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EFFECT OF ADDED SELENITE AND SELENATE ON THE SELENIUM CONTENT OF ITALIAN RYE GRASS (*LOLIUM MULTIFLORUM*) IN DIFFERENT SOILS

TOIVO YLÄRANTA

YLÄRANTA, T. 1983. Effect of added selenite and selenate on the selenium content of Italian rye grass (*Lolium multiflorum*) in different soils. Ann. Agric. Fenn. 22: 139—151. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

The uptake of selenium by Italian rye grass (*Lolium multiflorum* Lam.) from acid mineral and organogenic soils low in native selenium content was studied in a pot experiment. For the first crop 100 µg of selenium was added per 900 ml of soil in the form of either sodium selenite or selenate.

The first selenite crop obtained from the mineral soils had a mean selenium content of 0,2 mg/kg dry matter, while the first selenate crop contained 6 mg/kg. The third selenate crop contained only one-sixth as much selenium as the first crop, while the third selenite crop contained one-third as much as the first.

The three selenate crops from mineral soils took up an average of 44 % of the added selenium, while the three selenite crops took up only 2 %. The selenium contents of the crops and the uptake of selenium were of the same order of magnitude for both mineral soils and organogenic soils.

The additions of selenite and selenate did not affect the size of the rye grass yields. However, the selenium content of the crops was lower the higher the yield.

The content of iron extractable into acid ammonium oxalate solution explained 37 % of the variations in selenium contents of the first selenite crop and 51 % in the second.

Aside from the yield, the variations in the selenium contents of the selenate crops were best explained by the soils' acid ammonium oxalate extractable aluminium content and by the organic carbon content of the soils.

The organic carbon content was negatively correlated with the selenium contents of the crops, while the extractable aluminium content showed a positive correlation.

Index words: selenite and selenate application, selenium content of Italian rye grass, mineral soils, organogenic soils.

INTRODUCTION

The selenium content of plants can vary over a wide range, depending on factors such as the plant species, the stage of development of the plant, the type of soil, the selenium content of

the soil, its redox potential and physical and chemical properties in general.

Although selenium is suspected of stimulating plant growth (BROYER et al. 1966,

SINGH et al. 1976), selenium has not been shown to be an essential plant nutrient (BROYER et al. 1972, MOXON and OLSON 1974).

The minimum requirement for the selenium content of animal fodder is considered to be 0,1 mg/kg dry matter (AMMERMAN and MILLER 1975). On the other hand, the selenium content of plants is toxic if it exceeds 5 mg/kg dry matter (JOHNSON 1976).

The selenium content of crops grown in the Nordic countries is generally extremely low. Grasses grown in Finland contain on average 0,01 mg selenium per kg dry matter (OKSANEN and SANDHOLM 1970, SIPPOLA 1979).

Application of selenite or selenate either to the soil or to the plants is an effective means of raising their selenium content. Selenate is taken up from the soil by plants up to ten times more effectively than selenite (BISBJERG and GISSEL-NIELSEN 1969). There have thus been fears

that the selenium content of plants would reach toxic levels if selenates were used in fertilizers. In fact, research into selenium fertilizers has mainly concerned the use of selenite (GISSEL-NIELSEN 1977).

In Finland SYVÄLAHTI and KORKMAN (1978) and KORKMAN (1980) have used selenite-containing NPK compound fertilizers and sodium selenite, together with a mixture of salts containing several minerals, as the selenium source for cereals and potatoes. In these experiments the uptake of selenium by the plants amounted to only a few parts per thousand of the selenium added in the form of selenite. It was thus necessary to study, under controlled conditions, how plants take up selenium added to the soil in the form of selenite and selenate from different agricultural soils in order to be able to better assess the potential for using selenate as the source of selenium for crops.

MATERIAL AND METHODS

The experimental soils were obtained from plough layer samples of agricultural soils from different parts of Finland (Table 1). The treatment of the soil samples and the analysis of the physical and chemical properties presented in the table are described in detail in an earlier publication (YLÄRANTA 1983 c).

The experiment comprised 49 mineral soil samples and 17 samples of organogenic soil containing at least 11,8 % organic carbon. The clay content of the mineral soil samples ranged from 2,4 % to 52,3 % and the organic carbon content from 0,7 % to 8,8 %. The organic carbon content of the organogenic soils ranged from 11,8 % to 39,3 %. The pH(CaCl₂) of the mineral soils averaged 5,0 and that of the organogenic soils 4,5.

The selenium content of the soils averaged 0,2 mg/kg. In the case of mineral soils, an average of 4,8 % of this selenium was

extractable into hot water, the figure for the organogenic soils being 8,0 %. The mineral soils contained 1360—18 680 mg of iron extractable into 0,2 M (NH₄)₂C₂O₄, C₂H₂O₄ solution, pH 3,3, and 570—6230 mg of aluminium extractable into the same solvent per kilogram of soil dried for 16 hours at 105 °C. The corresponding figures for the organogenic soils were 2240—21 380 mg/kg and 810—7460 mg/kg.

Since the volume weight of the mineral soils ($\emptyset \leq 2$ mm), as determined using the method described by SIPPOLA and TARES (1978), was almost 1, the results of the analyses were roughly the same in both mass and volume units. The mean volume weight of the organogenic soils was only 0,52, so that the means given in Table 1 can be converted to volume units by dividing by two.

About 900 ml of air dried soil ($\emptyset \leq 2$ mm)

Table 1. Soil sample means (\bar{x}) and standard deviations (s) for pH(CaCl₂), organic carbon content (%), clay content of inorganic material (%), total (mg/kg) and hot water extractable ($\mu\text{g}/\text{kg}$) selenium content, acid ammonium oxalate extractable Fe and Al contents (mg/kg), bulk density (kg/l).

Soil group	Number of samples	pH(CaCl ₂)		Org. C (%)		Clay (%)		Total Se (mg/kg)		Hot water extr. Se ($\mu\text{g}/\text{kg}$)		Acid. amm.ox. extr.				Bulk density (kg/l)	
		\bar{x}	s	\bar{x}	s	\bar{x}	s	\bar{x}	s	\bar{x}	s	Fe (\bar{x})	Fe (s)	Al (\bar{x})	Al (s)	\bar{x}	s
Mineral soils	49	5,01	0,54	3,2	1,9	21,7	14,7	0,191	0,092	9,1	4,1	7200	3900	2650	1180	1,03	0,15
Organogenic soils	17	4,52	0,63	25,1	8,4	—	—	0,212	0,157	16,9	5,3	11100	4600	3660	1980	0,52	0,11

was weighed into one-litre polythene pots. The pots were square in cross section, the length of the side being 10 cm. There was no hole in the bottom of the pot. Soil was weighed into each pot to a depth of 9 cm. The dry weight of mineral soil per pot was 530—990 g and that of organogenic soil was 250—580 g. Six pots were prepared for each soil sample, giving a total of 396 pots.

Forty seeds of Italian rye grass (*Lolium multiflorum* Lam., variety Leda daehnfeldt) were planted in each pot. Italian rye grass was chosen for the experiment because of the ease with which it can be grown under experimental conditions on different soils. Rye grass also grows rapidly, producing several crops, which makes it possible to follow the effects and after-effects of selenium additions on several crops during a single growing season. The seeds were covered with a thin layer of the experimental soil. The seeds had a mean selenium content of 32 $\mu\text{g}/\text{kg}$, resulting in the introduction to each pot of 4,7 ng of selenium. Finally 200 g of quartz sand (\varnothing 0,2—0,5 mm) washed in 6 M HCl was spread on top of the soil, forming a layer about 1 cm thick. The pots were watered during three days to a pF value of 2 as determined from two parallel soil samples using a pH apparatus (Soil Moisture Equipment Co., California, USA). The water added to the mineral soils in this way totalled 16—70 % of the mass of the samples and to the organogenic soils 70—220 %. Because of the large number of pots, the experiment was set up on three consecutive days in batches of 22 soil samples at a time.

Three days after seeding, the pots were transferred outdoors to a growing frame. Six days after seeding, the first of which was done on May 27, 1980, the seedlings were thinned to 30 per pot. Nine days after seeding, two of the pots for each soil sample were treated with 10 ml Na₂SeO₃ solution (Merck, product number 6607), while two other pots were treated with an aqueous solution of Na₂SeO₄ (BDH 10262) containing 100 μg Se. The remaining two pots for each soil sample thus received no added selenium. The pots were watered twice with 50 ml of water in order to wash the selenium solution through the quartz sand and into the soil.

Fertilizer was applied to the pots on the day following addition of selenium. Aqueous solutions of different compounds were added to each pot as follows:

Nutrient	mg/pot	Compound
N	240	NH ₄ NO ₃
K	180	KCl, K ₂ SO ₄ , KH ₂ PO ₄
Mg	48	MgCl ₂ · 6H ₂ O
P	60	KH ₂ PO ₄
S	36	K ₂ SO ₄
Ca	30	CaCl ₂
Fe	1	FeNa-EDTA
Mn	2	MnCl ₂
Cu	2	CuCl ₂
Zn	1	ZnNa ₂ -EDTA
B	0,3	H ₃ BO ₃
Mo	0,3	Na ₂ MoO ₄ · 2H ₂ O

The chemicals used as fertilizer were analytical grade and supplied by Merck and BDH. The soils were not limed.

The pots were watered daily to a moisture content corresponding to about pF 2. The positions of the pots with respect to each other were changed every two days. At night and when it started raining the pots were covered with 0,15 mm transparent polythene sheet.

The first crop was cut at the silage stage four weeks after the seeds had been sown. The shoots were cut with scissors leaving about 1,5 cm of stubble. The crop was dried in paper bags in ovens provided with air circulation (Memmert Tv80uL) for four days at 50 °C.

The following nutrients were added to each pot the day after cutting the first crop: N 200 mg, K 150 mg, Mg 40 mg, P 50 mg and S 30 mg.

The second crop was cut three weeks after the first, and was given the same treatment. Application of N, K, Mg, P, S and Ca fertilizers was carried out as for the second crop. Micronutrients Fe, Mn, Cu, Zn, B and Mo were given as for the first crop. The third crop was cut and treated three weeks after cutting the second crop.

The mean temperature at the experimental site was 17 °C (4–27 °C) in June, 17 °C (7–29 °C) in July and 15 °C (3–29 °C) in August.

The amount of deionised water that had to be added exceeded 200 ml per pot per day in some cases.

Once the third crop had been cut 2,5 months after setting up the experiment, the contents of the pots were removed. Fresh mixed soil samples were used for determination of selenium content extractable into hot water. The selenium extraction was carried out by boiling 25 ml of soil in 100 ml of water for 30 minutes (YLÄRANTA 1982). Samples containing as little plant residues as possible were selected for selenium determinations. The selenium contents of the filtrates from hot water extraction and of each plant were determined using the hydride method (YLÄRANTA 1983 a). The equipment used consisted of a Perkin-Elmer 5000 atomic absorption spectrophotometer equipped with a deuterium background corrector, a Westinghouse electrodeless discharge lamp, a Westinghouse Power Supply and a W + W 1100 recorder.

Statistical analysis of the results was carried out using a VAX-11/780 automatic data processing system and SPSS software (NIE et al. 1975, JENKINS 1981).

RESULTS

The dry matter yields per pot obtained on the mineral soils ranged from 1,52 g to 6,56 g for the first crop, from 2,6 to 6,59 g for the second crop and from 2,49 g to 7,15 g for the third crop (Table 2). The corresponding figures for the organogenic soils were 1,66–6,59 g for the first crop, 2,96–6,30 g for the second crop and 2,06–6,12 g for the third crop (Table 3). The mean yields for the material as a whole ranged from the 4,17 g obtained for the second selenate crop on organogenic soils to the 5,23 g obtained for the second selenate crop on

mineral soils. The effect on the yield of the added selenium was investigated by means of variance analysis. No significant differences were found between the yields obtained for the control, selenite and selenate crops on either of the two types of soil at the 1 % level of significance.

The selenium content of the crops cut from pots without added selenium varied for the three crops obtained on mineral soils from 0,008 to 0,024 mg/kg dry matter and for the three crops from the organogenic soils from

Table 2. Mean yields of Italian rye grass for control, selenite and selenate pots (g/pot), crop selenium content (mg/kg dry matter) and selenium uptake ($\mu\text{g}/\text{pot}$) from 49 mineral soils.

Selenium added, crop		Yield (g/pot)		\bar{x}	Selenium content (mg/kg dry matter)		Selenium uptake ($\mu\text{g}/\text{pot}$)	
		\bar{x}	s		s	range	\bar{x}	s
No selenium added	I	4,98	0,98	0,014	0,003	0,008—0,024	0,069	0,020
	II	4,89	0,78	0,014	0,003	0,010—0,023	0,069	0,021
	III	4,54	0,80	0,012	0,002	0,009—0,018	0,055	0,014
Selenite	I	4,92	1,02	0,208	0,096	0,121—0,528	0,98	0,38
	II	4,81	0,79	0,096	0,038	0,058—0,236	0,45	0,16
	III	4,69	0,86	0,068	0,031	0,046—0,169	0,30	0,12
Selenate	I	4,99	0,96	6,22	1,52	3,02—10,120	30,5	8,09
	II	5,23	0,77	1,69	0,592	1,05—3,98	8,53	1,99
	III	4,93	0,86	1,07	0,405	0,544—2,24	5,02	1,18

0,008 to 0,018 mg/kg (Tables 2 and 3). The selenium contents of the selenite and selenate crops shown in the tables have been reduced by subtracting the selenium content of the crop taken from the corresponding control pot, so that all the selenium in these crops can be taken as being derived from the added selenium.

The mean selenium content of the first selenite crop on mineral soils was 0,208 mg/kg and that of the first selenate crop was 6,22 mg/kg. The crop obtained from the pots treated with selenate thus contained 30 times as much selenium as that from pots treated with selenite. The mean selenium content of the second selenate crop was 1,69 mg/kg compared with 0,096 mg/kg for the second selenite crop. The selenium content of the second selenite crop had thus fallen to half of that for the first

crop, while that of the second selenate crop had fallen to almost one quarter. The third selenate crop had a selenium content of only one sixth of that of the first crop on both mineral and organogenic soils. The fall in the amount of selenium taken up from the added selenite was not so rapid, as the third selenite crop contained one third as much selenium as the first crop on mineral soils and one quarter as much on organogenic soils. The lowest, highest and mean selenium contents were of the same order of magnitude on both types of soil.

There was no statistically significant correlation between yield and selenium content for the crops obtained from the control pots. The selenium content of the selenate and selenite crops on both types of soil was in many cases higher the lower the yield:

Table 3. Mean yields of Italian rye grass for control, selenite and selenate pots (g/pot), crop selenium content (mg/kg dry matter) and selenium uptake ($\mu\text{g}/\text{pot}$) from 17 organogenic soils.

Selenium added, crop		Yield (g/pot)		\bar{x}	Selenium content (mg/kg dry matter)		Selenium uptake ($\mu\text{g}/\text{pot}$)	
		\bar{x}	s		s	range	\bar{x}	s
No selenium added	I	4,39	1,36	0,013	0,003	0,009—0,018	0,057	0,022
	II	5,10	1,03	0,011	0,002	0,008—0,015	0,057	0,015
	III	4,48	1,01	0,011	0,002	0,008—0,015	0,051	0,015
Selenite	I	4,22	1,30	0,327	0,170	0,111—0,673	1,28	0,612
	II	4,57	0,92	0,120	0,074	0,060—0,311	0,517	0,262
	III	4,22	1,06	0,074	0,046	0,038—0,189	0,275	0,115
Selenate	I	4,17	1,34	5,83	1,79	2,32—9,86	23,5	8,86
	II	5,02	0,87	1,75	0,571	1,00—3,08	8,49	2,25
	III	4,84	1,18	0,945	0,284	0,558—1,43	4,30	0,849

Crop		Selenium content	
		Organogenic soils, r	Mineral soils, r
Selenite crop	I	-0,462 ^{ns}	-0,505 ^{***}
"	II	-0,517 [*]	-0,412 ^{**}
"	III	-0,779 ^{***}	-0,415 ^{**}
Selenate crop	I	-0,344 ^{ns}	-0,362 [*]
"	II	-0,632 ^{**}	-0,704 ^{***}
"	III	-0,858 ^{***}	-0,752 ^{***}

* P = 0,05, ** P = 0,01, *** P = 0,001

ns = not significant

Examination of the range of selenium contents of selenite and selenate crops shows the rather small variations found in rye grass grown on the different soils. The highest selenium contents of the first selenite crops on mineral soils were around 0,5 mg/kg, while the lowest were more than 0,1 mg/kg, in other words a four-fold difference. In the corresponding selenate crops the highest selenium content was 10 mg/kg and the lowest 3 mg/kg, a more than three-fold difference. The highest selenium content of each selenite and selenate crops grown on both mineral and organogenic soils was 2,6 to 6 times greater than the lowest selenium content.

The selenium uptake, calculated as yield x selenium content of the crop, had a mean value of 0,05–0,06 $\mu\text{g}/\text{pot}$ for pots containing mineral soil without added selenium, i.e. a mean of 0,19 $\mu\text{g}/\text{pot}$ for the three crops together. For the selenite pots, the mean uptake of selenium by the first crop was 0,98 $\mu\text{g}/\text{pot}$, i.e. about 1 % of the selenium added. The second and third crops together took up 0,85 % of the added selenium, which means that the three selenite crops had accumulated an average of 2 % of the added selenium. In the case of mineral soils treated with selenate, the mean uptake by the first crop was 30,5 $\mu\text{g}/\text{pot}$, by the second crop 8,5 $\mu\text{g}/\text{pot}$ and by the third crop 4,9 $\mu\text{g}/\text{crop}$, i.e. a total of about 44 % for the three crops together.

The uptake of selenium by rye grass from organogenic soils was of the same order of magnitude as from mineral soils for both control and selenite pots. However, the first crop of rye grass grown on organogenic soils treated with selenate took up less selenium than the corresponding crop grown on mineral soils. This is largely due to the fact that the average yield from the first crop on organogenic soils was much lower than that on mineral soils. The three selenate crops grown on organogenic soils together took up more than 36 % of the selenium added to the pots.

At the end of the growing part of the experiment the following amounts of the selenium added to the pots were extracted from the mineral soils by hot water:

Treatment	Se ng/g dry soil		Se $\mu\text{g}/\text{pot}$	
	\bar{x}	s	\bar{x}	s
No selenium added	6,4	3,7	5,0	2,5
Selenite	12,9	5,3	5,4	2,8
Selenate	42,5	15,0	28,7	8,8

The crops grown in the pots to which selenate was added had taken up 44,0 % of the selenium added, and a further 28,6 % was obtained from the remaining soil by extraction into hot water, together accounting for 72,6 % of the selenium added. Only 2 % of the selenite added was removed by the crops, while a further 5 % was extracted into hot water.

The corresponding figures for the organogenic soils were:

Treatment	Se ng/g dry soil		Se $\mu\text{g}/\text{pot}$	
	\bar{x}	s	\bar{x}	s
No selenium added	12,7	4,5	5,3	2,3
Selenite	25,5	7,1	4,7	2,2
Selenate	107,6	55,2	37,3	17,8

The amounts of selenium extracted per pot were about the same as those obtained for mineral soils. The mean selenium uptake by the plants accounted for 36,3 % of the selenate added, and a further 37,3 % was extracted from the soils into hot water, in other words 73,6 % of the selenium added to the pots was accounted for by measurement. This figure is very close to that obtained in the case of mineral soils.

To obtain an idea of the effects of the physical and chemical properties of the experimental soils on the selenium content of rye grass, multiple regression analyses were performed for the mineral soils. No such analysis was performed for the organogenic soils since there were only 17 samples.

As there were two control pots, two selenite pots and two selenate pots for each of the mineral soil samples, the mean values of the determinations carried out for parallel pots were used in the regression analysis. The following independent variables were used in the attempt to explain the selenium content (Y) of each crop:

x_1 = organic carbon content, % of dry (105 °C) soil

x_2 = clay fraction content, % of dry soil

x_3 = soil pH(CaCl₂) before the experiment

x_4 = iron extractable from soil into acid ammonium oxalate solution, mg/kg dry soil

x_5 = aluminium extractable from soil into acid ammonium oxalate solution, mg/kg dry soil

In addition to the above, the following variables were used in the attempt to explain the selenium present in the crops from the control pots:

x_6 = total selenium content of soil, mg/kg dry soil

x_7 = selenium extractable from the soil into hot water prior to start of experiment, mg/kg dry soil

Multiple regression analyses were performed using a stepwise "New Regression" program (JENKINS 1981). Variables with an F value in the equation significant at least the 5 % level were chosen for the equation model. In no cases was the absolute value of the correlations between the independent variables selected for the equations greater than 0,70, this being the value of the correlation between the iron content of the soil extractable into acid ammonium oxalate solution and the soil clay fraction content.

