# Plant-availability of soil and fertilizer zinc in cultivated soils of Finland

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# PREFACE

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The Zn status of cultivated soils of Finland was investigated by chemical analyses and bioassays. The effect on ryegrass of different Zn fertilizers and Zn rates was studied in pot experiments and their effect on barley and timothy in field experiments. In an uncontaminated surface soil material of 72 mineral soils and 34 organogenic soils, total Zn ($Zn_{tot}$) was 10.3 - 202 mg $kg^{-1}$ (median 66 mg $kg^{-1}$). In mineral soils, $Zn_{tot}$ correlated positively with clay content ($r = 0.81^{***}$) and in organogenic soils negatively with organic C ($r = -0.53^{***}$). Zinc bound by organic matter and sesquioxides was sequentially extracted by 0.1 M $K_4P_2O_7$ ($Zn_{py}$) and 0.05 M oxalate at pH 2.9 ($Zn_{ox}$), respectively. The sum $Zn_{py} + Zn_{ox}$, a measure of secondary Zn potentially available to plants, was 2 - 88% of $Zn_{tot}$ and was the lowest in clay (median 5%) and highest in peat soils (median 49%). Water-soluble and exchangeable Zn consisted of 0.3 - 37% (median 3%) of $Zn_{tot}$, the percentage being higher in acid soils, particularly in peat soils. Zinc was also extracted by 0.5 M ammonium acetate - 0.5 M acetic acid - 0.02 M $Na_2$-EDTA at pH 4.65 ($Zn_{Ac}$), the method used in soil testing in Finland. The quantities of $Zn_{Ac}$ (median 2.9 mg $dm^{-3}$, range 0.6 - 29.9 mg $dm^{-3}$) averaged 50% and 75% of $Zn_{py} + Zn_{ox}$ in mineral and organogenic soils, respectively, and correlated closely with $Zn_{py}$. In soil profiles, $Zn_{Ac}$ was with few exceptions higher in the plough layer (0 - 20 cm) than in the subsoil (30 - 100 cm).

In an intensive pot experiment on 107 surface soils, four crops of ryegrass took up 2 - 68% (median 26%) of $Zn_{py} + Zn_{ox}$. The plant-available Zn reserves were not exhausted even though in a few peat soils the Zn supply to grass decreased over time. Variation of Zn uptake was quite accurately explained by $Zn_{Ac}$ but increasing pH had a negative impact on Zn uptake. Application of Zn (10 mg $dm^{-3}$ of soil as $ZnSO_4 \cdot 7H_2O$) did not give rise to yield increases. In mineral soils, increase of plant Zn concentration correlated negatively with soil pH while $Zn_{Ac}$ was of secondary importance. In those organogenic soils in which the reserves of native Zn were the most effectively utilized, plant Zn concentration also responded most strongly to applied Zn.

In two 2-year field experiments, Zn application did not increase timothy or barley yields. Zinc concentration of timothy increased from 30 mg $kg^{-1}$ to 33 and 36 mg $kg^{-1}$ when 3 or 6 kg Zn $ha^{-1}$ was applied, respectively. The efficiency of $ZnSO_4 \cdot 7H_2O$ alone did not differ from that of a fertilizer where $ZnSO_4 \cdot 7H_2O$ was granulated with gypsum. Zinc concentration of barley grains increased by foliar sprays of $Na_2Zn$-EDTA but only a marginal response to soil-applied Zn (4.8 or 5.4 kg $ha^{-1}$ over three years) was detected in three 3-year experiments. High applications of Zn to soil (15 or 30 kg $ha^{-1}$ as $ZnSO_4 \cdot 7H_2O$) were required to increase Zn concentration of barley markedly.

In order to prevent undue accumulation of fertilizer Zn in soil, it is proposed that Zn fertilizer recommendations for field crops should be based on both soil pH and $Zn_{Ac}$. In slightly acid and neutral soils, even if poor in Zn, response of plant Zn concentration to applied Zn remains small while there is a high response in strongly acid soils.

Key words: soil analysis, vertical distribution of soil Zn, pot experiments, field experiments, liming, plant Zn concentration, barley, ryegrass, timothy

# 1 INTRODUCTION

Zinc is a trace element, the average concentration of which in the earth's crust is quoted as 70 mg kg$^{-1}$ (WEDEPOHL 1991). There are minerals containing Zn among olivines and pyroxenes, e.g. acmite-augite, and amphiboles, e.g. riebeckite. Also 2:1 clay minerals, mainly trioctahedral micas, contain Zn owing to isomorphic substitution of Mg or Fe ions for Zn at octahedral sites (RANKAMA and SAHAMA 1950, LINDSAY 1972, HUANG 1989). A substantial part of total Zn in soil occurs in clay and silt size particles (SHUMAN 1985), and total Zn content correlates with the content of clay or clay plus silt (SIPPOLA 1974, SCHLICHTING and ELGALA 1975, TJELL and HOVMAND 1978, BAGHDADY and SIPPOLA 1983, LIANG et al. 1990). Zinc is released into the soil solution from mineral structures through weathering reactions as $Zn^{2+}$ cation which is further adsorbed by various soil constituents and utilized by living organisms.

The significance of Zn as a nutrient of higher plants was shown in 1926 by SOMMER and LIPMAN. Zinc is involved in several enzymatic reactions of protein and carbohydrate metabolism of plants (MARSCHNER 1986). Zinc deficiency in crop production is extensive in calcareous soils (SILLANPÄÄ 1982), but insufficient Zn supply to dryland crops occurs also in acid soils for example in several states of the USA (JUNUS and COX 1987, BOSWELL et al. 1989), Brazil (LINS and COX 1988), Australia (BRENNAN and GARTRELL 1990) and Zambia (BANDA and SINGH 1989). Zinc deficiency induced by liming has also been reported (KOWALENKO et al. 1980, MACNAEIDHE et al. 1986, MYHR 1988). In Finland, the average Zn concentration of timothy ranges from 24 to 32 mg kg$^{-1}$ (LAKANEN 1969, KÄHÄRI and NISSINEN 1978) and in cereal grains from 26 to 36 mg kg$^{-1}$ (JAAKKOLA and VOGT 1978, VARO et al. 1980) although means as high as 54 mg kg$^{-1}$ have been reported in cereals (PESSI et al. 1974, SYVÄLAHTI and KORKMAN 1978). The Zn concentration in the crops of Finland is above the minimum physiological requirement of gramineous plants or clover, 10 - 20 mg kg$^{-1}$ of plant dry matter (e.g. MARSCHNER 1986, BRENNAN and GARTRELL 1990, CARSKY and REID 1990). Hence Zn applications have not increased yields in field experiments with cereals and forage crops (JAAKKOLA and VOGT 1978, SYVÄLAHTI and KORKMAN 1978, SILLANPÄÄ 1990). However, Zn concentration of crops grown in Finland is almost always below 50 mg kg$^{-1}$, a desirable level in the fodder of ruminants (NJF 1975, SALO et al. 1990).

Worldwide, annual industrial consumption of Zn ranks fifth among metals after Fe, Al, Mn and Cu (KABATA-PENDIAS and PENDIAS 1984). In Finland, 160 000 tons of Zn is manufactured annually (Tilastokeskus 1992), and 20% is consumed in the domestic markets mainly in galvanization (S. Karlman 1991, Outokumpu Oy, pers. commun.). Zinc is dispersed in the environment as emissions of metal industry and through the use of Zn-containing products. Elevated contents of Zn are found in soils of industrial areas, especially around Zn mines (BERGHOLM and STEEN 1989), smelters (ANDERSSON and NILSSON 1976, ELSOKKARY and LÅG 1978, MILLER and McFEE 1983), along highways (DELAUNE et al. 1989), under electric pylons (AL - HIYALY et al. 1990) and in urban areas in general (SALOMONS 1984) owing to traffic and combustion of fossil fuels (CASS and MCRAE 1983). Sludge application also gives rise to elevated Zn contents of soil (WIKLANDER and VAHTRAS 1977, CHRISTIE and BEATTIE 1989). Atmospheric deposition of anthropogenic origin is considered a major source of Zn input to the soil of rural areas in southern Sweden and western Norway (ÖBLAD and SELIN 1986, STEINNESS et al. 1989). The annual precipitation in southern and central Sweden and Finland is 100 - 140 g Zn ha$^{-1}$ (ROSS 1987, ERVIÖ et al. 1990) and an increasing accumulation of Zn in lake sediments of Finland has been observed during the last 100 years (MYLLYMAA and MURTONIEMI 1986, VERTA et al. 1989).

Zinc input into the cultivated soils of Finland has probably increased over time, but intensified cultivation has elevated Zn uptake by the crop especially in grasslands (RINNE et al. 1974). A decrease of soil Zn concentration in northern Finland has been observed in timothy fields when the same fields were analyzed in 1974 and again 14 years later (ERVIÖ et al. 1990). This has been regarded as an indication of gradual decline of plant-available Zn in intensive grassland cultivation. Also farm-level observations indicate insufficient supply of Zn to crop or domestic animals. Grasslands on peat soils have commonly shown poor growth after 10 years of intensive cultivation, and Zn deficiency has been suggested as an explanation to this (URVAS and SOINI 1984). In northern Finland, cattle have exhibited symptoms of Zn deficiency which disappeared with Zn injections. One way of contributing to a sufficient Zn supply to the cattle would be the elevation of the Zn content of forage crops and fodder cereals by Zn fertilization.

Zinc fertilization is in Finland recommended especially to fodder crops (Viljavuuspalvelu 1992). Before 1982, less than 30 000 kg of Zn (below 15 g ha$^{-1}$) was applied annually in mineral fertilizers. The first macronutrient fertilizer (18-3-12% N-P-K) containing also 0.3% Zn was introduced in 1982 and a separate granular Zn fertilizer in 1984. Since 1982, 180 000 - 420 000 kg, or 80 - 210 g Zn ha$^{-1}$ has been spread annually in mineral fertilizers, more than 90% of which incorporated in macronutrient fertilizers (Kemira 1992). The principal areas of fertilizer Zn consumption have been the provinces of Vaasa, Mikkeli, Kuopio and especially the provinces of Oulu and Lappi where 500 g Zn ha$^{-1}$, as compared to 20 - 50 g ha$^{-1}$ in the southernmost provinces, has been applied annually in chemical fertilizers. Even though field experiments on Zn fertilization have been carried out in Finland, the influence of soil characteristics on the response to applied Zn has not been investigated previously. Neither has the efficiency of different commercial Zn fertilizers been compared.

The purpose of the present investigation was to examine the content and solubility of Zn in cultivated soils of Finland and the effect of Zn fertilizers on cultivated plants. Information on the soil characteristics controlling the solubility and plant-availability of native and added Zn was sought. The study did not concentrate on soils suspected to be poor in Zn; the soil material collected represented all kinds of cultivated soils of Finland. The emphasis was in the plough layer, but the vertical distribution of Zn was also investigated. In addition to the characterization of soil Zn by soil analyses, the availability of soil Zn was studied in a pot experiment. The effect of Zn application on the Zn content of forage was examined in pot and field experiments. Also barley, the most important fodder cereal in Finland, was included in the field experiments. The ability of soil analysis to explain Zn uptake by ryegrass and to predict the response of plant Zn concentration to Zn applications was critically studied in pot experiments. In field experiments, the efficiency of different Zn fertilizers and application methods were compared, not forgetting environmental aspects.

# 2 METHODS OF ANALYSIS

## 2.1 Testing the methods of soil Zn determination

Soils from a material of 13 cultivated soils (Appendix 1) were mainly used for testing the methods of soil analysis. A few soils from a larger material (Appendix 2) were occasionally used.

### 2.1.1 Total Zn

In order to determine the total Zn content ($Zn_{tot}$) in the soil, the solid matrix needs to be dissolved. Hydrofluoric acid (HF) is required for complete decomposition of silicate minerals, and perchloric acid ($HClO_4$) is a strong oxidizing agent for organic materials. Procedures with and without these hazardous chemicals were tested for the digestion of $Zn_{tot}$.

In the aqua regia procedure (1), a 300-mg soil sample (four replicates) was digested with 4 ml of aqua regia (AR, 1 ml of concentrated $HNO_3$ and 3 ml of concentrated HCl). The sample was heated for 2 hours in a platinum crucible on a hot plate and allowed to react overnight. The next morning the residue was washed with warm dilute HCl into a volumetric flask. In the procedure of LIM and JACKSON (1982) employing aqua regia and HF (2), a 300-mg soil sample (four replicates) was digested with 4 ml of AR for 2 hours at 200°C in a 100-ml volumetric flask in a sand bath. Thereafter, 5 ml of HF was added and digestion was continued for 1 hour after which 50 ml of saturated $H_3BO_3$ was added to dissolve the possibly precipitated metal fluorides. After cooling, the bottle was filled with deionized water. In the $HNO_3$ - HF - $H_2SO_4$ procedure (3), a 500-mg soil sample (four replicates) was digested with 20 ml of $HNO_3$ in a teflon crucible on a hot plate until dry. Then, 5 ml of $H_2SO_4$ and 15 ml of HF were added and evaporated to dryness. In order to completely remove fluoride, 5 ml of concentrated $H_2SO_4$ was added and evaporated to dryness. The residue was washed into a volumetric flask with warm dilute HCl. From three soils, AR dissolved 55 - 70% of the quantity of Zn dissolved by the two mixtures containing HF (Table 1).

In an experiment with 12 surface soils (4, 11, 23, 30, 32, 35, 60, 61, 67, 69, 88, 105 in Appendix 2), the effect of $HClO_4$ addition was tested in the $HNO_3$ - HF - $H_2SO_4$ procedure. After the digestion with $HNO_3$, 3 ml of $HClO_4$ and 3 ml of $H_2SO_4$ were added and warmed until fumes evolved and heating was continued for 10 more minutes. Then, HF and $H_2SO_4$ were added as described above. Inclusion of the additional digestion phase into the procedure increased the average quantities of Zn extracted from 82.2 to 84.6 mg kg$^{-1}$ (+2.9%). According to the paired t-test, the difference was not statistically significant ($t = 1.856^{n.s.}$), but in further digestions also $HClO_4$ was added in order to ensure effective oxidation of organic matter.

Table 1. Soil Zn dissolved by aqua regia (AR), AR-HF and $HNO_3$-HF-$H_2SO_4$.[1]

| Soil | Zn (mg kg$^{-1}$) dissolved by | | |
|---|---|---|---|
| | AR | AR-HF | $HNO_3$-HF-$H_2SO_4$ |
| 209 Very fine sand | $46.0^{b}$ | $82.8^{a}$ | $82.8^{a}$ |
| 211 Fine sand | $40.3^{b}$ | $72.1^{a}$ | $70.1^{a}$ |
| 212 Mull | $50.2^{b}$ | $76.4^{a}$ | $71.7^{a}$ |

[1] Results of each soil were tested separately. Means marked with the same superscript do not differ at P = 0.05.

Table 2. Recovery of Zn added to a mull soil (212) digested according to the $HNO_3$-$HClO_4$-HF-$H_2SO_4$ procedure.[1]

| Zn addition | Zn | Recovery of added Zn | |
|---|---|---|---|
| mg kg$^{-1}$ | mg kg$^{-1}$ | mg kg$^{-1}$ | % |
| 0 | $74.9^{c}$ | - | - |
| 50 | $122.7^{b}$ | 47.8 | 96 |
| 100 | $168.6^{a}$ | 93.7 | 94 |

[1] Means marked with different superscripts differ at P = 0.05.

An experiment was carried out to study possible Zn loss and contamination during the digestion procedure. Portions (500 mg) of carefully homogenized mull soil (212) were weighed into nine teflon crucibles. Next, 1) 10 ml of water, 2) 5 ml of a solution containing 5 mg Zn dm$^{-3}$ as $ZnSO_4 \cdot 7H_2O$ ($ZnSO_4$) plus 5 ml of water and 3) 10 ml of the Zn solution were pipetted into three crucibles each. The quantities of Zn added were 0, 50 and 100 mg kg$^{-1}$ of soil, respectively. The soil samples were digested according to the $HNO_3$ - $HClO_4$ - HF - $H_2SO_4$ procedure as described above, and the Zn concentration in the digests was determined. No marked net loss or contamination occurred during the digestion (Table 2).

### 2.1.2 Fractionation of soil Zn

In order to characterize the chemical forms of soil Zn, it is commonly separated into fractions differing in solubility. The fractionation makes the basis for the estimation of potentially mobile Zn reserves and availability of soil Zn to plants. The sizes of the fractions are defined operationally as quantities of Zn which are extracted, often sequentially, with solutions supposed to displace Zn from the exchange complex or dissolve certain soil components resulting in a solubilization of Zn retained by them. The following fractions are commonly distinguished: (1) Zn in the soil solution, (2) exchangeable Zn, (3) adsorbed, chelated or complexed Zn, (4) Zn in secondary clay minerals and insoluble metal oxides, and (5) residual Zn bound by primary minerals (VIETS 1962).

There are no specific extractants for Zn, but various solutions are used for a simultaneous extraction of several elements, e.g. Zn, Cu, Mn, Fe, Al, Ni, Co. The sequential extraction procedures are usually combinations of single extraction methods developed earlier for specific purposes. The most frequently applied procedure in non-calcareous soils utilizes neutral salt solutions (e.g. 0.05 M $CaCl_2$, 1 M $MgCl_2$) to extract water-soluble and exchangeable Zn, pyrophosphate solutions (0.1 M $K_4P_2O_7$ or $Na_4P_2O_7$) for the extraction of Zn bound by organic matter, and ammonium oxalate - oxalic acid solutions for the dissolution of Zn bound by Fe, Al and Mn oxides (sesquioxides). This procedure was first used for the fractionation of soil Cu (McLaren and Crawford 1973) and has later been used also for the fractionation of Zn in non-calcareous soils (Elsokkary and Låg 1978, Iyengar et al. 1981, Bjerre and Shierup 1985, Haynes and Swift 1985, Liang et al. 1990). $H_2O_2$ or NaOCl may be used instead of pyrophosphate for the dissolution of Zn bound by organic matter (Shuman 1979, Nielsen et al. 1986, Sims 1986, Singh et al. 1988). A common feature for all the fractionation procedures is that residual Zn ($Zn_{res}$), remaining in the soil after removal of oxide-bound Zn and consisting mainly of Zn in the primary minerals, is dissolved with concentrated acids according to the same procedures as used in the digestion of $Zn_{tot}$.

The same fractionation procedure is seldom used in more than one study, which complicates the comparison of results. Depending on the research objectives, different fractions are determined. In some studies a fraction of Zn supposed to be specifically adsorbed on inorganic sites has been extracted by 2.5% acetic acid (Elsokkary and Låg 1978, Iyengar et al. 1981, Bjerre and Shierup 1985) or $Pb(NO_3)_2$ (Liang et al. 1990). Further, Zn bound by Mn oxide has been extracted together with Zn bound by Fe and Al oxides (Elsokkary and Låg 1978, Shuman 1979) or separately (Sims and Patrick 1978, Iyengar et al. 1981, Miller and McFee 1983, Shuman 1985, Sims 1986, Liang et al. 1990). Zinc bound by poorly crystalline Fe and Al oxides can be extracted separately from Zn bound by crystalline oxides (Miller and McFee 1983, Shuman 1985, Sims 1986) as opposed to extracting only one fraction, referring to Zn bound by oxide materials. In addition to differences in the extracting solutions, the same soil sample may be used throughout the procedure (Elsokkary and Låg 1978, Shuman 1979, Nielsen et al. 1986) or after the determination of water-soluble and exchangeable Zn a new sample is weighed for the determination of the more sparingly soluble secondary fractions (Sims and Patrick 1978, Iyengar et al. 1981).

In the present study, $MgCl_2$ solution was used for the extraction of water-soluble and exchangeable Zn, $K_4P_2O_7$ for the extraction of Zn bound by organic matter and oxalate for the dissolution of Zn bound by Fe, Al and Mn oxides. The residual Zn was digested by the $HNO_3$ - $HClO_4$ - HF - $H_2SO_4$ procedure.

### *a. Water-soluble and exchangeable Zn*

Zinc cations ($Zn^{2+}$) can be retained by the negatively charged sites by non-specific electrostatic forces. This fraction of Zn is exchangeable with other cations. For theoretical reasons, $Mg^{2+}$ salts have been considered suitable in the extractants for exchangeable $Zn^{2+}$ because the two cations are similar in radius and charge. It is therefore supposed that $Mg^{2+}$ effectively displaces exchangeable $Zn^{2+}$ from soil surfaces into the solution. Water-soluble Zn is simultaneously extracted. The 1 M $MgCl_2$ was first used for the determination of plant-available Zn by Stewart and Berger (1965) and Martens (1968). In those days, concentration of Zn was measured colorimetrically. Since the 1970's, Zn has invariably been determined by atomic absorption spectrophotometry (AAS) where a high salt concentration in the solution analyzed may cause a high background absorption as well as crusting of the burner. Owing to low concentration of Zn in the extract, dilution as a means of reducing the salt concentration may not be feasible. Therefore the use of less concentrated salt solutions as extractants would be desirable.

The effect of $MgCl_2$ concentration on the extraction of Zn from eight soils (201, 203, 204, 206, 209 and 210 in Appendix 1; 10 and 73 in Appendix 2) was studied. Soil samples (10 g, two replicates) were shaken for 2 hours with 25-ml aliquots of 1 M or 0.5 M $MgCl_2$ solution. The suspensions were filtered and analyzed for Zn. The means and ranges of Zn extracted (mg $kg^{-1}$) were as follows:

| Solution | Mean | Range |
|---|---|---|
| 1 M | 1.71 | 1.2 - 2.7 |
| 0.5 M | 1.13 | 0.7 - 2.0 |

The less concentrated solution extracted 65% (range 53 - 74%) of that extracted with the 1 M solution. According to the paired t-test, the difference between the quantities of Zn extracted with the two solutions was highly significant ($t = 14.758^{***}$), but the results correlated closely ($r = 0.99^{***}$). The mean deviation of the two replicates was 5.2%, range 0.3 - 22.2%.

The recovery of added Zn was studied on the extract obtained from soil 201 with 0.5 M $MgCl_2$ at the soil-to-solution ratio of 1:5 (weight/volume, w/v). Into three 180-ml portions of the extract, obtained by combining extracts of several subsamples, 20-ml aliquots of water or solution of $ZnSO_4$ were added to produce concentrations theoretically differing by 0.05 and 0.20 mg Zn $dm^{-3}$. The measured concentrations (four subsamples) showed accurate recovery of added Zn (Table 3).

*b. Zinc bound by organic matter*

The use of pyrophosphate solution as the extractant for Zn bound by organic matter is based on the ability of pyrophosphate to solubilize humic substances (Bremner and Lees 1949, Mortvedt and Osborn 1977) and on the ability of pyrophosphate anion to form soluble complexes with Zn (Asher and Bar-Yosef 1982, Bar-Yosef and Asher 1983). It has been hypothesized that polyvalent cations complexed to organic matter are responsible for keeping organic matter in a flocculated and water-insoluble state. These cations can be removed by complexing with pyrophosphate anion, resulting also in the solubilization of humus (Stevenson 1982, p. 40). However, the mechanism responsible for the solubilization of humic substances and cations in the pyrophosphate extraction has not been fully established (Borggaard 1988).

Recovery of Zn added into the pyrophosphate extracts of a mull soil (212) was studied. Soil samples were shaken with 0.1 M $K_4P_2O_7$ (pH 10) at the soil-to-solution ratio of 1:25 (w/v) for 18 hours, and the suspensions were centrifuged. Zinc was added to the extracts as has been described earlier. Added Zn was accurately recovered (Table 3).

The commercial $K_4P_2O_7$ chemical contained 6 mg Zn $kg^{-1}$ resulting in a Zn concentration of 0.2 mg $dm^{-3}$ in the 0.1 M solution. It is possible to purify the reagent with a solvent extraction (Shuman 1979) or with a cation exchange resin (Shuman 1985). However, the reagent may be used without purification if Zn in the extraction solution remains completely in the liquid phase during the extraction. The influence of Zn in the pyrophosphate reagent was indirectly examined with four surface soils (Appendix 2) by studying the adsorption of added Zn to soil suspended in the 0.1 M $K_4P_2O_7$ solution (pH 10). In the experiment, 2.5-g soil samples (four replicates) were shaken for 18 hours in the following solutions:

1) 0.1 M $K_4P_2O_7$
2) 0.1 M $K_4P_2O_7$ + 0.2 mg Zn $dm^{-3}$ as $ZnCl_2$
3) 0.1 M $K_4P_2O_7$ + 0.4 mg Zn $dm^{-3}$ as $ZnCl_2$

Table 3. Recovery of Zn added to 0.5 M $MgCl_2$, pyrophosphate and oxalate extracts.

| Zn addition | $MgCl_2$[1] | | Pyrophosphate[2] | | Oxalate[2] | |
|---|---|---|---|---|---|---|
| mg $dm^{-3}$ | Zn, mg $dm^{-3}$ | Recovery, % | Zn, mg $dm^{-3}$ | Recovery, % | Zn, mg $dm^{-3}$ | Recovery, % |
| 0 | 0.02 | - | 0.15 | - | 0.34 | - |
| 0.05 | 0.07 | 98 | - | - | - | - |
| 0.20 | 0.22 | 101 | 0.35 | 102 | 0.54 | 100 |
| 0.40 | - | - | 0.55 | 101 | 0.75 | 101 |

[1] Extract of soil 201
[2] Extract of soil 212

Table 4. Effect of Zn addition to the pyrophosphate solution on the concentrations of Zn measured in the soil extract.

| Soil | Zn added to the extracant, mg dm$^{-3}$ | Zn in the extract, mg dm$^{-3}$ | Recovery of added Zn | |
|---|---|---|---|---|
| | | | mg dm$^{-3}$ | % |
| 18[1] | 0 | 0.11 | - | - |
| Clay | 0.20 | 0.31 | 0.20 | 98 |
| loam | 0.39 | 0.50 | 0.39 | 99 |
| 34[1] | 0 | 0.23 | - | - |
| Loam | 0.21 | 0.45 | 0.22 | 101 |
| | 0.45 | 0.69 | 0.45 | 100 |
| 78[1] | 0 | 0.29 | - | - |
| Mull | 0.24 | 0.53 | 0.24 | 100 |
| | 0.46 | 0.76 | 0.47 | 102 |
| 104[1] | 0 | 0.84 | - | - |
| Carex | 0.24 | 1.09 | 0.24 | 103 |
| peat | 0.46 | 1.35 | 0.51 | 111 |

[1] Soils from the surface soil material (Appendix 2)

Zinc additions to the extractant corresponded to 4.1 - 9.2 mg Zn kg$^{-1}$ of soil and were recovered in the extract (Table 4), showing that added Zn was not adsorbed by the soil. The results are in agreement with those of ASHER and BAR-YOSEF (1982) who observed that at pH 9 Zn was not adsorbed onto a Ca-montmorillonite suspended in a 0.0096 M pyrophosphate solution containing 8.0 mg Zn dm$^{-3}$. It can thus be concluded that Zn of the commercial chemical is not adsorbed either but only gives rise to a high background absorption. The 0.1 M $K_4P_2O_7$ was therefore used in the extraction of Zn without purification.

### *c. Zinc bound by sesquioxides*

Since the work of TAMM (1922), acid oxalate solutions have been widely used for the extraction of Fe and Al oxides in soil. In the dark, acid oxalate is supposed to extract only poorly crystalline oxides; in UV light, also crystalline Fe oxide is extracted. The oxalate solutions are assumed to dissolve components occluded into the Fe and Al oxides, and oxalate has therefore been used for the extraction of soil Zn. To avoid crusting of the burner of AAS, a 0.05 M oxalate solution was selected instead of more concentrated solutions commonly used in the fractionation procedures.

The extraction of Zn from four soils with 0.05 M oxalate solutions was investigated at pH 2.0, 2.9, 3.3 and 4.0. The pH values were created by different ratios of oxalic acid and ammonium oxalate. Before the oxalate treatment, the samples (2.5 g, four replicates) were extracted with pyrophosphate and washed with water. The remaining samples were shaken for 4 hours with 50-ml aliquots of the four oxalate solutions, the suspensions were centrifuged and the extracts analyzed for Zn. The solution which had the lowest pH was the most efficient extractant for Zn (Table 5), probably owing to a substantial dissolution of structural Zn. There was a considerable decrease in the extractability of Zn in three soils with an elevation of pH from 2.0 to 2.9, but an additional increase in pH affected the results less markedly. A solution of pH 2.9 (0.024 M and 0.026 M in oxalic acid and ammonium oxalate, respectively) was used in the rest of the oxalate extractions.

The recovery of Zn added to the oxalate extract obtained from a mull (212) was studied. Prior to oxalate extraction the soil samples (2.5 g) were shaken with pyrophosphate and washed with water. The remaining samples were shaken in 50-ml aliquots of 0.05 M oxalate (pH 2.9) for 4 hours and the suspensions were centrifuged. Zinc was added to

Table 5. Soil Zn extracted by 0.05 M oxalate at different pH values.[1]

| Soil | Zn (mg kg$^{-1}$) extracted at pH | | | | HSD$_{0.05}$ |
|---|---|---|---|---|---|
| | 2.0 | 2.9 | 3.3 | 4.0 | mg kg$^{-1}$ |
| 201 Fine sand | 3.1$^{a}$ | 2.4$^{b}$ | 2.1$^{bc}$ | 2.0$^{c}$ | 0.39 |
| 209 Very fine sand | 4.1$^{a}$ | 2.5$^{b}$ | 2.5$^{b}$ | 2.0$^{b}$ | 0.63 |
| 212 Mull | 2.7$^{a}$ | 1.5$^{b}$ | 1.4$^{b}$ | 1.1$^{b}$ | 0.64 |
| 213 Mull | 2.0$^{a}$ | 1.7$^{ab}$ | 1.3$^{bc}$ | 1.1$^{c}$ | 0.42 |

[1] Results of each soil were tested separately. Means marked with the same superscript do not differ at P = 0.05.

the extracts as was described earlier. Added Zn was accurately recovered (Table 3).

*d. Repeated pyrophosphate extraction*

The effect of repeated pyrophosphate extraction on the quantities of Zn dissolved sequentially with oxalate was studied with two soils (211, 213). The 2.5-g soil samples (four replicates) were extracted once, twice or three times with 50-ml aliquots of pyrophosphate, washed with water and extracted once with a 50-ml aliquot of oxalate (pH 2.9). In both soils, the first pyrophosphate treatment extracted more than did the second and the third treatment (Table 6). Repeated pyrophosphate extractions tended to reduce the quantities of Zn extracted by oxalate in the mull (213), suggesting that the two solutions dissolved Zn to some extent from a common pool. An alternative but less likely explanation is that part of the sample was lost in the successive washings, resulting in a smaller quantity of soil remaining in the oxalate extraction. The number of pyrophosphate extractions did not have a consistent effect on the results of the oxalate extraction in the mineral soil 211. In soil 211, the quantities of Zn extracted by oxalate were substantially larger than those dissolved with the second and third extraction by pyrophosphate. In this soil there was obviously a pool of Zn which was extractable by oxalate but which was resistant even to repeated pyrophosphate washings.

Table 6. Soil Zn extracted with one, two or three sequential treatments by pyrophosphate and a successive extraction by oxalate. I, II and III refer to the first, second and third pyrophosphate extraction.[1]

| Soil | | Zn ($mg\ kg^{-1}$) extracted by pyrophosphate | | | Zn ($mg\ kg^{-1}$) extracted by oxalate |
|---|---|---|---|---|---|
| | | I | II | III | |
| 211 | | $3.5^a$ | - | - | $2.2^b$ |
| | | $3.6^a$ | $0.7^c$ | - | $2.5^a$ |
| | | $3.6^a$ | $0.8^{bc}$ | $1.0^b$ | $2.1^b$ |
| | $HSD_{0.05}$ | 0.2 | | | 0.1 |
| 213 | | $5.1^a$ | - | - | $1.6^a$ |
| | | $4.9^a$ | $1.4^b$ | - | $1.4^{ab}$ |
| | | $4.9^a$ | $1.4^b$ | $0.9^c$ | $1.2^b$ |
| | $HSD_{0.05}$ | 0.2 | | | 0.2 |

[1] Results of pyrophosphate and oxalate extractions were tested separately. The two soils were tested separately. Means marked with the same superscript do not differ at P = 0.05.

*e. Reproducibility and additivity of the results of sequential extractions*

The reproducibility of the results of pyrophosphate and oxalate extractions was studied with 13 soils (201, 202, 206, 207, 208, 209, 210, 211 and 212 in Appendix 1; 10, 73, 90 and 100 in Appendix 2). The 2.5-g soil samples (two replicates) were extracted in sequence with 50-ml aliquots of 0.1 M pyrophosphate, washed with water and extracted with 50 ml of 0.05 M oxalate (pH 2.9). Another two replicates were sequentially extracted and analyzed for Zn a few days later. The results of the first extraction were designated Py 1 and Ox 1, those of the second extraction Py 2 and Ox 2. The differences between Py 1 (5.12 $mg\ kg^{-1}$) and Py 2 (5.20 $mg\ kg^{-1}$) as well as between Ox 1 (2.15 $mg\ kg^{-1}$) and Ox 2 (2.17 $mg\ kg^{-1}$) were not statistically significant according to the paired t-test. In the 13 soils, the difference between the two means of $Zn_{py}$ ranged from -0.65 to 0.38 $mg\ kg^{-1}$ and that of $Zn_{ox}$ from -0.30 to 0.25 $mg\ kg^{-1}$. The coefficient of variation of the four individual determinations in the 13 soils ranged 2.8 - 12.4% (mean 5.3%) and 0.6 - 13.4% (mean 4.5%) for $Zn_{py}$ and $Zn_{ox}$, respectively.

