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# SULPHUR IN CULTIVATED ORGANIC SOILS

Rikki viljellyissä eloperäisissä maissa

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In mould soils the concentration of acid ammonium acetate extractable sulphur ( $S_{AAAc}$ ) was 33 mg/l on average and total sulphur ( $S_{tot}$ ) was 833 mg/l. Corresponding contents in peat soils were 45 and 1209 mg/l, respectively. Average extractability of sulphur was 4.2 % in mould soils and 3.7 % in peat soils. In both soil types the extractability was highest when pH was lowest. Increasing humus contents decreased slightly the extractability of sulphur.

Key words: humus, mould soil, peat soil, pH, extractable and total sulphur

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#### INTRODUCTION

The problem of excess sulphur was encountered in Finland during the 1940s after coastal areas of the Gulf of Bothnia were reclaimed for agricultural use (Purokoski 1959). Iron sulphide in the subsoils had oxidized into sulphate after drainage and caused the soil to become too acidic for cultivation. Heavy liming has improved these soils, but the extractable sulphur concentration in such gyttja-containing soils is still generally very high, with concentrations mostly ranging from 250 to 1200 mg/l (Erviö 1991). No problems have been observed with respect to sulphur in other parts of the country.

The widespread use of industrial fertilizers containing sulphur, in addition to farmyard manure, has maintained an adequate sulphur status of agricultural soils (Salonen et al. 1965, Korkman 1973). Thus interest in the determination of sulphur in soil has been slight. Recently, however, the need to determine sulphur has increased as a result of the further intensification and specialization of agriculture. In addition, the cultivation of sulphur demanding plants (the family *Brassicaceae*) has become more common.

Changes in the sulphur balance of soils due to atmospheric sulphur deposition by rainfall have emphasized the need to determine the sulphur contents of soils. Improved methods for sulphur determination are needed in Finland as well.

In other parts of Europe, the sulphur contents in air, plants and soils have been studied since the 1970s (Schnug 1991). However, very few total sulphur determinations have been made of Finnish soils (Salonen et al. 1965 Korkman 1973). The determination of extractable concentration has been more common instead. Purokoski and Lakanen (1959) tried to find a method for the determination of plant available sulphur. Dilute calcium chloride and acid ammonium acetate have been studied as extractants. Since the 1970s Viljavuuspalvelu Oy (Soil Analysis Service Ldt) has determined sulphur by gravimetric measurement using calcium chloride as the extractant (Salonen et al. 1965). Plasma emission spectrometers (ICP) became available in Finland during the 1980s. In order

to save costs, the possibilities were studied for the simultaneous determination of sulphur and other nutrient contents from a soil filtrate extracted by acid ammonium acetate (AAAc method, Vuorinen and Mäkitie 1955). According to the results of one comparison, the CaCl<sub>2</sub>method extracted two-thirds of that extracted by AAAc method (Yli-Halla 1987).

The Institute of Soils and Environment, Agricultural Research Centre of Finland (FARC) has used the AAAc method for the determination of sulphur since 1986. Viljavuuspalvelu Oy has used this method since 1991, but no results have been published. An other comparison between acid ammonium acetate and acid ammonium acetate-EDTA (Lakanen and Erviö 1971) as the extractant in sulphur analysis has also been carried out (Urvas 1994). AAAc-EDTA is a stronger extractant than AAAc alone. The ratios of results obtained by these methods for different soils vary from 1:1.5 to 1:1.9.

In the recommendations for sulphur fertilization (Viljavuustutkimuksen... 1991), Viljavuuspalvelu Oy has used the fertility classes based on the studies of Korkman (1973) and Yli-Halla (1987). In addition to knowing the extractable sulphur concentration in soils, however, it is also necessary to quantify the total sulphur resources in soils. The object of this study was to determine how much of the total sulphur in mould and peat soils is extractable.

#### MATERIAL AND METHODS

Soil samples were collected from the Ruukki and Sotkamo Research Stations, the Jokioinen Estate, the Juva district and from Lapland. Altogether, 111 soil samples were collected from plough layers (0–20 cm). According to soil type classification there were 59 samples of mould soil (humus content 20–40 %) and 52 samples of *Carex* peat (humus content over 40 %). Samples were air-dried, crushed and then passed through a 2-mm sieve before analysis.

Extractable sulphur was determined by acid ammonium acetate (pH 4.65) method (Vuorinen and Mäkitie 1955). Total sulphur content was analysed after wet combustion (Huang and Schulte 1985). Sulphur concentration of the extracts was determined by ICP-ARL. For comparison of the results, the total sulphur contents (mg/kg soil) were transformed into mg/l using bulk density determined in laboratory. The material was then classified according to the extractable sulphur, humus percentages and  $pH(H_2O)$  values obtained (Table 1). Humus percentages were calculated by multiplying the organic carbon percentages by 1.724.