None of the variables selected significantly explained the variations in the selenium content of the crops from the control pots.

The iron extractable into acid ammonium oxalate solution explained 41,6 % of the variations in the selenium content of the first selenite crop ($R^2 = 0,416$, $F = 33,47^{***}$) and 36,8 % of the variations in the selenium content of the second selenite crop ($F = 27,40^{***}$) (Table 4).

The clay fraction content of the soil explained 24,4 % of the variations in the selenium content of the third selenite crop ($F = 15,19^{***}$). The organic carbon content of the soil explained 10,5 % of the variations in the selenium content of the first selenate crop ($F = 5,518^*$). The pH(CaCl₂), acid ammonium oxalate extractable aluminium and the organic carbon content of the soil together explained 45,2 % of the variations in the selenium content of the second selenate crop ($F = 12,36^{***}$):

$$Y = 3,45 - 0,391x_3 + 0,246 \times 10^{-3}x_5 - 0,139x_1$$

$$R^2 = 0,452$$

S (standard error of estimate of the regression equation) = 0,453

n (number of samples) = 49

The soil pH(CaCl₂) explained 16,3 % of the variations in the selenium content of the crop, organic carbon content of the soil explained 22,2 % and acid ammonium oxalate extractable aluminium 23,5 % (Table 4).

Table 4. Coefficients of partial correlation between plant selenium content (mg/kg dry matter) of selenite and selenate yields and soil variables in 49 mineral soil.

Selenium added, crop		Fe (mg/kg)	Al (mg/kg)	pH(CaCl ₂)	Org. C (%)	Clay (%)	R ² (%)	F
Selenite	I	-0,645***	—	—	—	—	41,6	33,47***
"	II	-0,607***	—	—	—	—	36,8	27,40***
"	III	—	—	—	—	-0,494***	24,4	15,19***
Selenate	I	—	—	—	-0,324*	—	10,5	5,518*
"	II	—	0,485***	-0,404**	-0,471***	—	45,2	12,36***
"	III	—	0,557***	-0,492***	-0,446***	—	54,5	17,98***

*** P = 0,001, ** P = 0,01, * P = 0,05

Soil pH(CaCl₂), acid ammonium oxalate extractable aluminium, and organic carbon content of the soil explained 54,5 % of the variations in the selenium content of the third selenate crop (F = 17,98***), i.e. the same variables as in the case of the second crop:

$$Y = 2,40 - 0,311x_3 + 0,185 \times 10^{-3}x_5 - 0,812x_1$$

$$R^2 = 0,545$$

$$S = 0,282$$

$$n = 49$$

Soil pH(CaCl₂) explained 24,2 % of the variations in the selenium content of the crop, organic carbon content of the soils explained 19,9 % and acid ammonium oxalate extractable aluminium 31,6 % (Table 4).

Addition of selenite or selenate had no effect on the yields of rye grass obtained. However, the selenium content of the crops was lower the higher the yield. The yields correlated best with the soil pH(CaCl₂):

Crop		r
Selenite crop	I	0,420**
"	II	0,468***
"	III	0,518***
Selenate crop	I	0,424**
"	II	0,612***
"	III	0,537**

Since the physical and chemical properties of the soil affect the selenium content and yield of rye grass, and since this latter also affected the selenium content of the crop, it would have been extremely difficult to explain the uptake of selenium by the crops. Instead, an effort was made to explain the selenium content of the crops by including the yield (x₆, g/pot) alongside variables x₁ — x₅. Inclusion of the yield as an independent variable significantly raised the coefficient of determination (Table 5).

Yield and acid ammonium oxalate extractable iron together explained 63,7 % of the variations in the selenium content of the first selenite crop (F = 40,35***) and 47,7 % of the variations in the selenium content of the second selenite crop (F = 20,94***). Yield, soil pH(CaCl₂) and clay fraction together explained 43,1 % of the variations in the selenium content of the third selenite crop (F = 11,35***).

Yield and organic carbon content of the soil together explained 23,8 % of the variations in the selenium content of the first selenate crop (F = 7,167**). Yield, acid ammonium oxalate extractable aluminium and organic carbon content of the soil together explained 62,7 % of the variations in the selenium content of the second selenate crop (F = 25,21***) and 74,4 % of that of the third selenate crop (F = 43,67***).

DISCUSSION

The selenium contents of the rye grass grown in the selenite pots were surprisingly low. One of the reasons for this could be the way in which the selenium solution was applied to the surface of the soil.

During the experiment a total of 10–20 l of water was added to each pot, so that the selenium was leached downwards by an amount of water equivalent to a water column of 1–2 m. In a laboratory experiment carried out by YLÄRANTA (1982) water equivalent to 500 mm of rain was added to clay soil, fine sand and peat soil. The leaching of both selenite and selenate through 20 cm high columns of clay and fine sand during the three-month experiment was negligible. On the other hand, 7 % of the selenium added in the form of selenite to unlimed *Carex* peat passed through the soil.

In the present pot experiment the selenium content of the rye grass crops grown on organogenic soils was little higher than that of crops grown on mineral soils. It is thus clear that the addition of selenite to the surface of the soil could not have had any great effect on the final result of the experiment. This is confirmed by the fact that the roots of the rye grass were extremely evenly spread throughout the soil sample. In addition, the hot water extraction carried out at the end of the experiment indicated that much of the selenium added in the form of selenite was bound to the soil in a form that was poorly available to the plants. Adding selenium to the surface of the soil samples could hardly have had any importance in terms of the uptake of selenium from readily soluble selenate.

The high selenium contents found in the first selenate crop, up to 10 mg/kg dry matter, did not cause a decrease in the yield. It has been reported that the yield of barley only begins to fall when the selenium content exceeds 30 mg/kg dry matter (DAVIS et al. 1978). On the other hand, PRASAD and ARORA (1980) re-

ported that the dry matter yield of rice fell when the selenium content exceeded 2 mg/kg, while TRIPATHI and MISRA (1974) reported the same finding for wheat, mustard and bean.

The rapid fall-off in selenium contents in the second and third crops compared with the first indicates that a single addition of selenium does not produce plants with a consistent selenium content. In view of the fact that the variations in the selenium contents of the crops cut from pots to which selenium was added were comparatively small, a suitable chosen addition of selenate would probably not produce selenium contents toxic to animals. However, the addition would have to be made to each crop individually.

The results of this study only concern the uptake of selenium by Italian rye grass, of course. Grasses usually contain less selenium than other plants (PATEL and MEHTA 1970, WALKER 1971, KOLJONEN 1974, TRIPATHI and MISRA 1974). According to BISBJERG (1972) there is an average ten-fold variation in the selenium contents of different plant species. The highest selenium contents are found in plants of the *Cruciferae* and *Papilionaceae* families. In many field experiments the residual effect of selenium addition on the following crop and on the crops of the next years has been found to decrease rapidly, irrespective of whether the selenium was added in the form of selenite or selenate, either together with fertilizer or sprayed onto the plants (GRANT 1965, DAVIES and WATKINSON 1966, GISSEL-NIELSEN 1977, KORKMAN 1980, GUPTA et al. 1982).

In the present experiment 100 µg of Se was added per 900 ml of soil. Since the 20 cm plough layer of one hectare of agricultural land contains 20 million litres of soil, the selenium addition corresponds to 220 g of added selenium per hectare. It should also be pointed out that in a pot experiment, plants usually

take up the different elements from the soil more effectively than they do under normal agricultural conditions. On the other hand, the yield per unit area obtained from a pot experiment is higher than that obtained in the field. For example, the highest dry matter yields per pot in this study were 7 g, which corresponds to a yield of 7000 kg per hectare. The electrical conductivity of the soil in the pots at the end of the experiment in no case exceeded 6×10^{-2} S/m analysed according to SIPPOLA and TARES (1978), while the pH(CaCl₂) had fallen by an average of only 0,2 pH(CaCl₂) units. Since visual inspection of the plants also failed to reveal any abnormalities, the amount of fertilizer applied was apparently neither too high nor too low, nor was the fertilizer incorrect in any other respect. Viewed in this light, the selenium contents of the crops can be compared to those prevailing under actual farming conditions.

More than 30 % of the selenium added in the form of selenate to pots containing mineral soils was found in the first crop. The high uptake of selenium by the first crop thus adversely affected the chances of the next crops taking up large amounts of selenium. However, the three crops took up a total of 44 % of the selenium added in the form of selenate. If the selenium extracted into hot water at the end of the experiment is included, a total of 73 % of the selenium added to the pots as selenate was measured. The total selenium measured from pots containing organogenic soil treated with selenate was about the same. In view of the fact that parts of the rye grass above the ground, and all of the plants below the ground were excluded from the analysis, the selenium in the form of selenate can be said to be readily available to plants.

The corresponding analysis of selenium added in the form of selenite revealed only one tenth of that added, which indicates that this selenium was in a form that was not readily available to the plants. In a pot experiment

carried out by GISSEL-NIELSEN and HAMDY (1978) six crops of Italian rye grass grown on five acid and neutral mineral soils with natural selenium contents of 0,14—0,58 mg/kg and clay fraction contents no greater than 18 % took up a total of 5—7 % of the corresponding addition of selenium. In contrast to the present study, GISSEL-NIELSEN and HAMDY (1978) found the highest selenium contents of 0,15—1,2 mg/kg dry matter to be contained in the second, third or fourth crops. In addition, a considerable proportion of the selenium found in the rye grass (20—40 %) was derived from the soil's native selenium.

Large amounts of sulphur in the form the sulphate have been shown to drastically reduce the uptake of selenium from selenate by plants (GISSEL-NIELSEN 1973). The fertilizer given to the first rye grass crop contained 36 mg of sulphur per pot in the form of potassium sulphate, while the second and third crops received 30 mg per pot. The high uptake of selenium by the rye grass from the added selenate shows that the uptake has not been greatly affected by the amounts of sulphur added as sulphate during the experiment; the amounts of sulphur were adequate for the needs of the plants.

The native selenium content of soil is usually higher in clay soils than in coarse mineral soils (YLÄRANTA 1983 c). According to GISSEL-NIELSEN (1975) the uptake of selenium by plants from the soil's native selenium reserves increases as the clay fraction of the soil increases. In this study the selenium contents and their variations in the rye grass crops were very small in the case of pots to which no selenium was added. This was one reason why no close correlation was obtained between the clay fraction content of the soil or the other independent variables and the selenium content of the rye grass.

The selenium contents of the first and second rye grass crops were closely negatively correlated with the soils' contents of acid

ammonium oxalate extractable iron (Tables 4 and 5). This is not surprising in view of the fact that the selenites fix strongly with the active iron oxides in the soil. In fact the main poorly soluble selenium compounds in the soil are $\text{Fe}_2(\text{SeO}_3)_3$ and $\text{Fe}_2(\text{OH})_4\text{SeO}_3$ (ALLAWAY et al. 1967, GEERING et al. 1968).

The tendency of the clay fraction of the soil to fix selenite applied as fertilizer (GISSEL-

NIELSEN 1971, YLÄRANTA 1983 b) became evident in the third selenite crop. The soil $\text{pH}(\text{CaCl}_2)$ explained 12,6 % of the variations in the selenium content of the third selenite crop (Table 5). This is perhaps explained by the fact that the rise in the soil pH has rendered the added selenite more soluble and hence more readily available to the plants (YLÄRANTA 1983 b).

Table 5. Coefficients of partial correlation between plant selenium content (mg/kg dry matter) of selenite and selenate yields, both soil variables, and yields in 49 mineral soils.

Selenium added, crop		Yield (g/pot)	Fe (mg/kg)	Al (mg/kg)	pH(CaCl ₂)	Org. C (%)	Clay (%)	R ² (%)	F
Selenite	I	-0,615***	-0,716***	—	—	—	—	63,7	40,35***
"	II	-0,414**	-0,608***	—	—	—	—	47,7	20,94***
"	III	-0,491***	—	—	0,355**	—	-0,406**	43,1	11,35***
Selenate	I	-0,385**	—	—	—	-0,351**	—	23,8	7,167**
"	II	-0,656***	—	0,498***	—	-0,374**	—	62,7	25,21***
"	III	-0,758***	—	0,517***	—	-0,325*	—	74,4	43,67***

*** P = 0,001, ** P = 0,01, * P = 0,05

The selenium content of the first selenate crop showed a close negative correlation with the organic carbon content of the soil, but no other close correlations. This poor explanation of the variation in the selenium content of the crop was presumably due to the high solubility of selenate in the soil. Many chemical reactions take place only slowly. Hence the tendency of organic matter to fix selenate (CARY et al. 1967, HAMDY and GISSEL-NIELSEN 1976) is more apparent in the second and third crops, in which the organic matter content of the soil explained 22 % and 20 % of the variations in the selenium content of the rye grass, respectively (Table 4).

The significance of the soil $\text{pH}(\text{CaCl}_2)$ in explaining the selenium content of the plants of the second and third selenate crops was about the same as that of the organic carbon content (Table 4). This observation is not valid, however, as $\text{pH}(\text{CaCl}_2)$ was not included in the model equation, while the yield, which

explained 43,0 % and 57,5 % of the variations in the selenium content of the second and third selenate crops, respectively, was included as an independent variable (Table 5). The soil $\text{pH}(\text{CaCl}_2)$ correlated closely with the yield. An increase in the dry matter yields, however, resulted in a decrease in the selenium contents of the crops.

The close positive correlation between the content of aluminium extractable into acid ammonium oxalate solution and the selenium content of the second and third selenate crops is difficult to explain. In a study carried out by YLÄRANTA (1983 c) the total selenium content of Finnish agricultural soils was found to correlate closely with the acid ammonium oxalate extractable aluminium in the soil. It can be concluded from this that the active aluminium oxides would also fix selenite and selenate added to the soil. The results of this study, however, suggest that this is not the case.

Examination of the independent variables chosen for the regression equations to explain the selenium contents of the crops (Tables 4 and 5) shows a drop in the coefficient of determination from the first selenite crop to the third, but a rise in the coefficient of determination from the first selenate crop to the third. This may be due to the conversion of the

selenite added to the pots into a form that is poorly available to the plants, to a decrease in the amount of readily soluble selenate and to the conversion of the selenium from selenate into a form that is poorly available to the plants, in which case the physical and chemical properties of the soil have a greater effect.

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SELOSTUS

Maahan lisätyn seleniitin ja selenaanin vaikutus Italian raiheinän (*Lolium multiflorum*) seleenipitoisuuteen

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Lisäämällä maahan tai kasvustoon seleniitti- ja selenaatisuoloja voidaan viljelykasvien seleenipitoisuutta kohottaa. Kasvit ottavat maan kautta selenaatiseleeniä jopa kymmenen kertaa tehokkaammin kuin seleniittiseleeniä. Niinpä on pelätty kasvien seleenipitoisuuden saattavan kohota eläinten kannalta myrkyllisen korkeaksi, mikäli lannoituksessa käytettäisiin selenaatisuoloja. Kasvien seleniittiseleenin hyväksikäyttö on kuitenkin Suomessa ja ulkomailla suoritetuissa kenttäkokeissa ollut hyvin vähäistä. Tämän vuoksi oli tarpeen selvittää yhtenäisissä olosuhteissa, kuinka kasvi ottaa maahan lisättyä seleniitti- ja selenaatiseleeniä erilaisista viljelymaista, jotta voitaisiin paremmin arvioida selenaatisuolojen käyttöä viljelykasvien seleeninlähteenä.

Astiakokeessa tutkittiin Italian raiheinän seleenin ottoa 49 kivennäismaasta ja 17 eloperäisestä maasta, joihin oli ensimmäiselle sadolle lisätty seleeniä natriumseleniittinä tai selenaatina 100 µm/900 ml maata. Kokeessa korjattiin kolme satoa.

Ensimmäinen kivennäismaiden seleniittisato sisälsi seleeniä keskimäärin 0,2 mg/kg kuiva-ainetta ja selenaatiasato 6 mg/kg. Ensimmäinen sato oli ottanut selenaatiasioista keskimäärin 30 % ja seleniittiasioista 1 % lisätystä seleenistä. Seleeniäisyksien vaikutus raiheinän seuraaviin satoihin oli vähäinen: kolmas selenaatiasato sisälsi vain kuudennen osan ja kolmas seleniittiasato kolmannen osan ensimmäisen sadon seleenipitoisuudesta. Satojen seleenipitoisuudet ja seleenin otto olivat samaa suuruusluokkaa sekä kivennäismaissa että eloperäisissä maissa.

Kun satojen seleenipitoisuuksien vaihtelut eri maissa olivat melko vähäisiä, voidaan sopivasti valitulla selenaatiseleenillä tuottaa seleenipitoisuudeltaan halutunlaista kasviainesta. Selenaatiseleeni olisi kuitenkin annettava jokaiselle sadolle erikseen.

EFFECT OF LIMING AND SULPHATE ON THE SELENIUM CONTENT OF ITALIAN RYE GRASS (*LOLIUM MULTIFLORUM*)

TOIVO YLÄRANTA

YLÄRANTA, T. 1983. Effect of liming and sulphate on the selenium content of Italian rye grass (*Lolium multiflorum*). Ann. Agric. Fenn. 22: 152—163. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

The effect of liming and application of large amounts of sulphur, S 200 and 400 mg/l of soil in the form of sulphate, on the selenium content of Italian rye grass (*Lolium multiflorum* Lam.) grown on clay soil, fine sandy soil and Carex peat with naturally low selenium contents was studied in two pot experiments. Selenium was added to the first crop in the form of either sodium selenite or selenate and sulphur in the form of calcium sulphate.

The first rye grass crop took up 10—30 times more selenium from selenate than from selenite. Even the highest selenium contents, 30 mg/kg of dry matter, had no effect on the yield. Liming had little effect on the selenium content of the plants. Addition of sulphate had no effect on the selenium content of the rye grass grown on any of the soils when selenium was added to the soil in the form of selenite. On the other hand, the selenium content of the first crop grown of Carex peat soil in pots treated with selenate was only one fourth of that of rye grass grown without added sulphur or liming.

Index words: selenite and selenate application, liming, sulphate addition, selenium content of Italian rye grass.

INTRODUCTION

The selenium content of plants can be raised by adding selenites or selenates to the soil (GISSEL-NIELSEN and BISBJERG 1970, GISSEL-NIELSEN 1977, YLÄRANTA 1983 c).

Liming can be used to increase the solubility of selenium (YLÄRANTA 1983 b) and possibly to raise the amount of selenium available to the plants in the soil. According to CARY and GISSEL-NIELSEN (1973), sulphate has no significant effect on the solubility of selenium in

the soil. However, BROWN and CARTER (1969) and CARTER et al. (1969) reported that addition of sulphate to the soil raises the solubility of selenium in the form of selenate in alkali soils. On the other hand, the addition of sulphate to the soil greatly reduces the uptake by plants of fertilizer selenate and to a small extent that of fertilizer selenite (GISSEL-NIELSEN 1973).

In field experiments carried out in Finland,

plants have taken up only very small amounts of the selenium added to the soil in the form of selenite (SYVÄLAHTI and KORKMAN 1978, KORKMAN 1980). A pot experiment carried out by YLÄRANTA (1983 c) has, in fact, shown that Italian rye grass (*Lolium multiflorum* Lam.) takes up selenium from selenate in various

agricultural soils up to 30 times more effectively than selenite. The experiment did not examine the effect of liming and large amounts of sulphate on the selenium content of the plants, and this is thus the main aim of the present study.

MATERIAL AND METHODS

This study involved two pot experiments, the first of which (A) was carried out in 1979 and the second (B) in 1980. The soils used in experiment A were clay and fine sand, and these in experiment B clay and Carex peat. The clay soil contained 62 % of clay fraction $\text{Ø} < 0,002$ mm and 17 % fine sand. The Carex peat had a degree of humification of H_3 on the von POST scale and contained 8,6 % inorganic matter as determined by ignition at 500 °C. The clay soil contained 4,0 % organic carbon and the fine sand 2,2 %. The pH (CaCl_2) of the clay soil was 4,7 of the fine sand 4,9 and of the Carex peat 3,9. The determination of the physical and chemical properties of the experimental soils is described in detail in a previous publication (YLÄRANTA 1982). The natural selenium content of the clay soil was 0,37 mg/kg, of the fine sand 0,17 mg/kg and of the Carex peat 0,39 mg/kg (YLÄRANTA 1983 b).