In sequential fractionation procedures part of the sample may be lost during the numerous decantations. In order to study the importance of this source of error, 2.5-g samples (four replicates) of 13 soils were sequentially extracted by pyrophosphate for 18 hours, washed with water and extracted by oxalate for 4 hours. After the oxalate extraction, the remaining sample was washed with water, dried and ground, and a 500-mg sample (two replicates) was digested according to the $HNO_3$ - $HClO_4$ - HF - $H_2SO_4$ procedure, and residual Zn ($Zn_{res}$) was measured. Also $Zn_{tot}$ (two replicates) was determined. The sums of $Zn_{py}$, $Zn_{ox}$ and $Zn_{res}$ were compared with $Zn_{tot}$ (Table 7). In seven soils the sum of fractions was higher (1.1 - 13.6 $mg\ kg^{-1}$, 2 - 11%) than $Zn_{tot}$, while in six soils the sum of fractions was lower (0.1 - 10.5 $mg\ kg^{-1}$, 0.1 - 10%) than $Zn_{tot}$. The difference between $Zn_{tot}$ and the sum of

Table 7. Soil Zn extracted by pyrophosphate ($Zn_{py}$) and oxalate ($Zn_{ox}$) as well as residual Zn ($Zn_{res}$), and the sum of fractions ($Zn_{py}$ + $Zn_{ox}$ + $Zn_{res}$) and total Zn ($Zn_{tot}$) of 13 representative soils.

| Soil | $Zn_{tot}$ | $Zn_{py}$ | $Zn_{ox}$ | $Zn_{res}$ | Sum of fractions | |
|---|---|---|---|---|---|---|
| | mg $kg^{-1}$ | | | | mg $kg^{-1}$ | %[1] |
| 201 Heavy clay | 137.2 | 3.1 | 2.4 | 145.3 | 150.8 | 110 |
| 10[2] Gyttja clay | 109.1 | 4.2 | 2.0 | 109.3 | 115.4 | 106 |
| 202 Silty clay | 184.6 | 2.7 | 3.2 | 183.3 | 189.2 | 102 |
| 206 Very fine sand | 109.5 | 2.1 | 2.1 | 94.5 | 99.0 | 90 |
| 207 Very fine sand | 140.6 | 2.7 | 2.3 | 137.6 | 142.6 | 101 |
| 208 Very fine sand | 91.1 | 2.8 | 2.5 | 82.7 | 88.0 | 97 |
| 209 Very fine sand | 88.0 | 5.1 | 2.6 | 78.6 | 86.3 | 98 |
| 210 Silt | 151.5 | 3.9 | 3.0 | 150.6 | 157.5 | 104 |
| 211 Fine sand | 67.9 | 3.6 | 2.4 | 59.5 | 65.9 | 97 |
| 73[2] Sandy moraine | 15.7 | 3.2 | 1.2 | 13.0 | 17.3 | 110 |
| 212 Mull | 88.0 | 3.6 | 1.4 | 82.9 | 87.9 | 100 |
| 90[2] Carex peat | 42.2 | 12.3 | 1.5 | 33.2 | 47.0 | 111 |
| 100[2] Carex peat | 34.4 | 17.5 | 1.7 | 16.3 | 35.5 | 103 |
| Mean | 96.9 | 5.1 | 2.2 | 91.3 | 98.6 | 102 |

[1] Percent of $Zn_{tot}$

[2] Soil from surface soil material (Appendix 2)

the fractions was not statistically significant ($t = 0.897^{n.s.}$, paired t-test), showing that no major loss of the sample had occurred. The sum of the fractions correlated closely with $Zn_{tot}$ ($r = 0.99^{***}$).

## 2.2 Chemical and statistical analyses

### 2.2.1 Determination of Zn

All the extractions and digestions were performed in duplicate and were repeated when large deviations between the replicates occurred. In filtrations, Schleicher & Shüll 589[3] (Blue ribbon) filter paper was used unless otherwise mentioned. Silicon and polythene stoppers were used in capping centrifuge glass tubes and volumetric flasks because rubber stoppers were found to be sources of soluble Zn. The centrifugations were run for 10 min at 3000 G. Zinc concentrations of the $MgCl_2$ extracts were measured by atomic absorption spectrophotometry (AAS) using the standard addition method. Zinc concentration of the other extracts was measured by AAS using standard solutions matched for the matrix of the extracts.

*a. Total Zn and chemically specific fractions of Zn in soil*

*Total Zn.* A 500-mg soil sample was digested in a teflon crucible with 20 ml of $HNO_3$ until dry. Thereafter 3 ml of $HClO_4$ and 3 ml of $H_2SO_4$ were added and warmed until fumes evolved. Heating was continued for 10 minutes. Then, 5 ml of $H_2SO_4$ and 15 ml of HF were added and evaporated to dryness. To remove the fluoride, 5 ml of concentrated $H_2SO_4$ was added and evaporated to dryness. Finally, 20 ml of deionized water and 10 ml of concentrated HCl solution were added, and the mixture was warmed up and washed into a 100-ml volumetric flask.

*Water-soluble and exchangeable Zn* was extracted by shaking 10 g of soil for 2 hours with 50 ml of 0.5 M $MgCl_2$ in 100-ml polythene tubes in a reciprocating shaker, centrifuged and filtered.

*Extraction with 0.1 M $K_4P_2O_7$ solution (pH 10)* was performed by shaking 2.5-g samples of soil in 50 ml of pyrophosphate solution in a reciprocating shaker in centrifuge glass tubes. After 1 hour of shaking the suspensions were allowed to stand overnight (16 hours); the following morning the suspensions were shaken for 10 more minutes, centrifuged and filtered. The sample was washed by shaking with 50 ml of deionized water for 1 hour, and after centrifugation the solution was discarded.

*Oxalate extraction* was carried out sequentially after the pyrophosphate extraction. Oxalate solution (50 ml of 0.026 M ammonium oxalate, 0.024 M oxalic acid, pH 2.9) was added into the centrifuge glass tubes and shaken for 4 hours in daylight, centrifuged, filtered and analyzed for Zn.

### *b. Procedures used in soil fertility testing*

Contrary to the fractionation of soil Zn, determination of Zn in soil testing does not aim at extracting chemically specific fractions. These determinations do not involve assumptions of the bonding mechanism or soil constituent to which Zn is bound but attempt to obtain information on the size of Zn reserves available to plants. The solutions should ideally extract Zn from the same soil components which supply plants with Zn, and the quantities of Zn extracted should correlate with Zn uptake by plants. Mineral acids (HCl), neutral salts (1 M $MgCl_2$) and chelating agents (EDTA, DTPA) are commonly used for the extraction of Zn in soil testing. In the present study, methods presented in the literature were applied, and studies on the optimization of the procedures were not carried out.

In the *acid ammonium acetate procedure (AAAc)*, a solution containing 0.5 M $CH_3COONH_4$ and 0.5 M $CH_3COOH$ was made of acetic acid and $NH_4OH$, and the pH was adjusted to 4.65 with $NH_4OH$ or acetic acid. This solution is used in soil testing in Finland to extract Ca, Mg, K and P, and this was also used as an extractant for plant-available Zn by SILLANPÄÄ and LAKANEN (1966). In the present study, 20 ml of soil was shaken with 200 ml of the extractant in polythene bottles in a planar shaker for 1 hour, filtered and analyzed for Zn.

In the *AAAc-EDTA procedure*, the soil is extracted with a solution containing 0.5 M $CH_3COONH_4$, 0.5 M $CH_3COOH$ and 0.02 M $Na_2$-EDTA at pH 4.65 (LAKANEN and ERVIÖ 1971). Zinc, together with other metallic micronutrients, has been extracted with this solution in soil testing in Finland since 1986. In this procedure, 25-ml samples of soil were shaken with 250 ml of the extracting solution for 1 hour in a rotary shaker, filtered (Tesorp 04110, 130 g $m^{-2}$) and analyzed for Zn. Most extractions with AAAc-EDTA were performed routinely in duplicate at Viljavuuspalvelu Oy - Soil Analysis Service Ltd. Part of the extractions with AAAc-EDTA were carried out at Kemira Oy Espoo Research Centre and at the Department of Applied Chemistry and Microbiology, University of Helsinki.

For the *DTPA procedure*, developed by LINDSAY and NORVELL (1978) and commonly used as an extractant for metallic micronutrients in soil testing, a solution containing 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M triethanolamine (TEA) and 0.01 M $CaCl_2$ at pH 7.3 was prepared. In the extraction, 10 g of mineral soil or 10 ml of organogenic soil was shaken for 2 hours in polythene bottles, filtered and analyzed for Zn.

### *c. Zinc in plant material*

The Zn content of plant material was determined at Soil Analysis Service Ltd. Plant samples were dried at 60°C and ground. Prior to analysis, approximately 1.0 g of plant material was weighed into tared glass vessels and the exact weight was recorded. The sample was dried at 105°C for 4 hours, cooled and weighed, and the dry matter content was calculated. Simultaneously, another sample (approximately 1.0 g, exact weight recorded) was weighed for dry ashing. The sample was heated in a quartz crucible at 550°C for 4 hours until a white ash was obtained. After cooling, the ash was wetted with a few drops of deionized water, 10 ml of 4 M HCl was added, and the crucible was heated for 30 minutes in a sand bath. The contents of the crucible were transferred quantitatively into a 100-ml volumetric flask which was filled with water. After the remaining solid material had settled to the bottom, a 10-ml sample was taken and the Zn concentration of the solution was determined by AAS. The consistency of the results was checked by including one standard hay sample in every set of 40 samples. In 35 determinations, the mean Zn concentration of the standard sample was 22.5 mg $kg^{-1}$, range 19 - 31 mg $kg^{-1}$, standard deviation 2.56 mg $kg^{-1}$ and coefficient of variation 11.4%. In addition, in one determination the standard gave a value of 42 mg $kg^{-1}$, probably due to contamination at some point, resulting in repeated determinations of several samples of the set. Routinely, a duplicate determination was carried out with every eight samples.

*d. Zinc in fertilizers*

Fertilizer samples were dissolved with aqua regia to facilitate the determination of Zn. A sample (1.00 g) of ground fertilizer was weighed into a 250-ml beaker, and a few drops of water, 10 ml of concentrated $HNO_3$ and 30 ml of concentrated HCl were added and evaporated to dryness. After cooling, 10 ml of concentrated HCl was added and evaporated to dryness. Thereafter, 50 ml of water and 10 ml of concentrated HCl were added and boiled until the precipitation was dissolved. The solution was poured into a volumetric flask, filled and filtered if necessary and analyzed for Zn.

### 2.2.2 Other analyses

The soil organic carbon was determined by a modified wet digestion method (GRAHAM 1948). It was assumed that 80% of the carbon was oxidized in the treatment. The organic matter content was calculated by multiplying the organic C content by 1.724. The particle size composition of the mineral material in the soil samples was determined by the pipette method (ELONEN 1971). The determination was made for all mineral soils (organic matter content less than 20%) and for most mull soils (organic matter content 20 - 40%). Soil pH was measured in water (20 ml of soil, 50 ml of water) after 2 hours of equilibration. The bulk density of ground (<2 mm) soil was determined by weighing two 50-ml samples of soil.

Poorly crystalline Fe and Al oxides were extracted with 0.05 M oxalate solution at pH 3.3 (NISKANEN 1989). The concentrations of Fe and Al in the extracts were measured by AAS. The air-acetylene flame and acetylene-nitrous oxide flame were used in the determination of Fe and Al, respectively.

In order to determine the content of $Zn_{tot}$ in textural fractions, clay (<0.002 mm) and silt plus very fine sand (0.002 - 0.05 mm) fractions were separated in three soil samples. The flocculating and cementing agents were first removed with hydrogen peroxide ($H_2O_2$) and by a treatment with sodium dithionite ($Na_2S_2O_4$) and sodium citrate using $NaHCO_3$ as a pH buffer (pH 7.3) (OLSON and ELLIS 1982). The actual separation of the textural fractions was carried out by an automated procedure for the gravity sedimentation - decantation technique (RUTLEDGE et al. 1967) with the equipment of Texas A&M University (College Station, Texas, USA).

The contents of K, $NH_4^+$-N and $NO_3^-$-N in fertilizers were determined after dissolution of the fertilizer (20 g) with water (1 $dm^3$). The sum of $NH_4^+$-N and $NO_3^-$-N was taken as the concentration of total N. For the determination of total P, the fertilizer was dissolved in $H_2SO_4$ and $HNO_3$. The pH of the fertilizers was measured in a 10% solution (w/v).

The concentration of N in barley grains was measured by the near-infrared (NIR) technique. The vegetative parts were analyzed for N by the Kjeldahl method.

### 2.2.3 Statistical methods

The statistical analyses were mainly carried out according to the procedures presented by RANTA et al. (1991). The variation of the results was studied by calculating the mean deviations, $MD = \Sigma|x_i-\mu|/N$, or standard deviations, $s = \sqrt{[\Sigma(x_i-\mu)^2]/(n-1)}$. In assessing the variation of replicates, the mean deviations were calculated. Otherwise, standard deviations were used.

Fractiles of 10% ($F_{10\%}$) and 25% ($F_{25\%}$, quartiles) were formed in order to group the material in terms of various characteristics. Occasionally there were several equal results, all of them placed in the same fractile. Therefore the ultimate sizes of the fractiles may deviate from $F_{25\%}$ and $F_{10\%}$.

Means obtained from two populations were studied with the t-test. The effect of a treatment on several soils was studied by the t-test for paired measurements. Analysis of variance was used to test statistically significant differences between several means. The significance of the differences between individual means was tested by Tukey's test (HSD, $P = 0.05$). Means marked with the same superscript do not differ at $P = 0.05$.

The correlation between different characteristics of a population was studied. Owing to the skewed distribution of the results of several variables, logarithmic transformations (natural logarithms, $\log_e$) of results were commonly used. In addition to the linear correlation coefficients, Spearman rank correlation coefficients were calculated. The z-transformation test was applied to test the differences between the linear correlation coefficients.

Regression analyses were carried out in order to study the dependence between variables. Statistically not significant ($P = 0.05$) independent variables were excluded from the regression equation one by one and the equation was recalculated until all variables in the equation were significant. The significance of the multiple determination of the regression equations was tested by the F-test. The significance of each regression coefficient (b) was tested by the t-test. To depict the relative importance of statistically significant variables, the standard partial regression coefficients, or beta coefficients ($\beta$), were calculated as follows (STEEL and TORRIE 1981): $b' = b \cdot s_i/s_y$, where $s_i$ = standard deviation of an independent variable and $s_y$ = standard deviation of the dependent variable.

Statistical significance of various indices is indicated with asterisks. One asterisk ($^*$) indicates significance at the 5% risk level ($P = 0.05$), two asterisks ($^{**}$) at the 1% ($P = 0.01$) and three asterisks ($^{***}$) at the 0.1% level ($P = 0.001$); n.s. indicates no statistical significance ($P>0.05$).

# 3 ZINC IN SOIL

## 3.1 Experimental soils

Most laboratory studies and two pot experiments were carried out with soils of a material of 107 samples which were collected from plough layers ($A_p$ horizons) of cultivated fields in different parts of Finland. The samples were collected in 1987 and 1989 to represent the distribution of soil classes of cultivated soils of Finland as reported by KURKI (1982). The samples were taken from rural areas at least 100 m away from roads and electric wires. Moist soil samples were air-dried at room temperature and stored in plastic bags. Part of the sample was ground to pass a 2-mm sieve and stored in a cardboard box. Mineral soils except moraines were designated according to the textural classification of JUUSELA and WÄRE (1956). Clay refers to the fraction finer than 0.002 mm, silt to 0.002 - 0.02 mm, very fine sand to 0.02 - 0.06 mm and fine sand to 0.06 - 0.2 mm. Mineral soils containing ≥30% of clay are called clay soils. Occasionally, other mineral soils are collectively called coarse mineral soils. Organogenic soils (organic matter content ≥20%) were divided into mull and peat soils, with organic matter contents of 20 - 40 and ≥ 40%, respectively. The soil characteristics are presented in Appendix 2 and summarized in Table 8.

The vertical distribution of Zn was studied on seven soil profiles of cultivated fields (Appendix 3). Soil profiles were sampled according to visible horizon boundaries if present. Where the subsoil was apparently homogeneous, the samples were taken to represent 20-cm thick layers. Also 15 pairs of samples taken from the plough layer ($A_p$ horizon) and the respective subsoil (30 - 35 cm) (Appendix 4) were investigated. The two samples of the pair were usually of the same soil class. In one case, an organogenic soil had a fine sand subsoil and one case was the contrary.

Table 8. Distribution of surface soil samples into soil classes, and some chemical and physical properties of the experimental soils.

| Soil class | n | Organic C % | | Clay % | | pH | | $Fe_{ox}$ mmol kg$^{-1}$ | | $Al_{ox}$ mmol kg$^{-1}$ | | Bulk density[1] kg dm$^{-3}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| Clay | 25 | $3.5^{c}$ | 1.2-9.5 | $51^{a}$ | 32-74 | $6.0^{a}$ | 4.6-6.8 | $99^{a}$ | 55-172 | $79^{ab}$ | 47-172 | $0.96^{b}$ | 0.76-1.14 |
| Silt, loam, very fine sand | 20 | $2.5^{c}$ | 0.8-5.3 | $20^{b}$ | 6-29 | $5.9^{a}$ | 4.2-6.8 | $80^{ab}$ | 51-210 | $59^{b}$ | 26-137 | $1.00^{b}$ | 0.77-1.16 |
| Fine sand, moraine | 28 | $2.7^{c}$ | 0.7-6.1 | $6^{c}$ | 1-16 | $6.0^{a}$ | 4.9-7.4 | $51^{b}$ | 10-231 | $57^{b}$ | 9-178 | $1.15^{a}$ | 0.89,1.43 |
| Mull | 14 | $18.9^{b}$ | 12.4-22.6 | n.d. | - | $5.5^{ab}$ | 4.8-6.2 | $120^{a}$ | 54-249 | $107^{a}$ | 17-266 | $0.65^{c}$ | 0.53-0.77 |
| Peat | 20 | $38.0^{a}$ | 23.9-50.4 | n.d. | - | $5.0^{b}$ | 3.8-6.2 | $131^{a}$ | 29-252 | $91^{ab}$ | 10-249 | $0.37^{d}$ | 0.25-0.55 |

[1] Ground (<2 mm) soil

n.d. = Not determined

## 3.2 Zinc in surface soil

### 3.2.1 Total Zn

*a. Soil samples*

Total Zn ($Zn_{tot}$) in the surface soil samples ranged from 10 to 420 mg kg$^{-1}$, mean 71 mg kg$^{-1}$ (Appendix 5). In a fine sand soil (soil 71 from Harjavalta) there was a very high content of $Zn_{tot}$ (420 mg kg$^{-1}$), while the bulk of the results ranged rather uniformly between the second highest (202 mg kg$^{-1}$) and the lowest value (10.3 mg kg$^{-1}$). The ranges of $Zn_{tot}$ overlapped markedly in the five soil classes (Table 9). However, the average $Zn_{tot}$ in the clay soils was higher than that of silt, loam and very fine sand soils, and excluding soil 71, the $Zn_{tot}$ in fine sands and moraines was still lower. The mean $Zn_{tot}$ of the two organogenic soil classes did not differ significantly from one another or from the fine sand and moraine soils but was lower than that of the more fine-textured mineral soil classes. The mean deviation of the individual measurements of a soil sample averaged 1.8 mg kg$^{-1}$, i.e. 2.8% of the mean, range 0 - 17.6% of the mean. The mean deviation exceeded 5% in 18 soils which were poor in $Zn_{tot}$.

The results of $Zn_{tot}$ were divided into quartiles ($F_{25\%}$) (Table 10). The frequency of the different soil classes in each quartile demonstrates the abundance of $Zn_{tot}$ in clay soils and the small re-

Table 9. Total Zn in the surface soils.

| Soil class | n | Mean | s | Range |
|---|---|---|---|---|
| | | ------------ | mg kg$^{-1}$ | ------------ |
| Clay | 25 | $141.0^{a}$ | 37.0 | 66.4-202 |
| Silt, loam, very fine sand | 20 | $96.4^{b}$ | 34.5 | 58.0-201 |
| Fine sand, moraine | 28 | $62.1^{1}$ | 73.1 | 13.4-420 |
| -soil 71 excluded | 27 | $48.8^{c}$ | 20.9 | 13.4-102 |
| Mull | 14 | $48.7^{c}$ | 17.9 | 20.0-80.1 |
| Peat | 20 | $34.7^{c}$ | 20.3 | 10.3-85.6 |

[1] Mean not included in the statistical analysis.

Table 10. Limits of quartiles ($F_{25\%}$) of $Zn_{tot}$ and number of soils from different soil classes in each quartile.

| Soil class | Quartile of $Zn_{tot}$ and its limits mg kg$^{-1}$ | | | |
|---|---|---|---|---|
| | I<br>≥112 | II<br>109-66.8 | III<br>66.4-40.3 | IV<br>≤39.2 |
| Clay | 19 | 5 | 1 | 0 |
| Silt, loam, very fine sand | 6 | 11 | 3 | 0 |
| Fine sand, moraine | 1 | 6 | 11 | 10 |
| Mull | 0 | 4 | 6 | 4 |
| Peat | 0 | 1 | 6 | 13 |

serves of $Zn_{tot}$ in the coarsest mineral soils and organogenic soils. As many as 19 out of 25 clay soils occurred in the largest $F_{25\%}$, six out of the seven heavy clay soils (clay > 60%) containing more than 150 mg $Zn_{tot}$ $kg^{-1}$. The smallest $F_{25\%}$ contained 10 fine sand and moraine soils, and in these soils more than half (57 - 91%) of the mineral material was coarser than 0.06 mm (i.e. fine sand or coarser). However, the peat soils were poorest in $Zn_{tot}$. As many as 13 out of the 20 peat soils occurred in the smallest $F_{25\%}$.

When the results were transformed into milligrams per $dm^3$ of soil, the difference between mineral and organogenic soils became greater. The average $Zn_{tot}$ was 31 and 14 mg $dm^{-3}$ in mull and peat soils, respectively, while the results of the mineral soils were not altered by the transformation. The present material consisted of 11 Carex peat soils; eight of them contained less than 10 mg $Zn_{tot}$ $dm^{-3}$ of soil. The lowest $Zn_{tot}$ (3.2 mg $dm^{-3}$), occurring in a Carex peat soil of Sotkamo (97), corresponded to 6 kg $ha^{-1}$ in a 20 cm deep plough layer, while clay soils commonly contained as much as 300 kg $Zn_{tot}$ $ha^{-1}$.

Linear correlation coefficients were calculated between $Zn_{tot}$ (mg $kg^{-1}$) and some soil characteristics (Table 11). In mineral soils, excluding soil 71, $Zn_{tot}$ correlated positively with clay content and negatively with the content of coarse mineral material (>0.06 mm). There was also a positive correlation between $Zn_{tot}$ and $Fe_{ox}$, but the partial correlation between these two variables was not statistically significant when the effect of clay was eliminated. The dependence of $Zn_{tot}$ on clay content in mineral soils is presented in Figure 1. Some soils (17, 21, 38, 71) contained more $Zn_{tot}$ than the other soils of the same clay content. Inversely, the gyttja clay 12 (Vihti) and the silty clay 13 (Perniö) contained less Zn than expected. In soil 12 the organic C content (9.5%) was higher than average, resulting in a smaller quantity of mineral material and lower $Zn_{tot}$ in the sample weighed for the analysis. The low $Zn_{tot}$ of soil 13 may be due to the abundance of coarser materials which are usually poor in $Zn_{tot}$. In soil 13, 33% of the mineral material was coarser than 0.02 mm (very fine sand and coarser), while the average of these materials in clay soils was only 20%.

Table 11. Linear correlation coefficients (r) between $Zn_{tot}$ (mg $kg^{-1}$) and some soil properties of mineral and organogenic soils.

| Soil characteristic | Mineral soils n = 72 | Organogenic soils n = 34 |
|---|---|---|
| pH | $0.23^{n.s.}$ | $0.29^{n.s.}$ |
| Organic C | $0.00^{n.s.}$ | $-0.53^{**}$ |
| $Fe_{ox}$ | $0.40^{***}$ | $0.03^{n.s.}$ |
| $Al_{ox}$ | $0.24^{*}$ | $0.17^{n.s.}$ |
| Clay | $0.81^{***}$ | - |
| Silt | $0.38^{**}$ | - |
| $CF^1$ | $-0.79^{***}$ | - |

[1] CF = Coarse mineral fractions (>0.06 mm).

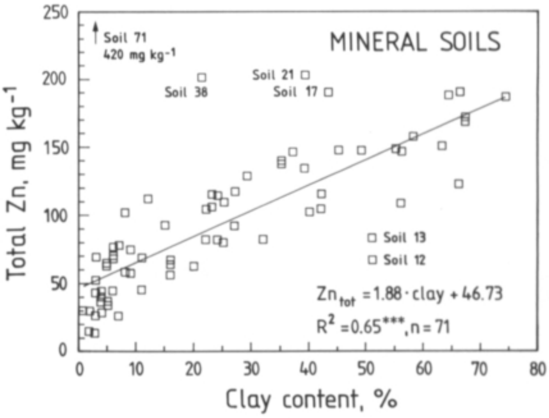

Fig. 1. Dependence of total Zn ($Zn_{tot}$) concentration of mineral soils on clay content.

In organogenic soils, there was a negative correlation between $Zn_{tot}$ and organic C. The content of mineral material is inversely reflected in the organic C content and the correlation between $Zn_{tot}$ and organic C thus indicates the fact that mineral material was richer in $Zn_{tot}$ than was organic matter. Figure 2 shows that all the soils which contained more than 35% organic C exhibited a very low concentration of $Zn_{tot}$.

The results of $Zn_{tot}$ were further studied by multiple regression analyses. In mineral soils $Zn_{tot}$ (mg $kg^{-1}$) increased with increasing content of clay and silt (%) and $Al_{ox}$ (mmol $kg^{-1}$). According to the regression analysis, an increase in organic C (C, %)

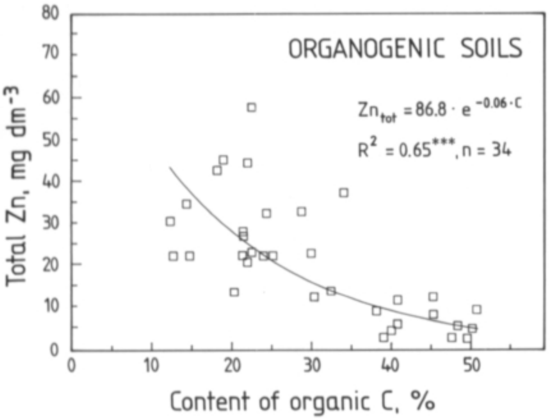

Fig. 2. Dependence of total Zn ($Zn_{tot}$) concentration of organogenic soils on the organic C content (C).

was coincident with the decrease in $Zn_{tot}$ even though there was no significant linear correlation between these two variables. The t-test of the regression coefficients and beta coefficients (β) of the independent variables showed that clay content was by far the dominant variable (Table 12). The regression equation was as follows (n = 72):

$$Zn_{tot} = 1.79\ Clay + 0.66\ Silt - 7.90\ C + 0.20\ Al_{ox} + 42.14$$
$$R^2 = 0.74^{***}$$

In organogenic soils, the dependence of $Zn_{tot}$ on different soil characteristics was weaker. In no equation did the coefficient of determination ($R^2$) exceed 0.30 when the results were expressed as milligrams or millimoles per kilogram of soil. However, when the regression analysis was carried out with results transformed into milligrams or millimoles per dm$^3$ of soil, a higher coefficient of multiple determination ($R^2$) was obtained. According to the following equation (n = 34), $Zn_{tot}$ (mg dm$^{-3}$) decreased with increasing organic C (%) while $Al_{ox}$ (mmol dm$^{-3}$) had a positive impact on $Zn_{tot}$:

$$Zn_{tot} = -0.69\ C + 0.11\ Al_{ox} + 36.75$$
$$R^2 = 0.60^{***}$$

Table 12. t-Values of the regression coefficients and beta coefficients (β) of the independent variables explaining the variation of $Zn_{tot}$ in mineral and organogenic soils.

| Independent variable | Mineral soils | | Organogenic soils | |
|---|---|---|---|---|
| | t | β | t | β |
| Clay | 11.469$^{***}$ | 0.77 | - | - |
| Silt | 3.224$^{**}$ | 0.21 | - | - |
| Organic C | -3.576$^{***}$ | -0.25 | -4.719$^{***}$ | -0.58 |
| $Al_{ox}$ | 2.056$^{*}$ | 0.14 | 2.635$^{*}$ | 0.33 |

The organic C content, being relatively the more important variable (Table 12), inversely reflects the abundance of mineral material in the soil, and $Al_{ox}$ may stand for the abundance of aluminosilicates. There was a negative correlation between organic C and $Al_{ox}$ ($r = 0.48^{**}$), showing that the $Al_{ox}$ decreased with decreasing mineral material, which obviously also resulted in a decrease of $Zn_{tot}$.

*b. Particle size fractions*

Of three silty clay soils (204 and 205 of Appendix 1; 10 of Appendix 2), clay and silt plus very fine sand were separated and analyzed for $Zn_{tot}$. The textural fractions separated had probably lost at least part of the secondary Zn during the pretreatments with hydrogen peroxide, citrate and dithionite. Therefore, the $Zn_{tot}$ of the soil fractions actually gives the quantity of Zn contained in primary minerals, while the results of the whole soil contained primary and secondary Zn. The clay fraction contained more $Zn_{tot}$ than did silt plus very fine sand (Table 13). In soil 205, the clay fraction was slightly poorer in $Zn_{tot}$ than in soil 204, while the

Table 13. Content of $Zn_{tot}$ (mg kg$^{-1}$) in clay and silt plus very fine sand fractions and in the whole soil in three soils.[1]

| Fraction | Soil | | |
|---|---|---|---|
| | 10 | 204 | 205 |
| Clay | 189.3$^{ab}$ | 199.5$^{a}$ | 178.8$^{b}$ |
| Silt plus very fine sand | 83.0$^{d}$ | 69.8$^{e}$ | 60.2$^{e}$ |
| Whole soil | 112.1$^{c}$ | 99.7$^{c}$ | 85.4$^{d}$ |
| $HSD_{0.05}$ | 12.8 | | |

[1] All means were tested simultaneously.

silt plus very fine sand of soil 10 was richer in $\mathrm{Zn_{tot}}$ than this fraction in the other two soils. The results of these analyses confirmed that the clay content largely determines the concentration of $\mathrm{Zn_{tot}}$ in a mineral soil but also silt and very fine sand seem to contribute substantially to $\mathrm{Zn_{tot}}$.

### 3.2.2 Fractions of soil Zn

In the fractionation of soil Zn, water-soluble and exchangeable Zn ($\mathrm{Zn_{ex}}$) were extracted by $\mathrm{MgCl_2}$. A new sample was weighed for the sequential extraction with pyrophosphate and oxalate which were assumed to dissolve Zn bound by organic matter ($\mathrm{Zn_{py}}$) and sesquioxides ($\mathrm{Zn_{ox}}$), respectively. Residual Zn ($\mathrm{Zn_{res}}$) remaining in the soil after the oxalate extraction was obtained as the difference of $\mathrm{Zn_{tot}}$ and $\mathrm{Zn_{py}} + \mathrm{Zn_{ox}}$.

*a. Water-soluble and exchangeable Zn*

Water-soluble and exchangeable Zn ($\mathrm{Zn_{ex}}$) ranged from 0.3 to 22.0 mg $\mathrm{kg^{-1}}$ (Appendix 5). The mean $\mathrm{Zn_{ex}}$ (Table 14) did not differ markedly from one mineral soil class to another, but the means in the two organogenic soil classes were considerably higher than those of the mineral soil classes. When studying the results expressed as milligrams of Zn per $\mathrm{dm^3}$ of soil, the difference between the means of the five soil classes were not statistically significant.

Table 14. Water-soluble and exchangeable Zn in surface soils.

| Soil class | n | Mean | s | Range |
|---|---|---|---|---|
| | | | mg $\mathrm{kg^{-1}}$ | |
| Clay | 25 | $1.7^{b}$ | 1.2 | 0.5-4.9 |
| Silt, loam, very fine sand | 20 | $1.3^{b}$ | 0.8 | 0.5-3.5 |
| Fine sand, moraine | 28 | $2.5^{1}$ | 4.3 | 0.3-22.0 |
| - soil 71 excluded | 27 | $1.8^{b}$ | 1.9 | 0.3-8.3 |
| Mull | 14 | $2.6^{b}$ | 2.0 | 0.9-7.0 |
| Peat | 20 | $5.2^{a}$ | 2.9 | 1.1-11.0 |

[1] Mean not included in the statistical analysis.

*b. Zinc bound by organic matter and sesquioxides*

In 106 soils, Zn extracted with pyrophosphate ($\mathrm{Zn_{py}}$) ranged from 1.4 to 53.8 mg $\mathrm{kg^{-1}}$. In addition, in soil 71 rich in $\mathrm{Zn_{tot}}$ there was also plenty of $\mathrm{Zn_{py}}$ (227 mg $\mathrm{kg^{-1}}$) (Appendix 5). The mean $\mathrm{Zn_{py}}$ was higher in peat soils than in the other four soil classes (Table 15). However, after transforming the results to milligrams per $\mathrm{dm^3}$ of soil, statistical differences between the soil classes were nonexistent with means of 4.9 and 5.3 mg $\mathrm{dm^{-3}}$ in the mull and peat soils, respectively.