## RESULTS AND DISCUSSION

The total sulphur ( $S_{tot}$ ) contents in this material varied from 310 to 8530 mg/kg air-dried soil. The average  $S_{tot}$  content in mould soils was 1327 mg/kg and in peat soils 3343 mg/kg. The resulting values of the present samples were somewhat higher than those obtained from the arable land samples of Korkman (1973). In his material the variation of mould and peat soils was 530–2160 mg/kg. In cultivated, so called acid sulphate soils from the coastal region of the Gulf of Bothnia, the average  $S_{tot}$  content in organic soils has been 2570 mg/kg (Erviö and Palko 1984).

When transformed with bulk density, the  $S_{tot}$  contents varied from 167 to 3241 mg/l. Mould soils contained 833 mg/l  $S_{tot}$  and peat soils 1209 mg/l on average (Table 2). The highest  $S_{tot}$  contents were found in samples from the Ruukki Research Station where high S contents in subsoils were previously encountered (Purokoski 1959).

The AAAc extractable sulphur ( $S_{AAAc}$ ) contents in mould soils averaged 33 mg/l, ranging from 11.3 to 171.0 mg/l. Peat soils had slightly higher S contents, 45 mg/l on average and the ranges were wider, from 10.5 to 441.0 mg/l. According

Table 1. Classes of acid ammonium acetate extractable sulphur, humus % and pH.

Taulukko 1. Happamaan ammoniumasetaattiin uuttuvan rikin, humusprosentin ja pH:n luokkarajat.

	Classes of extractable sulphur mg/l	Classes of pH	Classes of humus %
1.	10-24.9	3.60-4.99	20.1-39.9
2.	25-49.9	5.00-5.49	40.0-
3.	50-74.9	5.50-	
4.	75-		

<sup>1</sup>mould, <sup>2</sup>peat

Table 2. AAAc-extractable ( $S_{AAAc}$ ) and total sulphur ( $S_{tot}$ , m/l soil), and proportion of extractable S of the total S (%) in mould and peat soils classified according to extractable S (mean  $\pm$ SD).

Taulukko 2. HAA:iin uuttuva rikki, kokonaisrikki (mg/l) ja rikin liukoisuusprosentti multa- ja turvemaissa uuttuvan rikin mukaan luokiteltuna.

Classes of S <sub>AAAc</sub>	n	S <sub>AAAc</sub> mg/l	S <sub>tot</sub> mg/l	$\begin{array}{c} S_{AAAc} \ \% \\ of \ S_{tot} \end{array}$
Mould soil	s, multama	at		
1	19	$20.4 \pm 4.3$	658.1 ± 142.3	$3.2 \pm 0.7$
2	34	$32.1 \pm 5.5$	868.4 ± 163.1	4.2 ± 3.1
3	5	$60.1 \pm 7.5$	$1219.6 \pm 570.0$	5.6 ± 2.1
4	1	171.0	1120.0	15.3
Mean	59	$32.9 \pm 21.8$	833.2 ± 264.5	4.2 ± 3.0
Peat soils,	turvemaat			
1	19	$19.2 \pm 3.8$	847.9 ± 343.5	$2.6 \pm 1.0$
2	23	$36.8 \pm 7.5$	1451.5 ± 651.7	3.1 ± 1.8
3	7	$56.2 \pm 6.1$	$1093.5 \pm 75.3$	$5.2 \pm 0.7$
4	3	$242.4 \pm 182.5$	$1900.6 \pm 663.2$	$11.5 \pm 5.3$
Mean	52	$44.8 \pm 62.7$	$1208.7 \pm 589.8$	$3.7 \pm 2.7$

to the classifications used in Finland (Viljavuustutkimuksen... 1991), 80 % of this material belongs in the good fertility class (15–50 mg  $S_{AAAc}/I$ ) and only 4 % in the satisfactory class (10–15 mg/I).The  $S_{AAAc}$  contents of the other samples exceeded 50 mg/I.

In 1987, the Institute of Soils and Environment collected 1320 soil samples from Finnish cultivated fields and also determined them for sulphur concentrations. The mean value of the whole material was 19 mg/l S (Erviö et al. 1989). The  $S_{AAAc}$  concentrations of soil samples taken from cultivated fields in organic soils were lower than the present values, on average 24 mg/l, ranging from 4.3 to 269 mg/l.

As mentioned earlier, rather high S contents may occur locally in acid sulphate soils of the coastal region of the Gulf of Bothnia (Erviö and Palko 1984). The present samples from the Ruukki Research Station are from that area. The average content of the extractable sulphur in peat soil samples from Ruukki was 92 mg/l (14 samples). The mean  $S_{AAAc}$  content in the rest of the samples was only 27 mg/l, which is nearly the same as that reported by Erviö et al. (1989).

When the material was classified according to extractable sulphur, the proportion of  $S_{AAAc}$  compared to  $S_{tot}$  increased with increasing extractable S in both mould and peat soils (Table 2). The extractability percentages on average and in corresponding classes were slightly higher in mould soils than in peat soils. The

results are comparable with those of Korkman (1973). In his material, when the  $S_{AAAc}$  mean was 16 mg/l S, the extractability was 3.3 in mould soils, which is similar (3.2 mg/l) to Class 1, where the extractable S was between 10–25 mg/l.