One-litre polythene pots were used in both experiments. There were four replicates, the plan being as follows:

- S₀Ca₀ Control
- S₀Ca Liming
- SCa₀ Addition of sulphate
- SCa Liming and sulphate addition

In experiment A, 1100 g of air-dried clay soil and 1300 g of fine sand ($\text{Ø} \leq 2$ mm) were weighed out per pot. The depth of the soil in the pot was 10–11 cm. In experiment A there were three selenite additions for each soil type,

plus the controls, making a total of 128 pots. In experiment B, 900 g of clay soil and 170 g of Carex peat were weighed out per pot. In addition to the controls, this experiment also involved two additions of selenite and two of selenate, thus giving a total of 160 pots for the two soil types.

The liming (1), sulphate addition (2) and selenite (3) and selenate (4) additions were as follows:

	Experiment A		Experiment B	
	Clay	Fine sand	Clay	Carex peat
1. $\text{Ca}(\text{OH})_2$, g/pot	6,5	3,0	5,32	2,76
2. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, S mg/pot	200	200	400	400
3. Na_2SeO_3 , Se mg/pot	0, 0,1, 1, 10		0, 0,01, 0,1	
4. Na_2SeO_4 , Se mg/pot	—	—	0, 0,01, 0,1	

Liming was of the same magnitude in both experiments A and B, calculated per unit mass of soil. The purpose of liming was to raise the pH (CaCl_2) of the soils by around 1,5 pH units (YLÄRANTA 1982). Sulphur was added in the form of calcium sulphate as calcium is the most common exchangeable basic cation in the soil, and thus exerts the minimum effect on the experimental conditions. The amount of sulphur added as sulphate in experiment B was 400 mg, since the addition of 200 mg in the earlier experiment A had no effect on the selenium

content of the rye grass.

The $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ powder added to provide a source of phosphorus (P 100 mg/pot), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ was mixed carefully with the air-dried soil.

Forty seeds of Italian rye grass (*Lolium multiflorum* Lam., variety Leda daehnfeldt) were planted in each pot. The seeds were covered with a thin layer of the experimental soil. Finally, a layer of 200 g of quartz sand (\varnothing 0,2—0,5 mm) washed in 6 M HCl was placed on top of the soil, forming a layer about 1 cm deep. The water holding capacity of the soils corresponding to a water column of 100 cm was determined in 250 ml glass filter funnel (Schott & Gen. G 4) from two parallel samples. Over a period of five days the soils were watered to this pF value of 2, at which the clay soil contained 53 % (w/w) water, the fine sand 24 % water and the Carex peat 150 % water.

Four days after planting, the seedlings appeared and the pots were transferred outdoors to a growing frame. Seven days after planting, the seedlings were thinned to 30 per pot. Ten days after planting, each pot was treated with 10 ml aqueous Na_2SeO_3 solution (Merck, product number 6607) or 10 ml aqueous Na_2SeO_4 solution (BDH 10262).

Fertilizer was applied to the pots on the day following addition of selenium as follows:

Nutrient	mg/pot	Compound
N	240	NH_4NO_3
K	150	KCl
Mg	40	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Ca	30	CaCl_2
Fe	1	FeNa-EDTA
Mn	2	MnCl_2
Cu	2	CuCl_2
Zn	1	ZnNa ₂ -EDTA
B	0,3	H_3BO_3
Mo	0,3	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$

The chemicals applied as fertilizer and the other chemicals used in the experiment were

analytical grade chemicals supplied by Merck, Baker and BDH.

The pots were watered daily with deionised water to a moisture content corresponding to pF 2. The pots were weighed at every second watering and their position changed with respect to each other. No rain fell on the pots, since at night and when rain threatened they were covered with polythene sheet intended for covering greenhouses.

The first crop was cut at the silage stage four weeks after the seed had been sown. The shoots were cut with scissors leaving about 1,5 cm of stubble, and the crop dried in paper bags in ovens provided with air circulation (Memmert Tv80uL) for four days at 50 °C.

The following nutrients were added to each pot the day after cutting the first crop: N 150 mg, K 100 mg, Mg 25 mg and Ca 30 mg. The second crop was cut three weeks after the first, and was given the same treatment. Application of N, K, Mg and Ca fertilizers for the third crop was carried out as for the second crop. In addition each pot received 50 mg of phosphorus in the form of KH_2PO_4 . The third crop also received the same micronutrients as the first crop. Each pot in experiment B was also given 30 mg of sulphur in the form of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, since the second crop was small in those pots to which CaSO_4 was not added. The plants were also much paler, which suggests sulphur deficiency. A similar addition of sulphur was made to the fourth crop in experiment A for the same reasons.

Four crops were cut in experiment A and three crops in experiment B. The fourth crop of experiment A received N, K, Mg, P and Ca as for the third crop. The third and fourth crops were cut about three weeks after the preceding crops. The duration of experiment A from sowing the seeds to cutting the last crop was 102 days, while that for experiment B was 73 days.

Most of the rye grass grew during the period June-August. The mean temperatures for the

months during which the experiments were carried out were roughly the same in both years, although the mean temperatures for July and August were lower in 1979. In 1980 the mean temperature for June at the experimental site was 17 °C (4–27 °C), in July 17 °C (7–29 °C) and in August 15 °C (3–29 °C).

Apart from the suspected sulphur deficiency, no abnormalities were observed in the plants. Since the growth was intensive and carried out in small pots, great care was taken to avoid any errors in the application of fertilizer. The effect of fertilizer application was checked by including extra control pots, from which soil samples were determined for pH(CaCl₂) and electrical conductivity after cutting each crop.

At the end of the two experiments the contents of the pots were removed and the pH(CaCl₂) values determined. The selenium content of the soils in experiment A was determined by extraction into 0,01 M KH₂PO₄ solution, and that of the experiment B soils by

extraction into hot water. In experiment A the selenium extractable into 0,01 M KH₂PO₄ solution was obtained by shaking 10 ml of soil with 100 ml of the extractant for 2 hours. The hot water extraction was carried out by boiling 25 ml of soil with 100 ml of water for 30 min (YLÄRANTA 1982).

The selenium contents of the filtrates from hot water extraction and of each plant sample were determined using the hydride method (YLÄRANTA 1983 a). The measuring equipment used in experiment A was a Varian Techtron 1250 atomic absorption spectrophotometer and in experiment B a Perkin Elmer 5000.

Statistical analysis of the results was carried out using a VAX-11/780 data processing system with an SPSS software "Manova" programme (BURNS 1981).

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

RESULTS

The average dry matter yields per pot obtained on the clay and fine sand used in experiment A varied from 3,5 g to 6 g. Not even the highest selenium contents found for the rye grass (20–30 mg/kg dry matter) had reduced the size of the yield. The third crop grown on clay soil in pots given neither lime nor sulphur was only 2,5 g/pot, compared with 5 g/pot for the other pots, presumably because of the sulphur deficiency. No such deficiency was found in the pots that received lime, which means that liming had increased the amount of sulphur available to the plants through the soil. The sulphate added to the fourth crop brought the yield back up to the level of the other pots, and there were only very occasional statistically significant differences in the size of the yield.

The size of the first crop grown on both clay

and fine sand was less on average than that of the other crops. There were fewer statistically significant differences in yield on the fine sand than on clay. For example, no reduction in yield that could have been due to sulphur deficiency was observed. However, liming reduced the yield of the second crop grown on fine sand from an average of 5,3 g/pot to 4,4 g/pot. No significant differences were found in the third and fourth crops.

In the pots to which no selenium was added the mean selenium contents of the crops grown on clay and fine sand varied between 0,017 mg/kg and 0,040 mg/kg (Tables 1 and 2). The highest selenium contents were found in the first crop. None of the crops exhibited any statistically significant differences in selenium contents between the different treatments.

Table 1. Mean selenium contents of rye grass crops on clay soil in experiment A, mg/kg dry matter. Figures given for the different crops for each selenite addition not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Crops	Treatments	Se 0 mg/pot	Se 0,1 mg/pot	Se 1,0 mg/pot	Se 10 mg/pot
I	S ₀ Ca ₀	0,034 ^a	0,412 ^a	2,71 ^a	21,2 ^a
	S ₀ Ca	0,035 ^a	0,486 ^a	3,00 ^a	21,6 ^a
	SCa ₀	0,038 ^a	0,488 ^a	2,66 ^a	20,2 ^a
	SCa	0,039 ^a	0,474 ^a	3,12 ^a	19,3 ^a
II	S ₀ Ca ₀	0,021 ^e	0,076 ^e	0,436 ^e	4,11 ^e
	S ₀ Ca	0,020 ^e	0,081 ^e	0,412 ^e	3,70 ^e
	SCa ₀	0,020 ^e	0,095 ^e	0,466 ^e	3,67 ^e
	SCa	0,029 ^e	0,101 ^e	0,545 ^e	4,20 ^e
III	S ₀ Ca ₀	0,024 ^k	0,059 ^k	0,564 ^k	3,72 ^k
	S ₀ Ca	0,024 ^k	0,056 ^k	0,447 ^k	2,64 ^k
	SCa ₀	0,025 ^k	0,075 ^k	0,401 ^k	3,05 ^k
	SCa	0,023 ^k	0,072 ^k	0,460 ^k	2,97 ^k
IV	S ₀ Ca ₀	0,023 ^r	0,063 ^r	0,492 ^r	4,03 ^r
	S ₀ Ca	0,028 ^r	0,071 ^r	0,543 ^r	4,98 ^r
	SCa ₀	0,025 ^r	0,057 ^r	0,507 ^r	4,68 ^r
	SCa	0,026 ^r	0,056 ^r	0,519 ^r	4,60 ^r

The first crop grown on clay to which the least selenium was added (0,1 mg/pot) had a selenium content of 0,4—0,5 mg/kg dry matter, while the selenium contents of the second, third and fourth crops ranged between 0,06 and 0,1 mg/kg. When the selenium addition was 1,0 mg/pot, the selenium content of the first crop was 2,7—3,1 mg/kg and that of the other crops 0,4—0,6 mg/kg. In the case of the highest selenium addition (10 mg/pot) the first crop had a selenium content of 19—22 mg/kg, while that of the other crops averaged 2,6—5 mg/kg. The selenium contents of the second, third and fourth crops averaged one fifth to one sixth of the selenium content of the first crop. There were no significant differences in selenium content of the crops grown for any one particular selenium addition. This means that the selenium content of the rye grass grown on clay soil was not significantly reduced by addition of sulphate, nor was it significantly increased by liming.

The increase in the amount of selenite selenium added per pot from 0,1 mg to 10 mg did not raise the selenium content of the first

rye grass crops 100-fold, but only 50-fold. The effect of the selenium added to the first crops on the selenium content of the following crops diminished rapidly at all three levels of selenium addition. The first crop took up 1,6—1,9 % of the added selenium in the case of the lowest addition (0,1 mg/pot), while the other crops took up 0,1—0,4 %. For the 1,0 mg/pot selenium addition the first crop took up 1,0—1,1% and the other crops 0,2—0,3 %. In the case of the highest selenium addition (10 mg/pot) the first crop took up 0,6—0,7 % of the selenium and the other crops 0,1—0,3 %. Thus the second, third and fourth crops took up the same proportion of the added selenium at each of the three levels.

In experiment A the rye grass took up slightly more of the selenium added to the fine sand pots than of that added to the clay pots. The after-effect of the selenium addition on the second, third and fourth crops was also greater in the case of fine sand than clay.

For the lowest selenium addition (0,1 mg/pot) the selenium contents of the first crop grown on fine sand were 0,6—0,7 mg/kg dry

Table 2. Mean selenium contents of rye grass crops on fine sand in experiment A, mg/kg dry matter. Figures given for the different crops for each selenite addition not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Crops	Treatments	Se 0 mg/pot	Se 0,1 mg/pot	Se 1,0 mg/pot	Se 10 mg/pot
I	S ₀ Ca ₀	0,040 ^a	0,612 ^a	3,74 ^a	22,4 ^a
	S ₀ Ca	0,035 ^a	0,593 ^a	6,08 ^b	27,2 ^b
	SCa ₀	0,035 ^a	0,681 ^a	4,19 ^a	19,0 ^a
	SCa	0,036 ^a	0,705 ^a	5,59 ^b	20,8 ^a
II	S ₀ Ca ₀	0,023 ^c	0,137 ^c	0,908 ^c	9,03 ^c
	S ₀ Ca	0,021 ^c	0,165 ^c	0,986 ^c	7,42 ^c
	SCa ₀	0,022 ^c	0,157 ^c	1,21 ^f	9,25 ^c
	SCa	0,021 ^c	0,181 ^c	1,19 ^f	8,03 ^c
III	S ₀ Ca ₀	0,022 ^k	0,103 ^k	0,907 ^k	7,61 ^f
	S ₀ Ca	0,017 ^k	0,102 ^k	0,731 ^k	5,42 ^e
	SCa ₀	0,021 ^k	0,145 ^k	0,870 ^k	8,66 ^f
	SCa	0,025 ^k	0,143 ^k	0,801 ^k	5,59 ^e
IV	S ₀ Ca ₀	0,025 ^r	0,050 ^r	0,754 ^r	8,31 ^r
	S ₀ Ca	0,028 ^r	0,088 ^r	0,954 ^s	8,76 ^r
	SCa ₀	0,029 ^r	0,088 ^r	0,733 ^r	8,35 ^r
	SCa	0,029 ^r	0,079 ^r	1,027 ^s	8,18 ^r

matter, while those for the 1,0 mg/pot and 10 mg/pot additions were 3,7—6,1 mg/kg and 19—27 mg/kg, respectively. The selenium contents of the second, third and fourth crops were of the same order of magnitude at each selenium addition with the exception of the fourth crop grown with the lowest selenium addition; the selenium content of this crop averaged only 0,10—0,18 mg/kg, which is rather more than half of that for the second and third crops. The selenium contents of the second, third and fourth crops which received 1,0 mg/pot of selenium were 0,7—1,2 mg/kg, while those in pots given the highest selenium addition of 10 mg/pot were 5,4—9,3 mg/kg. The first crop had taken up 1,7—2,4 % of the smallest amount of added selenium, 1,5—1,9 % of the selenium added at the rate of 1,0 mg/pot and 0,6—0,8 % of the highest amount of selenium added. The other crops took up 0,2—0,7 % of the various selenium additions.

There were no significant differences in selenium content between the crops grown on fine sand in pots that received 0,1 mg/pot of selenium. For a selenium addition of 1,0

mg/pot the highest selenium contents of the second crop were found in pots that received added sulphate. In the first and fourth crops the highest selenium contents were found in pots that received lime. There was also a reduction in the yield due to liming. The same applied to the first crop grown with the highest selenium addition. In the third crop grown with the highest selenium addition, the lowest selenium contents were found in those pots that received lime.

The statistically significant differences in selenium content observed were not sufficiently logical or clear to permit conclusions to be drawn. Thus the selenium content of the rye grass crops was neither reduced by addition of sulphate nor increased by liming, even on fine sand.

The pH(CaCl₂) of the unlimed clay soils at the end of the experiment averaged 4,6 and that of the limed clay soils 6,3. The corresponding pH values for fine sand were 4,4 and 5,8. There were no statistically significant differences in pH values between the different treatments for either type of soil.

Table 3. Mean amounts of selenium ($\mu\text{g}/\text{pot}$) extracted from clay soil and fine sand into 0,01 M KH_2PO_4 solution at the end of experiment A. Figures given for each selenite addition not marked with a common letter differ from each other at 1 % level of significance (DUNCAN 1955).

Treatments	Se 0 mg/pot		Se 0,1 mg/pot		Se 1,0 mg/pot		Se 10 mg/pot	
	Clay	Fine sand	Clay	Fine sand	Clay	Fine sand	Clay	Fine sand
S_0Ca_0	2,9 ^a	6,5 ^k	5,3 ^a	11,6 ^k	11,9 ^a	28,5 ^k	95,5 ^a	315 ^k
S_0Ca	6,3 ^a	8,7 ^k	6,9 ^{ab}	15,5 ^k	18,1 ^b	66,3 ^l	191 ^b	488 ^l
SCa_0	5,3 ^a	7,7 ^k	8,7 ^{ab}	19,5 ^k	10,3 ^a	26,1 ^k	105 ^a	305 ^k
SCa	3,8 ^a	8,0 ^k	11,9 ^b	18,6 ^k	18,4 ^b	49,6 ^l	218 ^b	597 ^l

Liming raised the $\text{pH}(\text{CaCl}_2)$ values of the clay soil by an average of 1,7 pH units and of the fine sandy soils by 1,4 pH units. This was also seen in the pots that received the higher selenium additions (1,0 and 10 mg/pot), since at the end of the experiment the amount of selenium extracted from the limed soils into 0,01 M KH_2PO_4 solution was twice that for the unlimed soils (Table 3).

In experiment B the yields of the first crops grown on clay were 3,6—4,2 g/pot, of the second crops 4,6—5,1 g/pot and of the third crops 5,1—6,4 g/pot. There were no significant differences in yield in any crop caused by liming, sulphate addition or selenium addition.

The yields of the first crops grown on Carex peat were 2,6—3,2 g/pot, of the second crops 3,7—4,2 g/pot (with sulphate) and 3,0—3,2

g/pot (without sulphate), and of the third crops 3,9—5,1 g/pot. The addition of sulphate thus raised the size of the yield of the second crop grown on Carex peat. All pots received sulphate fertilizer prior to the third crop, and hence the differences in yield disappeared. There were no significant differences in the yields obtained from Carex peat as a result of liming or of addition of selenite or selenate. The yields obtained from the third crops in the limed pots were on average 0,5 g/pot higher than those in unlimed pots, although even this difference was not significant at the 1 % level.

In experiment B pots to which no selenium was added, the selenium contents of the crops grown on clay and peat soils varied from 0,014 mg/kg to 0,022 mg/kg of dry matter (Tables 4 and 5). On neither of these soils were there any

Table 4. Mean selenium contents of rye grass crops on clay soil in experiment B, mg/kg dry matter. Figures given for the different crops for each selenite and selenate addition not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Crops	Treatments	Se 0 mg/pot	Se 0,01 mg/pot		Se 0,1 mg/pot	
		Selenite/Selenate	Selenite	Selenate	Selenite	Selenate
I	S_0Ca_0	0,020 ^a	0,058 ^a	0,819 ^a	0,276 ^a	9,22 ^a
	S_0Ca	0,018 ^a	0,068 ^a	0,900 ^a	0,283 ^a	10,1 ^a
	SCa_0	0,020 ^a	0,072 ^a	0,796 ^a	0,401 ^b	10,3 ^a
	SCa	0,020 ^a	0,073 ^a	0,713 ^a	0,410 ^b	8,00 ^a
II	S_0Ca_0	0,017 ^k	0,020 ^k	0,132 ^k	0,091 ^k	1,62 ^k
	S_0Ca	0,017 ^k	0,021 ^k	0,138 ^k	0,086 ^k	1,51 ^k
	SCa_0	0,019 ^k	0,026 ^k	0,240 ^l	0,121 ^l	1,98 ^k
	SCa	0,019 ^k	0,019 ^k	0,167 ^k	0,095 ^k	1,62 ^k
III	S_0Ca_0	0,020 ^r	0,019 ^r	0,066 ^s	0,068 ^s	0,554 ^s
	S_0Ca	0,021 ^r	0,022 ^r	0,036 ^r	0,074 ^s	0,385 ^r
	SCa_0	0,019 ^r	0,018 ^r	0,083 ^r	0,046 ^r	0,611 ^s
	SCa	0,020 ^r	0,022 ^r	0,068 ^s	0,060 ^s	0,429 ^r

significant differences in selenium content between the various treatments.

The addition of 10 μg of selenium in the form of sodium selenite raised the selenium contents of the rye grass crops grown on clay to 0,04—0,05 mg/kg and of those grown on peat soil to 0,06—0,07 mg/kg. The corresponding addition of selenate had raised the selenium content of the first crop to 0,7—0,9 mg/kg, in other words by ten times as much as the selenite addition. There were no significant differences in selenium content between plants from different treatments in any of the crops on clay soil with addition of selenite or in the first selenite crop grown on Carex peat. The addition of sulphate had reduced the selenium content of the first selenate crop grown on Carex peat from 1,3 mg/kg to 0,2—0,3 mg/kg. The selenium contents of the first selenite crop given the highest addition of selenium (100 $\mu\text{g}/\text{pot}$) were 0,4 mg/kg for crops that received sulphate and 0,3 mg/kg for crops that received no sulphate. The selenium contents of the corresponding selenate crops were 8—10 mg/kg, without any statistically significant differences.

