCl}_2)$  value in both layers is 0,5 pH units lower than the mean  $\text{pH}(\text{H}_2\text{O})$  value, but the basic shapes of the distribution curves are the same (Fig. 3a).

The range of the electrical conductivity distribution is almost the same in both soil horizons, whereas the peak for the topsoil samples comes at a somewhat higher value. This is mostly due to the drift of cations (cations being counterions to sulphate) to the upper layer.

The most significant difference between the layers lies in the distribution of calcium, the majority of the subsoil samples (approx. 70 %) falling below 500 mg/l, while a similar propor-

tion of the topsoil samples come between 500 and 1500 mg/l (Fig. 3a).

There is no marked difference in potassium and sodium between these soil horizons, but magnesium and phosphorus concentrations in the subsoil layer are about half of those in the topsoil layer (Figs. 3a and 3b).

Subsoil zinc and manganese concentrations are about one third and iron and aluminium values about half of those in the topsoil samples (Fig. 3b and 3c). Most of the high iron values in both horizons come from gyttja soils (org. matter content > 2 %) which are typical of Litorina sediments.

Although the sulphate S content in subsoil is somewhat greater than in topsoils, the same number of samples (approx. 60 %) exceed the 100 mg/l level in both cases. ERVIÖ (1975) reports a greater difference between the soil horizons in the River Kyrönjoki drainage basin where, in general, the sulphate concentration of topsoils is lower. According to KORKMAN (1973), there is no difference in sulphate sulphur between the horizons in average Finnish cultivated soils.

The ranges of variation in total sulphur content in both the topsoils and subsoils are wide, with most of the values (approx. 70 %) falling between 50 and 2000 mg/kg. There are some subsoils, however (usually gyttja soils), with extremely high contents of total sulphur (Fig. 3c).

The average cobalt content of the topsoils is more than twice that of the subsoils and the peak in the distribution of cobalt lies at about 0,9 mg/l in the topsoil samples, compared with about 0,4 mg/l in the subsoil samples (Fig. 3c).

The only acidic cations whose concentrations do not clearly differ between the topsoil and subsoil samples are copper and chromium. The peak below the concentration value of 1 mg/l in the subsoil sample distribution curve for copper represents coarse mineral soils, the amounts of copper in which are markedly lower than those in the topsoil samples. The mean chromium content of the subsoils is higher than that of the topsoils and varies over a wider range (0,1—2,0 mg/l, Fig. 3c).

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## SELOSTUS

### Happamien sulfaattimaiden pää- ja hivenravinnepitoisuudet Limingan Tupoksen alueella.

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Tyypillisellä sulfaattimaa-alueella Limingan Tupoksen kylässä selvitettiin viljelymaan alkuainepitoisuuksia vertaamalla niitä tavanomaisten suomalaisten maiden vastaaviin pitoisuuksiin.

Noin 40 km<sup>2</sup>:n alueelta koottiin 212 kohdasta muokkauserroksen (0—20 cm) ja pohjamaan (50—70 cm) maanäytteet. Näytteistä määritettiin pH ja johtoluku sekä analysoitiin helppoliukoiset kalsium, kalium, magnesium, natrium, fosfori, boori, kupari, sinkki, mangaani, koboltti, alumiini,

rauta, kromi ja sulfaattirikki sekä kokonaisrikki.

Alueen maaperä on Litorina-merivaiheen aikana syntyneitä sedimenttejä, joita nimitetään happamiksi sulfaattimaiksi alhaisen pH:n ja suuren rikkipitoisuutensa vuoksi. Muokkauserroksen Ca-, K- ja P-pitoisuudet eivät poikenneet suomalaisten maiden keskimääräisistä pitoisuuksista. Sen sijaan Mg:a ja n.s. happamia kationeja (Fe, Mn, Cu, Zn, Cr ja Co) oli runsaammin ja alumiinia niukemmin kuin viljelymais-