Soil Zn extracted by oxalate ($\mathrm{Zn_{ox}}$) sequentially after the pyrophosphate treatment ranged in 106 soils from 0.5 to 13.0 mg $\mathrm{kg^{-1}}$, while soil 71 contained 115 mg $\mathrm{Zn_{ox}}$ $\mathrm{kg^{-1}}$ (Appendix 5). The mean $\mathrm{Zn_{ox}}$ (Table 15) was higher in clay soils than in fine sand and moraine soils or in organogenic soils. When expressing the results as milligrams of Zn per $\mathrm{dm^3}$ of soil, the organogenic soil classes were by far poorer in $\mathrm{Zn_{ox}}$ than were the mineral soils with means of 1.2 and 0.9 mg $\mathrm{dm^{-3}}$ in mull and peat soils, respectively. In nine out of the 25 clay soils, $\mathrm{Zn_{ox}}$ was higher than $\mathrm{Zn_{py}}$. In soils other than clay, $\mathrm{Zn_{ox}}$ was lower than $\mathrm{Zn_{py}}$ with only two exceptions; in organogenic soils $\mathrm{Zn_{py}}$ was four to five times higher than $\mathrm{Zn_{ox}}$.

The average mean deviation of the replicates of $\mathrm{Zn_{py}}$ was 0.33 mg $\mathrm{kg^{-1}}$, or 5.5% of the mean and ranged from 0 to 18.9% of the mean in the 107 surface soils. The mean deviation of $\mathrm{Zn_{ox}}$ averaged 0.16 mg $\mathrm{kg^{-1}}$, or 4.8% of the mean, ranging from 0 to 25.2%. The mean deviation exceeded 10% in 15 and eight soils in the determination of $\mathrm{Zn_{py}}$ and $\mathrm{Zn_{ox}}$, respectively.

The lowest results of $\mathrm{Zn_{py}}$ ($F_{11\%}$) were distributed over all mineral soil classes, while those of $\mathrm{Zn_{ox}}$ ($F_{10\%}$) occurred in fine sand and moraine soils (eight soils) as well as in organogenic soils (three soils). There was no soil in common to the smallest $F_{11\%}$ of $\mathrm{Zn_{py}}$ and the smallest $F_{10\%}$ of $\mathrm{Zn_{ox}}$. The mineral soils poorest in $\mathrm{Zn_{ox}}$ were characterized by a coarse texture and low $\mathrm{Fe_{ox}}$ content. In the eight fine sand and moraine soils of the smallest $F_{10\%}$ of $\mathrm{Zn_{ox}}$ the average concentration of $\mathrm{Fe_{ox}}$ was 22.0 mmol $\mathrm{kg^{-1}}$ which was less ($t = 3.598^{**}$) than in the rest of the fine sand and moraine soils (mean 62.3

Table 15. Soil Zn extracted sequentially by pyrophosphate ($Zn_{py}$) and oxalate ($Zn_{ox}$) as well as residual Zn ($Zn_{res}$).[1]

| Soil class | n | $Zn_{py}$, mg kg$^{-1}$ | | $Zn_{ox}$, mg kg$^{-1}$ | | $Zn_{res}$, mg kg$^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range |
| Clay | 25 | 4.9$^b$ | 1.4-23.1 | 3.5$^a$ | 1.2-13.0 | 132.0$^a$ | 62.6-193 |
| Silt, loam, very fine sand | 20 | 3.4$^b$ | 1.4-6.7 | 2.5$^{ab}$ | 1.4-5.0 | 90.5$^b$ | 54.2-192 |
| Fine sand, moraine | 28 | 12.7$^2$ | 1.4-227 | 6.1$^2$ | 0.6-115 | 43.3$^2$ | 10.2-96.9 |
| -soil 71 excluded | 27 | 4.8$^b$ | 1.4-23.9 | 2.0$^b$ | 0.6-8.8 | 42.0$^c$ | 10.2-96.9 |
| Mull | 14 | 7.8$^b$ | 1.6-26.9 | 1.8$^b$ | 1.0-3.5 | 39.1$^{cd}$ | 15.7-69.8 |
| Peat | 20 | 14.1$^a$ | 2.2-53.8 | 2.4$^{ab}$ | 0.5-10.3 | 18.7$^d$ | 3.9-53.0 |

[1] Results were tested separately for $Zn_{py}$ and $Zn_{ox}$.

[2] Mean not included in the statistical analysis.

Table 16. Complexed Zn calculated as the difference between $Zn_{py}$ and $Zn_{ex}$ (i.e. $Zn_{py}$-$Zn_{ex}$).

| Soil class | n | Mean | s | Range | $(Zn_{py}-Zn_{ex})/Zn_{py}$ |
|---|---|---|---|---|---|
| | | -------------------- | mg kg$^{-1}$ | -------------------- | % |
| Clay | 25 | 3.1$^b$ | 3.4 | 0.5-18.2 | 43-84 |
| Silt, loam, very fine sand | 20 | 2.2$^b$ | 1.6 | 0.6-4.8 | 16-85 |
| Fine sand, moraine | 28 | 10.2$^1$ | 38.3 | 0.6-205 | 22-90 |
| - soil 71 excluded | 27 | 3.0$^b$ | 3.5 | 0.6-18.7 | 22-85 |
| Mull | 14 | 5.1$^{ab}$ | 4.8 | 0.3-6.1 | 19-78 |
| Peat | 20 | 8.9$^a$ | 9.8 | 0.7-43.0 | 19-80 |

[1] Mean not included in the statistical analysis.

mmol kg$^{-1}$, n = 20). The highest results ($F_{10\%}$) of $Zn_{py}$ occurred with three exceptions in organogenic soils, while those of $Zn_{ox}$ ($F_{10\%}$) were the most common in clay soils.

### *c. Complexed Zn*

Water-soluble and exchangeable Zn extracted with $MgCl_2$ was probably included also in Zn extracted by pyrophosphate ($Zn_{py}$). Therefore the results of the pyrophosphate extraction can be divided into two parts: (1) water-soluble and exchangeable Zn bound by non-specific electrostatic forces and (2) Zn presumably bound mainly by organic matter in complexed forms by covalent forces. The quantities of complexed Zn were calculated as the difference of $Zn_{py}$ and $Zn_{ex}$ (i.e. $Zn_{py} - Zn_{ex}$) (Table 16). This fraction was larger in peat soils than in the mineral soil classes but, again, there were no differences between the soil classes when the results were expressed as milligrams of Zn per dm$^3$.

The percentage of $Zn_{py}$ which was bound by covalent forces, i.e. the ratio $100 \cdot (Zn_{py} - Zn_{ex})/Zn_{py}$, ranged 14 - 90% (Table 16) and correlated with soil pH ($r = 0.65^{***}$). The fractile ($F_{10\%}$) of the smallest percentage (14 - 38%) of $Zn_{py}$ in complexed forms consisted of six organogenic soils (pH 3.8 - 5.6) and of five coarse mineral soils (pH 4.2 - 5.8). The four fine sand and moraine soils of this group had only a moderate acidity (pH 4.9 - 5.8) and a very low content of clay (≤4%) as well as $Fe_{ox}$ and $Al_{ox}$. Three of these soils (72, 73, 74) were those of the coarsest texture in the whole soil material. For comparison, the most acid clay soils (10, 20, 26) had nearly the same pH (4.6, 5.2, 5.0, respectively) but a higher percentage (52 - 62%) of $Zn_{py}$ was not water soluble or exchangeable, indicating a difference in bonding of Zn in acid clay soils and acid fine sands.

### *d. Residual Zn*

Residual Zn ($Zn_{res}$) (Table 15) represents the fraction bound in the mineral lattices. This fraction was the largest in clay soils and decreased in mineral soils with decreasing clay content; 11 soils richest in clay were also in the largest $F_{25\%}$ of $Zn_{res}$. The lowest results occurred in organogenic soils; 15 out of 20 peat soils, especially those of the highest organic C content, and five out of 14 mull soils were in the smallest $F_{25\%}$ of $Zn_{res}$. The smallest $F_{25\%}$ also contained seven fine sand and moraine soils which were very coarse in texture, containing only 1 - 7% clay and 3 - 13% silt. The pH of these seven soils (4.9 - 6.3, mean 5.5) was lower ($t = 3.295^{**}$) than in the rest of the fine sand and moraine soils (mean 6.2). When the results of $Zn_{res}$ were transformed into milligrams per $dm^3$ of soil, the difference between organogenic and mineral soils became greater with means of 25.4 and 8.0 mg $dm^{-3}$ for mull and peat soils, respectively, while the transformation did not have a marked influence on the results of mineral soils.

### *e. Relationship between Zn fractions and other soil properties*

Owing to the skewed distribution of the results of secondary Zn fractions ($Zn_{ex}$, $Zn_{py}$, $Zn_{py}$ - $Zn_{ex}$ and $Zn_{ox}$), the linear correlation coefficients were calculated using the natural logarithms ($\log_e$) of the results (Table 17). In order to eliminate the effect of the skewness of the material, also the Spearman rank correlation coefficients were calculated between the various Zn fractions and soil properties. The two correlation coefficients were similar and only the linear ones are presented. Soil 71, extremely rich in Zn, was not included in the calculations.

In mineral and organogenic soils, $Zn_{ex}$ correlated negatively with soil pH. The correlation was made weaker by a few soils which in spite of a pH above 6.5 contained plenty of $Zn_{ex}$. $Zn_{ex}$ correlated closely with $Zn_{py}$, but it should be taken into account that $Zn_{ex}$ is actually a part of $Zn_{py}$; the correlation between $Zn_{ex}$ and complexed Zn ($Zn_{py}$ - $Zn_{ex}$) remained lower than that between $Zn_{ex}$ and $Zn_{py}$. Organic C content seemed to correlate with $Zn_{ex}$, reflecting the lower

Table 17. Linear correlation coefficients between Zn fractions and some other soil properties. Tabulations were carried out using natural logarithms of concentrations of Zn, Fe and Al, expressed as mg $kg^{-1}$ (Zn) or mmol $kg^{-1}$ (Fe, Al).

| | $Zn_{ex}$ | $Zn_{py}$-$Zn_{ex}$ | $Zn_{py}$ | $Zn_{ox}$ | $Zn_{res}$ |
|---|---|---|---|---|---|
| Mineral soils (n = 72): | | | | | |
| Clay | $0.05^{n.s.}$ | $0.07^{n.s.}$ | $0.03^{n.s.}$ | $0.47^{***}$ | $0.76^{***}$ |
| Organic C | $0.30^{**}$ | $0.10^{n.s.}$ | $0.23^{n.s.}$ | $-0.13^{n.s.}$ | $-0.04^{n.s.}$ |
| pH | $-0.70^{***}$ | $0.11^{n.s.}$ | $-0.29^{*}$ | $0.28^{*}$ | $0.23^{n.s.}$ |
| $Fe_{ox}$ | $0.09^{n.s.}$ | $0.07^{n.s.}$ | $0.12^{n.s.}$ | $0.57^{***}$ | $0.64^{***}$ |
| $Al_{ox}$ | $0.03^{n.s.}$ | $0.26^{*}$ | $0.14^{n.s.}$ | $0.26^{*}$ | $0.38^{**}$ |
| $Zn_{tot}$ | $-0.02^{n.s.}$ | $0.23^{n.s.}$ | $0.12^{n.s.}$ | $0.76^{***}$ | $0.99^{***}$ |
| $Zn_{res}$ | $-0.10^{n.s.}$ | $0.16^{n.s.}$ | $0.04^{n.s.}$ | $0.69^{***}$ | |
| $Zn_{ox}$ | $0.22^{n.s.}$ | $0.61^{***}$ | $0.53^{***}$ | | |
| $Zn_{py}$ | $0.78^{***}$ | $0.87^{***}$ | | | |
| $Zn_{py}$-$Zn_{ex}$ | $0.40^{***}$ | | | | |
| Organogenic soils (n = 34): | | | | | |
| Organic C | $0.48^{**}$ | $0.22^{n.s.}$ | $0.34^{*}$ | $0.11^{n.s.}$ | $-0.80^{***}$ |
| pH | $-0.54^{***}$ | $0.07^{n.s.}$ | $-0.14^{n.s.}$ | $0.04^{n.s.}$ | $0.39^{*}$ |
| $Fe_{ox}$ | $0.02^{n.s.}$ | $0.11^{n.s.}$ | $0.08^{n.s.}$ | $0.03^{n.s.}$ | $0.22^{n.s.}$ |
| $Al_{ox}$ | $-0.20^{n.s.}$ | $-0.34^{n.s.}$ | $-0.33^{*}$ | $-0.15^{n.s.}$ | $0.33^{n.s.}$ |
| $Zn_{tot}$ | $0.13^{n.s.}$ | $0.36^{*}$ | $0.33^{n.s.}$ | $0.48^{**}$ | $0.79^{***}$ |
| $Zn_{res}$ | $-0.28^{n.s.}$ | $-0.07^{n.s.}$ | $-0.15^{n.s.}$ | $-0.05^{n.s.}$ | |
| $Zn_{ox}$ | $0.50^{**}$ | $0.68^{***}$ | $0.69^{***}$ | | |
| $Zn_{py}$ | $0.85^{***}$ | $0.95^{***}$ | | | |
| $Zn_{py}$-$Zn_{ex}$ | $0.65^{***}$ | | | | |

pH in soils rich in organic C ($r = -0.45^{***}$ and $-0.44^{**}$ in mineral and organogenic soils, respectively). Soils rich in $Zn_{py}$ tended also to be rich in $Zn_{ox}$. $Zn_{ox}$ and $Zn_{res}$ correlated closely with $Zn_{tot}$ in mineral soils but more weakly ($z = 2.219^{*}$ and $12.642^{***}$ for $Zn_{ox}$ and $Zn_{res}$, respectively) in organogenic soils. In mineral soils $Zn_{ox}$ correlated with clay, $Fe_{ox}$ and $Zn_{res}$. Contrary to mineral soils, $Zn_{ox}$ did not correlate with $Zn_{res}$ or $Fe_{ox}$ in organogenic soils but there was a significant negative correlation between $Zn_{res}$ and organic C.

The relationships between $Zn_{ex}$ and other fractions of secondary Zn were further studied by regression analyses using the natural logarithms of Zn concentrations. Both in mineral and organogenic soils $Zn_{ex}$ (mg kg$^{-1}$) increased with increasing $Zn_{py}$ (mg kg$^{-1}$) and/or decreasing soil pH. Even though there was a statistically significant linear correlation between $Zn_{ex}$ and $Zn_{ox}$ in organogenic soils, $Zn_{ox}$ remained insignificant in the regression analysis, owing to the positive correlation between $Zn_{ox}$ and $Zn_{py}$. The t-values and the beta coefficients (Table 18) show that pH and $Zn_{py}$ were relatively of equal importance in explaining the variation of $Zn_{ex}$. The regression equations were as follows:

Mineral soils (n = 72):

$$\log_e Zn_{ex} = -0.66\ pH + 0.73 \log_e Zn_{py} + 3.21$$
$$R^2 = 0.85^{***}$$

Organogenic soils (n = 34):

$$\log_e Zn_{ex} = -0.54\ pH + 0.66 \log_e Zn_{py} + 1.13$$
$$R^2 = 0.84^{***}$$

Dependence of $Zn_{py}$, $Zn_{py}$ - $Zn_{ex}$ and $Zn_{ox}$ on soil characteristics was studied by regression analyses. The regression equations consisting of $Zn_{tot}$, organic C, pH, $Fe_{ox}$, $Al_{ox}$ and in mineral soils clay content explained less than 10% of the variation of $Zn_{py}$ and $Zn_{py}$ - $Zn_{ex}$. Instead, a considerable part of the variation of $Zn_{ox}$ (mg dm$^{-3}$) was explained by $Zn_{tot}$ (mg dm$^{-3}$) (n = 106):

$$\log_e Zn_{ox} = 0.65 \log_e Zn_{tot} - 2.00$$
$$R^2 = 0.71^{***}$$

### *f. Distribution of soil Zn into different fractions*

The distribution of soil Zn into different fractions, expressed as percentages of $Zn_{tot}$, was studied (Table 19). In clay and silt soils the residual fraction ($Zn_{res}$) commonly accounted for more than 90% of $Zn_{tot}$. The distribution of Zn in the mineral soil classes did not differ significantly from one class to another even though in a few coarse mineral soils a larger part of Zn was in the secondary fractions

Table 18. t-Values of the regression coefficients and beta coefficients (β) of the independent variables explaining the variation of log $Zn_{ex}$ in mineral and organogenic soils.

| Independent variable | Mineral soils | | Organogenic soils | |
|---|---|---|---|---|
| | t | β | t | β |
| pH | $-10.550^{***}$ | -0.52 | $-6.826^{***}$ | -0.51 |
| log $Zn_{py}$ | $12.822^{***}$ | 0.63 | $8.995^{***}$ | 0.67 |

Table 19. Distribution of soil Zn (%) into different fractions expressed as percentages of $Zn_{tot}$.[1]

| Soil class | $Zn_{ex}$ | | $Zn_{py}$-$Zn_{ex}$ | | $Zn_{ox}$ | | $Zn_{res}$ | |
|---|---|---|---|---|---|---|---|---|
| | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| Clay | $1.3^{b}$ | 0.3-3.6 | $2.2^{c}$ | 0.5-9.6 | $2.5^{b}$ | 1.4-6.8 | $94.0^{a}$ | 81.0-97.2 |
| Silt, loam, very fine sand | $1.5^{b}$ | 0.3-5.5 | $2.3^{bc}$ | 0.6-4.9 | $2.6^{b}$ | 1.5-4.3 | $93.6^{a}$ | 87.6-97.3 |
| Fine sand, moraine | 4.7[2] | 0.4-27.0 | 7.5[2] | 1.4-48.8 | 4.8[2] | 2.0-27.4 | 83.0[2] | 18.6-95.2 |
| -soil 71 excluded | $4.8^{b}$ | 0.4-27.0 | $6.0^{bc}$ | 1.4-23.9 | $4.1^{b}$ | 2.0-11.3 | $85.1^{ab}$ | 50.5-95.2 |
| Mull | $5.7^{b}$ | 2.2-17.9 | $10.4^{b}$ | 0.7-26.3 | $3.9^{b}$ | 1.9-7.1 | $80.0^{b}$ | 59.7-94.0 |
| Peat | $17.7^{a}$ | 2.6-37.4 | $25.1^{a}$ | 2.5-54.5 | $8.0^{a}$ | 2.8-12.0 | $49.2^{c}$ | 12.2-84.0 |

[1] Each fraction was tested separately.

[2] Mean not included in the statistical analysis.

($Zn_{ex}$, $Zn_{py}$ - $Zn_{ex}$, $Zn_{ox}$) than in the rest of the mineral soils. In mull soils the percentage of $Zn_{res}$ was significantly smaller than in the two most fine-textured mineral soil classes. In peat soils the percentages of the secondary fractions were substantially greater and $Zn_{res}$ smaller than in the other soil classes. In the 13 soils richest in organic C (34 - 50%) the sum $Zn_{py} + Zn_{ox}$ corresponded to as much as 68 - 88% of $Zn_{tot}$. In mineral soils, the ratio $(Zn_{py} + Zn_{ox})/Zn_{tot}$ which reflects the relative abundance of secondary fractions did not correlate with soil properties, but in organogenic soils there was a close correlation between this ratio and organic C ($r = 0.81^{***}$).

Fractions of Zn were studied separately in mineral and organogenic soils in which $Zn_{py}$ exceeded 10 mg $kg^{-1}$ (mineral soils) or 20 mg $kg^{-1}$ (organogenic soils) (Table 20). In these soils, the secondary Zn fractions ranged from 19% in clay soil 17 to 88% in peat soil 102 and were relatively larger than those in the respective soil class on average. Inquiries concerning the farming operations revealed that large quantities of farm-yard manure had been spread to the fields from where soils 53, 70, 85 and 95 originated (V. Haataja, P. Luoma and J. Nieminen 1991, Kemira Oy, I. Kallioniemi 1991, Suomen Säästöpankki, Pori, pers. commun.). It is likely that the abundance of secondary Zn also in soil 17 can be attributed to the use of farm-yard manure, because the respective field was located at Viikki 0.2 km from the barn of the farm of the University of Helsinki. Soil 71 of Harjavalta had been taken about 2 km from the smelter of Outokumpu Oy. No slag or farm-yard manure had been transported to the field for several years (I. Kallioniemi 1991, Suomen Säästöpankki, Pori, pers. commun.), suggesting that the abundance of Zn was airborne. Information of the farming of soils 74, 101 and 102 was not available.

Table 20. Soil $Zn_{py}$ and $Zn_{ox}$ as well as the ratio (%) between secondary and $Zn_{tot}$, i.e. $100 \cdot (Zn_{py} + Zn_{ox})/Zn_{tot}$, in soils exceptionally rich in $Zn_{py}$.

| Soil | $Zn_{py}$ mg $kg^{-1}$ | $Zn_{ox}$ mg $kg^{-1}$ | $(Zn_{py} + Zn_{ox})/Zn_{tot}$ % |
|---|---|---|---|
| 17, 53, 70, 74 | 18.3 | 7.1 | 36 |
| 71 | 227 | 115 | 81 |
| 85, 95, 101, 102 | 33.8 | 5.0 | 70 |

### 3.2.3 Zinc extracted by AAAc-EDTA

In soil testing in Finland plant-available Zn is extracted by AAAc-EDTA at pH 4.65. Therefore, this method was applied also to the present surface soil material, and relationships between Zn extracted by AAAc-EDTA ($Zn_{Ac}$) and chemically more specific fractions of soil Zn were investigated. Soil $Zn_{Ac}$ ranged from 0.6 to 165 mg $dm^{-3}$ (Appendix 5). The highest result occurred for the same fine sand soil (71) which was rich in Zn according to all indices determined. The second highest result was 29.9 mg $dm^{-3}$ and the median of the whole material was 2.9 mg $dm^{-3}$. The means of $Zn_{Ac}$ did not differ statistically significantly from one soil class to another (Table 21). The mean deviation of the replicates averaged 0.25 mg $dm^{-3}$, or 4.4% of the mean, range 0 - 20.8%. Soil 71 excluded, the mean deviation averaged 0.15 mg $dm^{-3}$. $Zn_{Ac}$ corresponded on average to 45% (range 18 - 76%) and 75% (range 43 - 200%) of the sum $Zn_{py} + Zn_{ox}$ (mg $dm^{-3}$) in mineral and organogenic soils, respectively.

The 15 soils ($F_{14\%}$) poorest in $Zn_{Ac}$ (≤ 1.5 mg $dm^{-3}$) consisted of two clay soils, 10 coarse mineral soils and three organogenic soils. The pH of the 12 mineral soils of this group was 5.4 - 6.9, and in nine of these soils, the pH was above or equal to 6.0, which was the mean pH for mineral soils. There

Table 21. Soil Zn extracted by AAAc-EDTA from surface soils.

| Soil class | n | Mean | s | Range |
|---|---|---|---|---|
| | | ------------ | mg $dm^{-3}$ | ------------ |
| Clay | 25 | 3.7 | 3.2 | 1.1-18.0 |
| Silt, loam, very fine sand | 20 | 2.6 | 1.5 | 0.8-5.7 |
| Fine sand, moraine | 28 | 9.9 | 30.9 | 0.9-165 |
| -soil 71 excluded | 27 | 4.1 | 5.8 | 0.9-29.9 |
| Mull | 14 | 4.0 | 3.2 | 0.8-14.0 |
| Peat | 20 | 4.6 | 4.0 | 0.6-19.4 |

was thus a slight tendency of the soils poor in $Zn_{Ac}$ to have a pH higher than average. There were, however, several soils of high pH which contained plenty of $Zn_{Ac}$.

Linear correlation coefficients were calculated between $Zn_{Ac}$ and other indices of soil Zn using the natural logarithms of the results (mg $dm^{-3}$). The $Zn_{Ac}$ correlated most closely with $Zn_{py}$ ($r = 0.87^{***}$ and $0.95^{***}$ in mineral and organogenic soils, respectively). The correlation was statistically highly significant also with $Zn_{ex}$ ($r = 0.76^{***}$ and $0.79^{***}$) and $Zn_{ox}$ ($r = 0.61^{***}$ and $0.60^{***}$). In the organogenic soils there was a significant correlation also between $Zn_{Ac}$ and $Zn_{tot}$ ($r = 0.42^{*}$). Like $Zn_{py}$, $Zn_{Ac}$ did not correlate with soil pH or with the content of clay or organic matter. Despite the highly significant correlation of $Zn_{Ac}$ both with $Zn_{py}$ and $Zn_{ox}$, $Zn_{py}$ (mg $dm^{-3}$) alone explained statistically significantly the variation of $Zn_{Ac}$ (mg $dm^{-3}$) in the regression analysis, and $Zn_{ox}$ was not a significant variable. The equation was as follows (n = 106):

$$\log_e Zn_{Ac} = 0.89 \log_e Zn_{py} - 0.090$$
$$R^2 = 0.80^{***}$$

When the regression analyses were tabulated separately for mineral and organogenic soils, slightly different equations were obtained for the two soil groups. In organogenic soils, $Zn_{py}$ alone explained 89% of the variation of $Zn_{Ac}$ (equation not shown); other soil characteristics were not significant. In the equation for mineral soils (n = 72), the contents (%) of clay and organic C were also significant variables, while $Zn_{py}$ (mg $dm^{-3}$) was relatively the most important:

$$\log_e Zn_{Ac} = 0.91 \log_e Zn_{py} + 0.0064\ \text{Clay} - 0.049\ \text{C} - 0.19$$
$$R^2 = 0.81^{***}$$

| | t | β |
|---|---|---|
| $\log_e Zn_{py}$ | $16.642^{***}$ | 0.89 |
| Clay | $3.860^{***}$ | 0.21 |
| Organic C | $-2.106^{*}$ | -0.12 |

The above equation shows that at a given level of $Zn_{py}$, increasing clay content enhanced the extraction power of AAAc-EDTA. The negative regression coefficient of C suggests that, at a given $Zn_{py}$ level, increasing organic C reduced the extraction power of AAAc-EDTA in relation to that of pyrophosphate.

Also the relationships between $Zn_{Ac}$ (mg $dm^{-3}$) and $Zn_{ex}$ (mg $dm^{-3}$) were studied by multiple regression analyses. According to the beta coefficients (β) (Table 22), $Zn_{ex}$ was relatively the most important variable explaining the variation of $Zn_{Ac}$ both in mineral and organogenic soils. The equation below shows that the relative efficiency of AAAc-EDTA to extract Zn increased with increasing soil pH. In mineral soils, also the clay content increased the efficiency of AAAc-EDTA as an extractant for soil Zn as compared to $MgCl_2$. The equations were as follows:

Mineral soils (n = 72):

$$\log_e Zn_{Ac} = 0.98 \log_e Zn_{ex} + 0.62\ \text{pH} + 0.0041\ \text{Clay} - 3.03$$
$$R^2 = 0.78^{***}$$

Organogenic soils (n = 34):

$$\log_e Zn_{Ac} = 1.05 \log_e Zn_{ex} + 0.48\ \text{pH} - 1.69$$
$$R^2 = 0.76^{***}$$

Table 22. t-Values of the regression coefficients and beta coefficients (β) of the independent variables explaining the variation of log $Zn_{Ac}$ in mineral and organogenic soils.

| Independent variable | Mineral soils | | Organogenic soils | |
|---|---|---|---|---|
| | t | β | t | β |
| log $Zn_{ex}$ | $15.235^{***}$ | 1.11 | $9.779^{***}$ | 0.93 |
| pH | $7.586^{***}$ | 0.56 | $4.149^{***}$ | 0.39 |
| Clay | $2.402^{*}$ | 0.14 | - | - |

## 3.3 Vertical distribution of soil Zn

Plant roots penetrate far below the plough layer and therefore Zn reserves also deeper in the soil may be important in providing the plant with Zn. Therefore, the vertical distribution of Zn was studied by

Table 23. Total Zn ($Zn_{tot}$) and Zn extracted by AAAc-EDTA ($Zn_{Ac}$) in samples taken from various depths in seven soil profiles.[1]

| Depth<br>cm | $Zn_{tot}$<br>mg kg$^{-1}$ | $Zn_{Ac}$<br>mg dm$^{-3}$ | Depth<br>cm | $Zn_{tot}$<br>mg kg$^{-1}$ | $Zn_{Ac}$<br>mg dm$^{-3}$ |
|---|---|---|---|---|---|
| *Profile 1:* loam/clay loam | | | *Profile 2:* silt | | |
| 0-30 | 82.3$^{d}$ | 2.3$^{b}$ | 0-27 | 93.9$^{a}$ | 1.9$^{a}$ |
| 32-38 | 88.2$^{d}$ | 0.7$^{e}$ | 30-40 | 62.9$^{b}$ | 0.3$^{c}$ |
| 38-46 | 97.4$^{d}$ | 0.7$^{e}$ | 40-50 | 68.7$^{b}$ | 0.4$^{c}$ |
| 50-60 | 116.8$^{c}$ | 1.3$^{d}$ | 50-70 | 71.9$^{b}$ | 0.6$^{c}$ |
| 65-80 | 132.2$^{bc}$ | 1.9$^{c}$ | 70-90 | 43.7$^{c}$ | 0.3$^{c}$ |
| 85-100 | 146.5$^{b}$ | 2.0$^{bc}$ | 90-100 | 71.7$^{b}$ | 0.6$^{c}$ |
| 105-120 | 165.9$^{a}$ | 5.0$^{a}$ | 110-120 | 96.8$^{a}$ | 1.5$^{b}$ |
| $HSD_{0.05}$ | 19.0 | 0.4 | $HSD_{0.05}$ | 11.0 | 0.4 |
| *Profile 3:* silty clay/heavy clay | | | *Profile 4:* fine sand | | |
| 0-30 | 129.0$^{d}$ | 4.3$^{a}$ | 0-30 | 22.6$^{b}$ | 6.7$^{a}$ |
| 30-40 | 129.1$^{d}$ | 2.4$^{c}$ | 30-40 | 9.2$^{e}$ | 0.8$^{b}$ |
| 40-60 | 137.6$^{c}$ | 1.2$^{d}$ | 40-45 | 11.7$^{de}$ | 0.7$^{b}$ |
| 60-80 | 159.0$^{b}$ | 3.3$^{b}$ | 45-60 | 13.7$^{cde}$ | 0.3$^{bc}$ |
| 80-100 | 191.9$^{a}$ | 3.5$^{b}$ | 60-80 | 17.3$^{bcd}$ | 0.2$^{c}$ |
| 100-120 | 192.6$^{a}$ | 3.8$^{ab}$ | 80-110 | 20.1$^{bc}$ | 0.2$^{c}$ |
| $HSD_{0.05}$ | 6.3 | 0.7 | 110-120 | 30.5$^{a}$ | 0.2$^{c}$ |
| | | | $HSD_{0.05}$ | 7.2 | 0.5 |
| *Profile 5:* Carex peat | | | *Profile 6:* Carex peat/mud/heavy clay | | |
| 0-20 | 42.3$^{a}$ | 0.9$^{a}$ | 0-25 | 65.2$^{c}$ | 2.7$^{b}$ |
| 20-30 | 6.1$^{c}$ | 0.6$^{a}$ | 30-40 | 41.8$^{d}$ | 1.6$^{c}$ |
| 30-40 | 6.6$^{c}$ | 0.9$^{a}$ | 40-45 | 90.3$^{b}$ | 6.3$^{a}$ |
| 40-60 | 5.0$^{c}$ | 0.4$^{a}$ | 50-70 | 191.8$^{a}$ | 2.4$^{a}$ |
| 60-80 | 8.3$^{c}$ | 0.5$^{a}$ | 70-80 | 199.4$^{a}$ | 2.7$^{b}$ |
| 80-100 | 9.9$^{c}$ | 0.5$^{a}$ | $HSD_{0.05}$ | 23.4 | 0.7 |
| 100-120 | 34.3$^{b}$ | 1.0$^{a}$ | | | |
| 120-130 | 29.6$^{b}$ | 1.1$^{a}$ | | | |
| $HSD_{0.05}$ | 5.2 | 0.7 | | | |
| *Profile 7:* Carex peat/fine sand | | | | | |
| 0—30 | 13.0$^{a}$ | 6.7$^{a}$ | | | |
| 30—50 | 6.4$^{b}$ | 1.7$^{b}$ | | | |
| 50—70 | 2.4$^{b}$ | 1.5$^{b}$ | | | |
| 70—90 | 2.9$^{b}$ | 0.7$^{b}$ | | | |
| 90—110 | 3.5$^{b}$ | 0.8$^{b}$ | | | |
| 110—125 | 14.3$^{a}$ | 0.8$^{b}$ | | | |
| $HSD_{0.05}$ | 5.9 | 1.8 | | | |

[1] Each profile was tested separately for $Zn_{tot}$ and $Zn_{Ac}$.

investigating soil profiles as well as sample pairs consisting of a sample from the plough layer and the subsoil.