The extractability of peat soils in the earlier material (Korkman 1973) was lower (1.3 %), but so were the  $S_{AAAc}$  (5.1 mg/l) and the  $S_{tot}$  (395 mg/l) contents too. These values fit well into the lowest class in the  $S_{AAAc}$  classification of Table 2. A comparable S extractability (3.7%) in organic soils was also found in another material collected from experimental fields (Salonen et al. 1965). When the  $S_{AAAc}$  contents increased in mould soils the  $S_{tot}$  values also increased, but in peat soils the  $S_{tot}$  did not change regularly.

In both soil types the extractable sulphur content was the highest when pH was between 3.6-5.0 (Table 3). When the acidity decreased in both soils the S<sub>AAAc</sub> and the solubility of S decreased, too.

When classified according to humus content the results showed, that  $S_{AAAc}$  and  $S_{tot}$  contents increased with increasing humus content (Table 2), but the extractability of S decreased. The total percentages were quite small, averaging 4.2% in mould soils and 3.7% in peat soils. The S extractability was higher in samples collected from the Ruukki Experimental station than others (Fig. 1). The extractability was 7.6% in mould soils of Ruukki and 6.2% in peat soils on average, but in other samples 3.3% and 2.7%, respectively.

pH Classes	n	S <sub>AAAc</sub> mg/l	S <sub>tot</sub> mg/l	${f S_{AAAc}}\ \% \ of \ {f S_{tot}}$
Mould so	ils, multamad	<i>at</i>		
1	2	$56.6 \pm 23.4$	$808.8 \pm 124.8$	$6.8 \pm 1.8$
2	27	$37.0 \pm 28.7$	$798.9 \pm 219.5$	$5.0 \pm 4.0$
3	30	$28.0 \pm 10.2$	868.7 ± 302.7	$3.3 \pm 0.8$
Peat soils	, turvemaat			
1	16	66.6 ± 109.6	$1040.5 \pm 661.8$	$5.3 \pm 4.0$
2	22	$41.0 \pm 17.2$	$1353.7 \pm 574.7$	$3.3 \pm 1.6$
3	14	$26.0 \pm 9.4$	$1173.0 \pm 503.9$	$2.4 \pm 0.9$

Table 3.  $S_{AAAc}$  and  $S_{tot}$  (mg/l soil), and proportion of extractable S of the total S (%) in mould and peat soils classified according to soil pH(H<sub>2</sub>O) (mean ± SD).

Taulukko 3. Uuttuva ja kokonaisrikki (mg/l) sekä liukoisuusprosentti multaja turvemaissa luokiteltuna  $pH(H_2O):n$  mukana.



Fig. 1. Ratio of AAAc extractable S and total S (%) as function of humus %.

The AAAc method has been found to extract only a very small portion of the total sulphur. The major portion of soil sulphur is in organic form and is released during decomposition. Sulphur reserves are substantial and the rate of decomposition determines how fast it becomes available to plants. However, its importance is increasing when the atmospheric deposition of sulphur is decreasing due to restrictions set for industry.

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Kuva 1. Rikin liukoisuusprosentit esitettyinä humusprosentin mukaan.

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#### TIIVISTELMÄ:

## RIKKI VILJELLYISSÄ ELOPERÄISISSÄ MAISSA

Suomessa todettiin 1940-luvulla olevan liikaa rikkiä ns. alunamailla Pohjanlahden rannikolla. Varsinaisissa viljelymaissa rikin puutosta havaittiin vasta 1980-luvulla ennen muuta viljeltäessä ristikukkaisia kasveja. Rikin analyysimenetelmiä on kehitetty, mutta tulokset ovat jääneet vähälle huomiolle.

Kasveille käyttökelpoisen rikin määrittäminen hapanammoniumasetaattiuutteesta (pH 4.65) otettiin käyttöön MTT:n ympäristöntutkimuslaitoksella vuonna 1986 ja Viljavuuspalvelussa vuoden 1991 alussa. Lannoitussuositukset tehdään nykyään tällä menetelmällä saatujen analyysitulosten mukaan.

Liukoisen rikin osuutta turpeiden ja multamaiden sisältämästä rikistä on tutkittu aikaisemmin vähän, minkä vuoksi tässä tutkimukessa muokkauskerroksesta otetuista 59 multamaasta ja 52 saraturpeesta analysoitiin happamaan ammoniumasetaattiin uuttuvan rikin lisäksi kokonaisrikki märkäpoltolla.

Multamaissa oli happamaan ammoniumasetaattiin uuttuvaa rikkiä keskimäärin 33 mg/l ja kokonaisrikkiä 833 mg/l. Saraturpeissa vastaavat määrät olivat 45 ja 1209 mg/l. Multamaissa liukoisen rikin osuus kokonaisrikistä oli 4.2 % ja turpeissa vielä vähän pienempi eli 3.7 %, ts. eloperäisen aineksen määrän eli humusprosentin kasvaessa rikin liukoisuus happamaan ammoniumasetaattiin pieneni. Molemmilla maalajeilla happamuuden lisääntyminen lisäsi rikin liukoisuutta.

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