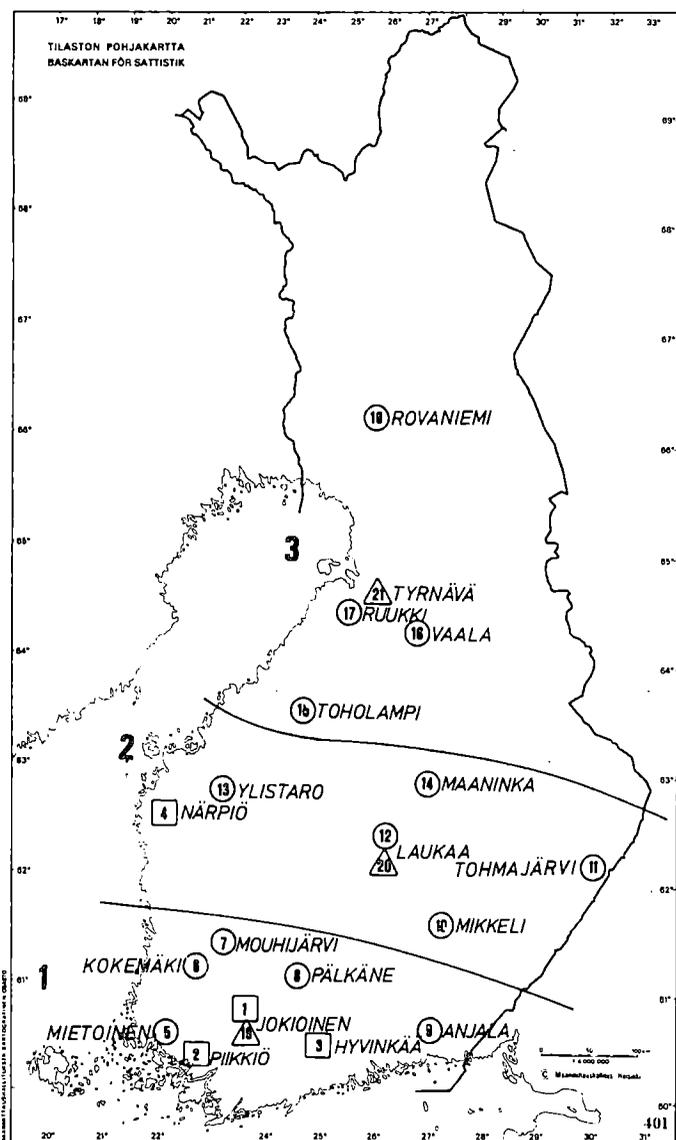
samme yleensä.

Eloperäisissä maissa oli useimpia liukoisia ravinteita enemmän kuin kivennäismaissa. Poikkeuksen tästä tekivät K, Na, P, Cu ja Cr. Karkeissa kivennäismaissa taas oli hienoihin kivennäismaihin nähden enemmän fosforia, kuparia ja kromia, mutta vähemmän natriumia.

Useimpien pohjamaan ravinteiden määrät olivat pintamaan määriä alhaisempia. Vain SO<sub>4</sub>-rikki- ja kokonaisrikkimäärät olivat pohjamaassa selvästi suurempia kalsiumin, natriumin ja kromin määrien ollessa pintamaan kanssa samaa tasoa.

## CONTENTS

YLÄRANTA, T. Raising the selenium content of spring wheat and barley using selenite and selenate ...	75
— Effect of selenium fertilization and foliar spraying at different growth stages on the selenium content of spring wheat and barley .....	85
— Effect of selenite and selenate fertilization and foliar spraying on selenium content of timothy grass .....	96
PAASIKALLIO, A. The effect of time on the availability of <sup>90</sup> Sr and <sup>137</sup> Cs to plants from Finnish soils....	109
ERVIÖ, R. & PALKO, J. Macro- and micronutrient status of cultivated acid sulphate soils at Tupos, Finland .....	121



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## SISÄLLYS — CONTENTS

YLÄRANTA, T. Raising the selenium content of spring wheat and barley using selenite and selenate ...	75
Selostus: Kevätvehnän ja ohran seleenipitoisuuden kohottaminen seleniitillä ja selenaatilla .....	84
— Effect of selenium fertilization and foliar spraying at different growth stages on the selenium content of spring wheat and barley .....	85
Selostus: Seleeni-lannoituksen ja seleeniruiskutuksen vaikutus kevätvehnän ja ohran seleenipitoisuuteen .....	95
— Effect of selenite and selenate fertilization and foliar spraying on selenium content of timothy grass .....	96
Selostus: Timoteinurmirehun seleenipitoisuuden kohottaminen ruiskuttamalla ja lannoittamalla .....	108
PAASIKALLIO, A. The effect of time on the availability of <sup>90</sup> Sr and <sup>137</sup> Cs to plants from Finnish soils ...	109
Selostus: Ajan vaikutus kasvin strontium-90:n ja cesium-137:n ottoon suomalaisesta peltomaasta .....	120
ERVIO, R. & PALKO, J. Macronutrient and micronutrient status of cultivated acid sulphate soils at Tupos, Finland .....	121
Selostus: Happamien sulfaattimaiden pää- ja hivenravinnepitoisuudet Limingan Tupoksen alueella .....	133