### 3.3.1 Total Zn

The seven profiles differed greatly in the content of total Zn ($Zn_{tot}$) (Table 23). In profiles P1, P3 and P6, where the entire profile or a part of it consisted of clay soil, the peak $Zn_{tot}$ exceeded 150 mg kg$^{-1}$. In turn, in profile P4 dominated by fine sand as well as in the Carex peat profiles P5 and P7, all layers contained less than 50 mg $Zn_{tot}$ kg$^{-1}$, most layers even less than 10 mg kg$^{-1}$. The $Zn_{tot}$ of organogenic layers was dependent on the $Zn_{tot}$ of the mineral subsoil. This was demonstrated in profile P7 which had a Carex peat topsoil very poor in $Zn_{tot}$ and a fine sand subsoil which also was poor in $Zn_{tot}$. On the contrary, in profile P6 the soil below the organogenic surface horizons was heavy clay rich in $Zn_{tot}$, and also the surface horizons were richer in $Zn_{tot}$ as compared with the other two organogenic soil profiles.

The content of $Zn_{tot}$ showed marked changes in relation to the depth within each soil profile. The highest $Zn_{tot}$ occurred either in the plough layer or in the deepest horizon sampled. The lowest $Zn_{tot}$ occurred between these horizons, with the exception of profile P1 (silty clay) and P3 (silt) where it was in the two or three uppermost horizons sampled. In the other five profiles (P2, P4, P5, P6, P7) $Zn_{tot}$ was markedly higher in the plough layer than in the next layer below. In all profiles but one (P5) was the content of $Zn_{tot}$ in the bottom of the profile at least as high as that in the plough layer. Mineral soil had obviously been mixed in the plough layer of Carex peat profile P5, increasing the $Zn_{tot}$ in the plough layer of this profile. An evidence of the external source of the mineral matter was the presence of clay (9%). Moreover, the uppermost layer contained only 9% organic C, while in the layer below there was as much as 52% of organic C.

The $Zn_{tot}$ of the mineral soil profiles P1, P2 and P3 correlated closely with the clay content ($r = 0.89^{**} - 0.99^{***}$); in profile P4, $Zn_{tot}$ correlated ($r = 0.81^{*}$) with very fine sand which was the finest textural fraction present in abundance. In the organogenic profiles P5 and P7, $Zn_{tot}$ correlated negatively with organic C, $r = -0.92^{**}$ and $r = -0.77^{n.s.}$, respectively.

### 3.3.2 Zinc extracted by AAAc-EDTA

Within a soil profile, the sampled layers differed markedly from one another in terms of Zn extracted by AAAc-EDTA ($Zn_{Ac}$, Table 23). In all profiles except P5 and P6 was the content of $Zn_{Ac}$ higher in the plough layer than in the next few underlying ones. In the Carex peat profile P5, all the horizons were equally poor in $Zn_{Ac}$. In profile P6, consisting of an organogenic surface horizon and a heavy clay subsoil, the maximum $Zn_{Ac}$ was measured in the upper part of the mineral subsoil which is the former soil surface currently covered by organic materials. In the three mineral soil profiles (P1, P2 and P3) dominated by clay or silt there was a tendency that deeper in the soil profile $Zn_{Ac}$ first decreased, increasing again in the deepest horizons. In profile P1, $Zn_{Ac}$ was highest in the deepest layer sampled. On the contrary, in the coarse mineral soil profile (P4) and in the two Carex peat profiles there was no increase of $Zn_{Ac}$ in the deeper layers.

In 14 out of the 15 plough layer and subsoil sample pairs, the subsoil was poorer in $Zn_{Ac}$ than was the respective plough layer (Table 24, details in Appendix 4). According to the t-test for paired measurements, the difference in $Zn_{Ac}$ between the plough layer and subsoil was highly significant ($t = 4.804^{***}$, $n = 15$). The only exception was the sample pair from Forssa which consisted of a mull plough layer and a subsoil of heavy clay which was richer in $Zn_{Ac}$. In the other sample pairs, $Zn_{Ac}$ in the subsoil averaged 39% of that in the plough layer. Only in heavy clay subsoils did $Zn_{Ac}$ exceed 2.0 mg $dm^{-3}$.

Table 24. Soil Zn extracted by AAAc-EDTA ($Zn_{Ac}$) from the plough layer and subsoil samples.

| Soil class[1] | n | $Zn_{Ac}$, mg $dm^{-3}$ | |
|---|---|---|---|
| | | Plough layer | Subsoil |
| Clay soils | 6 | 4.4 | 2.0 |
| Coarse mineral soils | 4 | 2.4 | 0.7 |
| Organogenic soils | 5 | 3.0 (3.0)[2] | 1.2 (0.6)[2] |

[1] Soil class of the plough layer.

[2] Results of the sample pair of Forssa not included.

## 3.4 Extractability of Zn added to soil

The ability of common extractants to dissolve Zn from soil was studied on four surface soils (18, 34, 78, 104). Deionized water or $ZnSO_4$ solution was added to weighed portions of air-dry soil (three replicates, 200 ml each), and the samples were incubated at an approximate field capacity for two weeks after which the samples were air-dried and ground with a porcelain mortar and a pestle. The soil samples of the first incubation (Zn addition

9.06 mg dm$^{-3}$) were extracted (two replicates) with the following solutions:

1. 0.5 M $MgCl_2$
2. 0.5 M ammonium acetate - 0.5 M acetic acid at pH 4.65 (AAAc)
3. 0.5 M ammonium acetate - 0.5 M acetic acid - 0.02 M $Na_2$-EDTA at pH 4.65 (AAAc-EDTA)
4. DTPA - TEA - $CaCl_2$ at pH 7.3 (DTPA)

The unbuffered $MgCl_2$ solution extracted exchangeable Zn ($Zn_{ex}$) at soil pH, AAAc at a constant pH of 4.65. The results of AAAc-EDTA demonstrate the effect of the addition of a chelating agent. The use of DTPA allows comparison to be made with an extractant containing the other widely used chelating agent.

The primary purpose of the second incubation experiment (Zn addition 9.26 mg dm$^{-3}$) was to study the extractability of added Zn in sequential extraction by 0.1 M $K_4P_2O_7$ and 0.05 M oxalate. In both experiments, the results of extractions for which the samples were weighed ($MgCl_2$, DTPA, pyrophosphate and oxalate) were transformed to milligrams per dm$^3$ of soil by multiplying the results by the bulk density determined for the incubated soil samples.

As far as native Zn is concerned, $MgCl_2$ was the weakest extractant in clay (18) which was the least acid (pH 6.2) of the four soils, while in the three more acid soils $MgCl_2$ and AAAc extracted equal quantities of native Zn (Table 25). In the clay soil, the higher efficiency of AAAc was probably due to its pH (4.65) which is 1.5 units below the soil pH. The acidity may have caused dissolution of Zn reserves which would not be exchangeable at native soil pH. From the other three soils AAAc probably extracted only the exchangeable Zn fraction.

Addition of EDTA to the AAAc solution markedly enhanced the extraction of native Zn. In clay (18) and organogenic soils (78, 104) the quantities dissolved were at least tripled, and in the highly acid loam (34) they increased by 50%. DTPA was a weaker extractant than AAAc-EDTA in the three soils except the peat (104) where DTPA and AAAc-EDTA extracted native Zn with an equal efficiency. The sequence of efficiency in mineral soils was thus:

$$MgCl_2 \leq AAAc = DTPA < AAAc\text{-}EDTA$$

In organogenic soils the sequence was as follows:

$$MgCl_2 = AAAc < DTPA \leq AAAc\text{-}EDTA$$

Table 25. Soil Zn (mg dm$^{-3}$) extracted by $MgCl_2$ ($Zn_{ex}$), AAAc ($Zn_{AAAc}$), AAAc-EDTA ($Zn_{Ac}$) and DTPA ($Zn_{DTPA}$) from soil samples incubated with or without added Zn. The percentage of added Zn which was extracted appears in parentheses. Zn+ = Zn added (9.06 mg dm$^{-3}$ of soil), Zn- = native Zn.[1]

| Soil | | $Zn_{ex}$ | $Zn_{AAAc}$ | $Zn_{Ac}$ | $Zn_{DTPA}$ | $HSD_{0.05}$ |
|---|---|---|---|---|---|---|
| 18 | Zn+ | 1.42$^{d}$ | 3.74$^{c}$ | 9.40$^{a}$ | 5.82$^{b}$ | 0.47 |
| | Zn- | 0.29$^{c}$ | 0.68$^{b}$ | 2.07$^{a}$ | 0.91$^{b}$ | 0.35 |
| | Difference | 1.13 (12%) | 3.06 (34%) | 7.33 (81%) | 4.91 (54%) | |
| 34 | Zn+ | 7.26$^{c}$ | 8.37$^{b}$ | 10.65$^{a}$ | 8.04$^{bc}$ | 0.97 |
| | Zn- | 1.90$^{b}$ | 1.99$^{b}$ | 2.95$^{a}$ | 1.93$^{b}$ | 0.29 |
| | Difference | 5.36 (59%) | 6.38 (70%) | 7.70 (85%) | 6.11 (67%) | |
| 78 | Zn+ | 4.04$^{c}$ | 4.65$^{c}$ | 11.75$^{a}$ | 8.29$^{b}$ | 1.06 |
| | Zn- | 0.94$^{c}$ | 1.08$^{c}$ | 3.46$^{a}$ | 1.79$^{b}$ | 0.48 |
| | Difference | 3.10 (34%) | 3.57 (39%) | 8.29 (92%) | 6.50 (72%) | |
| 104 | Zn+ | 4.76$^{b}$ | 4.18$^{b}$ | 10.66$^{a}$ | 10.42$^{a}$ | 0.83 |
| | Zn- | 1.00$^{b}$ | 0.95$^{b}$ | 3.34$^{a}$ | 3.70$^{a}$ | 0.54 |
| | Difference | 3.76 (42%) | 3.24 (36%) | 7.32 (81%) | 6.72 (74%) | |

[1] In each soil, the results of the samples incubated with and without added Zn were tested separately for each extraction.

Table 26. Soil Zn (mg dm$^{-3}$) extracted by pyrophosphate ($Zn_{py}$) and oxalate ($Zn_{ox}$) from samples incubated with or without added Zn. The percentages of added Zn which was extracted appear in parentheses. Zn+ = Zn added (9.26 mg dm$^{-3}$ of soil), Zn- = native Zn.[1]

| Soil | | $Zn_{py}$ | $Zn_{ox}$ | Sum | $HSD_{0.05}$ |
|---|---|---|---|---|---|
| 18 | Zn+ | $9.16^{a}$ | $4.34^{b}$ | | 0.69 |
| | Zn- | $1.39^{b}$ | $2.50^{a}$ | | 0.23 |
| | Difference | 7.77 (84%) | 1.84 (20%) | 9.61 (104%) | |
| 34 | Zn+ | $13.49^{a}$ | $3.34^{b}$ | | 0.21 |
| | Zn- | $4.71^{a}$ | $2.49^{b}$ | | 0.21 |
| | Difference | 8.78 (95%) | 0.85 (9%) | 9.63 (104%) | |
| 78 | Zn+ | $13.86^{a}$ | $1.03^{b}$ | | 0.68 |
| | Zn- | $5.01^{a}$ | $1.49^{b}$ | | 0.27 |
| | Difference | 8.85 (96%) | 0.46 (5%) | 9.31 (101%) | |
| 104 | Zn+ | $13.50^{a}$ | $0.98^{b}$ | | 0.14 |
| | Zn- | $4.14^{a}$ | $0.44^{b}$ | | 0.24 |
| | Difference | 9.36 (101%) | 0.54 (6%) | 9.91 (107%) | |

[1] In each soil, the results of the samples incubated with and without added Zn were tested separately for each extraction.

Adsorption of added Zn into the non-exchangeable form was observed especially in the clay soil (18) where as much as 88% of added Zn was not extracted with $MgCl_2$. This tendency was weaker in the loam (34) in which more than half of added Zn remained exchangeable. In mineral soils added Zn was more efficiently extracted by AAAc than by $MgCl_2$ but in the organogenic soils these two solutions extracted added Zn equally effectively. Despite the low pH of the organogenic soils, a considerable part of added Zn was adsorbed into forms not dissolved by $MgCl_2$ or AAAc. This may be due to the formation of organic complexes, and the extraction of this fraction seemed to require chelating agents (EDTA and DTPA).

AAAc-EDTA dissolved 81 - 92% of added Zn, being thus the strongest extractant for added Zn in the two mineral soils and in the mull. In peat, AAAc-EDTA and DTPA were equal in efficiency. Despite its high pH, DTPA was a strong extractant for native and added Zn in organogenic soils, but in mineral soils DTPA was relatively less effective. As for added Zn, the results of AAAc-EDTA extraction were less affected by soil characteristics than those of the other extractions.

Pyrophosphate extraction removed the bulk of added Zn from soil, the rest being dissolved by oxalate (Table 26). The residue of added Zn in the soil after pyrophosphate extraction seemed to be highest in the clay soil and lowest in the two organogenic soils. The recovery of added Zn was not affected by soil pH. The apparent recovery of added Zn seemed even to exceed 100% in all soils. The recovery was calculated as the difference between the sums of $Zn_{py} + Zn_{ox}$ extracted from soils incubated with and without added Zn. The confidence limits at the 95% level were 0.2 - 0.3 mg dm$^{-3}$ for $Zn_{py}$ and 0.1 - 0.2 mg dm$^{-3}$ for $Zn_{ox}$. The present results were within these limits.

## 3.5 Discussion

### 3.5.1 Total Zn

The $Zn_{tot}$ in the surface soil material was higher than the results of spectrographic determination of $Zn_{tot}$ published earlier in Finland (VUORINEN 1958, ERVIÖ and VIRRI 1965, SIPPOLA 1974). For example, in the study by SIPPOLA (1974) $Zn_{tot}$ ranged from 20 mg kg$^{-1}$ in sands to 78 mg kg$^{-1}$ in heavy clays. It is not likely that $Zn_{tot}$ of the soils in Finland has doubled in a few decades but the difference may be attributed to the different methodologies employed. Later $Zn_{tot}$ determinations carried out in Finland, based on digestion with HF-containing acid mixtures and measurement of Zn by AAS (BAGHDADY and SIPPOLA 1983, KOLJONEN and MALISA 1991), have yielded results of the same magnitude as those of the present study.

Because the methods of determining $Zn_{tot}$ give different results, the following references include only studies in which unpolluted mineral soil samples have been completely decomposed with HF-containing acid mixtures and analyzed for Zn by AAS. The $Zn_{tot}$ in soils of temperate climates, e.g. silt and clay loam soils of Denmark (TJELL and HOVMAND 1978), clay, loam and sandy soils of Germany (BAGHDADY and SIPPOLA 1983, LICHTFUSS and ANDRESEN 1983) and clay loam soils of various parts of Canada (BISHOP and MACEACHERN 1973, NIELSEN et al. 1986, LIANG et al. 1990), are similar to or slightly smaller than those in the respective textural classes of the present material. Clay and clay loam soils of warmer regions, e.g. Virginia and Georgia, USA (IYENGAR et al. 1981, SHUMAN 1985) and the Nile delta, Egypt (BAGHDADY and SIPPOLA 1983), have also had similar or slightly lower $Zn_{tot}$ than occurs in texturally corresponding soils of Finland. However, in unpolluted soils of other countries, $Zn_{tot}$ seldom exceeds 150 mg $kg^{-1}$, a value commonly found in clay soils of Finland. In coarse sandy soils of warmer climates, i.e. Georgia, USA (SHUMAN 1985), and Australia (BRENNAN and GARTRELL 1990), $Zn_{tot}$ is commonly below 10 mg $kg^{-1}$ which is less than in any of the coarse mineral soils of the present study.

A close correlation between clay content and $Zn_{tot}$ is likely to be a consequence of the differences in soil mineralogy in the textural fractions (SIPPOLA 1974). The analyses of clay and silt plus very fine sand of three soils directly showed that the coarser fraction was poorer in $Zn_{tot}$ than was clay. However, silt can occasionally be as rich in $Zn_{tot}$ as is clay (ANDERSSON 1979, ARMOUR et al. 1990). This may be the explanation why the unpolluted soils of Kuhmoinen (soil 21) and Hollola (soil 38) had a higher $Zn_{tot}$ than the other soils of similar clay contents.

The negative correlation between $Zn_{tot}$ and organic C in organogenic soils reflects the origin of $Zn_{tot}$ in mineral material. The studies on the vertical distribution of Zn emphasize that $Zn_{tot}$ in organogenic soils was dependent on $Zn_{tot}$ of the mineral soil below the organogenic layers. Organogenic soils (profile P6 from Jokioinen and the sample pair from Forssa) on a clayey subsoil were rich in $Zn_{tot}$. On the contrary, the Carex peat profile P7 (Muhos), most probably also profile P5 (Sotkamo), had developed on coarse mineral soils poor in $Zn_{tot}$ with the consequence that also the organogenic layers were poor in $Zn_{tot}$.

In mull and peat soils, the mean $Zn_{tot}$ was 48.7 and 35.1 mg $kg^{-1}$, respectively, while a higher mean of 65.5 mg $kg^{-1}$ was measured in 55 cultivated Histosols of Canada (LEVESQUE and MATHUR 1986). Nine out of the 20 peat soils of the present study contained less Zn than was the minimum (28.5 mg $kg^{-1}$) in the peat soils of Canada. This comparison confirms that soils extremely poor in $Zn_{tot}$ prevail among cultivated peat soils of Finland. Moreover, the results of URVAS et al. (1992) suggest that the peat soils of this study did not even contain the poorest ones occurring in Finland. However, $Zn_{tot}$ in cultivated peat soils of Finland commonly exceeds that in virgin peatlands of Germany where a $Zn_{tot}$ of 5 - 50 mg $kg^{-1}$ (mean 20 mg $kg^{-1}$) has been measured (TEICHER et al. 1987).

### 3.5.2 Fractions of soil Zn

The decreasing trend of $Zn_{ex}$ with increasing soil pH agrees with the results of several studies (SIMS and PATRICK 1978, NIELSEN et al. 1986, SIMS 1986, PALKO and YLI-HALLA 1990), reflecting the corresponding increase of specific adsorption of Zn. In mineral soils, $Zn_{ex}$ was of the same level as in other studies on acid mineral soils (IYENGAR et al. 1981, SHUMAN 1985, NIELSEN et al. 1986). Even in very acid clay soils Zn tended to be bound by covalent forces to a larger extent than in the coarsest mineral soils of similar pH. This may reflect the abundance of sites capable of specific adsorption of Zn in clay soils, which were richer in organic matter and Fe oxide, important components adsorbing Zn in acid soil (MCBRIDE and BLASIAK 1979, BRÜMMER et al.

1983, TILLER et al. 1984, PULFORD 1986). In organogenic soils, the high percentage of $Zn_{tot}$ in exchangeable form was probably attributable to the strong acidity in these soils. In a few peat soils, more than 30% of $Zn_{tot}$ was exchangeable, which suggests that the small native reserves of Zn in these soils may even be susceptible to leaching.

A few observations corroborate that sequential pyrophosphate and oxalate extractions dissolved Zn by and large from different soil components. First, $Zn_{py}$ (mg $dm^{-3}$) was approximately equal in all soil classes while $Zn_{ox}$ decreased in the mineral soils with decreasing clay content. Second, unlike $Zn_{py}$, $Zn_{ox}$ correlated significantly with $Zn_{tot}$. The fraction of $Zn_{py}$ has been assumed to consist of Zn bound by organic matter. In the present study $Zn_{py}$ or complexed Zn ($Zn_{py}$ - $Zn_{ex}$) did not correlate with organic C, but the dark color of the pyrophosphate extracts and the appearance of the soil after the extraction suggest effective removal of organic matter, with the consequence that also most Zn bound by organic matter was probably extracted. Pyrophosphate may also dissolve Zn from other sources. Oxides of Fe, Al and Mn are major adsorbents for Zn added to soil (e.g. MULLINS et al. 1982, MCBRIDE 1989). In an incubation experiment of the present study the bulk of Zn added to soil was extracted with pyrophosphate and only a minor part was recovered as $Zn_{ox}$ which was supposed to represent sesquioxide-bound Zn. This observation indirectly suggests that at least some Zn from sesquioxides is extracted with pyrophosphate. The hypothesis is supported by an observation that pyrophosphate dissolves Fe from sesquioxides (BASCOMB 1968).

There was some evidence that in mineral soils the occurrence of $Zn_{ox}$ may indeed be connected to Fe oxides. There was a correlation between $Zn_{ox}$ and $Fe_{ox}$, and the lowest $Zn_{ox}$ exclusively occurred in the mineral soils poorest in $Fe_{ox}$. Several organogenic soils were also rich in $Fe_{ox}$, but contrary to the mineral soils this was not connected to the abundance of $Zn_{ox}$. Moreover, in organogenic soils $Zn_{ox}$ did not correlate with $Zn_{res}$ or organic C which reflect the quantity of mineral material in the soil. Therefore, the source of $Zn_{ox}$ in organogenic soils requires further research.

The mean percentage of $Zn_{ox}$ was low compared to the results of comparable sequential extraction studies from Georgia and Virginia, USA (SHUMAN 1979, IYENGAR et al. 1981), and from the Nile delta, Egypt (ELSOKKARY 1979). In those soils, scarce in organic matter and rich in crystalline Fe oxide, $Zn_{ox}$ was the major fraction of secondary Zn, amounting to 25% of $Zn_{tot}$. Inversely, in the temperate soils of Canada (NIELSEN et al. 1986, LIANG et al. 1990) the $Zn_{ox}$ fraction was of the same magnitude (below 5% of $Zn_{tot}$) as in the present material. Oxalate is not selective for poorly crystalline oxides but over time also crystalline oxides are dissolved (BORGGAARD 1979, 1992). In the present sequential extraction, poorly crystalline oxides and Zn bound by them may have been removed already in the pyrophosphate treatment and only the Zn bound to more crystalline oxides may have remained in the successive oxalate extraction. The scarcity of $Zn_{ox}$ in temperate soils may thus be attributed to the small quantity of crystalline oxides, owing to the young age and high content of organic matter which retards crystallization. The hypothesis presented above may be valid especially in organogenic soils most of which were poor in $Zn_{ox}$.

Pyrophosphate and oxalate extractions completely removed Zn which had recently been added to the soil. The strong extraction power of these solutions was also shown by PAYNE et al. (1988) who observed that Zn added to a Rhodic Paleustult (560 kg Zn $ha^{-1}$ during 17 years) was recovered as $Zn_{py}$ and $Zn_{ox}$, but there was no accumulation in the residual fraction. It seems therefore justified to regard the sum $Zn_{py}$ + $Zn_{ox}$ as the quantity of secondary Zn.

In most studies from other countries, the percentage of $Zn_{res}$ in mineral soils has been lower than that in the present mineral soils where approximately 90% of soil Zn occurred as $Zn_{res}$. For example, in soils of the British Columbia and Saskatchewan, Canada (NIELSEN et al. 1986, LIANG et al. 1990), $Zn_{res}$ amounted to 71% and 83% (ranges 46 - 93% and 69 - 91%, respectively). Results of that level have also been obtained in soils of Delaware and Georgia, USA (IYENGAR et al. 1981, SHUMAN 1985), while in alluvial soils of Egypt, $Zn_{res}$

was only 45% of $Zn_{tot}$ (range 39 - 61%) (ELSOKKARY 1979). The higher percentage of $Zn_{res}$ in the present study reflects the young age of soils of Finland. The result also shows that the cultivated soils of Finland are not polluted with Zn because in polluted soils $Zn_{res}$ represents a smaller fraction of $Zn_{tot}$ (LÅG and ELSOKKARY 1978, RÄSÄNEN and HÄMÄLÄINEN 1991). The high percentage of secondary Zn in the organogenic soils reflects the scarcity of primary minerals in these soils.

Application of manures, sludges and Zn-containing mineral fertilizers as well as atmospheric deposition of Zn can result in excessive accumulation of secondary Zn in surface soil (BERNDT and KERSHAW 1989, DRIEL and SMILDE 1990). Owing to mineral additives of fodder, manures in Finland commonly contain more than 200 mg Zn $kg^{-1}$ in the dry matter (KEMPPAINEN 1989). The present results showed that also in Finland there are soils where abundant use of manure has resulted in elevated reserves of secondary Zn. The high concentration of Zn in soil 71 of Harjavalta was probably due to atmospheric deposition of Zn from the local metal industry which for example in 1988 emitted 100 000 kg of Zn, approximately 17% of all industrial Zn emissions of the country (AUNELA and LARJAVA 1990). Even though this single soil sample is not necessarily representative, this observation warrants concern for excessive Zn content of soil in the vicinity of metal industry. However, the Zn concentration of this sample was much lower than the extreme values exceeding 1000 mg $kg^{-1}$ in the secondary fractions in soils heavily polluted by Zn (ELSOKKARY and LÅG 1978, FOLKESON and ANDERSSON-BRINGMARK 1988, DELAUNE et al. 1989, JORDAO and NICKLESS 1989). Also in Finland, highly elevated concentrations of Zn have earlier been reported in lake shore sediments and surface soils of industrial areas (RÄSÄNEN and HÄMÄLÄINEN 1991).

### 3.5.3 AAAc-EDTA extractions

In unpublished material of Soil Analysis Service Ltd., the means of $Zn_{Ac}$ were 5.0, 6.1 and 4.9 mg $dm^{-3}$ in the 1262, 10240 and 11701 analyses carried out in 1986, 1987 and 1988, respectively (results available at Soil Analysis Service Ltd., P.O. Box 500, FIN-50101 MIKKELI). Also the means and distributions of $Zn_{Ac}$ in 2015 cultivated grassland soils of Finland (SIPPOLA and TARES 1978) were of the same magnitude as those of the present material. On the contrary, SILLANPÄÄ (1982) and URVAS et al. (1992) presented results on 90 mineral soils and 112 organogenic soils in which $Zn_{Ac}$ was considerably smaller (mean 2.7 and 2.1 mg $dm^{-3}$, respectively). Because the present results correspond to those of the large materials of Soil Analysis Service Ltd. and SIPPOLA and TARES (1978), it is justified to conclude that the observations made on the material can be extended to the cultivated soils of Finland in general.

The extractant AAAc-EDTA consists of three components: (1) acetic acid, (2) ammonium acetate and (3) $Na_2$-EDTA. The chemical nature of $Zn_{Ac}$ can be assessed by studying the fractions which might be extracted by each component alone. It is likely that the aqueous solution extracts water-soluble Zn, and $Zn^{2+}$ bound by electrostatic forces is exchanged by $NH_4^+$ cations of the solution. AAAc-EDTA extracted more Zn than did $MgCl_2$, the difference being especially pronounced at the high pH range of the experimental soils. In several studies, 2.5% $CH_3COOH$ has been used in the extraction of Zn specifically adsorbed on the surfaces of sesquioxides (ELSOKKARY and LÅG 1978, IYENGAR et al. 1981, PAYNE et al. 1988). In AAAc-EDTA, the concentration of acetic acid is 3% and therefore it is likely that specifically adsorbed Zn is extracted also by AAAc-EDTA. This assumption is supported by the observation that increasing clay content enhanced the extraction power of AAAc-EDTA in relation to $MgCl_2$ in mineral soils. In clay soils the number of sites available for specific adsorption of Zn is probably higher than in coarse mineral soils, owing to the higher contents of $Fe_{ox}$ and $Al_{ox}$.

EDTA has been added to the AAAc solution in order to enhance the extraction of metallic trace elements (LAKANEN and ERVIÖ 1971). However, the Zn-EDTA complex is most stable at pH 6.5 (LINDSAY 1972), and pH 4.65 should theoretically be far from ideal in order to facilitate effective extraction of Zn by EDTA. Yet, the extraction experiment (Section 3.4) showed that EDTA increased the extractability of both native and added Zn especially from organogenic soils as compared to the extraction by AAAc alone. Moreover, the extraction power of AAAc-EDTA was at least equal to that of DTPA where the pH 7.3 corresponds to the pH of maximum stability of the Zn-DTPA complex (LINDSAY 1972). EDTA is an effective extractant for organically bound Cu (RASHID 1974, STEVENSON 1982, p. 40). It has also been observed that the addition of EDTA in the Mehlich 2 extractant ($CH_3COOH$ - $NH_4Cl$ - $NH_4F$ - HCl) enhanced the extractability of soil Zn especially when the content of organic matter increased (MEHLICH 1984). It may thus be assumed that also AAAc-EDTA extracts Zn bound by organic matter even at pH 4.65. However, organic matter is more effectively extracted by pyrophosphate than by EDTA (McLAREN and CRAWFORD 1973). This observation seems to apply also to organically bound Zn because in mineral soils the extraction power of AAAc-EDTA decreased in relation to pyrophosphate with increasing content of organic C. The close correlation between $Zn_{Ac}$ and $Zn_{py}$ suggested that AAAc-EDTA extracted Zn mainly from the same sources as did pyrophosphate. It may thus be concluded that, in addition to water-soluble and exchangeable Zn, the AAAc-EDTA extracts Zn specifically adsorbed by sesquioxides and organic matter.

GOLDSCHMIDT (1937) observed in Germany and HIBBARD (1940) in California, USA higher concentrations of Zn extracted from surface soils as compared to the subsoil. They both suggested independently that this may be due to bioaccumulation as a result of uplift of Zn from deeper layers by plant roots. When plant residues are decayed, Zn from plant tissue is mineralized and retained in the surface soil. The hypothesis of bioaccumulation is also corroborated by the observations on the present mineral soil profiles and earlier in a more extensive material of peat soils of Finland (URVAS 1986). In the present fine-textured mineral soil profiles, the minimum $Zn_{Ac}$ occurred in the upper part of subsoil, and a higher concentration of $Zn_{Ac}$ was measured deeper in the profile. Zinc uptake by plant roots may have depleted the reserves of $Zn_{Ac}$ in the upper part of subsoil but not in the deeper layers because roots of herbaceous plants do not penetrate to a considerable extent deeper than 1 m (DWYER et al. 1988). This observation also suggests that bioaccumulation of Zn is an important factor contributing to $Zn_{Ac}$ in the plough layer. Absence of correlation between $Zn_{res}$ and $Zn_{Ac}$ also suggests that a considerable part of secondary Zn in the surface soil may not have been released from the primary minerals residing in the plough layer but may have been brought there from external sources, e.g. by bioaccumulation and atmospheric deposition.

# 4 AVAILABILITY OF SOIL AND FERTILIZER ZINC TO RYEGRASS IN POT EXPERIMENTS

## 4.1 Availability of soil Zn

### 4.1.1 Experimental

In order to examine the potential of soil to supply plants with Zn, a pot experiment was arranged with 107 plough layer samples (Appendix 2). Four crops of Italian ryegrass (*Lolium multiflorum*, Lam.) were grown in plastic boxes containing 0.2 $dm^3$ of ground (< 2 mm) soil (two replicates). Nutrients, except Zn, were applied to each crop at the following rates (mg $dm^{-3}$ of soil) as analytical grade chemicals:

| Element | Rate, mg $dm^{-3}$ | Compound |
|---|---|---|
| N | 300 | $NH_4NO_3$ |
| P | 80 | $KH_2PO_4$ |
| K | 200 | KCl, $KH_2PO_4$ |
| Mg | 50 | $MgSO_4 \cdot 7H_2O$ |
| S | 67 | $MgSO_4 \cdot 7H_2O$ |

Micronutrient fertilization, including 5 mg S dm$^{-3}$, was applied at the beginning of the experiment and after the second harvest at the following rates:

| Element | Rate, mg dm$^{-3}$ | Compound |
|---|---|---|
| Cu | 3 | $CuSO_4 \cdot 5H_2O$ |
| Mn | 4 | $MnSO_4 \cdot 4H_2O$ |
| Fe | 2 | $FeSO_4 \cdot 7H_2O$ |
| B | 0.5 | $H_3BO_3$ |
| Mo | 1 | $Na_2MoO_4 \cdot 2H_2O$ |

At the beginning of the experiment, the fertilizer solutions were mixed in the soil. For the subsequent crops they were pipetted onto the surface of the soil. To prevent a decrease of pH in the course of the trial due to N fertilization and root exudates, 250 mg of $Ca(OH)_2$ (6.8 meq dm$^{-3}$) was mixed into each pot. The seeds (250 mg per pot) were covered with 150 ml of quartz sand washed with 3 M HCl. The pots were watered with deionized water once or twice a day. The first crop was cut 29 days after sowing, and the average growing period of the successive crops was 24 days. The yields were dried at 60°C, weighed and analyzed for Zn. At the end of the experiment, the pH of the soil in the pot was determined. In spite of the lime application, soil pH decreased during the experiment (Table 27).

Table 27. Change in pH during the pot experiment in the five soil classes.

| Soil class | Change in pH | | |
|---|---|---|---|
| | Mean | s | Range |
| Clay | -0.24$^{b}$ | 0.21 | -0.57 – 0.06 |
| Silt, loam, very fine sand | -0.31$^{b}$ | 0.22 | -0.61 – 0.10 |
| Fine sand, moraine | -0.35$^{b}$ | 0.15 | -0.66 – -0.05 |
| Mull | -0.19$^{ab}$ | 0.19 | -0.40 – 0.13 |
| Peat | -0.10$^{a}$ | 0.15 | -0.36 – 0.18 |

### 4.1.2 Dry matter yields

The mean deviation of the total dry matter yield between the two replicates was 0.30 g per pot, or 3.1% of the average yield. The average total dry matter production (sum of four crops) in clay, silt loam and very fine sand soils was slightly higher than that of the organogenic soils (Table 28). Dry matter yields did not correlate with any of the indices of secondary Zn of soil. Dry matter production in mineral soils was positively correlated with $Zn_{tot}$ ($r = 0.48^{***}$) and soil pH ($r = 0.34^{***}$). The correlation between $Zn_{tot}$ and the yield reflects the trend that fine sand and moraine soils, poorer in $Zn_{tot}$ than the clay soils, tended to produce smaller yields than did the more fine-textured soils. In organogenic soils, dry matter yield did not correlate significantly with the soil properties measured.