The selenium content of the first crop grown on Carex peat with the highest selenite

addition plus liming averaged 0,8 mg/kg; the figure for the other pots was significantly lower at 0,4—0,5 mg/kg. In the corresponding selenate crop grown on Carex peat the addition of sulphate caused the selenium content to fall from 12—13 mg/kg to one fourth of this value, i.e. to 2,6—2,9 mg/kg.

In experiment B the selenium content of the second selenite crop on clay soil had fallen in those pots given the lower selenium addition to the same level as those crops grown without added selenium, i.e. to 0,018—0,026 mg/kg. In the pots containing clay soil given the higher selenium addition the selenium content of the second selenite crop was less than a quarter of the selenium content of the first crop, while that of the third crop was about one fifth. The selenium contents of the crops grown on Carex peat fell slightly more slowly than those grown on clay soil. Thus it was not until the third crop of rye grass grown on Carex peat with the 10 μg addition of selenite selenium that the selenium content of the crop fell to 0,017—0,022 mg/kg. The selenium content of the second crop grown on Carex peat plus the higher selenite addition (Se 100 $\mu\text{g}/\text{pot}$) was 0,41—0,66 mg/kg, i.e. almost as high as the selenium content of the first crop. The

Table 5. Mean selenium contents of rye grass crops on Carex peat in experiment B, mg/kg dry matter. Figures given for the different crops for each selenite and selenate addition not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Crops	Treatments	Se 0 mg/pot		Se 0,01 mg/pot		Se 0,1 mg/pot	
		Selenite/Selenate	Selenite	Selenite	Selenate	Selenite	Selenate
I	S ₀ Ca ₀	0,022 ^a	0,081 ^a	1,25 ^b		0,441 ^a	12,1 ^b
	S ₀ Ca	0,021 ^a	0,095 ^a	1,38 ^b		0,826 ^b	13,3 ^b
	SCa ₀	0,022 ^a	0,074 ^a	0,294 ^a		0,436 ^a	2,93 ^a
	SCa	0,021 ^a	0,079 ^a	0,240 ^a		0,464 ^a	2,62 ^a
II	S ₀ Ca ₀	0,015 ^k	0,054 ^l	0,472 ^m		0,449 ^k	5,53 ^m
	S ₀ Ca	0,014 ^k	0,053 ^l	0,414 ^{lm}		0,663 ^l	4,59 ^{lm}
	SCa ₀	0,015 ^k	0,047 ^{kl}	0,330 ^l		0,409 ^k	3,74 ^{kl}
	SCa	0,016 ^k	0,041 ^k	0,220 ^k		0,487 ^k	2,63 ^k
III	S ₀ Ca ₀	0,022 ^r	0,020 ^r	0,108 ^r		0,197 ^r	0,572 ^r
	S ₀ Ca	0,019 ^r	0,022 ^r	0,090 ^r		0,208 ^r	0,479 ^r
	SCa ₀	0,020 ^r	0,021 ^r	0,178 ^s		0,217 ^r	1,45 ^t
	SCa	0,020 ^r	0,017 ^r	0,107 ^r		0,289 ^s	1,06 ^s

selenium content of the third crop was about half of this. Although there were statistically significant differences in the selenium contents of the second and third selenite crops on both soil types, the differences failed to show any consistent trend or magnitude. With the exception of the first selenate crops grown on Carex peat, it was not possible to demonstrate with any certainty the effect of either liming or addition of sulphate on the selenium contents of the rye grass crops.

For the third crop grown on Carex peat plus the higher selenate addition, the selenium content of crops given additional sulphate was

clearly higher than that of the other crops. At the end of the experiment the amount of selenium extractable into hot water from soils treated with sulphate was 20—30 $\mu\text{g}/\text{pot}$, compared with 1—2 $\mu\text{g}/\text{pot}$ for the others (Table 6). This could be partly due to the fact that since the first crop had taken up so much selenium from the soil, there was considerably less selenium remaining for the later crops to take up, with the exception of those crops treated with sulphate. The first crops on clay soil and Carex peat took up more than 40 % of the selenium added as selenate, but only 1—3 % of that added as selenite. The addition of a

Table 6. Mean amounts of selenium ($\mu\text{g}/\text{pot}$) extracted from Carex peat into hot water at the end of experiment B. Figures given for each selenite and selenate addition not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Treatments	Se 0 mg/pot		Se 0,01 mg/pot		Se 0,1 mg/pot	
	Selenite/Selenate	Selenite	Selenite	Selenate	Selenite	Selenate
S ₀ Ca ₀	1,3 ^a	1,3 ^a	1,0 ^k	1,6 ^a	1,4 ^k	1,4 ^k
S ₀ Ca	1,2 ^a	1,0 ^a	1,4 ^k	2,0 ^a	2,3 ^k	2,3 ^k
SCa ₀	1,1 ^a	1,0 ^a	3,8 ^l	2,0 ^a	28,9 ^l	28,9 ^l
SCa	1,1 ^a	1,0 ^a	4,8 ^l	3,1 ^b	35,4 ^l	35,4 ^l

large amount of sulphate may also have increased the amount of selenium available to the plants, as the selenium contents of the plants grown in pots to which sulphate was added, including the first crop grown on clay soil given the higher selenite addition, were significantly higher than those for the other pots. At the end of the experiment the amounts of selenium extractable into hot water from the clay soil were only 50 % higher in pots given the lower selenium addition and 100 % higher in pots given the higher selenium addition than the corresponding figures for pots to which no selenium was added. There were no statistically significant differences in the amounts of selenium extracted (3—8 $\mu\text{g}/\text{pot}$) from the various clay soil treatments.

The selenium contents of the selenate crops grown on both clay soil and Carex peat fell much more rapidly than the selenium contents of the selenite crops. The selenium content of the first crop grown on clay soil with the lower selenate addition (10 $\mu\text{g}/\text{pot}$) was 0,7—0,9 mg/kg, but fell to 0,13—0,24 mg/kg in the second crop and to 0,04—0,08 mg/kg in the third crop. The second selenate crop grown on clay soil treated with the higher selenium addition contained 1,5—2,0 mg Se/kg, which is about one sixth of that of the first crop. The third crop contained only about one twentieth of the selenium content of the first crop. The average selenium contents of the second and third selenate crops grown on Carex peat were clearly greater than those grown on clay soil.

The mean pH(CaCl₂) value for unlimed clay soils at the end of the experiment was 4,6, while that for limed clay soils was 6,1. The corresponding pH values for the Carex peat

soils were 3,6 and 5,1. Liming thus raised the pH(CaCl₂) values of each soil type by 1,5 pH units.

DISCUSSION

Plants take up selenate more rapidly and in larger amounts than selenite (ASHER et al. 1977, YLÄRANTA 1983 c). Sulphate has been reported to inhibit the uptake by plants of selenate selenium (BROWN and SCHRIFT 1982). However, according to the study by ASHER et al. (1977) excess sulphate had no detectable effect on the selenate component of selenium transport in selenite-fed plants. In the tentative model for the selenium transport in tomato root systems ASHER et al. (1977) propose that oxidation of selenite to selenate is an essential feature of the absorption and long-distance transport of selenite selenium.

If sulphate really does reduce the uptake by plants of selenate selenium to the extent reported (e.g. GISSEL-NIELSEN 1973), any attempt to raise the selenium content of cereal crops by applying selenates to the soil would be rather risky. However, even the high amounts of sulphate added in this experiment, corresponding S to 200—400 mg/litre of soil, do not appear to adversely affect the uptake of selenite or selenate selenium in mineral soils. On the other hand, large amounts of sulphate may reduce the uptake of selenate selenium from certain organogenic soils. FLEMING (1962) also found that superphosphate added to naturally seleniferous peat soil decreased the selenium content of the herbage. However, the role of the calcium sulphate present in the superphosphate in reducing the selenium contents of the plants was not established. WILLIAMS and THORNTON (1972) have reported conflicting results for the uptake of selenium by perennial rye grass and red clover from two acid peat soils (Se 93 and 230 mg/kg). In their study

ammonium sulphate and elemental sulphur markedly reduced the selenium content of herbage. Potassium sulphate, on the other hand, raised the selenium content of the plants.

In Finland, organogenic soils with sulphate contents high enough to interfere with the uptake of selenate selenium by plants under favourable oxidation conditions are found in certain areas along the coast of the Gulf of Bothnia. However, these account for only a small proportion of Finland's agricultural land, so that any problem arising during application of selenate fertilizer due to sulphate would be very localised.

The NPK compound fertilizers normally used in Finland are supplemented with 2—11 % sulphur, which has usually proved to be a sufficient source of sulphur for the plants. In certain studies conducted outside Finland, in which there has apparently been a reduction in the selenium content of plants due to application of sulphate, there has in fact been a need of sulphur fertilization (DAVIES and WATKINSON 1966, PERDOMO et al. 1966, WESTERMANN and ROBBINS 1974). While sulphur fertilizer raised the yield, the selenium content of the crop fell, though without reducing the uptake of selenium by the plants. 30 mg of sulphate sulphur per litre of soil was applied to the fourth crops in experiment A of this study and to the third crops of experiment B in order to rectify the obvious sulphur deficiency. This amount of sulphur was sufficient to bring the dry matter yields up to the same size. No changes in the selenium contents of the rye grass were observed, however.

The addition of sulphate may even increase

the uptake of selenate selenium on alkali soils, since large amounts of sulphate can increase the amount of selenium available to the plants in the soil (CARTER et al. 1969). In the present study, the selenium content of the third rye grass crop grown on *Carex* peat to which 10 $\mu\text{g}/\text{pot}$ of Se was added as sodium selenate increased as a result of addition of sulphate as well as liming and sulphur addition. The most

likely reason for this was the large amount of available selenium in these treatments resulting from the low selenium uptake by the other crops. Although liming has been shown to increase the amount of readily soluble selenium in the experimental soils used in this study (YLÄRANTA 1983 b), it had no effect on the selenium content of rye grass.

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SELOSTUS

Kalkituksen ja sulfaatin vaikutus Italian raiheinän (*Lolium multiflorum*) seleenipitoisuuteen

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Lisäämällä maahan selenaatitsuoloja voidaan viljelykasvien seleenipitoisuutta kohottaa jopa kolmekymmentä kertaa tehokkaammin kuin seleniittisuoloilla. Ulkomaisissa tutkimuksissa on todettu sulfaattirikin vähentävän tehokkaasti kasvin selenaatiseleenin mutta vain vähäisessä määrin seleniittiseleenin ottoa. Tämä on lisännyt epävarmuutta selenaatiseleenin soveltuvuudesta maan kautta annettuna kasvien seleenin lähteeksi.

Kahdessa astiakokeessa tutkittiin kalkituksen ja suurien sulfaattirikkimäärien vaikutusta Italian raiheinän seleenipitoisuuden savimaassa, hietamaassa ja saraturpeessa. Seleni lisättiin ensimmäiselle sadolle natriumseleniittinä tai -senaattina.

Kalkituksen vaikutus raiheinän seleenipitoisuuteen oli vähäinen. Sulfaattirikkilisäys ei vaikuttanut kasvin seleenipitoisuuteen missään maalajissa, kun seleni lisättiin maahan seleniittinä. Sen sijaan annettaessa seleni maahan selenaatina sulfaattirikkilisäys vähensi ensimmäisen raiheinäsadon seleenipitoisuuden saraturpeessa neljanteen osaan ilman rikkilisäystä kasvaneen raiheinäsadon seleenipitoisuudesta.

Käytännön viljelyssä sulfaatin vaikutus kasvin seleenipitoisuuteen jäänee vähäiseksi kivennäismaissa, mutta suuret sulfaattirikkimäärät saattavat pienentää kasvien seleenipitoisuutta joissakin eloperäisissä maissa.

EFFECT OF APPLIED SELENITE AND SELENATE ON THE SELENIUM
CONTENT OF BARLEY (*HORDEUM VULGARE*)

TOIVO YLÄRANTA

YLÄRANTA, T. 1983. Effect of applied selenite and selenate on the selenium content of barley (*Hordeum vulgare*). Ann. Agric. Fenn. 22: 164—174. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

A field experiment was carried out to investigate whether the selenium content of barley (*Hordeum vulgare* L.) grown on clay soil can be raised by the application of compound fertilizers containing selenium and by spraying the plants with aqueous solutions of sodium selenite and selenate. A pot experiment was carried out with seeds treated with selenite and selenate to determine the effect on the selenium content of barley.

The selenium content of barley can be raised effectively by applying NPK compound fertilizers containing selenate. A grain selenium content of 0,1—0,2 mg/kg can be obtained by applying 10—20 g/ha of selenium in the form of selenate. To achieve the same result using selenite, the amount of Se necessary would be more than 100 g/ha, even if the placement technique were used for the fertilizers.

The results obtained by foliar application onto cereals are largely determined by the spraying conditions, the growth stage of the plants and the selenium compound used. When the plants were sprayed at the mid-tillering stage selenate fertilizer and selenate spray both raised the selenium content of the barley to the same level. As some of the selenate applied in the form of spray may be taken up by the plants via the soil, selenate spraying is more effective than selenite spraying. The residual effect of selenite and selenate on the following year's crop would probably be small.

Of the selenium treatments used for the seed, only selenate treatment appears to have any potential in practice.

Index words: selenite and selenate fertilization, spraying, seed treatment, selenium content of barley.

INTRODUCTION

In a series of pot experiments YLÄRANTA (1983 c, d) has shown that the selenium content of plants grown on Finnish agricultural soils, which are naturally acidic and have a low sele-

mium content, can be increased by adding selenium to the soil in the form of either selenite or selenate. In these experiments rye grass was found to take up selenate selenium

up to 30 times more effectively than selenite selenium.

The idea of using readily soluble selenate as the selenium source for plants has not been generally accepted everywhere in the world, however (GISSEL-NIELSEN 1977). The reasons for this are the fear that plants may attain selenium contents high enough to be toxic to animals, and knowledge that selenium uptake by plants can be adversely affected by many factors. A high sulphate content in the soil, for example, can interfere with the uptake of selenate by plants far more than that of selenite (GISSEL-NIELSEN 1973). On the other hand, YLÄRANTA (1983 c) has shown that the selenium content of rye grass grown on different Finnish agricultural soils varies little. Liming and sulphate have also been shown to have little effect on the selenium content of rye grass on mineral soils (YLÄRANTA 1983 d).

In view of the fact that attempts by SYVÄ-LAHTI and KORKMAN (1978) and KORKMAN (1980) to raise the low selenium content of

Finnish plants, which is usually in the range 0,01—0,02 mg/kg dry matter, through the application of fertilizers containing selenite required large amounts of selenium it was considered essential to include selenate in the field experiments.

The selenium content of plants can be raised by adding selenium to fertilizers, spraying selenium onto the plants or treating the seeds with aqueous solutions of selenium compounds. The purpose of the field experiment was to obtain preliminary information for more detailed experiments into what the selenium content of NPK compound fertilizers should be in terms of selenite or selenate, or how much selenite or selenate should be sprayed onto the plants to attain the target of Se 0,1—0,2 mg/kg of dry matter. A pot experiment was carried out to determine whether the selenium content of cereal crops can be increased by treating the seeds with aqueous solutions of sodium selenite or selenate.

MATERIAL AND METHODS

The field experiment was carried out in Jokioinen in southern Finland on clay soil in 1980. The residual effect of the selenium treatments was studied in 1981. The plot size in the factorial experiment was 2 m × 12 m. There were four replicates for each treatment.

The experiment with fertilizers involved the use of the granular NPK compound fertilizer, which is the type most widely used in Finland and which contains 16 % nitrogen, 7 % phosphorus, 13 % potassium and 2 % sulphur. At Kemira's experimental fertilizer factory uncoated grains of commercial fertilizer manufactured by the ammonium phosphate

method were sprayed with an aqueous solution containing sodium selenite or sodium selenate. The selenated fertilizers prepared in this way contained 0,002—0,21 % selenium.

The plough layer of the experimental soil had an average pH(CaCl₂) of 6,1, an organic carbon content of 2,5 % and a clay fraction content of the inorganic material of 41 % as measured before sowing from samples taken from eight plots in different parts of the field. The same samples were used to determine the Ca, K, Mg and P extractable from the soil into acid ammonium acetate solution (0,5 M CH₃-COONH₄, 0,5 M CH₃COOH, pH 4,65)

(VUORINEN and MÄKITIE 1955). The mean amounts extracted per litre of soil were: calcium 2800 mg, potassium 340 mg, magnesium 370 mg and phosphorus 41 mg. The fairly high pH value and extractable K, Mg and P contents showed the field to be in good growing condition.

The field experiment had the following treatments:

- A. Fertilizing with NPK compound fertilizer containing added sodium selenite or sodium selenate.
1. No Se addition, Se 0,000015 % 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
- B. Spraying the plants with aqueous solutions of either sodium selenite or sodium selenate. Fertilizing with NPK compound fertilizer with no added selenium.
1. No selenium spraying
 2. Se 5 g/ha as selenite
 3. Se 50 g/ha as selenite
 4. Se 500 g/ha as selenite
 5. Se 5 g/ha as selenate
 6. Se 50 g/ha as selenate
 7. Se 500 g/ha as selenate

The aim was to prepare selenated NPK fertilizers containing 0,01, 0,05 and 0,25 % selenium as selenite and 0,001, 0,01 and 0,1 % selenium as selenate. The selenate fertilizers contained less selenium than the selenite fertilizers because selenate is far more readily available to plants (YLÄRANTA 1983 c, d).

In 1980 the selenated fertilizers were used in a field experiment with barley (*Hordeum vulgare* L., variety Pomo) both to provide

nutrients and as a source of selenium. The amount of selenated NPK fertilizer used was 500 kg per hectare. The fertilizer was applied to the soil using a combined seed and fertilizer drill, an implement commonly used in Finland and which places the fertilizer between every second row of seeds at a depth of 8 cm. The barley seeds, which contained an average of 0,013 mg/kg selenium, were sown at the rate of 200 kg/ha.

Foliar applications of selenite and selenate were carried out at stage 4 on the FEEKES scale (LARGE 1954). The amount of water used without surfactant was 400 l/ha. Spraying was carried out using an AZO-propane experimental sprayer.

The plants were cut plot by plot using a Sampo 25 experimental harvester. The entire 2 m wide area was cut leaving a stubble 10 cm high. No straw cutter was used. The straw and grain obtained from each plot were weighed. A representative sample of about 1 kg of grain and 300 g of straw was taken from each plot. The samples were dried at 50 °C. The selenium contents of the grain and straw were determined, together with the sulphur content of the grain.

The stalks were cleared from the field and autumn ploughing carried out across the width of the plots using a 2-blade Kverneland lea plough to a depth of 20 cm.

To establish the residual effect of the selenium treatment the experimental field was harrowed in spring 1981 in the longitudinal direction of the plots to prevent selenium from being transferred into adjacent plots. The unselenated NPK fertilizer was applied and the barley sown as in the previous year.

The crops were harvested using a Walter & Wintersteiger Nursery Master experimental harvester with a cutting width of 1,5 m. The crop was treated and samples taken as in the previous year.

The weather during the 1980 growing season was favourable, with the exception of a heavy

shower on June 10th, when about 80 mm of rain fell. This heavy rain damaged the barley, though it recovered rapidly to give a good yield. In the 1981 growing season the early part of the summer was dry while the last part of the summer was very wet, the result being a smaller yield than the previous year. In 1980 and 1981 MCPA herbicides were sprayed onto the field by tractor spray, together with 400 l/ha of water. Weed spraying was carried out in 1980 when the crop was at the three-leaf stage, while selenium spraying was carried out at the mid-tillering stage, which means there was an interval of 14 days between sprayings.