### 4.1.3 Zinc concentration and uptake

The mean Zn concentration of the grass within each yield (Table 29) did not differ markedly from one soil class to another (HSD values not presented).

Table 28. Dry matter yields of ryegrass.[1]

| | | Successive crop, g per pot | | | | Sum of yields, g per pot | |
|---|---|---|---|---|---|---|---|
| Soil class | n | I | II | III | IV | Mean | Range |
| Clay | 25 | 2.27 | 3.36 | 2.52 | 2.13 | 10.28$^{ab}$ | 9.13-11.52 |
| Silt, loam, very fine sand | 20 | 2.41 | 3.39 | 2.48 | 2.15 | 10.43$^{a}$ | 9.45-11.48 |
| Fine sand, moraine | 28 | 2.26 | 2.97 | 2.38 | 2.10 | 9.71$^{bc}$ | 7.96-11.43 |
| Mull | 14 | 2.15 | 2.90 | 2.34 | 2.00 | 9.39$^{c}$ | 7.69-10.39 |
| Peat | 20 | 2.11 | 2.78 | 2.34 | 1.97 | 9.20$^{c}$ | 7.78-11.31 |

[1] Means in each column were tested separately.

Table 29. Zinc concentration (mg kg$^{-1}$) of ryegrass in the pot experiment. The results of the fine sand and moraine soils excluding those of soil 71 are presented in parentheses.[1]

| Soil class | Crop | Mean | s | Range |
|---|---|---|---|---|
| Clay | I | $32.4^{a}$ | 10.6 | 13.5-49.5 |
| n = 25 | II | $23.4^{b}$ | 6.9 | 12.0-34.5 |
| | III | $36.2^{a}$ | 11.2 | 19.0-64.5 |
| | IV | $36.8^{a}$ | 11.5 | 16.5-61.0 |
| | $HSD_{0.05}$ | 4.0 | | |
| Fine silt, loam, very fine sand | I | $27.5^{b}$ | 10.4 | 11.5-50.5 |
| n = 20 | II | $20.6^{c}$ | 6.8 | 11.0-38.0 |
| | III | $31.8^{a}$ | 7.6 | 18.5-42.0 |
| | IV | $29.4^{ab}$ | 7.8 | 16.0-44.0 |
| | $HSD_{0.05}$ | 3.9 | | |
| Fine sand, moraine | I | $30.1^{b}$ ($28.5^{b}$) | 13.7 (10.7) | 14.0-75.5 (54.5) |
| n = 28 | II | $27.0^{b}$ ($24.9^{b}$) | 18.7 (10.2) | 11.0-109 (52.0) |
| | III | $38.6^{a}$ ($34.1^{a}$) | 26.1 (13.3) | 17.5-154 (67.0) |
| | IV | $42.0^{a}$ ($36.3^{a}$) | 34.2 (15.7) | 16.0-198 (76.0) |
| | $HSD_{0.05}$ | 7.8 (5.3) | | |
| Mull | I | $35.0^{a}$ | 5.9 | 21.5-42.0 |
| n = 14 | II | $25.1^{b}$ | 6.0 | 13.0-35.5 |
| | III | $31.4^{a}$ | 8.7 | 15.5-47.0 |
| | IV | $30.6^{a}$ | 9.1 | 15.5-46.0 |
| | $HSD_{0.05}$ | 4.8 | | |
| Peat | I | $34.3^{a}$ | 10.2 | 17.0-56.5 |
| n = 20 | II | $28.2^{b}$ | 8.7 | 13.0-49.0 |
| | III | $30.8^{ab}$ | 10.8 | 11.5-57.5 |
| | IV | $30.0^{b}$ | 10.0 | 12.0-53.3 |
| | $HSD_{0.05}$ | 3.6 | | |

[1] Results of each soil class have been tested separately.

Table 30. Mean Zn uptake of grass by the four yields.[1]

| Soil class | Zn uptake (µg dm$^{-3}$) by successive crops | | | | $HSD_{0.05}$ µg dm$^{-3}$ |
|---|---|---|---|---|---|
| | I | II | III | IV | |
| Clay | $400^{a}$ | $380^{a}$ | $400^{a}$ | $410^{a}$ | 74 |
| Silt, loam very fine sand | $330^{b}$ | $350^{ab}$ | $400^{a}$ | $320^{b}$ | 51 |
| Fine sand, moraine | $330^{b}$ | $400^{ab}$ | $440^{a}$ | $450^{a}$ | 81 |
| -soil 71 excluded | $310^{b}$ | $370^{ab}$ | $400^{a}$ | $380^{a}$ | 61 |
| Mull | $380^{a}$ | $370^{a}$ | $370^{a}$ | $310^{b}$ | 50 |
| Peat | $360^{a}$ | $390^{a}$ | $360^{a}$ | $290^{b}$ | 49 |

[1] Results of each soil class have been tested separately.

Each soil class, particularly fine sand and moraine, contained a few soils (especially soil 71) which produced grass very rich in Zn as compared to the bulk of the material. There was a tendency of Zn concentration to be the lowest in the second crop in which the largest quantity of dry matter was produced. In peat soils, the mean Zn content in the fourth crop was lower than that in the first one, while in the mineral soils Zn concentration in the last two crops was at least as high as in the first one.

Uptake of Zn (Table 30) was calculated by multiplying the dry matter yield with Zn concentration of the respective grass sample. Because the roots were not weighed and analyzed, Zn uptake represents the quantity of Zn transported to the aboveground parts of ryegrass. In clay soils, Zn uptake remained constant from crop to crop, whereas in silt, loam and very fine sand soils, the maximum Zn uptake occurred in the third crop. Instead, in the fine sand and moraine soils, Zn uptake increased towards the end of the experiment, despite decreasing dry matter production. Because both Zn concentration and uptake increased, the Zn supply to plants can be assumed to increase over time in these soils. In organogenic soils, Zn uptake by the fourth crop was smaller than that by the three earlier ones. In peat soils, both concentration and uptake were smaller in the fourth crop, which may reflect a decreased Zn supply to the plants. Within a crop, the only statistically significant difference in Zn uptake between the five soil classes occurred in the fourth crop in which Zn uptake from clay soils was greater than that from the peat soils (HSD values not presented).

The cumulative Zn uptake in the four yields ranged from 620 to 6190 µg dm$^{-3}$ of soil, mean 1470 µg dm$^{-3}$. The mean deviation in Zn uptake between the replicates was 52 µg dm$^{-3}$, corresponding to 3.7% of the mean. The differences in Zn uptake were much greater within each soil class than between the classes which did not differ significantly from one another. Correlation between plant Zn concentration and Zn uptake was very close in each of the four crops ($r = 0.87^{***} - 0.96^{***}$) but negligible between the cumulative dry matter yield and Zn uptake ($r = 0.08^{n.s.}$ and $r = 0.26^{n.s.}$ in mineral and organogenic soils, respectively). Thus, the quantity of Zn taken up was by and large determined by the Zn concentration of the plant material.

Table 31. Linear correlation coefficients between soil characteristics and Zn uptake by the four ryegrass crops. Natural logarithms of soil Zn concentrations (mg dm$^{-3}$) were used in the calculations.

|  | Mineral soils n = 72 | Organogenic soils n = 34 |
|---|---|---|
| $Zn_{Ac}$ | $0.89^{***}$ | $0.80^{***}$ |
| $Zn_{py}$ | $0.82^{***}$ | $0.83^{***}$ |
| $Zn_{ox}$ | $0.51^{***}$ | $0.60^{***}$ |
| $Zn_{ex}$ | $0.77^{***}$ | $0.68^{***}$ |
| $Zn_{py}$-$Zn_{ex}$ | $0.64^{***}$ | $0.80^{***}$ |
| $Zn_{tot}$ | $0.18^{n.s.}$ | $0.37^{n.s.}$ |
| pH | $-0.27^{*}$ | $0.15^{n.s.}$ |
| Organic C | $-0.03^{n.s.}$ | $-0.11^{n.s.}$ |

### 4.1.4 Dependence of Zn uptake on soil properties

The correlation coefficients between a few soil characteristics and the cumulative Zn uptake in the four crops are presented in Table 31. In the calculations, natural logarithms ($\log_e$) of soil Zn concentrations (mg dm$^{-3}$) were used. The results of soil 71 were not included in the calculations. In organogenic soils, Zn uptake correlated most closely with $Zn_{py}$, $Zn_{Ac}$, $Zn_{ex}$ and $Zn_{py}$ - $Zn_{ex}$. In mineral soils, Zn uptake correlated more closely with $Zn_{Ac}$ than with $Zn_{ex}$ and $Zn_{py}$ - $Zn_{ex}$, and more closely with $Zn_{py}$ than with $Zn_{py}$-$Zn_{ex}$. The partial correlation coefficients between Zn uptake and $Zn_{py}$ - $Zn_{ex}$, when eliminating the effect of $Zn_{ex}$, were highly significant ($r = 0.56^{***}$ and $0.65^{***}$ in mineral and organogenic soils, respectively), suggesting that also complexed Zn contributed to plant-available Zn. The correlation coefficient with $Zn_{ox}$ was also significant, but the partial correlation coefficient between $Zn_{ox}$ and Zn uptake, when the effect of $Zn_{py}$ was eliminated, was not statistically significant. The relationship between $Zn_{Ac}$ and Zn uptake in mineral and organogenic soils is presented in Figures 3 and 4, respectively.

In the multiple regression analysis, $Zn_{Ac}$ (mg dm$^{-3}$), soil pH and organic C (%) explained 82% of the variation of the cumulative Zn uptake (µg dm$^{-3}$ of soil) in mineral soils. In an equation consisting of $Zn_{py}$ (mg dm$^{-3}$), $Zn_{ox}$ (mg dm$^{-3}$) and pH, the coefficient of multiple determination was slightly lower. At a given level of $Zn_{py}$, $Zn_{ox}$ and $Zn_{Ac}$, Zn uptake decreased with increasing soil pH. According to the beta coefficients (Table 32), $Zn_{Ac}$ and $Zn_{py}$ were by far the most important soil characteristics determining the magnitude of Zn uptake by the grass. The two equations for mineral soils (n = 72) were as follows:

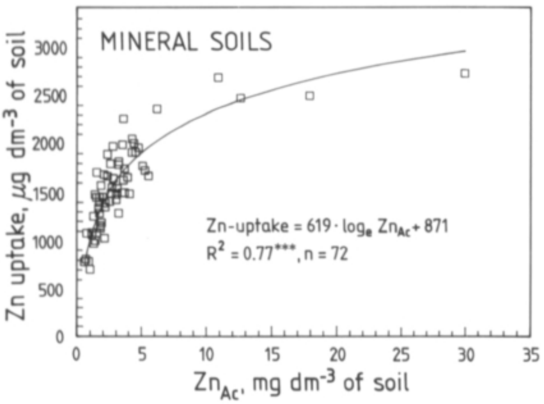

Fig. 3. Dependence of Zn uptake of four ryegrass crops on the concentration of soil Zn extracted by AAAc-EDTA ($Zn_{Ac}$) in mineral soils.

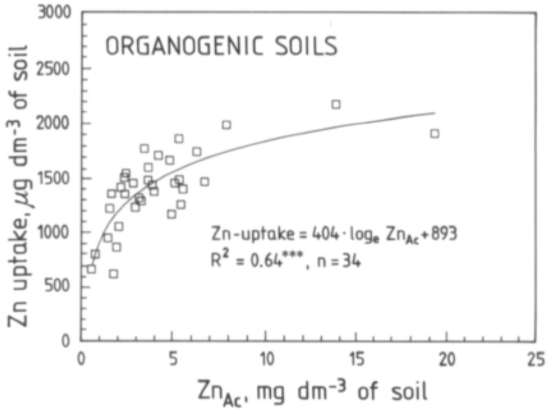

Fig. 4. Dependence of Zn uptake of four ryegrass crops on the concentration of soil Zn extracted by AAAc-EDTA ($Zn_{Ac}$) in mineral soil.

$$\text{Zn uptake} = 593 \log_e Zn_{Ac} - 188\,pH - 40.8\,C + 2150 \qquad R^2 = 0.82^{***}$$

$$\text{Zn uptake} = 439 \log_e Zn_{py} + 222 \log_e Zn_{ox} - 202\,pH + 1940 \qquad R^2 = 0.73^{***}$$

The dependence of Zn uptake of each crop on the characteristics of mineral soils was also studied. Within each crop, $Zn_{Ac}$ and $Zn_{py}$ ($\log_e$ of the results expressed as mg dm$^{-3}$) were the most important soil characteristics explaining the variation of plant Zn uptake (µg dm$^{-3}$ of soil) (Table 33). Soil pH was significant in the first two crops but lost significance towards the end of the experiment. Also the pH measured at the end of the experiment was used as an independent variable, but it did not prove statistically significant even in the last two crops. On the contrary, $Zn_{ox}$ was significant in the last crop. Increasing clay content (%) promoted Zn uptake, but increasing organic C (%) had a negative impact. When $Zn_{py}$ was divided into two components ($Zn_{ex}$ and $Zn_{py}$ - $Zn_{ex}$) they were both significant (beta coefficients not shown), and the equations had nearly the same coefficients of multiple determination as those containing $Zn_{py}$.

Table 32. t-Values of the regression coefficients and beta coefficients (β) of the independent variables of the regression equations explaining Zn uptake by ryegrass in mineral soils.

| Independent variable | t | β |
|---|---|---|
| $\log_e Zn_{Ac}$ | 16.270*** | 0.85 |
| pH[1] | -4.041*** | -0.24 |
| Organic C | -2.344* | -0.14 |
| $\log_e Zn_{py}$ | 6.837*** | 0.61 |
| $\log_e Zn_{ox}$ | 3.203** | 0.30 |
| pH[2] | -3.200** | -0.26 |

[1] in the equation with $\log_e Zn_{Ac}$ and organic C
[2] in the equation with $\log_e Zn_{py}$ and $Zn_{ox}$

In multiple regression analyses of the results of organogenic soils, the cumulative Zn uptake (µg dm$^{-3}$ of soil) was explained only by $Zn_{Ac}$ (mg dm$^{-3}$) or $Zn_{py}$ (mg dm$^{-3}$), without a statistically significant contribution of soil pH or $Zn_{ox}$. The two alternative regression equations were as follows (n = 34):

$$\text{Zn uptake} = 404 \log_e Zn_{Ac} + 894 \qquad R^2 = 0.64^{***}$$

$$\text{Zn uptake} = 389 \log_e Zn_{py} + 863 \qquad R^2 = 0.69^{***}$$

### 4.1.5 Utilization of soil Zn reserves

The relative utilization of $Zn_{tot}$, expressed as the percentage of $Zn_{tot}$ taken up by the four crops of ryegrass, averaged 5.1% of $Zn_{tot}$ (median 2.2%,

Table 33. Beta coefficients of independent variables explaining Zn uptake of the four ryegrass crops (I-IV) in mineral soils ($n = 72$), as well as the coefficients of multiple determination ($R^2$) of the respective regression equations. Natural logarithms of soil Zn concentrations (mg dm$^{-3}$) were used in the calculations.

| Crop | $Zn_{Ac}$ | $Zn_{py}$ | $Zn_{ox}$ | pH | Org. C, % | Clay, % | $R^2$ |
|---|---|---|---|---|---|---|---|
| I | 0.68 | - | - | -0.46 | n.s. | n.s. | $0.75^{***}$ |
| I | - | 0.64 | n.s. | -0.42 | n.s. | n.s. | $0.71^{***}$ |
| II | 0.76 | - | - | -0.37 | -0.16 | n.s. | $0.76^{***}$ |
| II | - | 0.68 | n.s. | -0.36 | -0.24 | 0.17 | $0.65^{***}$ |
| II | - | 0.66 | 0.24 | -0.36 | - | - | $0.62^{***}$ |
| III | 0.82 | - | - | n.s. | -0.22 | 0.14 | $0.77^{***}$ |
| III | - | 0.79 | n.s. | n.s. | -0.29 | 0.26 | $0.71^{***}$ |
| III | - | 0.66 | 0.21 | n.s. | - | - | $0.64^{***}$ |
| IV | 0.77 | - | - | n.s. | -0.24 | n.s. | $0.65^{***}$ |
| IV | - | 0.61 | 0.24 | n.s. | -0.21 | n.s. | $0.64^{***}$ |

- = Not included in the calculations.

Table 34. Relative utilization of $Zn_{tot}$ and secondary Zn ($Zn_{py} + Zn_{ox}$) by ryegrass in the pot experiment.[1]

| Soil class | n | Utilization of $Zn_{tot}$, % | | Utilization of $Zn_{py} + Zn_{ox}$, % | |
|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range |
| Clay | 25 | $1.3^{b}$ | 0.6-2.5 | 23.1 | 6.6-36.2 |
| Silt, loam, very fine sand | 20 | $1.6^{b}$ | 0.7-3.7 | 25.5 | 14.6-39.4 |
| Fine sand, moraine | 27 | $3.3^{b}$ | 0.8-8.6 | 24.5 | 6.4-48.6 |
| Mull | 14 | $5.1^{b}$ | 2.3-10.0 | 28.4 | 12.1-49.6 |
| Peat | 20 | $15.1^{a}$ | 3.7-40.3 | 33.1 | 6.8-68.8 |

[1] Means in each column were tested separately.

range 0.6 - 40.3%). It was greater in the peat soils as compared to the other soils (Table 34). In organogenic soils there was a correlation ($r = 0.80^{***}$) between organic C and utilization of $Zn_{tot}$, which is explained by the inverse relationship between organic C and $Zn_{tot}$. In five out of 20 peat soils Zn uptake exceeded 20% of $Zn_{tot}$. In mineral soils, decreasing pH promoted the utilization of $Zn_{tot}$ ($r = 0.42^{***}$), and clay content correlated negatively with the relative utilization of $Zn_{tot}$ ($r = -0.51^{***}$). This is because clay content correlated with $Zn_{tot}$, but Zn in the fine-textured mineral soils was to a higher extent in the residual fraction unavailable to plants.

In the short term, secondary Zn fractions serve as the reserve of plant-available Zn in soil. Therefore, rather than utilization of $Zn_{tot}$, it is more appropriate to investigate the use of secondary Zn reserves. Relative utilization of secondary Zn in soil is affected by the size of the reserves as well as by their availability. For example, a given Zn uptake by the crop corresponds to a stronger relative utilization of Zn in a soil which has small reserves as compared to another soil which contains more Zn in a plant-available form. Strong relative utilization of soil Zn may reflect the tendency of those reserves to be exhausted by plant uptake. Zinc uptake by ryegrass corresponded on average to 109% of $Zn_{ex}$ and ranged 15 - 535%. This result suggests that in addition to the water-soluble and exchangeable fraction, also less soluble Zn must have been taken up in several soils. Therefore the emphasis of studies on the relative utilization of soil Zn was in the $Zn_{py}$ and $Zn_{ox}$ fractions.

The relative utilization of secondary Zn was calculated as the ratio of Zn uptake (mg dm$^{-3}$) to the sum $Zn_{py} + Zn_{ox}$ (mg dm$^{-3}$), i.e. $100 \cdot$ Zn uptake/($Zn_{py} + Zn_{ox}$). Because the uptake of Zn in a pot experiment was used in the calculation of this index, the validity of the numerical values obtained is limited to this particular experiment. Zinc uptake amounted to 27.3% of $Zn_{py} + Zn_{ox}$, the range from 1.8% in soil 71 to 68.8% in peat soil 97 (Table 34). The secondary Zn fractions were utilized on average slightly more effectively in peat soils than in mineral soils, but the differences were not statistically significant. In 11 soils (two coarse mineral soils, two mull soils, seven peat soils) poor in Zn the relative utilization of secondary Zn reserves exceeded 40%.

Because correlation and regression analyses did not describe accurately the relationships between different soil characteristics and the relative utilization of secondary Zn, the quartiles of this index were investigated. The quartiles were designated I - IV according to increasing relative utilization of secondary Zn (Table 35). Coarse mineral soils were evenly distributed but in several clay soils Zn reserves tended to be poorly utilized, while in several organogenic soils strong relative utilization was observed.

The quartiles of relative utilization of secondary Zn were compared to those of Zn uptake. There were soils of all possible combinations of these two dimensions (Table 36). Large reserves of soil Zn were in most soils connected to a weak relative utilization, but small reserves were not necessarily effectively utilized by the grass. The four extreme groups of soils, shaded in the corners of Table 36, were studied in more detail. These soils were supposed to possess outstanding characteristics connected to given patterns of utilization of soil Zn. The rest of the soils were supposed to have the same characteristics less illustratively. The four extreme groups of soils were as follows:

Table 35. Distribution of soils of different classes into quartiles ($F_{25\%}$) of relative utilization of secondary Zn reserves ($Zn_{py} + Zn_{ox}$). The quartiles are designated I-IV according to increasing relative utilization of secondary Zn of soil.

| Quartile | Relative utilization of $Zn_{py} + Zn_{ox}$, % | Soil class | | |
|---|---|---|---|---|
| | | Clay soils | Coarse mineral soils | Organogenic soils |
| I | 1.8-19.5 | 6 | 13 | 8 |
| II | 19.6-25.5 | 11 | 9 | 7 |
| III | 25.7-30.9 | 5 | 16 | 6 |
| IV | 31.2-68.8 | 3 | 10 | 13 |

Table 36. Distribution of soils into quartiles ($F_{25\%}$) of Zn uptake by ryegrass and into quartiles of relative utilization of secondary Zn ($Zn_{py} + Zn_{ox}$) of soil.

| Quartile of relative utilization of secondary Zn[1] | Quartile of Zn uptake[2] | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| I | 12 | 7 | 3 | 5 |
| II | 7 | 7 | 9 | 3 |
| III | 6 | 7 | 4 | 11 |
| IV | 2 | 6 | 10 | 8 |

[1] The quartiles are designated I-IV according to increasing relative utilization of secondary Zn of soil.

[2] The quartiles are designated I-IV according to the decreasing Zn uptake

*Group 1*: combination of high Zn uptake (1720 - 6190 µg dm$^{-3}$) (quartile I) and weak relative utilization of secondary Zn (quartile I). The group consisted of 12 soils of large Zn reserves. All the seven soils containing more than 10 mg $Zn_{Ac}$ dm$^{-3}$ occurred in this group. Soil pH (5.3 - 7.2) was of minor importance in these soils with excessive reserves of plant-available Zn.

*Group 2*: high Zn uptake (quartile I) and strong relative utilization (39%) of secondary Zn (quartile IV). The group contained only one very fine sand (40) and one peat soil (99). These soils were acid (pH 4.2 and 5.5) and the $Zn_{Ac}$ (2.9 and 3.5 mg dm$^{-3}$) was around the median of the material. These soils are examples of rapid reduction of Zn reserves which were at least average in size. Owing to a small number of soils, this group was improperly portrayed.

*Group 3*: strong relative utilization of soil Zn (quartile IV) and low Zn uptake by plants (quartile IV). This group consisted of one gyttja clay (soil 12), three fine sands (50, 51 and 66) and four or-

Table 37. Soils showing a small Zn supply to ryegrass and strong relative utilization of secondary Zn reserves (group 3).

| Soil | Org. C % | pH | $Zn_{Ac}$ mg dm$^{-3}$ | $Zn_{py}+Zn_{ox}$ mg dm$^{-3}$ | Zn uptake µg dm$^{-3}$ | Utilization of $Zn_{py}+Zn_{ox}$, % |
|---|---|---|---|---|---|---|
| 12 | 9.5 | 5.4 | 1.5 | 2.9 | 950 | 33 |
| 50 | 1.3 | 6.3 | 2.1 | 3.8 | 1170 | 31 |
| 51 | 2.4 | 6.4 | 1.7 | 3.4 | 1060 | 31 |
| 66 | 6.1 | 5.4 | 1.3 | 2.2 | 1070 | 49 |
| 83 | 21.5 | 5.6 | 0.8 | 1.6 | 790 | 50 |
| 97 | 38.8 | 5.5 | 1.8 | 0.9 | 620 | 69 |
| 98 | 39.8 | 4.9 | 1.5 | 2.1 | 940 | 45 |
| 103 | 47.3 | 4.8 | 0.6 | 1.0 | 660 | 65 |

Table 38. Soils showing a small Zn supply to ryegrass and low relative utilization of secondary Zn reserves in soil (group 4).

| Soil | Org. C % | pH | $Zn_{Ac}$ mg dm$^{-3}$ | $Zn_{py}+Zn_{ox}$ mg dm$^{-3}$ | Zn uptake µg dm$^{-3}$ | Utilization of $Zn_{py}+Zn_{ox}$, % |
|---|---|---|---|---|---|---|
| 21 | 3.2 | 6.4 | 2.3 | 7.6 | 1020 | 13 |
| 28 | 0.8 | 6.6 | 0.8 | 4.5 | 760 | 17 |
| 38 | 4.8 | 6.4 | 1.4 | 6.6 | 1070 | 16 |
| 69 | 1.5 | 7.4 | 2.7 | 7.2 | 690 | 10 |

ganogenic soils (83, 97, 98, 103) (Table 37). These soils, except soil 50, belonged to the smallest quartile of $Zn_{Ac}$. The four organogenic soils were even within the $F_{10\%}$ of strongest relative utilization of secondary Zn as well as in the smallest $F_{10\%}$ of Zn uptake. Zinc uptake in these soils was thus limited by the small reserves.

*Group 4*: low Zn uptake (quartile IV) connected with weak relative utilization of soil Zn (quartile I). In the four mineral soils of this group (Table 38) soil pH was distinctly higher, and $Zn_{tot}$, $Zn_{py}$ + $Zn_{ox}$, and $Zn_{Ac}$ were higher than in group 3, but $Zn_{Ac}$ was below the median of the material (2.9 mg dm$^{-3}$). Zinc uptake by the grass was thus limited by relatively small reserves of Zn which, owing to a rather high pH, were poorly available.

In groups 3 (low uptake, strong relative utilization of secondary Zn ) and 1 (high uptake, weak relative utilization) the soils had the most distinctive characteristics. Also some characteristics of the combination of weak relative utilization and low Zn uptake (group 4) could be defined. Groups 3 and 4 exhibited two different combinations of characteristics resulting in a limited Zn supply to plants. Group 3 contained soils with small Zn reserves which, owing to the strong acidity, had a high availability to plants, resulting in a strong relative utilization. In turn, the soils of group 4 had larger Zn reserves which, owing to a higher pH, showed a poorer availability resulting in a weak relative utilization of these reserves. These conclusions are supported by the different patterns of Zn concentrations of grass grown in the organogenic soils of group 3 and in the mineral soils of group 4 (Figure 5). In the organogenic soils of group 3, the Zn concentration of grass decreased from crop to crop, suggesting declining reserves of plant-available Zn in soil. In group 4, the Zn concentration of plants increased during the experiment, suggesting increased availability, probably owing to acidification of the soil in the course of the experiment.

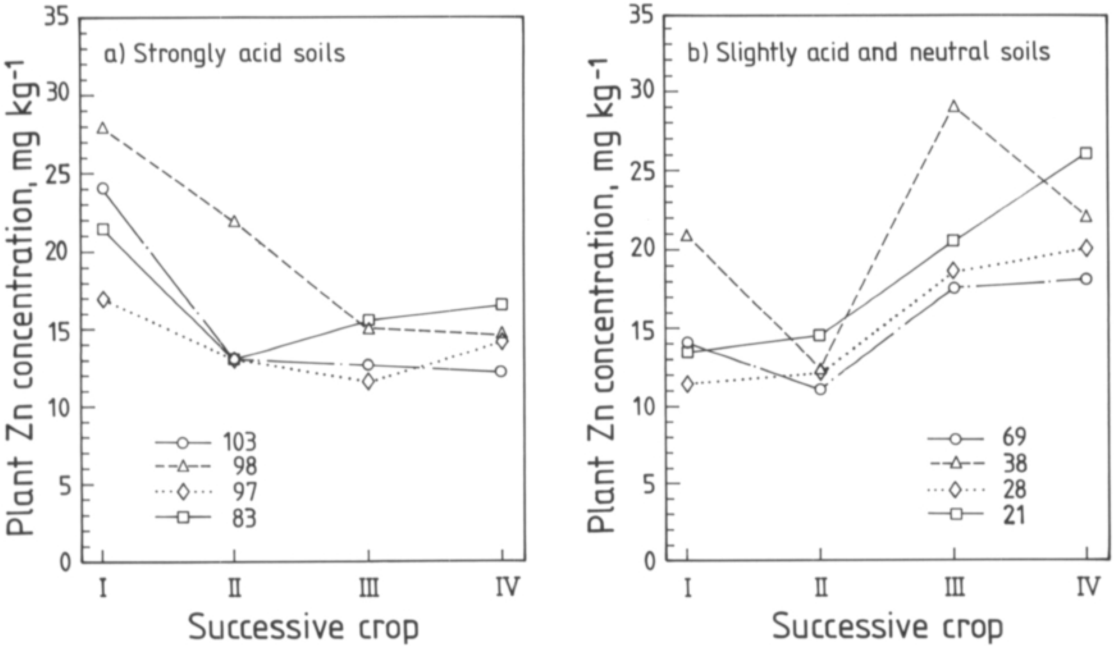

Fig. 5. Zinc concentration of four ryegrass crops grown (a) in very acid peat soils (group 3) where a strong relative utilization of secondary soil Zn was measured and (b) in slightly acid and neutral mineral soils (group 4) where a weaker relative utilization of secondary soil Zn occurred.

## 4.2 Effect of Zn application on plant Zn concentration

### 4.2.1 Experimental

A pot experiment was carried out in order to study the relationships between soil characteristics and the effect of Zn application on Zn concentration of ryegrass. The experiment was carried out in the same way as the one presented earlier (Section 4.1) with the exception that the pots were not limed. Zinc (10 mg dm$^{-3}$ of soil) was applied as a solution of $ZnSO_4$. One crop of Italian ryegrass was grown for 30 days in polythene boxes containing 0.2 dm$^3$ of soil. There were two pots of each soil to which Zn was applied; two pots were grown without added Zn. Of the 107 surface soils (Appendix 2), 101 soils were available for this trial. Those not available (15, 27, 29, 51, 88, 107) were of average characteristics.

### 4.2.2 Dry matter yields and plant Zn concentrations

The average dry matter production was 3.23 g per pot; the highest yields were nearly double the lowest ones (Table 39). The mean deviation of dry matter yield between the two replicates was 0.10 g per pot, or 3.1% of the average yield. The yields grown without added Zn correlated closely ($r = 0.88^{***}$) with the yields fertilized with Zn. According to the paired t-test, Zn application did not affect the size of the yield in any of the soil classes. The yields were not increased by Zn application even in soils producing grass with the lowest Zn concentration.

The mean deviation of Zn concentration between the two replicates was 1.6 mg kg$^{-1}$ and 1.0 mg kg$^{-1}$ in pots grown with and without applied Zn, corresponding to 4.5% of the mean in both treatments. The average Zn concentration of grass grown in mineral soils without applied Zn (19.5 mg kg$^{-1}$) was

Table 39. Dry matter yields, Zn concentration and Zn uptake of ryegrass in a pot experiment. Zn- = no Zn applied, Zn+ = Zn applied.

| Soil class | | Dry matter g per pot | | Zn concentration mg kg$^{-1}$ | | Zn uptake µg dm$^{-3}$ |
|---|---|---|---|---|---|---|
| | | Mean[1] | Range | Mean[2] | Range | Mean[2] |
| Clay | Zn- | 3.32$^{a}$ | 2.79-3.86 | 21.8$^{de}$ | 11.5-35.0 | 360$^{cd}$ |
| n = 25 | Zn+ | 3.34$^{a}$ | 2.12-3.77 | 32.5$^{b}$ | 19.0-53.0 | 530$^{ab}$ |
| Silt, loam, very | Zn- | 3.41$^{a}$ | 2.67-4.20 | 18.7$^{de}$ | 10.5-29.5 | 310$^{cd}$ |
| fine sand, n = 18 | Zn+ | 3.48$^{a}$ | 2.85-4.14 | 34.9$^{ab}$ | 25.0-63.0 | 600$^{ab}$ |
| Fine sand, moraine | Zn- | 3.11$^{ab}$ | 2.14-3.59 | 18.3$^{e}$ | 7.5-38.0 | 280$^{d}$ |
| n = 26 | Zn+ | 3.10$^{ab}$ | 1.76-3.80 | 33.0$^{b}$ | 13.5-81.5 | 500$^{b}$ |
| Mull | Zn- | 2.91$^{b}$ | 2.46-3.63 | 25.5$^{cd}$ | 18.5-33.5 | 360$^{cd}$ |
| n = 13 | Zn+ | 3.06$^{b}$ | 2.35-3.83 | 39.0$^{ab}$ | 31.0-48.5 | 590$^{ab}$ |
| Peat | Zn- | 2.89$^{b}$ | 1.86-3.77 | 28.4$^{c}$ | 9.0-55.0 | 410$^{c}$ |
| n = 18 | Zn+ | 2.88$^{b}$ | 1.99-3.77 | 44.3$^{a}$ | 21.0-62.0 | 630$^{a}$ |

[1] All means in the column were tested simultaneously.

[2] Means of Zn- (superscripts c, d and e) and Zn+ (superscripts a and b) were tested separately.

Table 40. Increase of Zn concentration upon application of Zn and utilization of added Zn.[1]

| Soil class | n | Increase of Zn concentration, mg kg$^{-1}$ | | Utilization of added Zn, % | |
|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range |
| Clay | 25 | 10.8 | 1-30 | 1.7$^{b}$ | 0.5-4.8 |
| Silt, loam, very fine sand | 18 | 16.3 | 6-35 | 2.9$^{a}$ | 1.7-4.2 |
| Fine sand, moraine | 26 | 14.5 | 4-53 | 2.1$^{ab}$ | 0.8-4.5 |
| Mull | 13 | 13.4 | 2-24.5 | 2.3$^{ab}$ | 0.3-3.9 |
| Peat | 18 | 15.8 | 4.5-28.5 | 2.2$^{ab}$ | -0.4-4.0 |

[1] Means in the two columns were tested separately.

lower ($t = 4.072^{***}$) than that in the corresponding organogenic soils (27.1 mg kg$^{-1}$). In all soil classes, Zn application elevated Zn concentration of ryegrass significantly (t-values of the paired t-test not presented). The Zn concentration of the grass fertilized with Zn was lower ($t = 3.276^{**}$) in mineral soils (34.0 mg kg$^{-1}$) than in organogenic soils (42.1 mg kg$^{-1}$). Zinc uptake correlated closely with the Zn concentration of the grass ($r = 0.84^{***}$ and $r = 0.93^{***}$ in pots grown with and without Zn application, respectively), but there was no correlation between plant Zn concentration and dry matter yield.

### 4.2.3 Influence of soil characteristics on the response to applied Zn

The average increase of Zn concentration caused by Zn application did not differ statistically from one soil class to another (Table 40), and the utilization of added Zn by the grass was low in all soil classes. The increase (mg kg$^{-1}$) in Zn concentration of grass correlated slightly negatively with the dry matter yield ($r = 0.44^{***}$), showing that the Zn concentration of a smaller yield was more strongly increased than that of a larger one. In soils where grass of low Zn concentration was produced without added Zn,

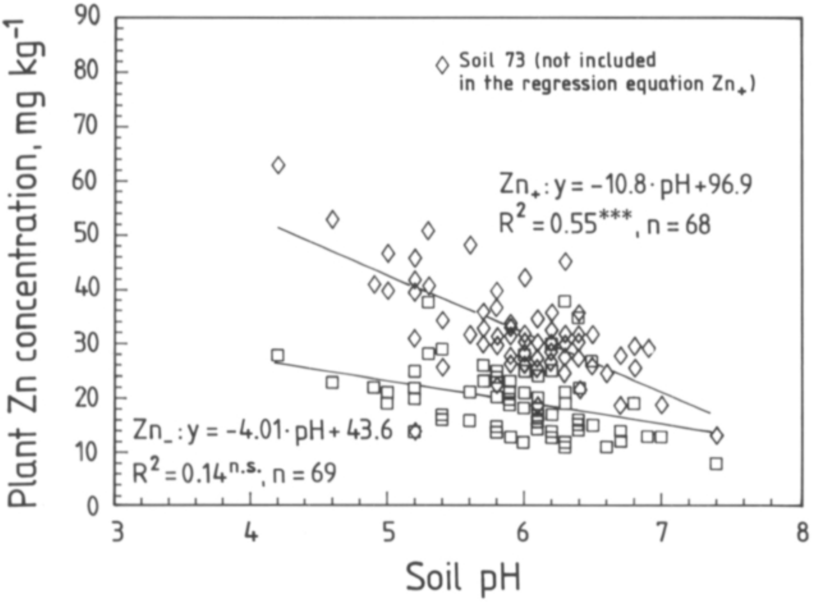

Fig. 6. Dependence of Zn concentration of ryegrass on soil pH in mineral soils fertilized with 10 mg Zn dm$^{-3}$ ($Zn_+$, symbol ◇) and those not fertilized with Zn ($Zn_-$, symbol □).

a high response to applied Zn was not necessarily measured, and even in soils producing grass of high Zn concentration a large response to applied Zn was occasionally observed. This resulted in a nonexistent correlation ($r = -0.06^{n.s.}$) between Zn concentration of grass grown without applied Zn and the increase of Zn concentration.

It can be seen in Figure 6 that in soils fertilized with Zn, soil pH had a more marked impact on plant Zn concentration as compared to soils not fertilized with Zn. In neutral and slightly acid soils the effect of added Zn on plant Zn concentration was much smaller than in the more acid soils. The relationship between soil properties and response of plant Zn concentration to applied Zn in mineral soils was studied in more detail by multiple regression analyses. The results of soils 71 and 73 were not included in the tabulation, because soil 71 had an excessive $Zn_{Ac}$ concentration and in soil 73 the increase of plant Zn concentration (+53 mg kg$^{-1}$) was much higher than in any other soil. The effect of added Zn on plant Zn concentration (y, mg kg$^{-1}$) decreased upon increasing soil pH which, according to the beta coefficients (Table 41), was relatively the most important independent variable. The equations below show that the increase of plant Zn concentration due to Zn application diminished with increasing soil pH at any level of native soil $Zn_{Ac}$ (mg dm$^{-3}$) or $Zn_{py}$ (mg dm$^{-3}$). On the other hand, at any pH the response was the greater the lower was the native $Zn_{Ac}$ or $Zn_{py}$ in soil. Also the clay and organic C content (%) had a slightly negative effect on the response. The regression equations for mineral soils (n = 68) were as follows:

$$y = -7.58\ \text{pH} - 0.070\ \text{Clay} - 4.45\ \log_e Zn_{py} + 66.06 \quad R^2 = 0.59^{***} \qquad \text{(Equation 1)}$$

$$y = -8.23\ \text{pH} - 0.77\ \text{C} - 3.95\ \log_e Zn_{Ac} + 68.52 \quad R^2 = 0.54^{***} \qquad \text{(Equation 2)}$$

In organogenic soils the relationship between soil pH and plant Zn concentration was inconsistent. As a matter of fact, the grass of the lowest Zn concentration was produced in the two most acid organogenic soils (100, pH 3.8; 105, pH 4.1), which is a striking difference from mineral soils where acidity enhanced Zn uptake by the grass. In the two

Table 41. t-Values of regression coefficients and beta coefficients (β) of independent variables in the regression equations explaining the variation of increase in Zn concentration upon Zn addition. Equation 1 and Equation 2: see text.

| Independent variable | Equation 1 | | Equation 2 | |
|---|---|---|---|---|
| | t | β | t | β |
| pH | -8.374*** | -0.69 | -7.694*** | -0.74 |
| Clay | -2.929** | -0.24 | - | - |
| $\log_e Zn_{py}$ | -5.329*** | -0.44 | - | - |
| $\log_e Zn_{Ac}$ | - | - | -4.699*** | -0.41 |
| Organic C | - | - | -1.929[1] | -0.19 |

[1] Significant at P = 0.058.

peat soils 100 and 105, the Zn concentrations of the grass not fertilized with Zn were as low as 11 and 9 mg $kg^{-1}$, respectively, and no higher than 21 mg $kg^{-1}$ in grass fertilized with Zn. In organogenic soils the increase (mg $kg^{-1}$) of plant Zn concentration was not explained by other soil properties, either. Instead, the response was dependent on the relative utilization (%) of native $Zn_{py}$ in the pot experiment (100 · Zn-uptake/$Zn_{py}$) (Figure 7). In other words, grass grown in soils where native $Zn_{py}$ was easily available and strongly utilized responded strongly to added Zn and vice versa. The grass grown in three soils (77, 87 and 101) responded to added Zn markedly less than would be expected on the basis of the relative utilization of $Zn_{py}$. In soils 77 and 101, the deviation between the replicates was large, possibly contributing to the inconsistent results; soil 87 was rich in clay (69%), possibly reducing the availability of added Zn. Omission of the three soils increased the coefficient of determination ($R^2$) from 0.48 to 0.68.

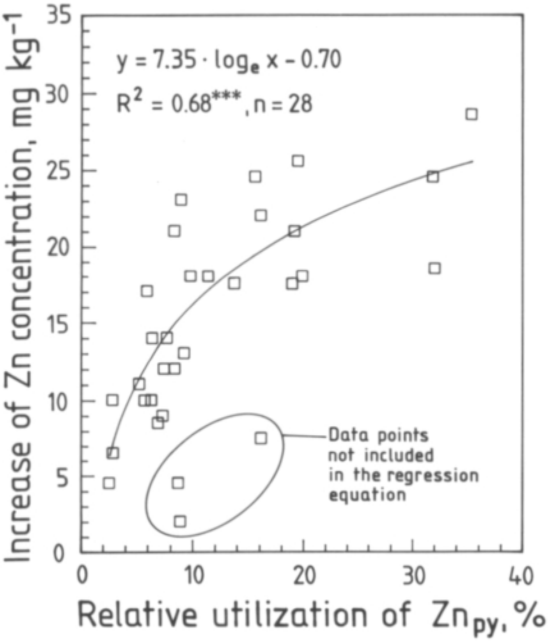

Fig. 7. Relationship between relative utilization (%) of Zn extracted by pyrophosphate ($Zn_{py}$) and increase of Zn concentration of ryegrass upon application of 10 mg Zn $dm^{-3}$ in 34 organogenic soils.

### 4.2.4 Response of ryegrass to applied Zn in soils poor in $Zn_{Ac}$

The need for Zn fertilization is in Finland currently assessed on the basis of soil $Zn_{Ac}$. It is assumed that the need for Zn fertilization of a soil is the greater the less $Zn_{Ac}$ is extracted from the soil. It might further be presumed that the greatest responses in plant Zn concentration would occur in soils poorest in $Zn_{Ac}$. According to the previous regression analyses, a decrease in $Zn_{Ac}$ indeed enhanced the response of plant Zn concentration to added Zn, but the regression equations did not accurately explain the variation of the response. Therefore the increases of Zn concentration were divided into quartiles ($F_{25\%}$) which were compared with the quartiles of soil $Zn_{Ac}$. Because, according to the present recommendations, Zn fertilization is most commonly applied to soils poorest in $Zn_{Ac}$, the effect of Zn application on plant Zn concentration grown on these soils was studied with particular care.

There were 19 mineral soils in the smallest quartile of $Zn_{Ac}$ ($Zn_{Ac} \leq 1.85$ mg $dm^{-3}$, Table 42). Only in three of these mineral soils was there a strong response (the largest $F_{25\%}$, quartile I) of plant Zn concentration to applied Zn. In the bulk of these mineral soils the increase of plant Zn concentration was smaller, placing them in the second or third quartile of response, but in none of the mineral soils concerned was the increase of Zn concentration of the grass very small (quartile IV). Within the group of these 19 mineral soils, the increase of plant Zn concentration did not correlate with soil $Zn_{Ac}$, but

Table 42. Soil $Zn_{Ac}$ and pH in mineral and organogenic soils poorest in $Zn_{Ac}$ ($Zn_{Ac} \leq 1.85$ mg dm$^{-3}$). The soils are divided into groups according to quartiles ($F_{25\%}$) of the increase of Zn concentration of ryegrass when 10 mg Zn dm$^{-3}$ was added to the respective soil.

| Increase of Zn concentration, mg kg$^{-1}$ | Soil | $Zn_{Ac}$, mg dm$^{-3}$ | | pH | |
|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range |
| ≥18[1]<br>(Quartile I) | *Mineral soils:*<br>44, 52, 66 | 1.3 | 0.8-1.8 | 5.5 | 5.2-6.0 |
| | *Organogenic soils:*<br>83, 94, 97, 98, 103 | 1.3 | 0.6-1.8 | 5.2 | 4.8-5.6 |
| 13-17.5[1]<br>(Quartile II) | *Mineral soils:*<br>3, 13, 23, 28, 38, 45<br>48, 49, 54, 61, 63, 65 | 1.4 | 0.8-1.9 | 6.3 | 5.8-6.9 |
| 9-12.5[1]<br>(Quartile III) | *Mineral soils:*<br>12, 37, 41, 64 | 1.6 | 1.5-1.9 | 6.0 | 5.4-6.5 |
| | *Organogenic soils:*<br>105 | 1.6 | - | 4.1 | - |
| ≤8.5[1]<br>(Quartile IV) | None | | | | |

[1] Limits of quartiles were set based on the pot experiment with 101 surface soils.

the observed response was to some extent explained by soil pH. The three soils responding strongly to added Zn (44, 52, 66) had a pH equal to or below 6.0, while in most of the soils in which a smaller response was observed the pH was commonly above 6.0 which was the average of the mineral surface soils. It should be pointed out that in the whole material (n = 101) the greatest increases (30 - 53 mg kg$^{-1}$) in plant Zn concentration occurred in very acid (pH 4.2 - 5.4) mineral soils (10, 40, 52, 73) containing 1.8 - 3.8 mg $Zn_{Ac}$ dm$^{-3}$, and only one of these (52) was among the soils poorest in $Zn_{Ac}$ (within the smallest $F_{25\%}$). This observation further confirms that low $Zn_{Ac}$ does not guarantee strong response of plant Zn concentration to applied Zn.

There were six organogenic soils in the smallest $F_{25\%}$ of $Zn_{Ac}$, all of which were very acid (Table 42). In five of those, a strong response (quartile I) of plant Zn concentration to applied Zn was measured. In all the five organogenic soils, secondary Zn reserves were quite effectively (the largest $F_{10\%}$) utilized. Thus, in organogenic soils a very low concentration of $Zn_{Ac}$ resulted in a large increase in plant Zn concentration as a consequence of Zn application. The only exception was the extremely acid soil 105 (pH 4.1) in which the grass responded less strongly. In this soil, the pH was as low as 3.8 at the end of the experiment.

## 4.3 Effect of liming and different rates of Zn application on ryegrass

### 4.3.1 Experimental

The effect of liming and different rates of applied Zn on the yield and Zn concentration of ryegrass was investigated on clay, fine sand, Carex peat and Sphagnum peat (Appendix 6) in a pot experiment. The Sphagnum peat was commercial light-colored peat; the other experimental soils were taken from cultivated fields. The pots (four replicates) were filled with 7.5 dm$^3$ of Sphagnum peat or 7 dm$^3$ of the other three soils. Lime was mixed into the assigned pots at the beginning of the experiment three days before the actual fertilization. In clay, fine sand and Carex peat, one rate of $Ca(OH)_2$ (clay and fine sand: 7.0 g per pot, Carex peat: 14 g per pot) was applied to elevate soil pH by one unit. The Sphagnum peat was originally extremely acid ($CaCl_2$-pH 2.8) and the grass did not grow without liming. Therefore two rates of $Ca(OH)_2$ (16 and 23 g per pot) were applied to Sphagnum peat and no unlimed pots were grown.

Zinc was applied in a $ZnSO_4$ solution to clay, fine sand and Carex peat at the rates of 0, 2.7, 10, 20 and 40 mg Zn $dm^{-3}$ and to Sphagnum peat at the rates of 0, 5, 10, 20, 50 and 100 mg Zn $dm^{-3}$. The excessive Zn rates were applied in order to get information on Zn tolerance of ryegrass. At the beginning of the experiment, the following quantities (mg $dm^{-3}$ of soil) of other nutrients were mixed in the entire soil of the pot as analytical grade chemicals:

| Nutrient | Rate, mg $dm^{-3}$ | Compound |
|---|---|---|
| N | 200 | $NH_4NO_3$ |
| P | 50 | $Ca(H_2PO_4)_2 \cdot H_2O$ |
| K | 200 | KCl |
| Mg | 50 | $MgSO_4 \cdot 7H_2O$ |
| S | 68 | mainly $MgSO_4 \cdot H_2O$ |
| Cu | 2 | $CuSO_4 \cdot 5H_2O$ |
| Mn | 2 | $MnSO_4 \cdot H_2O$ |
| Fe | 2 | $FeSO_4 \cdot 7H_2O$ |
| B | 0.5 | $H_3BO_3$ |
| Mo | 0.5 | $Na_2MoO_7 \cdot H_2O$ |

Ca was added to the soil at different rates depending on the liming. The macronutrients were mixed in the soil as solids and the micronutrients as solutions. The quantity of seed sown was 2.5 g per pot. The pots were grown in a greenhouse and watered daily with deionized water. In clay, fine sand and Carex peat, two crops were grown without reseeding. For the second crop, N, P and K solutions ($NH_4NO_3$, KCl and $KH_2PO_4$) were pipetted onto the surface of the soil in four portions at intervals of four to five days, resulting in a total of 200, 50 and 200 mg of N, P and K per $dm^3$ of soil, respectively. For Sphagnum peat, the experiment continued for two years. Three crops were grown in the first summer. During the winter the pots were stored outdoors covered with plastic foil, and in the second spring fertilized and reseeded. Then, two more crops were grown in pots to which 5, 20, 50 or 100 mg Zn $dm^{-3}$ had been applied. At two rates of Zn application (0 and 10 mg Zn $dm^{-3}$) five crops were grown in the second year. In clay, fine sand and Carex peat, each crop was analyzed for Zn. In Sphagnum peat, a few crops were pooled in the second year in order to reduce the number of analyses. At the end of the experiment, soil samples of each pot were analyzed for $Zn_{Ac}$ and pH.

During the experiment, atmospheric deposition of Zn was monitored in the greenhouse. Six Petri dishes (area 60.8 $cm^2$) were kept open in the greenhouse compartment where the pots were grown and six capped Petri dishes served as controls. After two months the Petri dishes were washed with 25 ml of 1 M HCl and the extracts were analyzed for Zn.

### 4.3.2 Dry matter yields and plant Zn concentrations

The total dry matter yields, not presented in detail, were 33.6, 27.3 and 28.3 g per pot in clay, fine sand and Carex peat, respectively, and they were not affected either by Zn application or by liming. In Sphagnum peat the grass tended to be paler green at the highest Zn rate (100 mg $dm^{-3}$) throughout the experiment as compared to the other pots. There seemed to be a slight yield decrease towards the higher rates of Zn application (Table 43), which may be an indication of excess of Zn. The dry matter production in Sphagnum peat at the higher liming rate was 5% higher than that at the lower rate

Table 43. Sum of five yields (g per pot) grown in Sphagnum peat.[1]

| Zn application, mg $dm^{-3}$ | Liming rate I | Liming rate II |
|---|---|---|
| 0 | $124.2^{a}$ | $129.9^{a}$ |
| 5 | $119.8^{ab}$ | $129.8^{a}$ |
| 10 | $125.2^{a}$ | $129.9^{a}$ |
| 20 | $122.3^{ab}$ | $127.5^{ab}$ |
| 50 | $119.6^{ab}$ | $125.4^{ab}$ |
| 100 | $115.1^{b}$ | $121.6^{b}$ |
| $HSD_{0.05}$ | 8.1 | 6.3 |

[1] Results of the two liming rates were tested separately.

($F = 47.083^{***}$). The additional three crops grown in pots of 0 or 10 mg Zn $dm^{-3}$ increased the total dry matter yield to an average of 181 g per pot, with no differences between the treatments.

Application of Zn elevated the Zn concentration of grass substantially in all soils (Figure 8). In Sphagnum peat Zn addition increased the Zn concentration of grass most effectively. For example, Zn application of 10 mg $dm^{-3}$ elevated the Zn concentration of grass by 65 mg $kg^{-1}$ in the first crop in Sphagnum peat and by 107 - 145 mg $kg^{-1}$ in the next ones, while in clay, fine sand and Carex peat the corresponding increase was only 10 - 31 mg $kg^{-1}$. The highest Zn concentrations of plants at the Zn application rate of 40 mg $dm^{-3}$ remained below 100 mg $kg^{-1}$ in clay and Carex peat. This level was slightly exceeded in the first crop in the limed fine sand, while 200 mg $kg^{-1}$ was reached at the highest application rate in the unlimed fine sand. The regression curves of Sphagnum peat showed that the grass grown in that soil would have contained as much as 250 - 400 mg Zn $kg^{-1}$ at the application rate of 40 mg Zn $dm^{-3}$. The maximum application rate in Sphagnum peat (100 mg $dm^{-3}$) gave rise to Zn concentrations exceeding 500 mg $kg^{-1}$ at both liming rates.

The efficiency of applied Zn was assessed by studying the slopes of the regression lines calculated between the quantity of added Zn (mg $dm^{-3}$) and Zn concentration (mg $kg^{-1}$) of grass (Table 44). Despite the slight curvilinearity of the response in clay soil and in Carex and Sphagnum peat, the linear regression equations were used. The equations of Sphagnum peat were calculated using the results of the first and second crop and Zn additions up to 50 mg $dm^{-3}$. All possible pairs of the regression coefficients were tested separately for each crop and liming rate (RANTA et al. 1991, p. 395). According to the regression coefficients, the effect of Zn application was the greatest in Sphagnum peat, followed by fine sand. The effect was smaller in clay and still smaller in Carex peat, although the difference between these two soils was not significant in the second crop in the limed soils. Liming lowered the efficiency of Zn application in clay ($P = 0.001$) and especially in fine sand ($P = 0.001$) but had a relatively smaller but significant effect ($P = 0.05$) in the two peat soils. The efficiency of added Zn decreased in clay and unlimed fine sand from the first crop to the second one, while in Sphagnum peat the efficiency increased. In Carex peat and limed fine sand the efficiency was unchanged from the first to the second crop.

Despite substantial increases in Zn concentration of grass, the utilization (%) of added Zn in clay, fine sand and Carex peat remained low, ranging in the unlimed pots from 0.4 to 1.7% and in the limed pots from 0.0 to 1.4%. In the first two crops grown in Sphagnum peat, the utilization of added Zn ranged from 3.1% to 6.1%. In the total of five crops, the utilization ranged from 22 to 8%, decreasing steadily from the lowest to the highest rate of added Zn. In the pots grown for three more crops, the utilization of added Zn rose to 34.5% at the rate of 10 mg Zn $dm^{-3}$ without any indication of decreased Zn availability over time.

Table 44. Regression coefficients (b) and coefficients of determination ($R^2$) of the linear regression equations between Zn addition (mg $dm^{-3}$) and plant Zn concentration (mg $kg^{-1}$).

| Soil | Crop I | | | | Crop II | | | |
|---|---|---|---|---|---|---|---|---|
| | Unlimed[1] | | Limed[3] | | Unlimed[1] | | Limed[3] | |
| | b | $R^2$ | b | $R^2$ | b | $R^2$ | b | $R^2$ |
| Clay | 1.37 | 0.98 | 1.05 | 0.98 | 1.15 | 0.97 | 0.77 | 0.95 |
| Fine sand | 3.64 | 0.99 | 1.64 | 0.84 | 2.74 | 0.97 | 1.36 | 0.83 |
| Carex peat | 1.02 | 0.98 | 0.84 | 0.94 | 1.01 | 0.98 | 0.74 | 0.69 |
| Sphagnum peat | 5.09 | 0.97 | 4.35 | 0.97 | 7.53 | 0.99 | 6.80 | 0.98 |

[1] Liming rate I in Sphagnum peat.

[3] Liming rate II in Sphagnum peat.

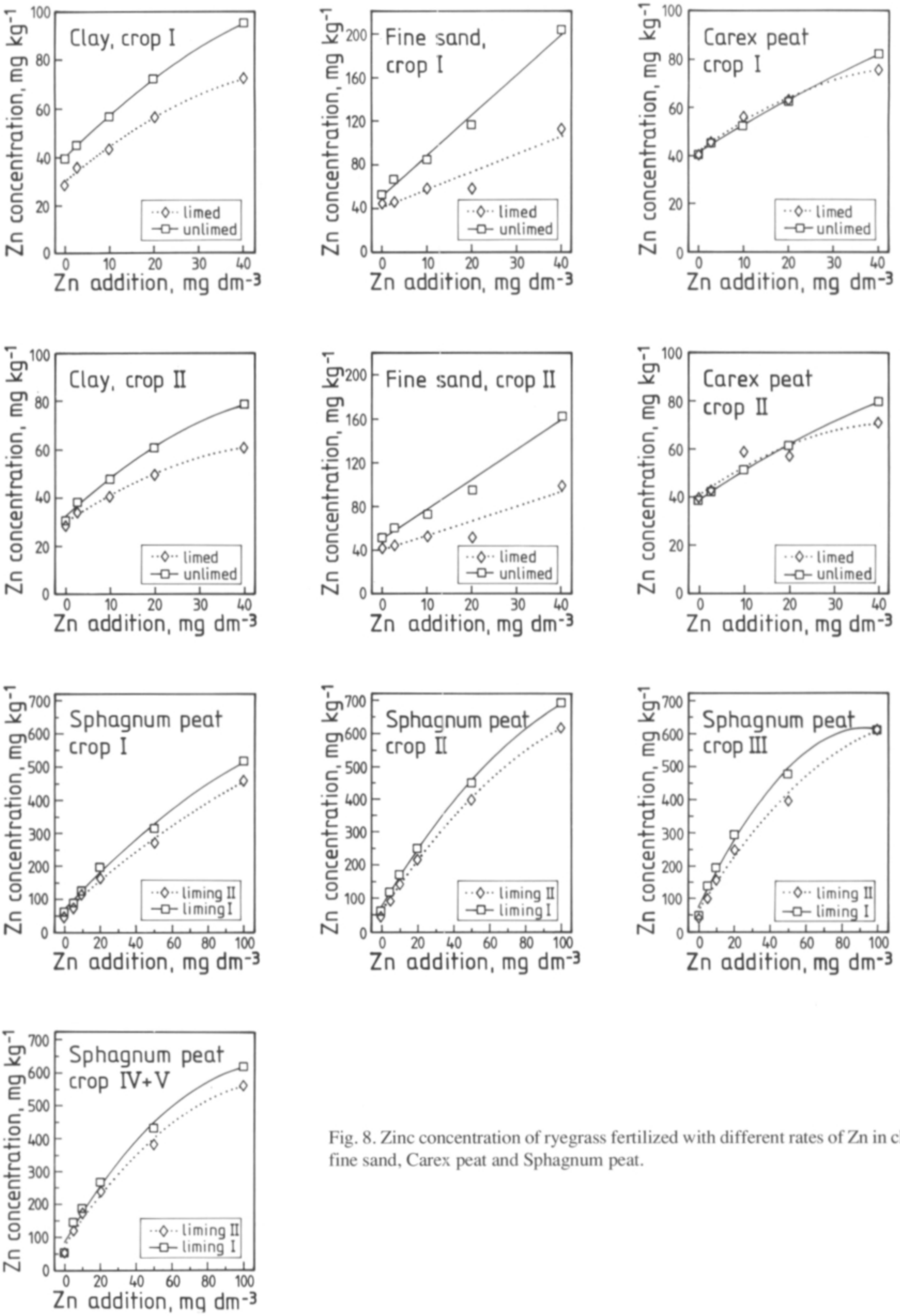

Fig. 8. Zinc concentration of ryegrass fertilized with different rates of Zn in clay, fine sand, Carex peat and Sphagnum peat.

### 4.3.3 Atmospheric deposition of Zn in the greenhouse

In the greenhouse, the quantities of Zn (mg m$^{-2}$) analyzed in the Petri dishes during two months were as follows:

| | Mean | Range |
|---|---|---|
| Open dishes | 1.34 | 0.54 - 2.11 |
| Capped dishes | 0.06 | 0.05 - 0.08 |

Assuming that the same deposition had fallen over the grassed pots (area 363 cm$^2$), a fallout of 49 µg per pot can be expected over 2 months. The average total uptake of Zn from the control pots of clay, fine sand and Carex peat ranged from 900 µg per pot in clay to 1500 µg per pot in fine sand. The deposited Zn thus ranged from 3 to 6% of the measured Zn uptake in the control pots. The deposition corresponded to 78 g ha$^{-1}$ over 12 months.

### 4.3.4 Soil analyses at the end of the experiment

Zinc addition to soil substantially elevated the quantities of $Zn_{Ac}$ determined at the end of the experiment (Table 45). The samples taken from clay soils to which 0 or 10 mg Zn dm$^{-3}$ had been applied were lost before the analysis. In all clay samples available, the final $Zn_{Ac}$ was lower than the amount of applied Zn plus the initial $Zn_{Ac}$, the difference being much greater than the Zn uptake by the grass. Inversely, in the unlimed fine sand the ultimate $Zn_{Ac}$ did not differ from the sum of Zn application plus the initial $Zn_{Ac}$. This difference between clay and fine sand may suggest retention of Zn in the clay soil into forms not extractable by AAAc-EDTA, while the availability of added Zn was maintained in the sand. In the two peat soils, on the contrary, the quantities of $Zn_{Ac}$ determined at the end of the experiment exceeded the sum of applied Zn and original $Zn_{Ac}$. This anomaly may be attributed to increasing bulk density of the organogenic soil during the experiment, owing to compaction and oxidation of organic matter.

Table 45. Soil pH and $Zn_{Ac}$ (mg dm$^{-3}$) at the end of the pot experiment.[1]

| Zn application, mg dm$^{-3}$ | $Zn_{Ac}$, mg dm$^{-3}$ | | pH | |
|---|---|---|---|---|
| | Unlimed[2] | Limed[3] | Unlimed[2] | Limed[3] |
| | ---------- Clay ---------- | | | |
| 0 | - | - | - | - |
| 2.7 | $2.0^{d}$ | $1.6^{d}$ | 5.5 | 6.0 |
| 10 | - | - | - | - |
| 20 | $11.2^{c}$ | $9.0^{c}$ | 5.6 | 6.0 |
| 40 | $25.4^{a}$ | $17.0^{b}$ | 5.6 | 6.0 |
| HSD$_{0.05}$[4] | 6.5 | | | |
| | ---------- Fine sand ---------- | | | |
| 0 | $3.3^{fg}$ | $2.9^{g}$ | 5.1 | 5.5 |
| 2.7 | $6.4^{f}$ | $4.1^{fg}$ | 5.1 | 5.9 |
| 10 | $10.6^{de}$ | $7.8^{ef}$ | 5.0 | 5.6 |
| 20 | $21.0^{c}$ | $12.9^{d}$ | 5.1 | 6.3 |
| 40 | $40.5^{a}$ | $32.1^{b}$ | 4.8 | 6.1 |
| HSD$_{0.05}$[4] | 3.2 | | | |
| | ---------- Carex peat ---------- | | | |
| 0 | $3.5^{d}$ | $2.6^{d}$ | 5.2 | 5.9 |
| 2.7 | $5.9^{cd}$ | $6.4^{cd}$ | 5.5 | 6.4 |
| 10 | $11.5^{c}$ | $10.7^{c}$ | 5.4 | 5.7 |
| 20 | $24.9^{b}$ | $25.1^{b}$ | 5.6 | 6.3 |
| 40 | $53.1^{a}$ | $49.8^{a}$ | 5.6 | 6.2 |
| HSD$_{0.05}$[4] | 7.0 | | | |
| | ---------- Sphagnum peat ---------- | | | |
| 0 | $1.5^{d}$ | $4.0^{d}$ | 4.6 | 5.2 |
| 5 | $10.5^{cd}$ | $6.9^{d}$ | 4.5 | 5.3 |
| 10 | $12.5^{cd}$ | $11.7^{cd}$ | 4.7 | 5.2 |
| 20 | $22.5^{c}$ | $25.5^{c}$ | 4.7 | 5.3 |
| 50 | $56.5^{b}$ | $57.6^{b}$ | 4.7 | 5.2 |
| 100 | $123.0^{a}$ | $108.5^{a}$ | 4.5 | 5.1 |
| HSD$_{0.05}$[4] | 15.5 | | | |

[1] Results of each soil were tested separately.
[2] Liming rate I in Sphagnum peat.
[3] Liming rate II in Sphagnum peat.
[4] HSD$_{0.05}$ for $Zn_{Ac}$

Determination of soil pH at the end of the experiment showed that there was a significant (t-value 4.56$^{**}$ - 15.85$^{***}$) difference in soil pH between the two liming levels in Sphagnum peat and between the limed and unlimed pots of the other three soils. The difference was greatest (0.8 pH units) in fine sand where liming lowered most effectively plant Zn concentration. In the other three soils the difference was 0.4 - 0.6 pH units. Liming also caused a decrease in $Zn_{Ac}$ determined at the end of the experiment in clay and fine sand (F = 14.019$^{**}$ and F = 41.763$^{***}$, respectively), while in Carex and Sphagnum peat the difference between the two liming rates was not statistically significant (P = 0.308 and P = 0.279, respectively).

## 4.4 Discussion

The adequacy of soil Zn supply to plant can be assessed by measuring the dependence of plant growth on the Zn status of soil (LINS and COX 1988, ARMOUR et al. 1990, BRENNAN and GARTRELL 1990). The critical level of Zn in soil has been determined as the quantity of extractable Zn above which no yield increase is obtained by Zn application. The present pot experiments did not allow to determine the critical level of $Zn_{Ac}$, because the dry matter production was not dependent on the status of soil Zn, and the yields were not increased by Zn application even though a few soils in the material were rated poor in $Zn_{Ac}$ (<1.0 mg $dm^{-3}$). The adequate size of the native Zn reserves was also displayed by the fact that in spite of the high growth intensity in the pot experiment, the average Zn concentration of the ryegrass grown in 107 soils was of the same magnitude as the average of field-grown timothy in Finland (30.8 ± 13.2 mg $kg^{-1}$ by LAKANEN 1969, 32.0± 8.5 mg $kg^{-1}$ by KÄHÄRI and NISSINEN 1978).