The vertical movement in the soil profile of the selenium added to the soil was also investigated in this experiment. For this purpose layer samples were taken before sowing the barley in spring 1980 and in autumn after cutting the crop, and again in autumn 1982 before ploughing the field. The area was allowed to remain fallow in 1982. Soil layer samples were taken to a depth of 90 cm. Soil samples were taken from the 16 plots that received selenite or selenate in the form of either fertilizer or spray. The samples were from the layers 0—5, 5—10, 10—20 and 0—20 cm in 20 places per plot and from the layers 20—40, 40—60 and 60—90 cm in eight places per plot. The samples taken in autumn 1980 were from the fertilizer rows. The samples taken from each plot were mixed still fresh. Samples of 0,5 l were put aside for analysis. The total selenium content was determined from dry (30 °C) milled ($\varnothing \leq 0,2$ mm) samples. In addition, the pH(CaCl₂), organic carbon and clay fraction content of the inorganic matter were determined for plots given the highest amount of selenate selenium in the fertilizer.

Seed treatment

The effect of treating barley seeds with sodium selenite or sodium selenate on the selenium content of the barley was studied in a pot

experiment. A small amount of an aqueous solution of either sodium selenite or sodium selenate was absorbed onto barley (variety Suvii) and the seeds allowed to dry at room temperature. The untreated seeds had a mean selenium content of 0,018 mg/kg, selenite-treated seeds a selenium content of 76 mg/kg and selenate-treated seeds a selenium content of 86 mg/kg.

Two-layer plastic Baumann pots (Kick-Brauckmann) were used. The experiment involved four replicates. As the experiment included seeds treated with selenite or selenate and untreated seeds, the total number of pots was 12. The soil used was fine sand with a clay fraction content of 8 % pH(CaCl₂) 5,5 and an organic carbon content of 4,1 %.

Into each pot was weighed 5,8 kg of air-dried soil ($\varnothing \leq 5$ mm) to which fertilizer had been applied as follows (mg/pot):

N	1600	NH ₄ NO ₃
P	500	Ca(H ₂ PO ₄) ₂ · H ₂ O, KH ₂ PO ₄
K	1300	K ₂ SO ₄ , KCl, KH ₂ PO ₄
Mg	280	MgCl ₂ · 6H ₂ O
S	200	K ₂ SO ₄
Cu	12	CuCl ₂
Mn	12	MnCl ₂
Fe	6	FeNa—EDTA
Zn	6	ZnNa ₂ —EDTA
B	4	H ₃ BO ₃
Mo	4	Na ₂ MoO ₄ · 2H ₂ O

The plant nutrients were applied in the form of solutions, with the exception of the calcium dihydrogen phosphate, which was a powder. All the chemicals were analytical grade.

1,00 g of barley seeds was planted into the soil surface, giving 25—28 seeds per pot. The seeds were covered with 0,7 kg of the experimental soil and the pots watered with deionised water from both below and above up to 60 % of the water holding capacity. The fact that the pots had two layers meant that watering could be carried out from the soil surface as well as

from the bottom of the pot. This watering procedure was used throughout the entire 80 day growing period. The plants were grown outdoors in a covered growing frame.

The crop was harvested by cutting the stalks to leave 3 cm of stubble. The straw and the heads were dried at 50 °C. The grain was separated from the chaff using a Saatmeister laboratory thresher. The selenium content was determined for the grain and the straw and the sulphur content for the grain. The pots were emptied and the selenium content of the soil determined by extraction into hot water.

Analytical methods

The $\text{pH}(\text{CaCl}_2)$ value of the soil samples was measured 2 hours after re-mixing from a suspension containing 25 ml of soil ($\varnothing \leq 2$ mm) and 62,5 ml of 0,01 M CaCl_2 solution. Organic carbon was determined using a LECO CR-12

carbon analyser (SIPPOLA 1982) and the particle size composition of the inorganic matter was analysed using the pipette method (ELONEN 1971). The selenium content of the soil extractable into hot water (YLÄRANTA 1982) and the selenium contents of the fertilizer, plant and soil samples were determined using the hydride method (YLÄRANTA 1983 a). The fertilizer and soil samples ($\varnothing \leq 0,2$ mm) were decomposed using the $\text{HNO}_3\text{—HClO}_4\text{—HF}$ method reported by AGEMIAN and BEDEK (1980). The selenium contents were then determined using Varian Techtron 1250 and Perkin Elmer 5000 atomic absorption spectrophotometers.

The sulphur content of the barley grains was determined from a 300 mg batch using a LECO SC-132 sulphur analyser.

For the analyses the grain was milled fine in a KT-30 grain mill, and the straw in a KT-120 hammer mill (Koneteollisuus Oy, Helsinki), fitted with a 2 mm sieve.

RESULTS

The grain crop harvested in the field experiment averaged 4900 kg/ha and the straw yield 2300 kg/ha. The use of selenium fertilizer had no effect on the size of the crop. The grain used in the control treatment contained Se 0,02 mg/kg dry matter (Table 1). The highest amount of selenium applied in the form of selenite fertilizer (1050 g/ha) had raised the selenium content of the grain to 1,56 mg/kg, while the 200 g/ha selenite selenium addition had raised it to 0,350 mg/kg. Since the smallest amount of selenium added to the fertilizer as selenite (50 g/ha) raised the selenium content of the grain to only 0,067 mg/kg, the experiment suggests that about 100 g/ha of selenite selenium would be required to achieve the target selenium content of 0,1 mg/kg dry matter.

Table 1. Effect of NPK compound fertilizers containing selenite (A2—A4) and selenate (A5—A7) on the selenium content of barley grain and straw (mg/kg dry matter) on clay soil in a field experiment in 1980. Residual effect of selenium treatments in 1981.

	Se (g/ha)	Se (mg/kg dry matter)			
		Grain		Straw	
		1980	1981	1980	1981
A1	0	0,022	0,017	0,019	0,016
A2	50	0,067	0,018	0,022	0,020
A3	200	0,345	0,029	0,170	0,025
A4	1050	1,56	0,070	0,830	0,044
A5	10	0,097	0,022	0,054	0,020
A6	50	1,12	0,020	0,813	0,017
A7	500	7,45	0,039	6,38	0,018

Spraying aqueous sodium selenite solution onto the plants at the mid-tillering stage was two or three times as effective in raising the selenium content of the plants as the application of selenite in the fertilizer. The highest selenite

application by spraying (Se 500 g/ha) raised the selenium content of the grain to 1,11 mg/kg (Table 2). Selenate, both in the fertilizer and sprayed onto the crop, raised the selenium content of barley grain more effectively than selenite. The highest amount of selenate selenium used (500 g/ha) raised the selenium content in both fertilizer and spray treatments to 7,5 mg/kg. Even 10 g/ha of selenate selenium in the fertilizer raised the selenium content of the grain to 0,10 mg/kg. On average, the selenate present in the fertilizer raised the selenium content of the barley over ten times more effectively than selenite, as the barley took up 4—10 % of the selenate contained in the fertilizer. The selenium contents of the straw were slightly lower than those of the grain, after both fertilizer application and spraying. The coefficient of variation for the selenium content of the grain between the different replicates averaged 13 % (5—17 %) and that for the straw averaged 14 % (5—24 %).

Table 2. Effect of foliar spraying with selenite (B2—B4) and selenate (B5—B7) on the selenium content of barley grain and straw (mg/kg dry matter) grown on clay soil in a field experiment in 1980. Residual effect of selenium treatments in 1981.

Se (g/ha)	Se (mg/kg dry matter)				
	Grain		Straw		
	1980	1981	1980	1981	
B1	0	0,021	0,013	0,021	0,017
B2	5	0,041	0,021	0,052	0,018
B3	50	0,183	0,018	0,126	0,018
B4	500	1,11	0,023	0,923	0,024
B5	5	0,040	0,021	0,038	0,018
B6	50	1,473	0,019	0,334	0,016
B7	500	7,52	0,036	6,79	0,020

The residual effects of selenite and selenate applications on the following year's crop was small. The highest selenium contents of 70 µg/kg dry matter were found in those plots that received 1050 g/ha selenium in the form of selenite (Tables 1 and 2). The residual effects of the highest selenate selenium addition in fertilizer (Se 500 g/ha) was to increase the sele-

mium content of the grain to 0,039 mg/kg. In the spraying treatment, only the highest amount of selenate (Se 500 g/ha) had raised the selenium content of the grain, which was found to be 0,036 mg/kg. There were no other statistically significant differences ($P = 0,01$, DUNCAN 1955) between the selenium contents of the grains. The straw with the highest selenium content (0,044 mg/kg) was found to be that given the highest amount of selenite fertilizer.

The grain yield from the 1981 field experiment averaged only 3000 kg/ha, while that of straw was 2800 kg/ha. There were no statistically significant differences in yields. In the residual effect part of the experiment the sulphur contents of the grains had risen from the 1980 mean of 0,129 mg/kg dry matter to 0,155 mg/kg. One reason for this was probably the fact that the yield was on average 1900 kg/ha lower than in the previous year. In neither year were there any statistically significant differences in sulphur content between the various treatments.

The selenium content of the soil used in the experiment was 0,35 mg/kg down to a depth of 40 cm (Table 3). The selenium content of the 40—60 cm layer was around 0,2 mg/kg and that of the 60—90 cm layer only 0,1—0,2 mg/kg. The clay fraction content of the plough layer averaged 41 %, though the figure increased with depth, and was 65 % in the 60—90 cm layer. The organic carbon content of the soil fell from the value of 2,5 % found in the plough layer to 0,3 % in the 60—90 cm layer. The pH(CaCl₂) was 6,1 in the 0—20 cm layer and 6,5 in the 60—90 cm layer (Table 4).

The selenium content of soil samples taken after harvesting the crop in autumn 1980 had clearly increased in samples from the plough layer as a result of application of selenium fertilizer and selenium spraying. Since fertilizer had been applied using the placement technique at a depth of 8 cm it was not surprising that the selenium content of the 10—20 cm layer

Table 3. Total selenium content of different soil layers ($\mu\text{g}/\text{kg}$) in a field experiment on clay soil. Selenium additions, A. selenium fertilizer, B. selenium foliar spray, carried out on barley in 1980. Selenium contents at the different sampling times for the soil layers not marked with the same letter differ from each other at the 1 % level of significance (DUNCAN 1955).

Sample depth (cm)	Se ($\mu\text{g}/\text{kg}$)		
	Spring 1980	Autumn 1980	Autumn 1982
A4 Se 1050 g/ha as selenite			
0—10	312 ^a	1987 ^b	597 [*]
10—20	294 ^e	414 ^f	597 [*]
20—40	328 ^k	325 ^k	377 ^k
40—60	204 ^r	214 ^r	194 ^r
60—90	—	—	115
A7 Se 500 g/ha as selenate			
0—10	346 ^a	503 ^b	410 [*]
10—20	263 ^e	431 ^f	410 [*]
20—40	336 ^k	391 ^k	344 ^k
40—60	249 ^s	268 ^s	197 ^r
60—90	—	—	123
B4 Se 500 g/ha as selenite			
0—5	348 ^a	651 ^b	443 [*]
5—10	350 ^e	404 ^f	443 [*]
10—20	231 ^k	356 ^l	443 [*]
20—40	339 ^r	312 ^r	320 ^r
40—60	202 ^t	185 ^t	176 ^t
60—90	—	—	114
B7 Se 500 g/ha as selenate			
0—5	354 ^a	534 ^b	433 [*]
5—10	343 ^e	435 ^f	433 [*]
10—20	280 ^k	383 ^l	433 [*]
20—40	351 ^r	358 ^r	339 ^r
40—60	199 ^t	182 ^t	195 ^t
60—90	—	—	129

* sample depth 0—20 cm

had also risen. Most of the selenite selenium applied in the fertilizer had remained in the 0—10 cm layer. Some of the selenium sprayed onto the cereal crops remains on the plants, though most of it finds its way to the surface of the soil. The selenium content of samples taken in autumn 1980 from plots treated by spraying was higher down to a depth of 20 cm than that of corresponding samples taken in spring. Before the autumn 1982 samples were taken the soil had been ploughed twice down to a depth of 20 cm and harrowed several times, both in spring and summer 1982 while the field was lying fallow. The selenium content of the plough layer soil had thus become uni-

form and it was not necessary to divide this layer into smaller parts. The results from autumn 1982 show that no selenium derived from either fertilizer or spray was observable below the plough layer.

Treatment of the barley seeds with either selenite or selenate produced no statistically significant differences in yield. The grain crop averaged 53 g/pot and the straw crop 46 g/pot. On the other hand, the selenium contents of the grain and the straw rose statistically significantly, with the exception of the straw in the selenite treatment. Selenite treatment of the seeds had raised the selenium content of the grain from the value of 0,020 mg/kg for the control to 0,042 mg/kg (Table 5). Selenate treatment was more than ten times more effective than selenite as it raised the selenium content of the grain to 0,305 mg/kg. Thus more than 18 % of the selenium applied in the form of selenate had accumulated in the grain. When the mean selenium content of the straw is also included (0,200 mg/kg) almost 30 % of the selenium from seeds treated with selenate was found in those parts of the barley above the ground. The result for selenite treatment, a 1,5 % accumulation in grain and straw, is extremely low when compared with selenate.

The sulphur content of the grain in the control treatments averaged 0,125 mg/kg dry matter, in the selenite treatments 0,126 mg/kg and in the selenate treatments 0,116 mg/kg. The difference between sulphur contents was not statistically significant ($P = 0,01$, DUNCAN 1955).

The following mean amounts of selenium ($\mu\text{g}/\text{pot}$) were extracted from the soils into hot water after the crops were cut:

Selenium treatment of seeds	\bar{x}	s
No selenium added	51	1,6
Selenite	65	4,9
Selenate	96	6,2

When the native selenium content of the soil is subtracted from the above figures, extraction

Table 4. Average particle size composition of the inorganic matter (%) of the various soil layers in the clay soil experimental field, organic matter content (%) and pH(CaCl₂) with standard deviations. Samples taken in autumn 1982.

Sample depth (cm)	Particle size composition (%)								Org. C (%)		pH(CaCl ₂)	
	< 0,002 mm		0,002—0,02 mm		0,02—0,2 mm		0,2—2 mm		\bar{x}	s	\bar{x}	s
	\bar{x}	s	\bar{x}	s	\bar{x}	s	\bar{x}	s				
0—20	41	2,7	27	2,1	23	2,1	8	2,7	2,5	0,17	6,1	0,15
20—40	50	4,4	24	2,4	20	2,7	6	1,4	1,6	0,12	6,1	0,14
40—60	62	1,5	21	1,1	16	1,7	1	0,6	0,51	0,02	6,2	0,10
60—90	65	5,5	20	3,8	14	2,5	1	0,4	0,31	0,03	6,5	0,00

accounted for 18 % of the added selenite and 52 % of the added selenate. This means that the selenate selenium found in the crop and the selenate selenium extracted from the soil together account for about 80 % of that added.

Table 5. Effect of selenium treatment of seeds on the selenium content of barley grain and straw (mg/kg dry matter) in a pot experiment with fine sand.

Treatment	Se (mg/kg dry matter)	
	Grain	Straw
No selenium added	0,020	0,017
Selenite	0,042	0,018
Selenate	0,305	0,200

DISCUSSION

These results, the results of pot experiments (YLÄRANTA 1983 c, d) and the results of field experiments carried out previously in Finland (SYVÄLAHTI and KORKMAN 1978, KORKMAN 1980) and abroad (GISSEL-NIELSEN 1981 a, GUPTA et al. 1982) show that plants take up only a small portion of the selenium added to soil in the form of selenite. The proportion taken up depends on factors such as the physical and chemical properties of the soil, the plant species and the mode of selenium application.

Although liming increases the amount of soluble selenium in the soil (YLÄRANTA 1983 b), it has little effect on the selenium content of plants (KORKMAN 1980, YLÄRANTA 1983 d). Since selenite selenium is known to be strongly sorbed in acid and neutral soils and hence to have little mobility in them (GISSEL-NIELSEN and BISBJERG 1970, YLÄRANTA 1982), it is understandable that selenite selenium applied to the soil surface is not available

to plants in the same way as selenium placed close to the roots. In Finland fertilizer is normally applied using the placement method, which was also the method employed in the field experiment in this study. It is presumably for this reason that the selenite was more readily available than in the field experiments carried out by SYVÄLAHTI and KORKMAN (1978), in which a mixture of salts containing selenite was applied to and mixed with the topsoil.

Many studies have looked into the residual effect of applying large quantities of selenite selenium, often up to several kilos per hectare, on the selenium content of crops grown in succeeding years. The purpose of applying large quantities of selenium has been to achieve a situation in which it would not be necessary to add selenium in order to raise the selenium content of the plants up to at least the target level of 0,1 mg/kg dry matter. On acid and neutral soils this level has usually been achieved

within only 2—3 years following treatment with 2—4 kg/ha of selenite selenium (CARY and ALLAWAY 1973, GUPTA et al. 1982). GISSEL-NIELSEN (1981 a) used 120 g/ha of selenite-containing PK fertilizers on 12—21 experimental fields over a period of four years, but failed to raise the selenium content of barley grain in any year to the level of 0,1 mg/kg dry matter. It should be borne in mind that selenium has not been shown to be essential to plants. Trying to raise the selenium content of plants is thus a very questionable practice when only several parts per thousand of the selenium applied are taken up.

The field experiment suggests that the use of fertilizers containing selenate could be a promising way of raising the selenium content of plants. To raise the selenium content of plant matter to 0,1 mg/kg dry matter would require more than 100 g of selenite selenium per hectare but possibly only one tenth of this amount if selenate selenium were used. TURNER (1981) also considers selenate the most likely form of selenium for adding to fertilizers in New Zealand.

The foliar application of selenium is more effective the more advanced the crop at the time of spraying. According to GISSEL-NIELSEN (1981 b) the selenium content of barley grain rises to 0,1 mg/kg if the plants are sprayed with 10 g/ha of selenite selenium at stage 4 on the FEEKES scale (LARGE 1954). The effectiveness of foliar spraying with selenium can be increased by the use of surfactants. Spraying in this study was restricted to aqueous solutions of sodium selenite and sodium selenate. Nevertheless, spraying with selenate proved almost as effective as the selenite spraying experiments carried out by GISSEL-NIELSEN (1981 b) in which a surfactant was used. In view of the fact that selenate is far more soluble than selenite, the barley clearly took up some of the selenate applied in the form of a spray via the soil in the field experiment carried out on clay soil at Jokioinen.

If spraying plants with selenium is considered worthwhile in practice it would be most economical to combine it with herbicide spraying. This may pose some problems, however, as spraying with herbicide is usually carried out at an earlier stage than that at which it would be worthwhile spraying with selenium.

The residual effect of the selenium treatments on the selenium content of barley crops grown in the following years was slight, as the highest amounts of selenate and selenite added to the soil were 0,5 and 1 kg/ha. Since only a small proportion of the selenium added to the soil was found in the crop, "the fate" of the selenium that remained in the soil was uncertain. One reason for the poor availability of fertilizer selenium was presumably the mixing of the selenium into the top 20 cm of soil during ploughing and spring preparation of the soil, which meant that it was no longer within easy reach of the plants roots in the way that selenium fertilizer applied using the placement method was. By determining the total selenium contents of the soil samples it was hoped to obtain further explanation for the selenium situation in the soil. The results indicated that the selenium had not leached below the plough layer, irrespective of whether it was applied as selenite or selenate.

Studies carried out earlier show that the volatilization of selenium is also unlikely (YLÄRANTA 1982). The low selenium content of barley grown in the years following selenium treatment of the soil thus confirms the supposition that both selenite and selenate selenium tend to be reduced and sorbed in Finnish soils.

According to GISSEL-NIELSEN (1975) the selenium treatment of seeds is equally ineffective in raising the selenium content of barley as selenium in fertilizer. The pot experiment carried out does not support the need to study the selenite treatment of seeds. Treatment of seeds with selenate, on the other hand, could be used in actual practice.

It has been suggested that high selenate

selenium contents in plants irreversibly combines with the enzymes necessary for the reduction of sulphate. In this way selenate would cause a shortage of essential organic sulphur compounds in the plants (GISSEL-NIELSEN 1982). On the other hand, there are some results showing that a high sulphate content of the soil reduces the uptake of selenate selenium by plants (GISSEL-NIELSEN 1973). However, the chemical forms of the selenium in the barley were not determined, and neither was the sulphate sulphur situation in the soil. Nevertheless, the crop was a good one and there were no statistically significant differences in either yield or sulphur content between the different treatments, although the selenium content of the barley in plots given the highest selenate additions was over 7 mg/kg. The uptake by barley of fertilizer selenate was so much greater than that of fertilizer selenite

that the former does not appear to be disrupted by anions from either the NPK fertilizer or the soil.