Zinc needs to enter the solution phase as $Zn^{2+}$ cation in order to be taken up by the plant. It is the fraction extracted with $MgCl_2$ that contains water-soluble and exchangeable Zn readily available to plants. However, the four crops of grass were able to take up more Zn than was originally extracted with $MgCl_2$ from several of the 107 surface soils especially in the higher pH range. It is feasible that during the experiment there was a flux of Zn from the more strongly bound fractions into the soluble one. This hypothesis is supported by the results of BAKHSH et al. (1990) and TORRES-MARTIN and GALLARDO-LARA (1991) who measured an increase in Zn extracted with 0.01 M $CaCl_2$ or 1 M $MgCl_2$ during the plant growth with a consequent decrease in the fraction bound by Fe oxide. As compared to the bulk of the soil, increased concentration of Zn in the rhizosphere of maize, wheat and barley has also been measured by LINEHAN et al. (1985) and MERCKX et al. (1986). The increase was attributed to the influence of the lower pH and the abundance of chelating root exudates in the rhizosphere, both mobilizing Zn from reserves less soluble than $Zn_{ex}$.

Some authors have reported a very close correlation between soil $Zn_{ex}$ and Zn concentration of plants grown in pot experiments (DAVIES 1985, NIELSEN et al. 1987) and in the field (MERKEL and KÖSTER 1977, SAUERBECK and STYPEREK 1985). Neutral salt solutions ($NaNO_3$, $CaCl_2$) have been proposed for extractants of Zn especially in polluted soils rich in Zn (HÄNI and GUPTA 1985, SAUERBECK and STYPEREK 1985, HOUBA et al. 1990). These solutions may not, however, be the most suitable in unpolluted soils where plants also utilize Zn reserves which are less soluble than $Zn_{ex}$. In the present study, Zn extracted by $MgCl_2$ did correlate significantly with Zn uptake by ryegrass, but in mineral soils AAAc-EDTA which dissolved also complexed Zn yielded results which correlated even more closely with Zn uptake by the grass. It was also observed by NIELSEN et al. (1987) that in non-contaminated soils poor in Zn, only $Zn_{DTPA}$, but not $Zn_{ex}$, correlated with Zn uptake by plants.

Soil $Zn_{Ac}$ and $Zn_{py}$, determined at the beginning of the pot experiment, were relatively the most important soil characteristics to explain the variation of the uptake of soil Zn throughout the four crops. AAAc-EDTA and pyrophosphate thus extracted Zn from the same fractions which serve as the source of Zn for plants. Contrary to $Zn_{ex}$ underestimating Zn supply in soils of high pH, $Zn_{Ac}$ and $Zn_{py}$ overestimated the Zn supplying power in the same mineral soils. It is possible that Zn unavailable to plants may be extracted by AAAc-EDTA buffered to pH 4.65 especially from soils which are less acid than the extractant. This assumption is supported by the results of JAHIRUDDIN et al. (1986) obtained in acid soils of Scotland. There, 1 M ammonium acetate, adjusted to different pH values, dissolved more Zn at pH 4.8 than did the solution adjusted to soil pH above 4.8, and the additional quantity of Zn dissolved at pH 4.8 was the greater the higher was the soil pH. The present study showed that also pyrophosphate at pH 10 was less sensitive than ryegrass to decreased Zn solubility induced by increasing pH. Corresponding observations have been reported earlier (HAQ and MILLER 1972, HORNBURG and BRÜMMER 1991) when extracting soil Zn with various EDTA and DTPA containing solutions.

The above findings support a pH-dependent interpretation of $Zn_{Ac}$, in principle suggested by SILLANPÄÄ (1982). This means that at a low pH a given result of $Zn_{Ac}$ corresponds to a larger Zn supply to plants than the same result in a soil of higher pH, and the more acid soil gets a higher rating in soil testing. A highly pH-dependent interpretation of $Zn_{DTPA}$ in soils of Australia has also been proposed (BRENNAN and GARTRELL 1990). However, when extracting soil Zn with chelating agents (EDTA and DTPA) the need of a pH correction is not as crucial as it is when mineral acids are used as extractants for Zn. For example, in the study of JUNUS and COX (1987) the results of Mehlich 3 extraction explained the variation of Zn uptake by soybean and corn from soils of North Carolina, USA, only when soil pH was taken into account.

In extremely intensive pot experiments also $Zn_{ox}$ was a source of plant-available Zn in mineral soils even though $Zn_{ox}$ has been considered virtually unavailable to plants (IYENGAR et al. 1981, PAYNE et al. 1988). The increase of plant Zn concentration towards the end of the experiment (Section 4.1) in the mineral soils may reflect the increased solubility of $Zn_{ox}$ over time. The decrease of soil pH during the experiment can have caused partial dissolution of the $Zn_{ox}$ fraction, which has been reported to respond to soil acidification (HAYNES and SWIFT 1985). In turn, in organogenic soils the decrease of plant Zn concentration during the trial may reflect the scarce $Zn_{ox}$ reserves in these soils.

In several previous studies (WEAR 1956, LEYDEN and TOTH 1960, AASEN 1981, SIMS 1986, JUNUS and COX 1987, BOSWELL et al. 1989) liming of an acid soil has been shown to reduce the fertilizer efficiency of added Zn. The same finding as well as an observation that $Zn_{Ac}$ decreased upon liming were made in this study in a pot experiment with clay and fine sand (Section 4.3). However, a more noteworthy observation of pH and fertilizer efficiency of added Zn was made in the larger material of mineral surface soils (Section 4.2) where soil pH proved a relatively more important characteristic than native $Zn_{Ac}$ in determining the effect of added Zn on plant Zn concentration. According to several studies, the equilibrium Zn concentration in soil solution or in the liquid phase of a soil suspension decreases and Zn adsorption increases with increasing pH of an acid soil (MCBRIDE and BLASIAK 1979, BRÜMMER et al. 1983, JEFFERY and UREN 1983, TILLER et al. 1984, PULFORD 1986, MSAKY and CALVET 1990). A decrease of Zn concentration in the soluble phase seems to indicate an increased specific adsorption (TILLER et al. 1984, SHUMAN 1986, SIMS 1986) which evidently results in a decreased tendency for desorption and lower plant-availability of Zn (EL - KHERBAWY and SANDERS 1984). Thus, soil pH by and large determines which part of fertilizer Zn remains plant-available and which is converted into unavailable forms.

Unlike mineral soils, $Zn_{py}$ or $Zn_{Ac}$ explained alone the variation of the uptake of Zn from organogenic soils by ryegrass without a significant contribution of other soil properties. The insignificance of other variables may partly be caused by the small number of organogenic soils and a narrower pH range, which may not have allowed the influence of soil pH to be observed as clearly as in mineral soils. It is also possible that the influence of soil pH on Zn solubility in organogenic soils is different from that in mineral soils. This conclusion can be drawn on the basis of the results of a pot experiment (Section 4.3) where liming highly affected the response of ryegrass to applied Zn in the two mineral soils but had only a minor influence in the two peat soils despite a significant increase in soil pH also in these soils. A similar observation was made by WOLTZ et al. (1953) in New Jersey, USA, where an elevation of the pH from 6.0 to 7.0 decreased the Zn uptake by red clover in mineral soils but did not do so in a peat soil. Also JEFFERY and UREN (1983) observed that mixing peat in an acid mineral soil reduced the decrease of Zn concentration in soil solution when the pH was elevated. MCBRIDE and BLASIAK (1979) attributed the pH-dependent increase of Zn adsorption in acid mineral soils to the reactions of Zn with Fe, Al and Mn oxides and considered the reactions with organic matter to be of minor importance. If this is true and the fraction of Zn bound by organic matter plays a more important role as a source of soluble Zn in organogenic soils, soil pH may in organogenic soils indeed have a less marked effect on Zn solubility than in mineral soils.

In organogenic soils, the AAAc-EDTA method was able to recognize soils which, according to the pot experiment, had the smallest reserves of plant-available Zn. In those peat soils native Zn reserves were most strongly utilized, and also added Zn remained available to plants, effectively elevating plant Zn concentration. However, the soil characteristics controlling the relative utilization of Zn in organogenic soils remained ambiguous. Moreover, in a very acid peat soil (100, pH 3.8) Zn concentration and uptake of ryegrass were low in spite of abundant $Zn_{Ac}$ reserves in the soil. In this soil and in another highly acid peat (105, pH 4.1), also the response to applied Zn was small even though at this pH the solubility of added Zn was inevitably high. An increase in $Al^{3+}$ concentration in a nutrient solution culture has been reported to reduce the concentration of Zn in ryegrass (RENGEL and ROBINSON 1989). It has also been observed that timothy grown in acid sulphate soils rich in exchangeable Al had a low Zn concentration in spite of a rather high $Zn_{Ac}$ in the respective soils (PALKO 1986). The adverse effects of Al may thus have caused the low Zn uptake of soil and fertilizer Zn in the two extremely acid peat soils.

## 5 FERTILIZERS AS ZINC SOURCES IN POT AND FIELD EXPERIMENTS

Qualitative relationship between soil and plant Zn can be studied in laboratory and pot experiments, but these studies do not tell the quantitative effect of applied Zn on the crop grown in the field where Zn fertilization is actually practiced. Moreover, in the pot experiments reported earlier in this study only $ZnSO_4$ was used as the source of Zn. In practice, the quantities of solid $ZnSO_4$ corresponding to Zn fertilizer recommendations are too small to allow uniform spreading, and therefore fertilizers of lower Zn concentration have been developed in which $ZnSO_4$ is incorporated in different carriers, facilitating uniform application with common machinery. In addition to the application to the soil, Zn fertilization of the crop can be carried out by foliar sprays. In order to study the effect of different sources, rates and application methods of Zn on the yield and Zn concentration of the crop, field experiments were carried out with timothy and barley at the Kotkaniemi Experimental Farm of Kemira Oy and in the neighboring fields in Vihti in southern Finland (60°22' N, 24°22' E). To complement the field experiments, a pot trial was conducted on the effect of different fertilizers on the Zn concentration of ryegrass.

### 5.1 Experimental

### 5.1.1 Fertilizers

The fertilizers consisted of commercial fertilizers as well as products specifically manufactured for the experiments (Table 46). The commercial Zn fertilizer 'Sinkkilannos' consists of $ZnSO_4$ mixed with gypsum, and the dry mixture is granulated. In addition to straight Zn fertilizers, there were four NPK fertilizers to which Zn was added as $ZnSO_4$. Addition of Zn to the commercial NPK fertilizer 'Vähäfosforinen Y-lannos' (18-3-12, N-P-K) is carried out by mixing $ZnSO_4$ in the fertilizer slurry resulting in the distribution of Zn in the entire granule. The coated NPK fertilizers containing Zn were made by coating grains of a commercial NPK fertilizers (17-6-12 or 25-4-4, % N-P-K) with $ZnSO_4$ in the pilot hall of Kemira Oy Espoo Research Centre. Based on the results of ELLIS et al. (1965), it was hypothesized that Zn might be more available when it is applied onto the granule as opposed to mixing in the slurry before granulation. After the field experiments were set up, it turned out that the fertilizer 18-3-12 contained 0.26% of Zn instead of

Table 46. Concentration of N, P, K and Zn as well as pH of the fertilizers used in the field experiments and in the respective pot experiment.

| Fertilizer | N | P | K | Zn | pH |
|---|---|---|---|---|---|
| | % | | | | |
| $ZnSO_4$ | - | - | - | 22.7 | - |
| $Na_2Zn$-EDTA | - | - | - | 15.0 | - |
| 'Sinkkilannos' | - | - | - | 2.6 | 4.3 |
| NPK 18-3-12[1] | 18.0 | 3.1 | 12.2 | 0.26 | 5.3 |
| Coated NPK I | 24.0 | 4.3 | 4.1 | 0.32 | 5.0 |
| Coated NPK II | 16.9 | 6.0 | 12.0 | 0.21 | 5.4 |
| Coated NPK III | 17.0 | 6.0 | 12.0 | 0.39 | 5.2 |
| NPK 25-4-4[2] | 24.6 | 4.5 | 4.7 | 0.0024 | 5.4 |
| NPK 20-4-8[3] | 20.1 | 4.2 | 7.8 | 0.0031 | 5.3 |
| NPK 17-6-12[4] | 17.5 | 5.8 | 12.3 | 0.0062 | 5.3 |
| NPK 14-9-10[5] | 14.2 | 8.4 | 9.9 | 0.0047 | 5.1 |
| KCl | - | - | 50.5 | 0.0016 | - |
| Triple superphosphate | - | 19.6 | - | 0.0144 | - |

The Finnish trade names of the commercial NPK fertilizers: [1] 'Vähäfosforinen Y-lannos', [2] 'Typpirikas Y-lannos 1', [3] 'Typpirikas Y-lannos 2', [4] 'Typpirikas Y-lannos 3', [5] 'Fosforirikas Y-lannos'

0.30% on which the experimental design was based. Therefore, Zn application to the plots receiving this fertilizer remained in reality slightly lower than intended.

Table 47. Applications of Zn in the pot experiment.

| Treatment | Zn, mg dm$^{-3}$ |
|---|---|
| 1. Control, no Zn application | 0 |
| 2. $ZnSO_4$ mixed in the soil | 2.7 |
| 3. 'Sinkkilannos' mixed in the soil | 2.7 |
| 4. 'Sinkkilannos' onto the soil | 2.7 |
| 5. Zn in NPK 18-3-12 onto the soil | 2.3 |
| 6. Zn in Coated NPK I onto the soil | 2.7 |
| 7. $ZnSO_4$ mixed in the soil | 10 |
| 8. 'Sinkkilannos' mixed in the soil | 10 |
| 9. 'Sinkkilannos' onto the soil | 10 |

### 5.1.2 Experiments with ryegrass and timothy

#### *a. Comparison of Zn fertilizers in a pot experiment*

Agronomic efficiency of a few Zn fertilizers used in the field experiments was tested in a pot experiment with ryegrass in clay, fine sand and Carex peat (Appendix 6). The clay and fine sand were taken from the sites were the field experiments with timothy were carried out. Zinc sulphate mixed in the soil served as reference fertilizer. The other treatments resembled the alternatives available in practical farming of forage crops. The commercial fertilizer 'Sinkkilannos' was mixed in the soil or was given as a topdressing, and the two Zn-containing NPK fertilizers were surface-applied (Table 47). The two Zn rates were 2.7 (2.3 in NPK 18-3-12) and 10 mg Zn dm$^{-3}$ of soil.

There was 7 dm$^3$ of soil per pot and four replicates. At the beginning of the experiment, the same quantities of nutrients were applied as in the experiment reported in Section 4.3. The nutrient sources were compound NPK fertilizers and/or analytical grade chemicals. The pots to which Zn-containing NPK fertilizers were added obtained the bulk of N, P and K in these compound fertilizers. For the second crop, N, P and K were provided at the rate of 200, 50 and 200 mg dm$^{-3}$, respectively. Nutrient solutions made of $NH_4NO_3$, KCl and $KH_2PO_4$ were pipetted onto the surface of all pots in four portions at a few days intervals. The pots were grown in a greenhouse and watered daily with deionized water. The grass yields were dried at 60°C and analyzed for Zn.

*b. Application of Zn fertilizers to timothy in the field*

The objective of the 2-year experiments, performed in clay and fine sand soils (Appendix 6), was to study whether Zn concentration of timothy was equally affected by a single application of straight Zn fertilizers and applications of Zn incorporated in NPK fertilizers spread for each yield. The swards were sown in 1990 and harvested in 1991 and 1992. During the experiment, all plots, except the control, received 3 or 6 kg Zn ha$^{-1}$ (5.2 kg ha$^{-1}$ in NPK 18-3-12) as a single dose or as multiple smaller applications. Foliar application of Zn to the growing sward was not made because Zn added that way can be adsorbed on the foliage without taking part in the reactions of the plant, which may cause irrelevant results of plant analysis. The different Zn applications, presented in detail in Appendix 7, were as follows:

1) Single application of a straight Zn fertilizer ($ZnSO_4$ or 'Sinkkilannos') at sowing (1990).
2) Single application of a straight Zn fertilizer ('Sinkkilannos') onto the sward in spring of the first year of cropping (1991).
3) Applications of Zn-containing NPK fertilizers (NPK 18-3-12, Coated NPK II or Coated NPK III) onto the sward in spring and after cutting the first crop in both years of harvest (1991 and 1992).

When setting up the experiments, the fields were harrowed twice. Then, the granular Zn fertilizer 'Sinkkilannos' was broadcast and $ZnSO_4$, dissolved in water, was sprayed on the appropriate plots. The NPK fertilization was applied with a fertilizer drill and timothy seeds were sown with a seed drill, simultaneously mixing 'Sinkkilannos' and $ZnSO_4$ in the soil. The next spring, granular 'Sinkkilannos' was top-dressed on the assigned plots. In both experimental years, all plots received N, P and K fertilization as a top dressing at the rates of 90, 32 and 64 kg ha$^{-1}$, respectively. As mentioned earlier, two of the NPK fertilizers contained added Zn. After the first cut in mid-June, when a few heads of timothy were emerging, NPK fertilization was applied again at the same rates and the swards were harvested for the second time later during the growing season. Owing to a drought in 1992, the experiment in clay soil was irrigated on June 30 (28 mm of water) and the latter cut of both experiments took place as late as the end of September. In addition to the actual Zn fertilization, all plots received 19 g Zn ha$^{-1}$ in the NPK fertilizer when the experiments were established. During the years of harvest, the plots received a maximum of 130 g Zn ha$^{-1}$ as impurities of NPK fertilization. This quantity corresponds to 5% of the smaller application of 3 kg Zn ha$^{-1}$ and can be considered negligible.

The stand was cut with a forage harvester. The yield of each plot was collected in a glass fibre box attached to the harvester. The plant samples, to be analyzed for Zn, N and moisture, were taken just before the actual harvesting. The samples, composed of two subsamples of 0.25 m$^2$ from each plot, were collected by hand using stainless steel scissors and weighed together with the harvested yield of the respective plot. Soil samples were taken from each plot and analyzed for pH and $Zn_{Ac}$ in the beginning and at the end of the experiment.

### 5.1.3 Field experiments with barley

*a. Comparison of Zn fertilizers*

The objective of the three 3-year field experiments carried out in 1990 through 1992 on clay, fine sand and mull soils (Appendix 6) was to establish whether Zn concentration of barley can be elevated with moderate Zn applications given in different fertilizers and whether a single application at the beginning of the experiments differs in efficiency from smaller annual applications. During the experiment, all plots, except the control, received 5.4 kg Zn ha$^{-1}$ (4.8 kg ha$^{-1}$ in NPK 18-3-12) either as a single application at the beginning or as three annual applications of 1.8 kg Zn ha$^{-1}$ (4 x 1.6 kg ha$^{-1}$ in NPK 18-3-12). The treatments, presented in detail in Appendix 8, were as follows:

1) Single application of a straight Zn fertilizer ($ZnSO_4$ or 'Sinkkilannos') in the first spring of the trials.

2) Annual doses of Zn incorporated in granular NPK fertilizers (NPK 18-3-12 or Coated NPK I).

3) Annual doses of $Na_2Zn$-EDTA sprayed each spring onto the soil.

4) Annual doses of $Na_2Zn$-EDTA sprayed on the foliage.

Each spring the soil was harrowed twice. After harrowing, the granular Zn fertilizer ('Sinkkilannos') was broadcast (in 1990 only), and $ZnSO_4$ (in 1990 only) and $Na_2Zn$-EDTA (annually) were sprayed on the appropriate plots as water solutions. These fertilizers were mixed in the soil with a combined seed and fertilizer drill in connection with sowing and application of the NPK fertilizers. The granular NPK fertilizers, including added Zn in two fertilizers, were applied by the placement method. At the Feekes 5 growth stage (LARGE 1954), when the plants had usually reached the height of 10 - 15 cm, water solution of $Na_2Zn$-EDTA was sprayed on the assigned plots. In 1992, the experiment on clay soil was irrigated with 13 mm of water on July 1. In addition to the actual Zn fertilization, the experiments on clay and fine sand received 37 g Zn ha$^{-1}$ as impurities of other fertilizers during three years, except the plot fertilized with the NPK 18-3-12 and Coated NPK I. In mull soil, the corresponding quantity was 120 g Zn ha$^{-1}$, owing to the larger Zn concentration of the NPK fertilizers used in that experiment.

The grain yield, harvested with an experimental harvester (Hege 125), was weighed and analyzed for moisture and Zn. Also the straw was analyzed for Zn and moisture. The straw yield was weighed in the last two experimental years.

*b. Application of different Zn rates*

The objective of the two 2-year field experiments with barley was to investigate the effect of high Zn rates (15 and 30 kg ha$^{-1}$) on the Zn concentration of barley at different growth stages. The experiments, presented in detail in Appendix 9, were carried out in the same fine sand and clay soil (Appendix 6) in which the different Zn fertilizers were experimented. After harrowing in the first spring (1991) of the experiment, powdery $ZnSO_4$ was applied by hand at the rate of 0, 15 or 30 kg Zn ha$^{-1}$ and mixed in the soil by harrowing for one more time. The NPK fertilizer was applied with the combined seed and fertilizer drill to supply N, P and K at the rates of 110, 22 and 44 kg ha$^{-1}$, respectively. In the second spring (1992), no Zn was added and the results of the second experimental year thus reflect the residual effect of the Zn fertilization. The quantity of Zn as impurity in the NPK fertilizer during the two years was 34 g ha$^{-1}$. In 1992, the experiment on clay soil was irrigated with 20 mm of water on July 1.

The plant samples were collected four times during the growing season from each plot by cutting the plants each time from two areas of 0.25 m$^2$. The stand was sampled at the beginning of tillering (Feekes 2), at the end of tillering (Feekes 5), at the end of flowering (Feekes 10.5) and at maturity. The number of days from sowing to these growth stages was 38 - 39 days, 50 - 52 days, 69 -70 days and 104 days, respectively, in 1991 and 26 - 28 days, 40 - 43 days, 61 days and 91 - 96 days, respectively, in 1992. The plant samples were dried and weighed. The grains were removed from the ears of mature plants by hand and the remnants of the ears were combined with the straw. The plant samples were analyzed for Zn; the grains and straw were weighed and analyzed separately. At the end of the experiments, a composite soil sample of each plot was analyzed for $Zn_{Ac}$.

### 5.1.4 Weather

Precipitation and temperature were measured at the Kotkaniemi Experimental Farm. The three growing seasons in which the field experiments were conducted differed strongly in weather of the early summer. In 1990 and 1992, May and June were dry and warm (Table 48). In 1992, the drought continued until the end of July, resulting in a shortage of water especially in the experiments on the clay

Table 48. Monthly mean temperatures and precipitations at the Kotkaniemi Experimental Farm during the months of growing seasons of the experimental years and means over a period of 18 years.

| Month | Temperature, °C | | | | Precipitation, mm | | | |
|---|---|---|---|---|---|---|---|---|
| | 1990 | 1991 | 1992 | 1974-91 | 1990 | 1991 | 1992 | 1974-91 |
| May | 11.9 | 8.5 | 11.4 | 10.5 | 27 | 27 | 16 | 33 |
| June | 16.0 | 13.8 | 16.1 | 14.8 | 14 | 58 | 16 | 44 |
| July | 16.0 | 19.2 | 19.1 | 16.6 | 88 | 41 | 32 | 68 |
| August | 16.5 | 16.7 | 16.6 | 15.0 | 49 | 98 | 90 | 76 |
| September | 9.2 | 10.5 | 13.2 | 9.6 | 82 | 53 | 61 | 65 |

Table 49. Concentration of Zn in ryegrass. I and II refer to the first and second crop, respectively.[1]

| Treatment | Zn added mg dm$^{-3}$ | Zn concentration (mg kg$^{-1}$) of grass grown in | | | | | |
|---|---|---|---|---|---|---|---|
| | | Fine sand | | Carex peat | | Clay | |
| | | I | II | I | II | I | II |
| Control | 0 | 52.9$^{c}$ | 51.6$^{d}$ | 40.7$^{d}$ | 38.8$^{e}$ | 39.8$^{cd}$ | 31.0$^{f}$ |
| $ZnSO_4$ | 2.7 | 66.6$^{b}$ | 60.8$^{cd}$ | 45.7$^{bc}$ | 42.5$^{de}$ | 45.4$^{b}$ | 38.4$^{de}$ |
| 'Sinkkilannos' | 2.7 | 65.1$^{b}$ | 57.6$^{d}$ | 42.3$^{cd}$ | 42.9$^{de}$ | 38.2$^{cd}$ | 37.5$^{e}$ |
| 'Sinkkilannos', s.a.[2] | 2.7 | 56.0$^{c}$ | 72.3$^{bc}$ | 41.2$^{d}$ | 44.2$^{cd}$ | 37.4$^{d}$ | 45.8$^{bc}$ |
| NPK 18-3-12, s.a.[2] | 2.3 | 51.8$^{c}$ | 51.9$^{d}$ | 39.8$^{d}$ | 42.0$^{de}$ | 38.6$^{cd}$ | 35.4$^{ef}$ |
| Coated NPK I, s.a.[2] | 2.7 | 54.4$^{c}$ | 55.1$^{d}$ | 39.3$^{d}$ | 43.3$^{cde}$ | 35.7$^{d}$ | 35.7$^{e}$ |
| $ZnSO_4$ | 10 | 84.7$^{a}$ | 73.5$^{b}$ | 52.7$^{a}$ | 51.3$^{b}$ | 56.7$^{a}$ | 48.0$^{b}$ |
| 'Sinkkilannos' | 10 | 85.6$^{a}$ | 75.0$^{b}$ | 46.1$^{bc}$ | 47.8$^{bc}$ | 52.2$^{a}$ | 42.5$^{cd}$ |
| 'Sinkkilannos', s.a.[2] | 10 | 65.0$^{b}$ | 88.5$^{a}$ | 46.8$^{b}$ | 58.8$^{a}$ | 43.2$^{bc}$ | 66.5$^{a}$ |
| | $HSD_{0.05}$ | 6.9 | 12.2 | 4.1 | 4.8 | 5.2 | 4.4 |

[1] Results of each soil and crop were tested separately.

[2] s.a. = surface-applied

soil. Inversely, in 1991 especially June was cooler and rainier than normal.

## 5.2 Comparison of Zn fertilizers, Zn rates and application practices with grass crops

### 5.2.1 Effect of Zn fertilizers on ryegrass in a pot experiment

Zinc application did not affect ryegrass yields in the pot experiment, and therefore only the mean yields obtained from each soil (g per pot) are presented:

| | Crop I | Crop II |
|---|---|---|
| Clay | 13.7 | 20.1 |
| Fine sand | 9.9 | 18.1 |
| Carex peat | 12.2 | 16.6 |

At the lower rate (2.7 or 2.3 mg Zn dm$^{-3}$), $ZnSO_4$ elevated Zn concentration of the first ryegrass crop in all soils (Table 49), but only in fine sand also the granular 'Sinkkilannos', mixed in the soil, had a significant effect. In the second crop, the effect of the fertilizers was different; granular 'Sinkkilannos' elevated plant Zn concentration relatively more efficiently than in the first crop, probably owing to a longer time available for the dissolution of the granules. In the second crop, the surface-applied 'Sinkkilannos' elevated plant Zn concentration in all soils at least as effectively as $ZnSO_4$ mixed in the soil. Actually, surface-applied 'Sinkkilannos' was the only fertilizer which elevated plant Zn concentration significantly at the lower application rate in the second crop in fine sand and Carex peat. The only significant effect of the two Zn-containing NPK fertilizers on plant Zn concentration was observed in the second crop in clay with the coated NPK I.

At the higher application rate (10 mg $dm^{-3}$) the increase of plant Zn concentration was substantially higher. In fine sand, 'Sinkkilannos' mixed in the soil was equal to $ZnSO_4$ in efficiency in both crops, but in the first crop in Carex peat and in the second crop in clay, $ZnSO_4$ was more efficient. Also at the higher Zn rate top-dressing of 'Sinkkilannos' was a less effective way of application than was mixing in the soil in the first crop in fine sand and clay soils. In the second crop the contrary was observed: topdressing of 'Sinkkilannos' was the most effective way of Zn application in all soils. The efficiency of the surface-application of 'Sinkkilannos' in the second yield was also emphasized when comparing the results obtained at the two Zn rates. Surface-applied 'Sinkkilannos' at the lower rate elevated Zn concentration of ryegrass as much as did the higher rate of 'Sinkkilannos' mixed in the soil. Despite substantial increases in Zn concentration of ryegrass, the utilization of added Zn remained at 1 - 2% in all soils.

### 5.2.2 Effect of Zn fertilizers on timothy in the field

All the four timothy yields (Table 50) obtained from the fine sand field during the two growing seasons were of normal size. Owing to poor growth, only two of the four blocks could be harvested in clay soil in the first experimental year and the first yields remained small also in the harvested blocks. Later, the yields obtained from the clay soil were of the same magnitude as those from the fine sand. The results concerning the clay soil represent the yield of those two blocks harvested in both years. Dry matter yields did not respond to Zn applications.

Table 50. Dry matter yields and raw protein (6.25 · N) contents of timothy. I and II refer to the first and second crop in the respective growing season.

| Soil | Successive crop | | | |
|---|---|---|---|---|
| | I/1991 | II/1991 | I/1992 | II/1992 |
| | Dry matter, kg $ha^{-1}$ | | | |
| Clay | 1115 | 4054 | 3695 | 2350 |
| Fine sand | 2568 | 3935 | 4320 | 2100 |
| | Raw protein, % | | | |
| Clay | 14.3 | 14.5 | 15.4 | 18.2 |
| Fine sand | 15.0 | 14.6 | 15.1 | 18.3 |

The results of Zn concentration and uptake were tested with the analysis of variance using Zn fertilization and the crop (I/1991, II/1991, I/1992, II/1992) as the two criteria of classification. The results of the blocks served as replicates. The F-values in Table 51 suggest that in both experiments the systematic differences between the Zn concentrations of the four crops were at least as significant as those caused by the different fertilization treatments.

In clay soil, Zn concentration of timothy varied in a rather narrow range in the four crops of each treatment (Table 51). In fine sand, the ranges were slightly wider mainly because the Zn concentrations of crop II/1992 were substantially higher than those of the other crops. In neither experiment did the lower Zn rate (3 kg $ha^{-1}$) elevate the mean Zn concentration of timothy significantly. At the higher Zn rate (6 kg $ha^{-1}$) 'Sinkkilannos', applied by mixing in the soil or by top-dressing, elevated Zn concentration of timothy significantly in both soils. In addition, Zn concentration of the grass fertilized with $ZnSO_4$ (6 kg Zn $ha^{-1}$) or with the coated NPK III (6 kg Zn $ha^{-1}$) differed significantly from the control in clay soil. 'Sinkkilannos' mixed in the soil seemed to be slightly more effective at both levels than $ZnSO_4$ alone, but the difference between these two fertilizers was not significant.

A decrease in the effectiveness of Zn application during the experiments was not detected. As a matter of fact, the greatest increases in Zn concentra-

Table 51. Zinc concentration and uptake of timothy in two 2-year experiments as means of the four crops.

| Treatment | Zn rate kg ha$^{-1}$ | Zn concentration, mg kg$^{-1}$ | | Zn uptake, g ha$^{-1}$ |
|---|---|---|---|---|
| | | Mean | Range | Mean |
| | | Clay | | |
| 1. Control | 0 | 28.0$^{c}$ | 25-31 | 80 |
| 2. $ZnSO_4$ | 3 | 30.1$^{bc}$ | 27-34 | 85 |
| 3. 'Sinkkilannos' | 3 | 32.4$^{abc}$ | 29-34 | 86 |
| 4. 'Sinkkilannos', s.a.[1] | 3 | 31.9$^{abc}$ | 27-37 | 87 |
| 5. Coated NPK II, s.a.[1] | 4×0.75 | 29.6$^{bc}$ | 25-32 | 79 |
| 6. $ZnSO_4$ | 6 | 33.6$^{ab}$ | 31-37 | 92 |
| 7. 'Sinkkilannos' | 6 | 35.6$^{a}$ | 33-38 | 98 |
| 8. 'Sinkkilannos', s.a.[1] | 6 | 36.5$^{a}$ | 36-38 | 100 |
| 9. NPK 18-3-12, s.a.[1] | 4×1.3 | 29.5$^{bc}$ | 27-33 | 82 |
| 10. Coated NPK III, s.a.[1] | 4×1.5 | 34.1$^{ab}$ | 31-37 | 99 |
| $HSD_{0.05}$ (fertilizations) | | 5.3 | | 27 |
| F (fertilizations) | | 5.612$^{***}$ | | 1.875$^{n.s.}$ |
| F (crops) | | 8.802$^{***}$ | | 152.840$^{***}$ |
| | | Fine sand | | |
| 1. Control | 0 | 34.9$^{cd}$ | 32-40 | 112$^{abc}$ |
| 2. $ZnSO_4$ | 3 | 35.9$^{bcd}$ | 30-41 | 121$^{abc}$ |
| 3. 'Sinkkilannos' | 3 | 40.0$^{abc}$ | 36-48 | 122$^{abc}$ |
| 4. 'Sinkkilannos', s.a.[1] | 3 | 38.9$^{bcd}$ | 34-46 | 136$^{ab}$ |
| 5. Coated NPK II, s.a.[1] | 4×0.75 | 34.1$^{d}$ | 31-40 | 100$^{c}$ |
| 6. $ZnSO_4$ | 6 | 37.6$^{bcd}$ | 34-44 | 124$^{abc}$ |
| 7. 'Sinkkilannos' | 6 | 41.0$^{ab}$ | 36-47 | 126$^{abc}$ |
| 8. 'Sinkkilannos', s.a.[1] | 6 | 44.6$^{a}$ | 37-55 | 140$^{a}$ |
| 9. NPK 18-3-12, s.a.[1] | 4×1.3 | 34.3$^{d}$ | 30-38 | 103$^{bc}$ |
| 10. Coated NPK III, s.a.[1] | 4×1.5 | 35.2$^{cd}$ | 32-41 | 108$^{abc}$ |
| $HSD_{0.05}$ (fertilizations) | | 5.3 | | 35.5 |
| F (fertilizations) | | 9.193$^{***}$ | | 2.937$^{**}$ |
| F (crops) | | 41.960$^{***}$ | | 35.745$^{***}$ |

[1] s.a. = surface application

tion of grass occurred in the last crop harvested. The effect of a given Zn rate was similar in both soils. As the mean of the two experiments, 'Sinkkilannos' increased plant Zn concentration by 4.4 and 8.5 mg kg$^{-1}$ at the application rate of 3 and 6 kg Zn ha$^{-1}$, respectively, corresponding to an increase of 1.4 mg kg$^{-1}$ for each kilogram of Zn applied.