In the search for methods of raising the selenium content of cereal crops that would be suitable for plant production, account should also be taken of the possible effects of selenium application on the environment. If only a small proportion of the selenium applied to the soil or the crop is removed each year along with the crop, the selenium content of the soil will increase. Selenate is far more readily available to plants than selenite. In other words, because of the small amounts that would be added, selenate would not raise the selenium content of the soil as much as selenite in the long term. The results of the field experiment and the pot experiment indicate the need for further studies on the use of selenate fertilizers and the selenate treatment of seeds.

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SELOSTUS

Maahan lisätyn seleniitin ja selenaatin vaikutus ohran (*Hordeum vulgare*) seleenipitoisuuteen

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Kenttäkokeessa savimaalla tutkittiin mahdollisuutta kohottaa ohran seleenipitoisuutta seleenipitoisin Normaali Y-lannoksin ja ruiskuttamalla natriumseleniitin ja -selenaatien vesiliuoksia kasvustoon. Seleniitillä ja selenaatilla käsiteltyjen siementen vaikutusta ohran seleenipitoisuuteen tutkittiin astiakokeessa.

Lisäämällä lannoitteessa maahan seleeniä 10—20 g/ha selenaatina kohotetaan ohran jyvien seleenipitoisuus 0,1—0,2 mg:aan/kg. Jotta päästäisiin samaan tulokseen seleenipitoisilla lannoitteilla, olisi seleeniä käytettävä todennäköisesti yli 100 g/ha.

Kasvustoruiskutusten vaikutus kasvin seleenipitoisuuteen riippuu suuresti ruiskutusolosuhteista, kasvin kehitysvaiheesta ja käytetystä seleeniyhdisteestä. Kun kasvustoruiskutus suoritettiin versonnan keskivaiheilla, kohotti lannoiteselenaatti ja ruiskuteselenaatti ohran seleenipitoisuuden samalle tasolle. Osan ruiskuteselenaatista kasvi voi ottaa maan kautta, joten selenaatiruiskutus oli seleeniruiskutusta tehokkaampi. Lannoitteessa maahan lisätyn tai kasvustoon ruiskutetun seleniitin ja selenaatien vaikutus seuraavan vuoden ohran seleenipitoisuuteen oli vähäinen.

Tutkituista siementen seleenikäsittelyistä vain selenaatikäsittelyllä lienee toteutumismahdollisuuksia käytännön viljelyssä.

TOTAL HEAVY METAL RECOVERY BY AQUA REGIA IN SOILS OF DIFFERENT ORIGIN

NABIL H. BAGHDADY and JOUKO SIPPOLA

BAGHDADY, N. H. and SIPPOLA, J. 1983. Total heavy metal recovery by aqua regia in soils of different origin. *Ann. Agric. Fenn.* 22: 175—185. (Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.)

In all soil types studied, the extraction of total Co, Cu, Mn and Zn with aqua regia (AR) gave values lower than with the HF—HClO₄—HNO₃ method (HHH) (73—100 % recovery). The AR mean values of total Co were 26,6, 9,3 and 4,5 mg/kg, total Cu 57,4, 31,1 and 18,3 mg/kg, total Mn 904, 512 and 425 mg/kg, and total Zn 78,4, 103,7 and 60,1 mg/kg for Egyptian, Finnish and German soils, respectively.

The total elemental content was closely correlated with the clay plus silt content of the soil. Linear equations were derived to allow estimation of total elemental content (HHH method) from concentrations in AR extracts.

Index words: total Co, Cu, Mn, Zn; aqua regia; HF—HClO₄—HNO₃; Egyptian, Finnish and German soils.

INTRODUCTION

A picture of the reserves of soil microelements is obtained by determining their total content, for which several methods are available. They include aqua regia (AR) extraction, which has been used extensively in soil pollution studies (BÜRGER 1978, KICK et al. 1980). AR can be used to determine the total content of series of elements except silicon (COTTENIE et al. 1982). This reagent is a strong extractant,

because of the presence of free chloride, a powerful oxidizing agent (MAXWELL 1968). In most instances about 80—90 % of soil elements are released (BÜRGER 1978, NASSEEM 1980). Elements bound in organic matter and in small particles or soft minerals are the most likely to be dissolved. Elements in acid resistant, large particle size minerals most likely can not be determined by this extraction method.

Only rare mineral species are known to be resistant to HF—HClO₄—HNO₃ digestion. Therefore, this method results in a more complete digestion than aqua regia, and values closer to the total content are obtained. In view of the fact that the aqua regia extraction is relatively simple to carry out (NASSEEM 1980, COTTENIE et al. 1982), it may be possible to use it instead of the more complex methods

such as HF—HClO₄—HNO₃ digestion. This investigation was therefore carried out to elucidate the effectiveness of aqua regia in the extraction of total content of Co, Cu, Mn and Zn in some soils from Egypt, Finland and Germany. The chemical and physical soil properties controlling the extractability were also studied.

MATERIAL AND METHODS

The investigated soil samples were collected from Egypt, Finland and Germany (Table 1). Eleven Egyptian soils (0—30 cm) representing the recent alluvial deposits of the Nile floods and the desert calcareous soils (Fig. 1), eighteen Finnish soils (0—20 cm) and six German soils were selected (Figs. 2 and 3).

The air-dried soil samples were passed through a 2 mm steel sieve. For the determination of total elemental content, representative subsamples were taken, ground in an agate mortar and sieved through a 0,1 mm plastic sieve. The pH values of these samples were measured in a soil:water suspension (1:2,5), and their humus content determined by a dry combustion method (SIPPOLA 1982). The

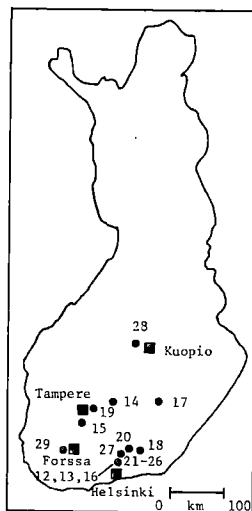


Fig. 2. Finland.

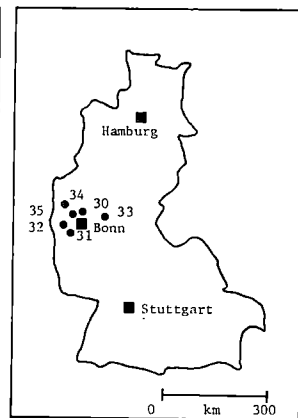


Fig. 3. West-Germany.

LOCATIONS OF THE INVESTIGATED SOILS

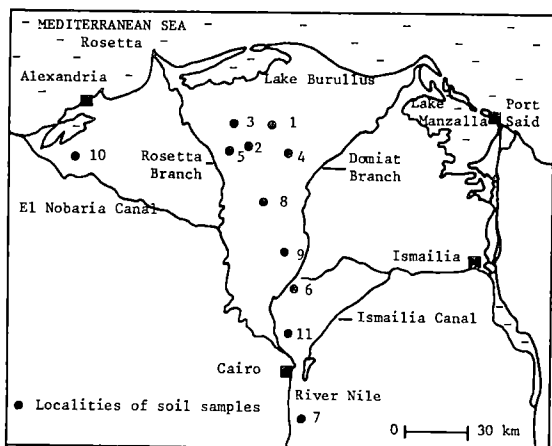


Fig. 1. Nile Delta of Egypt.

cation exchange capacity using the sodium acetate method and the total CaCO₃ content using the gasometric method were also determined (JACKSON 1958). The particle size distributions were determined by wet sieving and by a pipette method for the finer fractions.

The digestion with aqua regia (AR) was done according to BÜRGER (1978) as follows: 10 g of very finely ground, air-dried soil was weighed in a 250 ml round-bottomed flask and a small amount of de-ionized water (approx. 2—3 ml) was added to form a slurry. 40 ml of aqua regia (HCl—HNO₃, 3,5:1) was then gradually added in four portions to avoid any loss due to reaction with the organic matter in the sample. The sample was then left overnight and a 40 cm

Table 1. Some physical and chemical characteristics of the investigated soils.

Soil no.	Location	Mechanical analysis (%)			pH (H ₂ O)	Total CaCO ₃ %	Humus %	CEC me/100 g soil
		Sand 20–2000 μm	Silt 2–20 μm	Clay < 2 μm				
Egyptian soils:								
1	Baltim	21,7	39,6	38,7	7,55	1,4	0,6	60,0
2	Kafr El-Skiekh	15,1	21,4	63,5	8,22	3,1	1,4	62,5
3	Hamoul	16,5	41,1	42,4	7,82	1,7	0,5	57,5
4	Mahala	13,6	25,6	60,8	8,46	2,6	1,6	65,0
5	Desouk	13,4	25,3	61,3	8,47	3,4	1,6	60,0
6	Toch	19,0	25,7	55,3	8,33	3,7	2,2	57,5
7	Helwan	37,2	32,3	30,5	8,18	5,9	1,6	55,0
8	Tanta	21,6	22,6	55,8	7,83	3,1	2,3	55,0
9	Quesna	24,7	22,0	53,3	8,33	3,4	1,7	55,0
10	Nobaria	48,6	21,6	29,8	9,01	23,4	0,5	15,0
11	Kaha	25,9	22,5	51,6	8,29	3,4	1,9	47,5
Finnish soils:								
12	Vantaa	29,4	25,9	44,7	4,60	0	26,9	90,0
13	"	78,9	7,2	13,9	4,95	0	9,1	35,0
14	Jämsä	60,7	30,2	9,1	6,14	0	0,2	15,0
15	Lempäälä	8,1	43,1	48,4	5,90	0	1,0	32,5
16	Vantaa	88,7	3,6	7,7	5,10	0	3,0	25,0
17	Järvenpää	10,6	11,1	78,3	7,20	0	4,2	57,5
18	Pornainen	54,8	17,5	27,7	5,75	0	4,9	40,0
19	Orivesi	35,1	46,2	18,7	6,65	0	2,7	25,0
20	Mäntsälä	19,7	29,2	51,1	6,74	0	5,8	50,0
21	Vantaa	75,9	8,7	15,4	6,30	0	3,6	25,0
22	"	88,8	5,0	6,2	5,65	0	2,4	25,0
23	"	Mould	Mould	Mould	4,75	0	19,2	80,0
24	"	39,3	20,8	39,9	5,26	0	6,8	50,0
25	"	39,5	21,0	39,5	5,26	0	6,6	45,0
26	"	41,2	20,2	38,6	5,29	0	7,1	50,0
27	Mikkeli	82,5	13,0	4,5	5,58	0	6,7	40,0
28	Maaninka	Peat	Peat	Peat	5,39	0	26,7	155,0
29	Jokioinen	43,4	18,0	38,6	6,29	0	2,8	37,5
German soils:								
30	Meckenheim	58,9	25,9	15,2	6,53	0,5	0,9	30,0
31	Uedorf	90,8	4,6	4,6	6,37	0,5	0,8	22,5
32	Wahner Heide	94,4	2,8	2,8	6,10	0,3	0,9	22,5
33	Berrenrath	60,1	23,1	16,8	8,37	6,0	1,3	17,5
34	Viersen	85,3	8,6	6,1	6,46	0,3	1,8	15,0
35	Röttingen	50,5	30,2	19,3	4,80	0,3	0,4	15,0

reflux condenser was fitted on to the top of the flask. The mixture was gradually heated and boiled under reflux for three hours. After cooling, the condenser was washed with approx. 30 ml of de-ionized water into the flask. The diluted solution was filtered quantitatively using hot water washings into a 250 ml measuring flask.

The HF—HClO₄—HNO₃ (HHH) digestion was done as described by FISHER and FECHTER (1982). The soil extractants were analysed for Co, Cu, Mn and Zn using an

atomic absorption spectrophotometer with an air/acetylene flame. The coefficients of variation of the two methods (Table 3), based on double determinations, were of the same order for each element.

Results were analysed statistically using standard methods (STEEL and TORRIE 1960). Regression lines were calculated between the total elemental contents extracted with the AR and HHH methods. The factors affecting the rate of dissolution by the AR method and the soil properties were also examined statistically.

RESULTS AND DISCUSSION

Soils studied

The Egyptian soils of the study have a fine texture (Table 1). This is because they have been formed recently from alluvial deposits of the Niled floods (EL-ATTAR and JACKSON 1973). The soils were alkaline (pH 7,55—9,01) with an average pH 8,23, the organic C content was low, ranging from 0,5 to 2,2 %. The alluvial soils had a total CaCO_3 content of 1,4—3,4 % and the calcareous soil (No. 10) 23,4 % (limestone parent material). The cation exchange capacity (CEC) was high for the alluvial soils (47,5—62,5 me/100 g) and low for the calcareous soil (15 me/100 g). For Egyptian soils, results in the same range have been reported e.g. by SILLANPÄÄ (1982).

The Finnish soils are developed mainly from acidic magmatic rocks, pulverized by the continental ice sheet during the glacial period and from organic materials during the post-glacial period (SIPPOLA and TARES 1978). These soils are generally acidic (mean pH 5,70) with varying texture. The organic C content ranged from 0,2 to 27 % and CEC was relatively high with a mean of 48,8 me/100 g for mineral soils and 100 me/100 g for mould and peat soils. SILLANPÄÄ (1982) also gave similar data for the Finnish soils. The German soils were coarser in texture than the Egyptian or Finnish soils. The pH range was 4,8—8,4, total CaCO_3 0,3—6 %, organic C content 0,4—1,3 % and CEC 15—30 me/100 g.

Egyptian soils

Generally, the extraction of total soil Co, Cu, Mn and Zn (Tables 2 and 3) with AR gave lower values than the HHH method. The recovery of these elements amounted to 92,1, 91,9, 85,1 and 84,4 %, respectively, with the AR method. NASSEEM (1980) reported similar

findings, but with less recovery by the AR than the hydrofluoric acid method for Cu and Zn. This could be attributable to the technique used (i.e. no overnight reaction time, no reflux condenser and only 90 minutes' digestion time).

1. Cobalt. The calcareous soil gave a value of 6,0 mg/kg for Co extracted with AR, while in the alluvial soils values ranged from 24,0 to 29,5 mg/kg with an average of 26,8 mg/kg and mean deviation of 5,6 %. On the other hand, with the HHH extraction a range of 7—33 mg/kg with a mean value of 26,6 mg/kg was obtained (Tables 2 and 3). Similar results have been reported by ELSOKKARY and LÄG (1980). A highly significant correlation existed between the total Co determined with the AR and HHH methods (Fig. 4), giving the equation:

$$\text{Co}_{\text{HHH}} = 0,97 \text{Co}_{\text{AR}} + 2,7$$

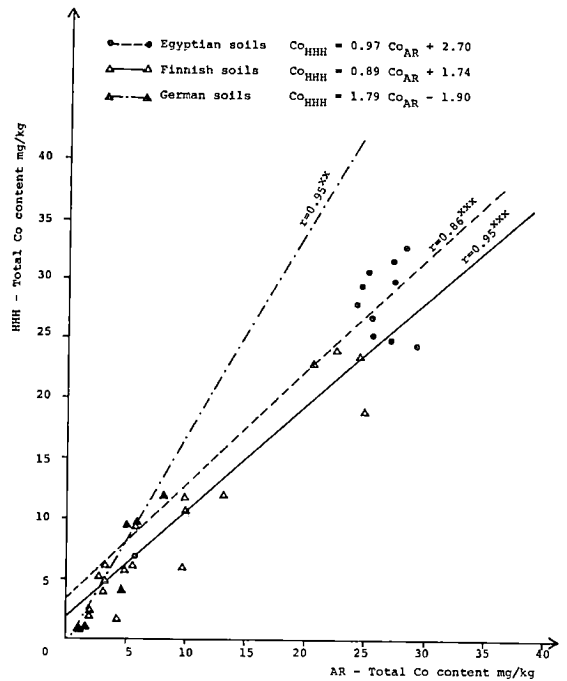


Fig. 4. Regression lines of total Co content extracted with AR and HHH in different soils.

Table 2. Mean values of total Co, Cu, Mn and Zn contents (mg/kg) digested with aqua regia (AR) and HF—HClO₄—HNO₃ (HHH) in investigated soils.

Soil no.	Co		Cu		Mn		Zn	
	AR	HHH	AR	HHH	AR	HHH	AR	HHH
Egyptian soils:								
1	25,5	27,0	53,2	60,3	672	802	69,0	90,6
2	27,0	32,0	59,1	61,2	929	1040	80,2	91,3
3	25,0	31,0	54,6	59,8	742	810	74,4	87,3
4	24,5	29,5	58,1	61,6	1121	1345	79,1	96,1
5	27,0	30,0	57,0	64,7	1118	1348	77,1	98,4
6	24,0	28,0	108,9	119,2	1109	1420	84,6	105,0
7	28,0	33,0	58,2	60,5	1017	1275	106,4	123,7
8	27,0	25,0	57,6	60,0	949	1106	88,5	94,5
9	29,5	24,0	57,5	61,4	1009	1108	78,6	91,7
10	6,0	7,0	10,8	13,7	299	326	32,4	38,3
11	25,5	25,5	56,5	63,2	976	1092	91,3	104,6
Finnish soils:								
12	2,0	2,0	18,9	23,0	113	162	33,4	33,3
13	3,5	5,0	14,4	18,1	114	339	37,2	45,8
14	3,0	6,0	10,8	12,8	319	397	30,7	41,0
15	22,5	24,0	32,2	35,3	1239	1363	137,1	142,1
16	3,0	4,0	9,4	12,6	211	407	42,3	52,1
17	24,0	23,5	58,7	58,9	638	647	164,7	168,2
18	10,0	6,0	17,1	20,1	262	340	71,6	78,1
19	10,0	12,0	20,6	20,7	1225	1147	123,8	115,8
20	25,0	19,0	43,9	46,9	907	968	227,6	256,8
21	5,0	6,0	39,2	33,9	347	420	200,4	211,2
22	3,0	5,0	10,8	13,5	205	335	40,3	55,6
23	9,7	11,3	68,6	72,9	1185	1097	142,5	157,6
24	8,0	12,0	32,0	33,5	302	382	93,9	98,5
25	6,0	8,0	45,3	45,7	307	370	144,6	139,8
26	6,0	9,0	59,3	59,0	319	383	195,8	186,2
27	2,0	2,0	7,2	10,9	150	285	21,7	27,5
28	3,3	2,0	35,1	34,0	187	179	28,2	30,5
29	21,0	23,0	36,9	37,3	1185	1098	131,4	146,6
German soils:								
30	8,0	12,0	14,9	16,1	724	687	57,2	56,1
31	4,5	4,0	10,8	14,4	358	370	90,6	89,2
32	2,0	1,0	3,5	6,0	116	116	21,6	26,5
33	5,0	9,0	9,4	12,7	454	515	32,2	38,0
34	1,5	1,5	61,0	61,0	327	357	117,2	120,6
35	6,0	9,5	10,2	13,8	572	500	41,9	51,4

There was a significant negative correlation between total Co extracted with AR and total CaCO₃ content ($r = -0,93^{***}$), and humus ($r = -0,77^{**}$), but a positive correlation with CEC ($r = 0,89^{***}$) and clay plus silt ($r = 0,67^{*}$).

2. Copper. The total copper content extracted by AR digestion varied from 10,8 to 108,9 mg/kg with a mean of 57,4 mg/kg. The HHH digestion resulted in Cu values ranging from 13,7 to 119,2 mg/kg with a mean of 62,5 mg/kg (Tables 2 and 3). The calcareous soil had lower value than the alluvial soils due to its lower

clay content and clay minerals poor in Cu (illite and kaolinite, KISHK et al. 1973, EL-DAMATY et al. 1973). The regression between the total Cu contents digested with AR and HHH (Fig. 5) showed a high positive correlation ($r = 0,99^{***}$), giving the equation:

$$Cu_{HHH} = 1,07 Cu_{AR} + 0,74$$

The same high significant correlation was also found by NASSEEM (1980). ELSOKKARY and LÄG (1980) and NASSEEM (1980) recorded a lower total Cu content for the alluvial soils than the present values, because they used a

Table 3. Ranges, mean values, mean deviation of double determinations for Co, Cu, Mn and Zn, and the recovery using the AR method in the tested soils.

Element	Soils		Minimum — (mean value) — maximum (mg/kg)				Mean dev. of double determinations		Recovery with AR method (HHH = 100)
	Origin	Total no.	aqua regia		HF—HClO ₄ —HNO ₃		AR	HHH	
Co	Egyptian	11	6,0 — (24,5) — 29,5	7,0 — (26,6) — 33,0	5,6	3,6	92,1		
	Finnish	18	2,0 — (9,28) — 25,0	2,0 — (9,99) — 24,0	2,9	1,2	92,9		
	German	6	1,5 — (4,5) — 8,0	1,0 — (6,17) — 12,0	6,1	5,2	73,0		
Cu	Egyptian	11	10,8 — (57,4) — 108,9	13,7 — (62,5) — 119,2	2,9	2,4	91,9		
	Finnish	18	7,2 — (31,1) — 68,6	10,9 — (32,7) — 72,9	3,8	4,3	95,1		
	German	6	3,5 — (18,3) — 61,0	6,0 — (20,7) — 61,0	2,6	2,7	88,6		
Mn	Egyptian	11	299 — (904) — 1121	326 — (1061) — 1420	5,3	5,5	85,1		
	Finnish	18	113 — (512) — 1239	162 — (573) — 1364	3,4	2,5	89,3		
	German	6	116 — (425) — 724	116 — (424) — 687	4,8	3,7	100		
Zn	Egyptian	11	32,4 — (78,4) — 106,4	38,3 — (92,9) — 123,7	2,9	4,3	84,4		
	Finnish	18	21,7 — (103,7) — 227,6	27,5 — (110,4) — 256,8	4,9	4,0	94,0		
	German	6	21,6 — (60,1) — 117,2	26,5 — (63,6) — 120,6	3,1	3,0	94,5		

less efficient technique. A significant negative linear correlation was found between Cu determined with AR and CaCO₃ content ($r = -0,66^*$) and a significant positive correlation with CEC ($r = 0,66^*$). This is in agreement with similar findings by FOLLET and LINDSAY (1970). No significant correlations with humus content were found.

3. Manganese. The Mn determined by AR ranged from 299 mg/kg for calcareous soil to 1121 mg/kg for alluvial soils, with an average of 904 mg/kg. With the HHH digestion, the range was from 326 mg/kg for calcareous soil to 1420 mg/kg for the alluvial soils, with an average of 1061 mg/kg. GHANEM et al. (1970) found that the range of total Mn extracted with HF—HClO₄ from Egyptian soils was from 116 to 1300 ppm and that calcareous soils have a lower Mn content than clay soils. These data are also in accordance with the findings of KARIM et al. (1960), SERRY and MAWARDI (1962), EL-DAMATY et al. (1971) and ELSOKKARY and LÄG (1980). A positive correlation (Fig. 6) was found between Mn determined by AR and HHH ($r = 0,98^{***}$), giving the equation:

$$Mn_{HHH} = 1,27 Mn_{AR} - 82$$

The manganese determined by AR correlated negatively with total CaCO₃ ($r = -0,74^{**}$), but positively with CEC ($r = 0,77^{**}$) and clay plus silt content ($r = 0,79^{**}$), while the humus content did not correlate. ELSOKKARY and LÄG (1980) found a significant correlation between total Mn and CaCO₃, clay content and also organic matter. GHANEM et al. (1970) reported a significant correlation between total

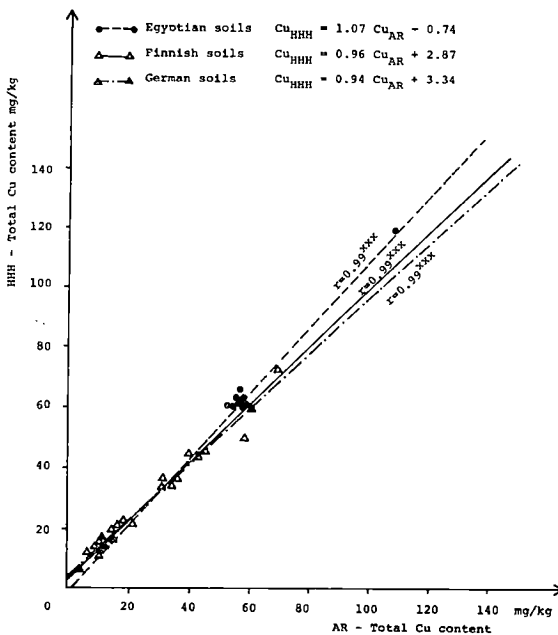


Fig. 5. Regression lines of total Cu content extracted with AR and HHH in different soils.

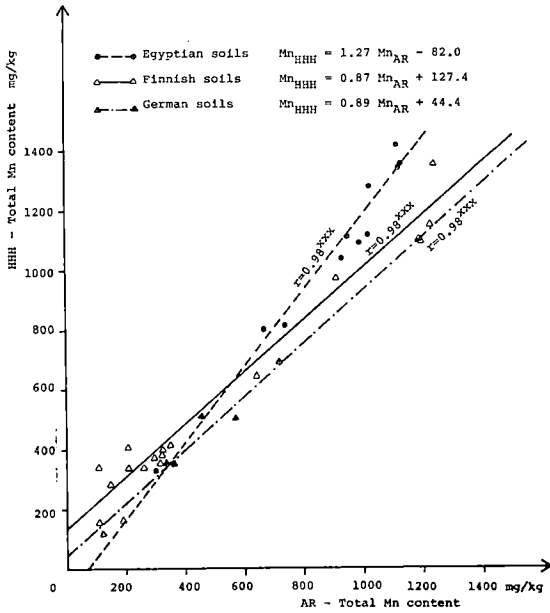


Fig. 6. Regression lines of total Mn content extracted with AR and HHH in different soils.

Mn and organic matter after the addition of manure to the soils. FOLLET and LINDSAY (1970) also obtained significant correlations between total Mn and CEC of soils.

4. Zinc. The total zinc extracted with AR ranged from 32,4 to 106,4 mg/kg, with a mean value of 78,4 mg/kg (Tables 2 and 3). On the other hand, for HHH extraction the range was from 38,3 mg/kg for calcareous soil to 123,7 mg/kg for alluvial soils, with a mean value of 92,9 mg/kg. This confirms earlier findings by ELSOKKARY and LÄG (1980). The correlation (Fig. 7) between total Zn determined using AR and HHH was significant ($r = 0,97^{***}$), giving the following regression equation:

$$Zn_{HHH} = 1,1 Zn_{AR} + 6,53$$

NASSEEM (1980) also found this significant correlation in his work with Egyptian soils. Zinc determined using AR was negatively correlated with total $CaCO_3$ content of the soil ($r = -0,75^{**}$), but positively correlated with

CEC ($r = 0,69^{**}$). Organic matter and clay plus silt contents, however, showed no significance. FOLLET and LINDSAY (1970) reported a higher correlation for total Zn and CEC. ELSOKKARY and LÄG (1980) also obtained significant correlations between total Zn and organic matter as well as $CaCO_3$ content in Egyptian soils.

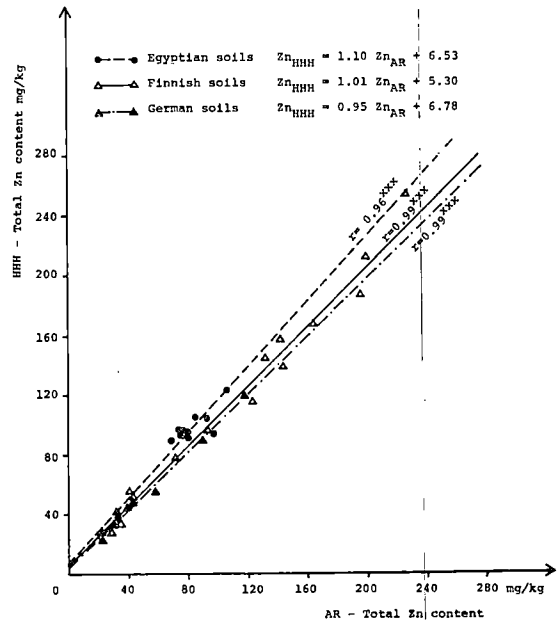


Fig. 7. Regression lines of total Zn content extracted with AR and HHH in different soils.

Finnish soils

In comparison to the HHH method, AR extraction recovered 92,5, 95,1, 89,3 and 94 % of Co, Cu, Mn and Zn, respectively.

1. Cobalt. Table 2 and 3 show that the cobalt content of Finnish soils determined using the AR method ranged from 2 to 25 mg/kg, with an average of 9,5 mg/kg. Similar ranges and mean value were also obtained with the HHH extraction. SIPPOLA (1974) also gave similar values. A close correlation existed between the

two methods of extraction ($r = 0,95^{***}$), giving the regression equation:

$$Co_{HHH} = 0,89 Co_{AR} + 1,74 \quad (\text{Fig. 4})$$

The cobalt contents determined using the AR method correlated with the clay plus silt content ($r = 0,74^{***}$), but no significant correlations were found with CEC or humus content. The correlation between total Co and clay content was also reported by SIPPOLA (1974).

2. Copper. The total Cu content determined using the AR method ranged from 7,2 to 68,6 mg/kg, with a mean value of 31,1 mg/kg, while the HHH method gave a range from 10,9 to 72,9 mg/kg, with an average of 32,7 mg/kg. Using spectrographic determination, VUORINEN (1958) reported lower values of total Cu content and SIPPOLA (1974) higher values. This variation in the total Cu content of Finnish soils most likely depends on the method of estimation. A highly significant correlation coefficient ($r = 0,99^{***}$) was found between the results of the two methods of determination of total Cu, and the following regression equation was obtained:

$$Cu_{HHH} = 0,96 Cu_{AR} + 2,87$$

The Cu content determined using the AR method and the clay plus silt content correlated significantly ($r = 0,59^{**}$), while no correlation was found with CEC or organic matter. These correlations were also in accordance with reports by SILLANPÄÄ (1962) and SIPPOLA (1974).

3. Manganese. The total Mn determined using the AR method ranged from 113 to 1239 mg/kg, with a mean value of 512 mg/kg, while that extracted with HHH ranged from 162 to 1364 mg/kg, with a mean value of 573 mg/kg (Tables 2 and 3). VUORINEN (1958) and SIPPOLA (1974) reported similar mean values for Finnish soils using a spectrographic method. The results of the investigated methods correlated

significantly ($r = 0,98^{***}$), and the following regression equation was obtained:

$$Mn_{HHH} = 0,87 Mn_{AR} + 127,4$$

Total Mn extracted with AR correlated with the clay plus silt content ($r = 0,63^{**}$). Total $CaCO_3$, humus content and CEC showed no significant correlation. This supports earlier findings by SILLANPÄÄ (1962) and SIPPOLA (1974).

4. Zinc. The total Zn in Finnish soils determined using the AR method ranged from 21,7 to 227,6 mg/kg, with a mean value of 103,7 mg/kg. The determination using the HHH method gave a range from 27,5 to 256,8 mg/kg, with a mean value of 110,4 mg/kg (Tables 2 and 3). Lower ranges of total Zn contents measured using a spectrographic method were given by VUORINEN (1958), SILLANPÄÄ (1962) and SIPPOLA (1974). The results of the two methods correlated closely ($r = 0,99^{***}$), and the following regression equation was obtained:

$$Zn_{HHH} = 1,01 Zn_{AR} + 5,3$$

Of the studied soil properties, the zinc content determined using the AR method correlated with the silt plus clay content ($r = 0,55^*$), while no correlation was found with organic matter content or CEC. Similar correlations with clay content were also found by SIPPOLA (1974) for Finnish soils.

German soils

With the exception of Mn, determinations using the AR method gave lower values than the HHH method. The recovery from AR extraction compared to the HHH method for total Co, Cu, Mn and Zn were 73, 88,6, 100 and 94,5 %, respectively.

1. Cobalt. The total Co contents determined using the AR method for German soils were

relatively lower than those in Egyptian and Finnish soils. The values ranged from 1,5 to 8,0 mg/kg, with a mean value of 4,5 mg/kg. Similarly, the HHH extraction gave a range from 1 to 12 mg/kg, with an average of 6,2 mg/kg (Tables 2 and 3). Nearly the same values were found for German soils by EL-BASSAM (1978), BÜRGER (1978) and KICK et al. (1980). The results of the two methods also correlated in this group of soils ($r = 0,95^{**}$) and the regression equation was as follows:

$$Co_{HHH} = 1,79 Co_{AR} - 1,9 \quad (\text{Fig. 4})$$

The total soil Co determined by AR showed no significant correlation with any soil properties.

2. Copper. The range of total Cu determined using the AR method in German soils was 3,5—61 mg/kg, with an average of 18,3 mg/kg (Tables 2 and 3). Approximately the same values were obtained with the HHH method and the correlation between the results of the two methods was close ($r = 0,99^{***}$). These results are in accordance with earlier studies by EL-BASSAM (1978), KICK et al. (1980) and FISHER and FECHTER (1982). The following regression equation was obtained to illustrate the relation between the two methods:

$$Cu_{HHH} = 0,94 Cu_{AR} + 3,4$$

The total soil Cu determined using the AR method gave no significant correlations with any other studied soil properties.

3. Manganese. The total Mn content determined using the AR method gave a range of 116 to 724 mg/kg, with a mean value of 425 mg/kg (Tables 2 and 3). Approximately the

same values were recorded using the HHH method. The results of the two methods correlated closely ($r = 0,98^{***}$) and the regression equation was:

$$Mn_{HHH} = 0,89 Mn_{AR} + 44,4 \quad (\text{Fig. 6})$$

The results of the AR method correlated with the clay plus silt content ($r = 0,85^*$), but not with other studied soil properties.

4. Zinc. Determination of total Zn using the AR method with German soils gave a range of 21,6—117,2 mg/kg, with a mean value of 60,1 mg/kg, but the extraction of total Zn with HHH gave the range 25,6—120,6 mg/kg, with an average of 63,6 mg/kg (Tables 2 and 3). Similar mean values were reported by BÜRGER (1978), KICK et al. (1980) and FISHER and FECHTER (1982). A highly significant correlation coefficient ($0,99^{***}$) was found between the results of the two methods giving the related regression equation:

$$Zn_{HHH} = 0,95 Zn_{AR} + 6,8$$

No significant correlation was found between the total Zn extracted with AR and the soil properties studied.

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SELOSTUS

Kuningasveden kyky uuttaa raskasmetalleja

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Maatalouden tutkimuskeskus

Kuningasvettä (väkevä HCl + väkevä HNO₃ suhteessa 3,5 : 1) käytetään hyvin yleisesti maaperän raskasmetallien kokonaispitoisuuksien määrittämiseen. Sitä on erityisesti käytetty tutkimuksissa, joissa on pyritty selvittämään maan saastuneisuutta. Kuningasvesi ei kuitenkaan pysty liuottamaan maassa esiintyviä suuria mineraalirakeita eikä siten määrityksessä saada kokonaismäärää täydellisesti. Tutkimuksen tarkoituksena olikin selvittää lähemmin kuningasveden uuttokykyä.

Saatujen tulosten mukaan kuningasvesi uutti kobolttia,

kuparia, mangaania ja sinkkiä 73—100 % fluorivetyhajoituksella saaduista määristä keskimäärin ollessa 90 %. Aineiston Suomesta otetuista näytteistä suhteellisesti vähiten uutui mangaania (89 %) ja eniten kuparia (95 %).

Aineiston perusteella laskettiin regressioyhtälöt, joiden avulla on mahdollista muuntaa kuningasvesiuuttoa käytäten saadut tulokset varsinaista totaalianalyysia vastaaviksi tuloksiksi. Määritetyistä maaperätekijöistä totaalipitoisuudet korreloivat parhaiten saveksen ja hiesulajitteen summan kanssa.

THE INFLUENCE OF DIFFERENT SUBSOIL TYPES ON THE Ca, K AND P STATUS, AND pH OF THE CORRESPONDING MOULD LAYER

LEILA URVAS

URVAS, L. 1983. The influence of different subsoil types on the Ca, K and P status, and pH of the corresponding mould layer. *Ann. Agric. Fenn.* 22: 186—192. (*Agric. Res. Centre, Inst. Soil Sci., SF-31600 Jokioinen, Finland.*)

The fertility of four mould soil groups with different subsoils was compared. The subsoils were coarse mineral, clay, gyttja and peat, and each had a different effect on the pH, Ca, K and P contents of the plough layers. The most significant influence of subsoil type was in the K content of the mould. The highest content (123 mg/l K) was in the mould with clay as subsoil, and was twice as high as the K content of the mould with peat as subsoil.

The mould soils with a clay subsoil were also the least acid (pH 5,37). Their average Ca content (1722 mg/l) was the highest, too. The mould soils with peat subsoil had a Ca content of 1711 mg/l, which was nearly the same as with the clay subsoil. However, their pH value of 5,07 was the lowest. The mould soils above the coarse mineral soils were the poorest in calcium (1267 mg/l), and the entire fertility of these was low.

The lowest P content (2,8 mg/l) was found in the mould soils above peat subsoil. The P contents of the other mould soil groups were a little higher than this and about the same as each other.

Index words: subsoil, mould, Ca, K, P, pH.

INTRODUCTION

The moulds, soils containing 20—40 % organic matter, are found mainly in cultivated areas in regions with a temperate climate. Mould is usually a man-made soil type; farmers have used mineral soils to improve peat soils and peat to improve mineral soils. Otherwise, mould is found in large areas where shallow peat soils have been reclaimed and the peat has been mixed with the underlying mineral soil

during the process of cultivation. The only original mould soils are found in grass-herb forests or areas liable to flooding.

The mineral component of mould can be clay, silt, fine sand, sand or till. Therefore there are considerable variations in the physical and chemical properties of mould soils (KURKI 1982). Where shallow peat soils have been cleared, as well as on the mould areas formed

when peat is worn out, the mineral component of the mould is the same soil type as the subsoil. We can thus assume that there is a definite influence of subsoil on the fertility of mould.

When AARNIO (1921) studied different subsoil types, his opinion was that the effect of the subsoil was very important to how well the plants thrived. The nutrients leached from the plough layer are absorbed into the subsoil layer. On the other hand, nutrients are raised by capillary motion from the lower layers to the subsoil. Deep-rooted plants in particular can then exploit the nutrient reservoirs below the plough layer.

In a field trial (KIVINEN 1935), with the same level of fertility in the plough layer, lower yields were obtained on plots where the subsoil pH was lower. When the pH of the subsoil changed from pH 5,8 to 4,6 the yields decreased by about 30 %.

MOON (1938) discussed a number of the effects of subsoils on plant growth when outlining the relationships between compact subsoils and productivity. For example, the subsoil may contribute significant amounts of nutrients and water if it is readily penetrated by plant roots.

According to WINTERS and SIMONSON (1951) most subsoils have a lower nitrogen content than the surface soils; the same applies to organic phosphorus and forms of phosphorus readily available to plant. On the other hand, the subsoils generally have higher con-

tents of calcium, magnesium and potassium available to plants than the plough layer. Where nutrient deficiencies are suspected, the levels present in the subsoil should also be investigated. The problems encountered in measuring and interpreting the fertility of subsoil fall within the range of those encountered in surface soils. It seems that these problems can be approached using the same general procedures.

The results obtained in the study of samples collected in connection with mapping of agricultural soils show that the extractable calcium and potassium contents are higher in fine textured than in coarse textured mineral soils (SILLANPÄÄ and URVAS 1966, VIRRI 1972, URVAS 1976). The trend is the same in both surface and lower layers. The phosphorus contents, on the other hand, are lower in clay soils than in other mineral soils, because the phosphorus is more closely bound to clays than to other soil types.

This discussion has so far concerned the differences between surface and subsoil layers which are formed from the same soil type. In the present investigation, the soil samples taken from the plough layer were moulds, but the soil types in the subsoil layer varied. The aim of this study was to discover how much the fertilities of mould layers on different soil types differ from each other and what is the influence of the subsoil nutrients on the fertility of mould.

MATERIAL AND METHODS

Soil samples were taken from the plough and subsoil layers in fields during a routine soil survey carried out by the Institute of Soil Science. Sample pairs from 593 sites were taken from 23 mapping areas (Fig. 1).

The sample pairs were classified according to the subsoil types (20—40 cm). Four groups of mould samples were found, as follows: 182 with coarse mineral subsoil (till, sand, fine sand and silt), 103 with clay subsoil, 80 with

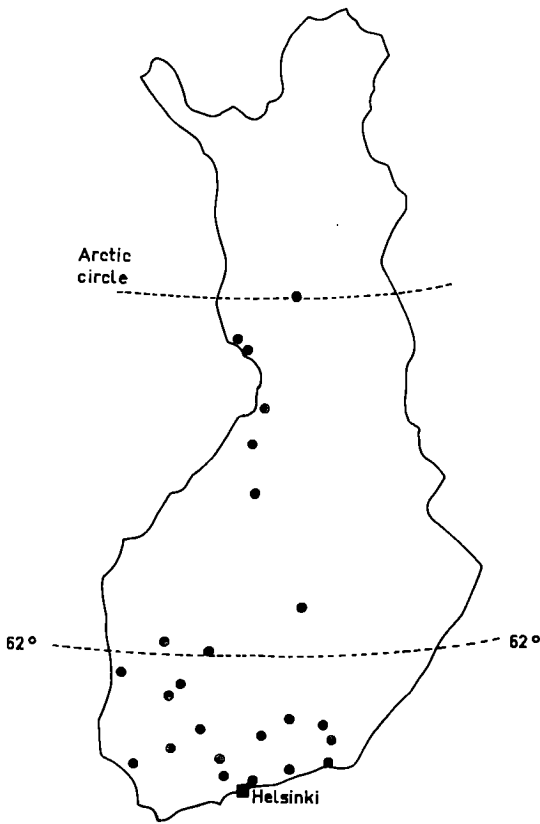


Fig. 1. The location of the agricultural soil map sites from which the mould soils samples were collected.

gyttja subsoil, and 228 with peat subsoil.

The macronutrients calcium, potassium, and phosphorus were determined by the soil testing method (VUORINEN and MÄKITIE 1955); the results are expressed on an elemental basis as mg/litre soil (KURKI et al. 1965). The soil pH was measured from a 1:2,5 soil:water suspension, organic matter by the dichromate method, and nitrogen by the Kjeldahl method.

The differences in the nutrient contents between the four mould groups as well as between the four subsoil groups were tested with a multiselection test using Tukey tables (STEELE and TORRIE 1960).

The influence of the subsoil soil type on the fertility of the overlying mould was studied using analysis of variance. In order to exclude the influence of a subsoil plant nutrient on the corresponding mould nutrient in normal regression analyses, that nutrient was taken as a factor in calculations.

The correlation between the plant nutrient in corresponding mould and subsoil samples is presented with regression lines. The parallelism of the regression lines was also tested (SNEDECOR and COCHRAN 1972).

RESULTS AND DISCUSSION

The average pH of all mould samples was 5,16, ranging from pH 3,9 to 6,6 and the corresponding values of subsoil layers was pH 5,11, ranging from pH 3,0 to 7,2 (Table 1). The influence of the subsoil type on the pH values of the mould was highly significant (Table 2).

The average pH of the mould layer on clay soil was the highest. The pH values of mould

on coarse mineral soils and those on gyttja soil were similar. The mould layer on the peat soil was more acid than these and differed significantly from all of the others. The pH of the clay subsoil was the highest (pH 5,63). The organic subsoils — gyttja and peat — were more acid than the coarse mineral subsoils. According to the correlation analysis the differences between the pH values of the mould

Table 1. The mean pH values and plant nutrient contents of four subsoil groups and the corresponding values of mould above them. The significances between the differences are denoted with letters; same letters = no difference, different letters = differ from each other with a probability $p = 0,99$.

Soil groups	Number of samples	pH	Calcium	Potassium mg/l	Phosphorus	Humus %	Nitrogen %	C/N ratio
Plough layer								
Mould on coarse mineral soils	182	5,15 ^b	1267 ^a	69 ^a	4,0 ^b	28,0 ^a	0,89 ^a	19 ^b
Mould on clay soils	103	5,37 ^b	1722 ^a	123 ^b	4,1 ^{ab}	26,9 ^a	0,87 ^a	18 ^{ab}
Mould on gytja soils	80	5,19 ^b	1340 ^a	112 ^b	4,1 ^{ab}	26,7 ^a	0,94 ^a	17 ^a
Mould on peat soils	228	5,07 ^a	1711 ^b	62 ^a	2,8 ^a	29,9 ^b	0,92 ^a	19 ^b
Mould soils average	593	5,16	1527	81	3,6	28,4	0,91	19
Subsoil layer								
Coarse mineral soils	182	5,20 ^b	538 ^a	41 ^a	2,1 ^b			
Clay soils	103	5,63 ^c	1608 ^c	114 ^b	1,5 ^{ab}			
Gyttja soils	80	4,91 ^a	1063 ^b	96 ^b	1,6 ^{ab}			
Peat soils	228	4,87 ^a	1636 ^c	31 ^a	1,3 ^a			
Subsoils average	593	5,11	1217	57	1,6			

and the corresponding subsoil depended only on the pH levels of the different soil types — the so-called differences in elevation were significant (Fig. 2).

In Finnish soils (SILLANPÄÄ and URVAS 1966, URVAS 1976 etc.), the fertility of surface layers is higher than in subsoils if the same soil type is considered. In the present study, the calcium, potassium and phosphorus contents of the mould layers were also higher than those of the underlying subsoils. This is caused by liming and fertilizing of the fields.

The moulds on the clay and peat soils had the highest calcium contents, but only the Ca values of the latter group deviated significantly from the other groups. The differences in calcium contents in the subsoil layers were

more distinct; the coarse mineral soils had the lowest calcium values — three times lower than in the clay and peat soils (Table 1).

The effect of the subsoil type on the calcium content of the mould was highly significant (Table 2). The coefficients of regression, which described the influence of subsoil Ca values on

Table 2. The test results of the pH and nutrient contents between different mould groups and their subsoils.

The tested property of mould soil	The influence of the subsoil soil type on the properties of mould tested by variance analyses, F-values	The correlation between the nutrient contents of subsoils and the nutrient contents of corresponding mould tested by regression analyses, F-values
pH	14,96 ^{***} (3,589)	4,24 ^{**}
Calcium	12,91 ^{***} (3,589)	3,74 [*]
Potassium	38,72 ^{***} (3,589)	0,15
Phosphorus	5,29 ^{**} (3,589)	3,58 [*]

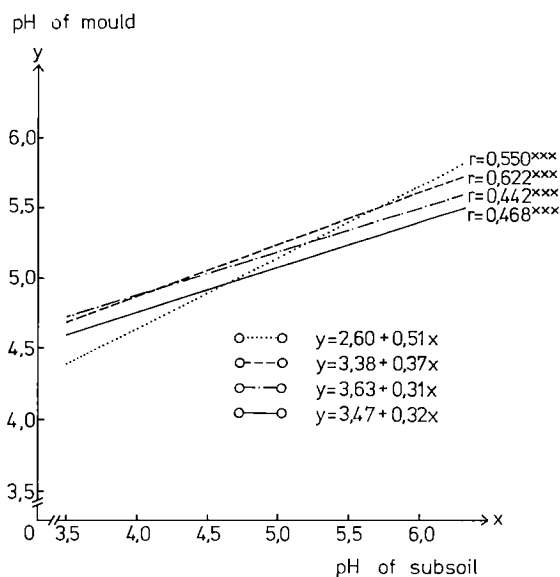


Fig. 2. The regressions of pH values of mould against those of the respective subsoil.

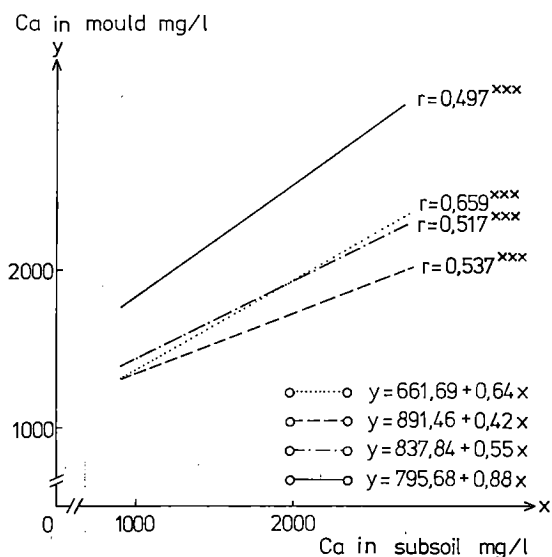


Fig. 3. The regressions of Ca contents of mould against those of the respective subsoil.

the mould Ca values, varied from 0,42 to 0,88, but elevation differences were relatively small. According to regression analysis (Table 2), no soil factors other than calcium in subsoil had an effect on the Ca content of mould (Fig. 3).

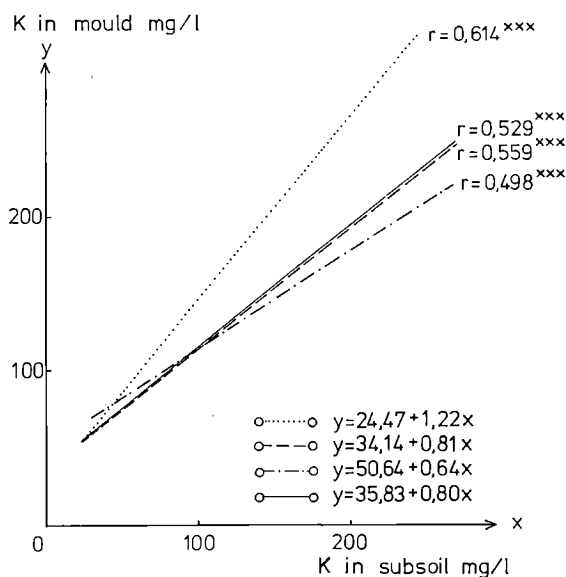


Fig. 4. The regressions of K contents of mould against those of the respective subsoil.

The potassium contents in the mould layer varied from 10 to 423 mg/litre soil, average 81 mg K/l, and that in subsoil 57 mg/l. The subsoils of coarse mineral and peat soils were poor in potassium, like the mould layers above them (Table 1). These characteristics clearly differed from the potassium contents of the groups with clay or gyttja subsoils and these are, again, similar to each other.

Statistically, the most significant effect was that of the subsoil type on the potassium contents in mould (Table 2, var.). The only reason for this might have been the mutual correlation between the potassium contents of mould and subsoil (Fig. 4), because the other properties of subsoil did not correlate with the K values of mould (Table 2, regr.).

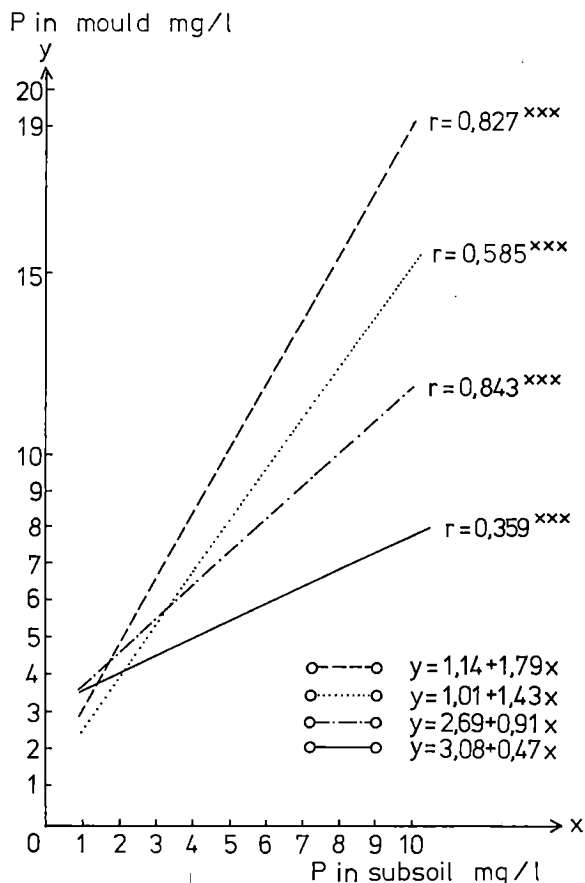


Fig. 5. The regressions of P contents of mould against those of the respective subsoil.

The influence of subsoil type on the phosphorus content in mould of the plough layer was not as evident as on the other nutrients (Table 2, var.). The lowest phosphorus contents (1,3 mg/l) were in peat subsoil and in the mould on it (2,8 mg/l), but statistically these values did not deviate significantly from the P contents of the clay and gyttja subsoils, and their corresponding moulds. The only statistically significant dissimilarity in the phosphorus contents was between the mould on coarse mineral soil and that on peat (Table 1). In the parallel test of the regression lines, the four mould groups had distinct trend differences (26,3***, Fig. 5). This means that, when the phosphorus content of the subsoil is increasing in the same way, the P content of the corresponding mould increases differently

in all four groups, as follows: most quickly in mould on gyttja, then peat and gyttja and slowest on the coarse mineral soils.

Humus and nitrogen determinations were performed on mould samples from the surface soil only, not from subsoils. The average humus content of mould on the peat soil (29,9 %) was only a little higher than the others (Table 1). In the different soil mapping areas, for example in Anjala-Kymi, the humus content of mould on peat soils was 15 percentage units higher than on clay soils (SILLANPÄÄ and URVAS 1966).

The average nitrogen content of mould was 0,91 per cent, ranging from 0,25 to 1,95. The C/N ratio in mould on gyttja soil differed significantly from this ratio only in mould on coarse mineral and peat soils.

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SELOSTUS

Jankon vaikutus multamaan ravinteisuuteen

LEILA URVAS

Maatalouden tutkimuskeskus

Tutkimuksen tarkoituksena oli selvittää jankon maalajin ja sen ravinteiden vaikutus muokkauskerroksena olevan multamaan ravinnepitoisuuksiin. Maaperäkartoitusaineistosta kerättiin 593 multamaan ja niiden alla olevan jankon viljavuusluvut, jaettiin aineisto jankon maalajin mukaan neljään ryhmään ja tarkasteltiin niiden ravinnepitoisuuksia. Jankon maalajiryhmät olivat karkeat kivennäismaat, savet, lieju ja turpeet.

Eri maalajien päällä olevien multamaiden viljavuusluvuisa oli selvät erot. Jankon maalajin vaikutus multamaan ravinteisiin näkyi parhaiten kaliumpitoisuuksissa ja heikoimmin fosforipitoisuuksissa.

Ne multamaat, joiden jankkona oli savi, olivat sekä happamuutensa että ravinteisuutensa puolesta parhaita. Niiden pH 5,37 edustaa Viljavuuspalvelun tulkinnan mukaan viljavuusluokkaa 4 eli tyydyttävä. Samaan viljavuusluokkaan ne kuuluvat myös sekä kalsium- että kaliumtasoltaan. Keskimääräinen Ca-luku oli 1722 mg/l ja K-luku 123 mg/l. Fosforipitoisuudet olivat samaa suuruusluokkaa karkeiden

kivennäismaiden ja liejujen päällä olevien multamaiden kanssa eli välttäviä.

Liejujankkoisten multamaiden kaliumpitoisuus oli ainoa, joka ylty viljavuusluokkaan 4, muut ominaisuudet jäivät viljavuusluokkaan 3.

Karkeiden kivennäismaiden päällä olevat multamaat olivat viljavuustasoltaan välttäviä. Niiden kalsiumpitoisuus 1267 mg/l oli alhaisin verrattuna muihin multamaaryhmiin. Myös karkeiden kivennäismaajankkojen Ca-pitoisuus 538 mg/l oli koko aineiston pienin.

Turvejankkoiset multamaat olivat happamimpia, pH 5,1. Niiden kaliumpitoisuus 62 mg/l oli myös alhaisin edustuen viljavuusluokkaa välttävä. Fosforipitoisuus 2,8 mg/l niin ikään oli pienin turvejankkoisilla multamailla. Viljavuuspalvelun tulkinnan mukaan se yltyä vain viljavuusluokkaan 2.

Multamaiden keskimääräinen humusprosentti vaihteli 26,9—29,9 ja oli korkein turpeiden päällä olevilla multamailla.

CONTENTS

YLÄRANTA, T. Effect of added selenite and selenate on the selenium content of italian rye grass (<i>Lolium multiflorum</i>) in different soils	139
— Effect of liming and sulphate on the selenium content of italian rye grass (<i>Lolium multiflorum</i>)	152
— Effect of applied selenite and selenate on the selenium content of barley (<i>Hordeum vulgare</i> L.)	164
BAGHDADY, N. H. & SIPPOLA, J. Total heavy metal recovery by aqua regia in soils of different origin	175
URVAS, L. The influence of different subsoil types on the Ca, K and P status and pH of the corresponding mould layer	186

ERRATA

Annales Agriculturae Fenniae, Vol. 22: 186—192 (1983)

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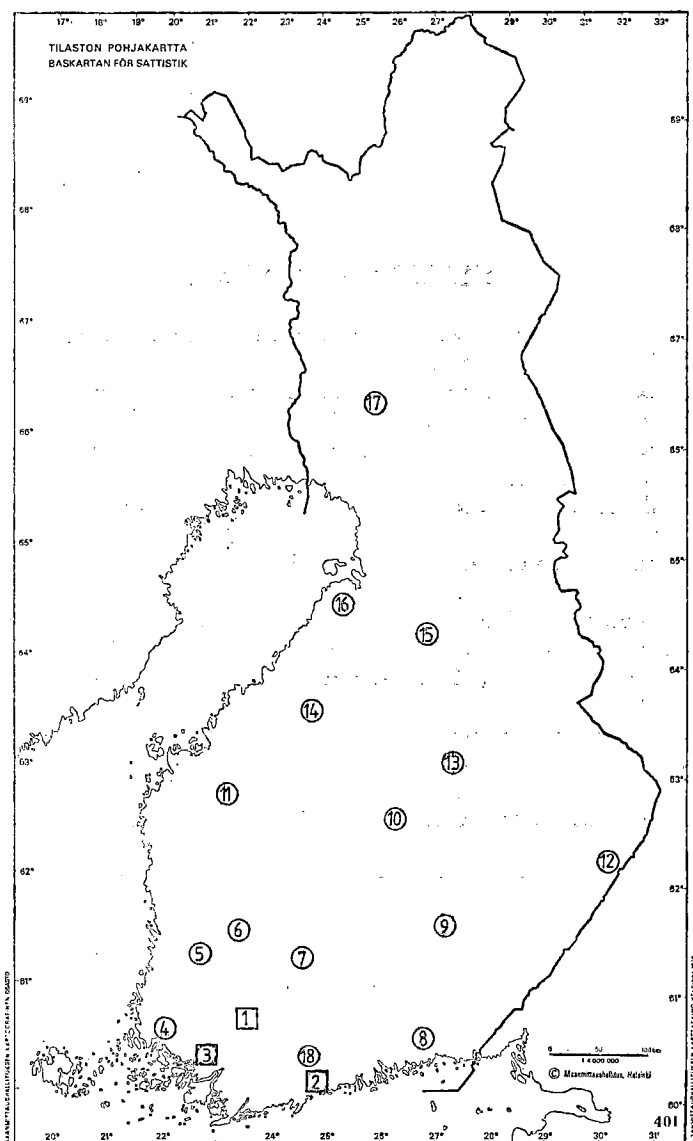
Addition to Fig. 2 on page 189.

o - - - o gyttja soil, o ····· o peat soil,

o ····· o clay soil, o ——— o coarse mineral soil,

corresponding explanations in Fig. 3, 4 and 5

Page 191 the second row on the right should be:
in mould on gyttja, then peat and clay and



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SISÄLLYS — CONTENTS

YLÄRANTA, T. Effect of added selenite and selenate on the selenium content of italian rye grass (<i>Lolium multiflorum</i>) in different soils	139
Selostus: Maahan lisätyn seleniitin ja selenaaatin vaikutus Italian raiheinän (<i>Lolium multiflorum</i>) seleenipitoisuuteen	151
— Effect of liming and sulphate on the selenium content of italian rye grass (<i>Lolium multiflorum</i>)	152
Selostus: Kalkituksen ja sulfaatin vaikutus Italian raiheinän (<i>Lolium multiflorum</i>) seleenipitoisuuteen	163
— Effect of applied selenite and selenate on the selenium content of barley (<i>Hordeum vulgare</i> L.)	164
Selostus: Maahan lisätyn seleniitin ja selenaaatin vaikutus ohran (<i>Hordeum vulgare</i> L.) seleenipitoisuuteen	174
BAGHDADY, N. H. & SIPPOLA, J. Total heavy metal recovery by aqua regia in soils having different origin	175
Selostus: Kuningasveden kyky uuttaa raskasmetalleja	185
URVAS, L. The influence of different subsoil types on the Ca, K and P status and pH of the corresponding mould layer	186
Selostus: Jankon vaikutus multamaan ravinteisuuteen	192