Cumulative Zn uptake in the four crops (4 x the means in Table 51) was 317 - 399 g ha$^{-1}$ and 400 - 561 g ha$^{-1}$ in clay and fine sand, respectively. Some treatments seemed to increase Zn uptake by the crop but in neither soil did any of the treatments differ significantly from the control. The apparent utilization of fertilizer Zn corresponded to 0.8 - 1.5% of added Zn in the treatments where the Zn concentration of the grass was significantly elevated.

Soil analyses carried out at the end of the experiments showed that Zn applications yielded slightly elevated $Zn_{Ac}$ in clay ($F = 12.584^{***}$). Owing to a large variation of the results in fine sand, the influence of Zn application on $Zn_{Ac}$ was not significant ($F = 1.742^{n.s.}$). Surface-application of granular Zn-containing fertilizers may have caused an uneven distribution of Zn in the soil, possibly resulting in a failure of representative sampling. The means of $Zn_{Ac}$ (mg dm$^{-3}$) at the various levels of added Zn, tested separately in clay and fine sand, were as follows:

| Zn, kg ha$^{-1}$ | Clay | Fine sand |
|---|---|---|
| 0 | 1.2$^{b}$ | 2.8 |
| 3 | 1.4$^{b}$ | 3.3 |
| 6 | 2.0$^{a}$ | 3.5 |

Table 52. Grain and straw yield (kg ha$^{-1}$) of barley in three field experiments.

| Yield | Year | Yield (kg ha$^{-1}$) obtained from | | |
|---|---|---|---|---|
| | | Clay | Mull | Fine sand |
| Grain[1] | 1990 | 4597 | 6361 | 6996 |
| | 1991 | 5222 | 5604 | 6414 |
| | 1992 | 1790 | 7051 | 5514 |
| Straw | 1991 | 2456 | 3435 | 3236 |
| | 1992 | 660 | 2782 | 3040 |

[1] Grain yields are presented at the moisture of 15%.

Table 53. Mean Zn concentration of barley grains and straw in three 3-year field experiments in which different Zn fertilizers were applied at the rate of 5.4 kg ha$^{-1}$ (4.8 kg ha$^{-1}$ in NPK 18-3-12).[1]

| Treatment | Zn concentration (mg kg$^{-1}$) in yield obtained from | | |
|---|---|---|---|
| | Clay | Mull | Fine sand |
| | ---------------- | Grain | ---------------- |
| Control | 29.3$^{b}$ | 39.4$^{b}$ | 17.6$^{b}$ |
| $ZnSO_4$[2] | 33.3$^{a}$ | 39.4$^{b}$ | 18.3$^{b}$ |
| 'Sinkkilannos'[2] | 33.8$^{a}$ | 40.3$^{b}$ | 18.6$^{b}$ |
| $Na_2Zn$-EDTA in soil[3] | 32.9$^{ab}$ | 39.2$^{b}$ | 18.2$^{b}$ |
| NPK 18-3-12[3] | 34.2$^{a}$ | 39.6$^{b}$ | 19.1$^{ab}$ |
| Coated NPK I[3] | 34.5$^{a}$ | 39.6$^{b}$ | 16.5$^{b}$ |
| $Na_2Zn$-EDTA, foliar[3] | 33.6$^{a}$ | 43.1$^{a}$ | 22.1$^{a}$ |
| $HSD_{0.05}$ | 4.0 | 2.9 | 3.5 |
| F (treatments) | 3.504$^{**}$ | 4.086$^{**}$ | 4.568$^{***}$ |
| F (years) | 37.251$^{***}$ | 10.783$^{***}$ | 2.849$^{n.s.}$ |
| | ---------------- | Straw | ---------------- |
| Control | 11.0$^{b}$ | 17.9$^{b}$ | 5.6$^{b}$ |
| $ZnSO_4$[2] | 14.5$^{ab}$ | 15.8$^{b}$ | 6.8$^{ab}$ |
| 'Sinkkilannos'[2] | 12.9$^{ab}$ | 17.6$^{b}$ | 6.2$^{b}$ |
| $Na_2Zn$-EDTA in soil[3] | 12.9$^{ab}$ | 18.7$^{b}$ | 6.0$^{b}$ |
| NPK 18-3-12[3] | 15.2$^{a}$ | 18.7$^{b}$ | 7.1$^{ab}$ |
| Coated NPK I[3] | 16.0$^{a}$ | 17.5$^{b}$ | 6.2$^{b}$ |
| $Na_2Zn$-EDTA, foliar[3] | 16.6$^{a}$ | 25.9$^{a}$ | 9.8$^{a}$ |
| $HSD_{0.05}$ | 4.1 | 6.1 | 3.3 |
| F (treatments) | 4.189$^{**}$ | 5.189$^{***}$ | 3.425$^{**}$ |
| F (years) | 7.344$^{***}$ | 71.063$^{***}$ | 7.194$^{***}$ |

[1] Results of grain and straw were tested separately in each soil.

[2] Applied only at the beginning of the experiment.

[3] Applied each year at the rate of 1.8 kg Zn ha$^{-1}$ (1.6 kg ha$^{-1}$ in NPK 18-3-12).

## 5.3 Comparison of Zn fertilizers, Zn rates and application practices with barley

### 5.3.1 Different fertilizers as Zn sources for barley

The growth of barley was ample in 1990 and 1991, but in 1992 the yields were reduced in clay by the drought (Table 52). In none of the experiments were grain or straw yields affected by Zn fertilization.

Zinc concentration of grain and straw (Table 53) was the highest in mull which had the lowest pH and highest content of $Zn_{Ac}$. Inversely, the lowest concentrations occurred in barley grown in fine sand which had the highest pH and was poorest in $Zn_{Ac}$. Zinc concentration of grain was, with few exceptions, at least twice the Zn concentration of the straw. Foliar application of $Na_2Zn$-EDTA elevated Zn concentration of grain and straw significantly in all experiments. The increase in Zn concentration of grain was 4.3, 3.7 and 4.5 mg kg$^{-1}$ in clay, mull and fine sand, respectively. In mull and fine sand, none of the soil-applied Zn fertilizers affected Zn concentration of grain or straw. On the contrary, in clay all soil-applied Zn fertilizers, except $Na_2Zn$-EDTA mixed in the soil, elevated Zn concentration of the grain and the two Zn-containing NPK fertilizers increased Zn concentration of the straw. No systematic difference could be detected in the effect of Zn fertilizers applied in the soil annually and that applied only at the beginning of the experiment. It should be pointed out that the Zn concentration of the crop did not correlate with dry matter yield. For example, in clay the highest yield in 1991 and the lowest one in 1992 had similar Zn concentrations in grain (mean of all plots 36.1

and 34.2 mg kg$^{-1}$ in 1991 and 1992, respectively) and straw (12.4 and 14.4 mg kg$^{-1}$, respectively).

In the three years, Zn concentration of grain of the control plots varied within a narrow range (3 mg kg$^{-1}$ in clay and mull, 1 mg kg$^{-1}$ in fine sand). In clay there was substantial annual variation in Zn concentration of grain in the plots fertilized with Zn. In the first experimental year, Zn concentration was below 30 mg kg$^{-1}$ in all treatments, while in the two following years the average concentrations of the different treatments ranged from 32 to 38 mg kg$^{-1}$. The annual variation of straw Zn concentration was by far the greatest in mull where the means were 27.4, 11.6 and 14.2 mg kg$^{-1}$ in 1990, 1991 and 1992, respectively, in plots other than those of $Na_2Zn$-EDTA application. In clay and fine sand the annual variation in Zn concentration of straw was less marked.

The mean annual Zn uptake by barley grains was 89, 212 and 94 g ha$^{-1}$ in the control plots of clay, mull and fine sand, respectively. In clay, all Zn fertilizers slightly increased Zn uptake but only the Coated NPK I gave rise to a significant increase (24 g ha$^{-1}$, +27%). In fine sand, foliar application of $Na_2Zn$-EDTA elevated Zn uptake significantly (by 23 g ha$^{-1}$, +24%); utilization of foliar-applied Zn in grain was 1.3%, 0.6% and 0.8% in clay, mull and fine sand, respectively. Mean annual Zn uptake by the straw in the control plots was 15, 42 and 17 g ha$^{-1}$ in clay, mull and fine sand, respectively. Foliar application of $Na_2Zn$-EDTA increased the quantity of Zn harvested in the straw by 12, 21 and 18 g ha$^{-1}$ in clay, mull and fine sand, respectively, corresponding to 0.7 - 1.1% of the foliar-applied Zn.

### 5.3.2 Plant Zn concentration as affected by different Zn rates

Zinc application of 15 or 30 kg Zn ha$^{-1}$ did not affect the dry matter yields at any growth stage, and only the means of the dry matter produced at different growth stages are presented (Table 54). There was a decreasing trend in Zn concentration of vegetative plant material in the course of the growing season (Table 55). In 1991, Zn concentrations in the samples taken at the Feekes 2 and 5 growth stages were higher than in the vegetative parts of the plants at later growth stages in both soils. In 1992, the samples taken at Feekes 2 growth stage had a significantly higher Zn concentration than the vegetative parts of the later growth stages. The higher Zn concentration in grain, as compared to that of straw, suggests an effective translocation of Zn from the vegetative parts. The phenomenon was pronounced in fine sand where Zn concentration of the straw was extremely low in 1992. Even though $Zn_{Ac}$ was of the same magnitude in both soils, Zn concentration of barley at any growth stage was higher in clay soil than in fine sand which had a higher pH.

In clay, Zn application elevated Zn concentration of barley only in the first experimental year (F = 12.503$^{***}$) and showed no residual effect in the second year. In fine sand where Zn application of 5.4 kg ha$^{-1}$ to the soil (see Section 5.3.1) did not affect Zn concentration of barley, the higher rates in the present experiment had a significant effect in the first year (F = 19.820$^{***}$) and there was an increase in plant Zn concentration (F = 4.107$^{**}$)

Table 54. Dry matter yields (kg ha$^{-1}$) produced by barley at different growth stages in two field experiments.

| Soil and year | Growth stage | | | | |
|---|---|---|---|---|---|
| | Feekes 2 | Feekes 5 | Feekes 10.5 | Grain[1] | Straw[1] |
| Clay: | | | | | |
| 1991 | 655 | 3579 | 5419 | - | - |
| 1992 | 587 | 1201 | 3113 | 2346 | 1757 |
| Fine sand: | | | | | |
| 1991 | 1942 | 4399 | 8146 | 5483 | 4814 |
| 1992 | 1012 | 3058 | 7420 | 5861 | 4391 |

[1] The grain and straw samples of 1991 from the experiment on the clay soil were destroyed by fire.

Table 55. Zinc concentration and uptake of barley at different growth stages in two field experiments. I, II and III refer to the plant samples taken at Feekes 2, 5 and 10.5 growth stages, respectively.[1]

| Soil and year | Zn application, kg ha$^{-1}$ | Zn (mg kg$^{-1}$) at various growth stages | | | | | Zn uptake (g ha$^{-1}$) at maturity[2] |
|---|---|---|---|---|---|---|---|
| | | I | II | III | Grain | Straw | |
| Clay 1991 | 0 | 37.8$^{b}$ | 31.8$^{b}$ | 18.3 | - | - | 106[2] |
| | 15 | 52.9$^{a}$ | 49.0$^{ab}$ | 25.0 | - | - | 132[2] |
| | 30 | 58.3$^{a}$ | 53.3$^{a}$ | 25.3 | - | - | 139[2] |
| | HSD$_{0.05}$ | 11.8 | 20.9 | 8.3 | | | 51 |
| Clay 1992 | 0 | 29.2 | 23.3 | 21.6 | 32.0 | 14.1 | 98 |
| | 15 | 27.7 | 23.8 | 21.3 | 36.8 | 15.9 | 110 |
| | 30 | 28.3 | 24.5 | 21.2 | 36.0 | 16.6 | 118 |
| | HSD$_{0.05}$ | 16.0 | 5.0 | 4.8 | 5.6 | 6.0 | 61 |
| Fine sand 1991 | 0 | 27.4$^{b}$ | 20.3 | 8.1 | 14.6$^{b}$ | 4.7 | 101$^{b}$ |
| | 15 | 31.9$^{ab}$ | 37.0 | 10.5 | 19.6$^{a}$ | 8.1 | 142$^{ab}$ |
| | 30 | 35.6$^{a}$ | 43.5 | 11.3 | 21.8$^{a}$ | 11.4 | 185$^{a}$ |
| | HSD$_{0.05}$ | 5.1 | 40.3 | 3.5 | 4.6 | 7.8 | 54 |
| Fine sand 1992 | 0 | 21.9 | 15.5 | 10.6 | 16.9 | 2.6 | 113 |
| | 15 | 22.5 | 16.7 | 13.0 | 18.1 | 3.2 | 118 |
| | 30 | 22.9 | 18.3 | 13.4 | 19.9 | 3.7 | 128 |
| | HSD$_{0.05}$ | 7.0 | 3.7 | 6.0 | 8.0 | 1.7 | 24 |

[1] Zinc concentration and uptake were tested separately in each soil, each year and growth stage.

[2] In 1991, Zn uptake in the clay soils refers to the sampling at Feekes 10.5 growth stage.

also in the second year. In neither of the soils did Zn concentration of the plants at Zn rate 15 kg ha$^{-1}$ differ from that at Zn rate 30 kg ha$^{-1}$. The utilization of applied Zn was extremely low, 0.2 - 0.3%. When the plant Zn concentrations were compared separately at each sampling (Table 55), the differences between the Zn rates were not always statistically significant even in the first year, owing to large variation in the Zn concentration of plants fertilized with Zn. The influence of Zn application on Zn concentration of barley was greater in the early growth stages than later in the growing season (Feekes 10.5), reflecting the accumulation of dry matter and suggesting that Zn was taken up at the early part of the growing season.

Soil analyses at the end of the experiments showed that the effect of the application of high rates of $ZnSO_4$ on soil Zn$_{Ac}$ was rather small and statistically insignificant both in clay ($F = 1.554^{n.s.}$) and in fine sand ($F = 2.298^{n.s.}$). The means of Zn$_{Ac}$ (mg dm$^{-3}$) at the different levels of added Zn, tested separately in clay and fine sand, were as follows:

| Zn, kg ha$^{-1}$ | Clay | Fine sand |
|---|---|---|
| 0 | 3.5 | 1.9 |
| 15 | 2.9 | 2.5 |
| 30 | 6.0 | 3.8 |

## 5.4 Discussion

The status of Zn$_{Ac}$ of the mineral soils where the field experiments were carried out was far below the average Zn$_{Ac}$ of cultivated soils of Finland (SIPPOLA and TARES 1978 and unpublished data of Soil Analysis Service Ltd.). In spite of the rather low Zn$_{Ac}$ concentration, timothy did not show any signs of Zn deficiency and had a Zn concentration similar to the mean value in samples collected from various parts of Finland (KÄHÄRI and NISSINEN 1978). Also Zn concentration of barley grains was well beyond the deficiency level in clay and especially in mull where the abundant Zn$_{Ac}$ reserves in the subsoil may have contributed to the high Zn concentration in barley grains. The sufficient supply of Zn from soil reserves explains the absent response of timothy and barley yields to added Zn. In the control plots of fine sand, Zn concentration of barley grains was below 20 mg kg$^{-1}$ but the growth was probably not limited by Zn deficiency because the yield was not increased by Zn applications. Moreover, the higher Zn concentration earlier in the growing season suggests that Zn supply for barley was at a very sufficient level during the intensive growth also in the fine sand.

The efficiency of $ZnSO_4$ to increase Zn concentration of timothy was similar to that observed in other field experiments carried out with forage grasses in acid mineral soils. For example, in two mineral soils (pH 5.6 and 5.8) in New Zealand (McLaren et al. 1991) an application of 4.6 kg ha$^{-1}$ as $ZnSO_4$ increased Zn concentration of herbage by 8.9 mg kg$^{-1}$. In the experiments of Jaakkola and Vogt (1978) in Finland the increase of Zn concentration of hay in the first experimental year corresponded to 1.3 mg kg$^{-1}$ for each kilogram of Zn applied, which agrees with the results of the present study. The response of plant Zn concentration is, however, strongly dependent on soil characteristics. The studies of Urvas (1986, 1992) on Zn fertilization of timothy show that the efficiency of fertilizer Zn can be much higher in strongly acid peat soil, and even a small application of Zn (0.55 kg ha$^{-1}$) may elevate plant Zn concentration significantly.

The low or absent response of Zn concentration of barley grains to 4.8 or 5.4 kg Zn ha$^{-1}$ applied to soil is in agreement with other Finnish field experiments where small rates (1.75 kg ha$^{-1}$) of Zn have been given (Jaakkola and Vogt 1978, Syvälahti and Korkman 1978). A higher Zn application (15 and 30 kg ha$^{-1}$) elevated Zn concentration of barley significantly in fine sand, but even then Zn concentration of grain remained around 20 mg kg$^{-1}$, reflecting the poor availability of Zn in neutral soil. However, the response was of the same level as has been observed in the neutral and slightly acid mineral soils of Norway and Canada where 50 and 20 kg Zn ha$^{-1}$, respectively, were applied to barley (Myhr 1988, Gupta 1989).

The drought in 1992 may partly explain the small residual effect of the high Zn rates (15 and 30 kg ha$^{-1}$) on barley. In the first year of the experiment (1991), there was plenty of rain in May and June, and the roots of barley were probably active in the plough layer, resulting in the observed response to applied Zn. Owing to the drought in the second year (1992), the plough layer was dry and plant roots were able to take up nutrients from that part of the soil less effectively. In 1992, the roots probably grew to a greater extent into the deeper soil layers where they were no more in contact with the applied Zn. This hypothesis is supported by the findings made in Canada by Dwyer et al. (1988) according to which the maximum rooting depth of barley and the quantity of roots in the deeper soil layers increase when there is shortage of water in the surface soil. The hypothesis does not, however, explain why there was some response by barley to soil-applied Zn also in 1992 in clay soil in the other experiment where the different Zn fertilizers were tested (Section 5.3.1).

Granulation and spot-placement commonly decrease the agronomic efficiency of $ZnSO_4$ added to neutral and calcareous soils (Brown and Krantz 1966, Allen and Terman 1967, Mortvedt and Giordano 1969a). However, in the present study, carried out in acid soils, the granulated 'Sinkkilannos' mixed into the soil elevated plant Zn concentration at the same rate as did $ZnSO_4$. In the granulated product, $ZnSO_4$ is incorporated in gypsum, and Zn cations seem to be readily released from the matrix into the soil solution. Also the top-dressed 'Sinkkilannos' increased Zn concentration of grass in the field and pot experiments at least as effectively as did the fertilizer mixed in the soil. Availability of Zn in granular fertilizers added onto the soil surface requires that Zn be dissolved from the granule and further to move into the soil and to get into contact with active plant roots. The rains in the early summer of 1991 right after broadcasting the fertilizers or the daily watering in the pot experiment probably resulted in an effective disintegration of the granules of 'Sinkkilannos' and enhanced the penetration of Zn into the root zone. In a short-term pot experiment, top-dressing retarded the fertilizer effect of 'Sinkkilannos', but in the field there was evidently enough time for the surface-applied granules of 'Sinkkilannos' to dissolve before the first harvest, and consequently there was no difference between the application methods.

The negligible agronomic efficiency of Zn contained in NPK fertilizers cannot solely be attributed to the granular form of the fertilizers because the granular 'Sinkkilannos' did elevate plant Zn concentration in the very same experiments. The low efficiency is rather due to the chemical reactions occurring in the fertilizer between Zn and the other components. During the manufacturing process of the present NPK fertilizers the acid orthophosphate slurry is ammoniated (KIVIOJA 1987), resulting in an elevation of pH. The accompanying decrease in the water-solubility and plant-availability of Zn added to the fertilizer as $ZnSO_4$ (MORTVEDT 1968, MORTVEDT and GIORDANO 1969b) is due to the precipitation of insoluble Zn compounds (e.g. Zn phosphates, Zn hydroxides) in the fertilizer grain (TERMAN et al. 1966, ALLEN and TERMAN 1967, MORTVEDT and GIORDANO 1969a). According to MORTVEDT (1968), above pH 5 the availability of Zn in ammoniated orthophosphate fertilizers is less than 20% of what is observed when $ZnSO_4$ is applied separately or incorporated in unammoniated (pH 3) orthophosphate fertilizer. The pH of the present NPK fertilizers ranged between 5.0 and 5.4, suggesting a low water-solubility of Zn in the fertilizer. The present field and pot experiments showed that the sparingly soluble Zn compounds are not necessarily dissolved during short-term experiments even in acid soils, resulting in an inconsistent fertilizer effect. Because the NPK fertilizers coated with $ZnSO_4$ had an equally low availability of Zn, it is likely that ionic activities also in the vicinity of the fertilizer granule exceed the solubility products of sparingly soluble Zn compounds.

The current results disagree with those of SILLANPÄÄ (1990) who applied Zn-containing NPK fertilizers to barley in ten field experiments in Finland. In those experiments, high Zn rate (11.6 kg $ha^{-1}$) and low soil pH ($CaCl_2$-pH 4.2 - 5.5) probably facilitated the mean increase of 8 mg $kg^{-1}$ in grain Zn concentration. Moreover, in the fertilizers of SILLANPÄÄ, part of Zn (2 kg $ha^{-1}$) had been added as Zn-EDTA. According to MORTVEDT and GIORDANO (1969a), the plant-availability of Zn added as Zn-EDTA in macronutrient fertilizers is not reduced as much as that of $ZnSO_4$.

Increased Zn concentration of barley straw by foliar sprays of $Na_2Zn$-EDTA can at least partly be caused by the adsorption of foliar-applied Zn on the surfaces of plant leaves. Therefore the increased Zn concentration of straw by this treatment must not be considered an indication of high fertilizer efficiency. Because $Na_2Zn$-EDTA was sprayed at an early growth stage before there was any shoot or ear in the crop, the increase of grain Zn concentration can be attributed to the introduction of applied Zn into the physiological reactions of the plant. However, soil pH strongly dominated the grain Zn concentration also in this treatment. In some studies application of Zn in a chelated form to neutral or calcareous soils has been at least twice as effective as application of $ZnSO_4$ (MORTVEDT and GIORDANO 1969a, BOAWN 1973, HERGERT et al. 1984). The difference between the two sources has not been significant in acid soils (HERGERT et al. 1984) and not always even in neutral soils (SCHNAPPINGER et al. 1972). Also in the present study, the soil-applied $Na_2Zn$-EDTA failed to increase plant Zn concentration, which shows that the observed effect of foliar application of $Na_2Zn$-EDTA can be attributed primarily to the application method rather than to the chelated form of Zn. This conclusion is supported indirectly by the results of PATERSON et al. (1991) who elevated Zn concentration of barley grains with foliar sprays of $ZnSO_4$, while the application of $ZnSO_4$ to the soil was without effect. Further, it needs to be pointed out that foliar application of $Na_2Zn$-EDTA was the only treatment increasing Zn concentration of barley grain in fine sand where insufficient Zn supply to barley may have been approached.

# 6 GENERAL DISCUSSION AND CONCLUSIONS

In spite of generally sufficient Zn reserves for plant growth the present material contained a few soils poor in Zn. Even though worldwide zinc deficiency is commonly connected to calcareous soils, low plant-availability of Zn may occur also in slightly acid and neutral mineral soils of Finland. Moreover, the soil testing method applied in Finland (AAAc-EDTA, pH 4.65) seems to overestimate the Zn supply to plants in these soils. However, the soils with the scarcest reserves were among Carex peat and Ligno Carex peat soils, which were poor in Zn also according to international comparisons. Owing to the small number of organogenic soils in the present material, it is not possible to draw conclusions on the geographic occurrence of Zn deficiency in Finland even though cultivated peat soils are the most common in the northern parts of the country. Peat soils constitute less than 10% of the cultivated area of Finland (KURKI 1982), but they are not all poor in Zn. Only 1.5% of samples analyzed for $Zn_{Ac}$ in soil testing in 1986 - 1988 contained $Zn_{Ac}$ less than 1.0 mg $dm^{-3}$ (unpublished data of Soil Analysis Service Ltd.) and were rated poor in Zn according to the current interpretation (Viljavuuspalvelu 1992). The present results as well as those of URVAS (1985, 1990) suggest that yield response to applied Zn is hardly observed in short-term experiments even in these soils. Consequently, a $Zn_{Ac}$ concentration below 1.0 mg $dm^{-3}$ in the soil does not necessarily indicate insufficient Zn supply to the crop. In accordance with the results of soil analyses and pot experiments, yield increases owing to Zn fertilization have not been detected in the field in Finland. Therefore, Zn fertilization in the great majority of cultivated soils of Finland is justified by the possible elevation of Zn concentration of the crop.

It seems feasible that in the poorest peat soils Zn reserves can be exhausted over time in intensive grassland cultivation. In the studies of SILLANPÄÄ and RINNE (1975) the quantity of Zn harvested in three cuttings of silage grass amounted to 280 g $ha^{-1}$ at the annual N fertilizer level of 300 kg $ha^{-1}$. At this rate, the uptake of Zn in 10 years amounts to 2.8 kg $ha^{-1}$, or 1.4 mg $dm^{-3}$ in a 20-cm layer. This corresponds to the reserves of secondary Zn in the poorest peat soils. Low pH of most peat soils further contributes to the high availability and effective utilization of soil Zn. The above calculation supports the recent finding by ERVIÖ et al. (1990) of the decline of $Zn_{Ac}$ in the cultivated soils of northern Finland.

Soil characteristics strongly affect the response of plant Zn concentration to Zn fertilization. In strongly acid soils Zn application elevates Zn concentration of grass, also facilitating the maintenance of sufficient supply of Zn to plants in peat soils under intensive grassland cultivation. But even high rates of Zn to slightly acid and neutral soils elevate the Zn content of the crop less effectively even if the soils were poor in $Zn_{Ac}$. In those soils, foliar sprays increase plant Zn concentration more effectively. In order to avoid applications of Zn to soil with no fertilizer effect, both soil pH and $Zn_{Ac}$ need to be taken into consideration when Zn fertilizer recommendations are given. Owing to the inconsistent effect of Zn-containing NPK fertilizers on Zn concentration of crop, the use of separate Zn fertilizers should be preferred.

The reserves of secondary Zn (10 - 20 kg $ha^{-1}$ in a 20-cm deep plough layer) were of the same magnitude as Zn fertilizer recommendations (5 - 20 kg Zn $ha^{-1}$, Viljavuuspalvelu 1992). The utilization of added Zn is commonly far below 5% and therefore the recommended application substantially increases the reserves of secondary Zn in soil. The low utilization is caused by the strong adsorption of Zn in the soil and not by the reluctance of the plants to take up Zn. This conclusion can be drawn on the basis of the results of pot experiments where high Zn concentration in the grass occurred when Zn was added to an unhumified Sphagnum peat and to strongly acid coarse mineral soils of obviously low Zn adsorption capacities.

The large variations of dry matter yield of timothy and barley in the field and ryegrass in the pot experiment were not reflected as a negative correlation between the size of the yield and the Zn concentration. This suggests that Zn uptake by the plants is probably not limited by the capacity factor (quantity of plant-available Zn in soil) but rather by intensity (Zn concentration in soil solution). The adsorbed Zn fraction is much larger than the dissolved one, resulting in a strong buffering of soil Zn concentration (ELGAWHARY et al. 1970). As Zn is taken up by plant roots from the soil solution, the decrease of concentration is readily replenished from the adsorbed fraction, provided the soil is not poor in Zn. It can therefore be concluded that plant uptake does not markedly reduce the Zn concentration of soil solution. Consequently, the Zn concentration of plant tissue grown in a given soil can be the same regardless of the size of the yield.

The average Zn concentration of cereal crops grown in Finland is at the same level as in other countries of temperate climates. In Norway, in Prince Edward Island, Canada and in southwestern Sweden, mean Zn concentrations of barley and oats have ranged between 28 and 48 mg Zn kg$^{-1}$ (FRØSLIE et al. 1983, WINTER and GUPTA 1987, ERIKSSON et al. 1990). Also timothy grown in Finland has on average at least the same Zn concentration as has been reported elsewhere (METSON et al. 1979, WINTER and GUPTA 1983, BOILA et al. 1985). Owing to the great variation in Zn concentrations of timothy and barley (JAAKKOLA and VOGT 1978, KÄHÄRI and NISSINEN 1978), it is likely that in areas of poor soil Zn, locally produced fodder may contain much less Zn than is the national average.

The level of dietary Zn (50 mg kg$^{-1}$) recommended for cattle in the Nordic countries (NJF 1975, SALO et al. 1990) appears to be high as compared to recommendations given elsewhere. In the USA, a concentration of 40 mg kg$^{-1}$ is recommended for dairy cattle (NRC 1978) and 20 - 30 mg kg$^{-1}$ for beef cattle (NRC 1976). In New Zealand, a recommendation of 15 - 25 mg kg$^{-1}$ for grazing livestock is given (TOWERS and GRACE 1983). In a compilation prepared in England (ARC 1980) 30 mg kg$^{-1}$ was regarded as the sufficient level in experimental conditions, but it was also pointed out that in studies made in the field higher concentrations have occasionally been of advantage. The average Zn concentration of timothy and barley occurring in Finland would thus be considered sufficient for cattle in most countries, and the evidence of a general need of a higher Zn level in fodder is not conclusive. Zinc concentration of timothy and barley at least in mineral soils does not reach the level recommended in Finland (50 mg kg$^{-1}$) without excessive Zn fertilization. Because high Zn rates result in an undue accumulation of Zn in the soil, it seems needless to aim at Zn concentrations beyond the current average level in the crop by increased Zn fertilization. The recommended Zn level in the diet should still be reached by direct supplementation into the fodder.

Besides soil Zn status, pH and Zn fertilization, also other factors affect the actual Zn concentration in fodder of domestic animals. Clover and other dicotyledons have a higher Zn concentration than gramineous fodder crops (REAY and MARSH 1976, YLÄRANTA and SILLANPÄÄ 1984, MCLAREN et al. 1991). Nitrogen fertilization has also been shown to elevate plant Zn concentration, probably owing to the decrease of pH (BOAWN et al. 1960, TERMAN et al. 1966). For example, in field experiments by RINNE at al. (1974) and SILLANPÄÄ and RINNE (1975) Zn concentration in the grass increased from 30 mg kg$^{-1}$ to 39 mg kg$^{-1}$ when the N fertilization was increased from nil to 600 kg ha$^{-1}$. On the other hand, the experiments of ETTALA and KOSSILA (1979, 1980) showed that on average 34% of Zn in silage grass was lost during the ensiling. These examples propose that the choice of crop as well as different agricultural practices other than Zn fertilization can affect the Zn content of the fodder at least as much as was commonly observed to be the effect of Zn application in the current field experiments with timothy.

Also excessive Zn concentration in plants need to be considered. The highest concentration in ryegrass grown without added Zn, occurring in the soil of Harjavalta, exceeded 100 mg kg$^{-1}$ and was of the same magnitude as was reported in grass grown in a Zn-contaminated harbor dredge in the Netherlands (SMILDE et al. 1982). High concentrations of Zn can thus occur locally in the neighborhood of industry also in Finland. The high concentration of the grass grown in the soil of Harjavalta also shows that Zn accumulated in the soil probably as a result of atmospheric deposition was plant-available. This conclusion is corroborated by findings showing that the bulk of Zn in the deposition both in urban

(Gatz and Chu 1984) and rural (Lindberg and Harriss 1981) environments is water-soluble. Various plants may exhibit symptoms of Zn toxicity when the Zn concentration of the plant exceeds 120 - 220 mg kg$^{-1}$ (Beckett and Davis 1977, Sauerbeck 1982) but according to the present study, as much as 500 - 700 mg Zn kg$^{-1}$ was tolerated by ryegrass with only slight adverse effects. This result agrees with those by Gerzabeck and Schaffer (1989) according to whom the toxicity limit in ryegrass was higher than 400 mg kg$^{-1}$. Tolerance to large doses of Zn by domestic animals appears to be even greater (Miller et al. 1965, Ott et al. 1966). According to Ott et al. (1966), toxicity symptoms occurred only when the dietary Zn concentration exceeded 900 mg kg$^{-1}$.

The highest Zn fertilization rate currently recommended in Finland is 20 kg ha$^{-1}$ (Viljavuuspalvelu 1992), corresponding to 10 mg dm$^{-3}$ in a 20-cm thick plough layer. The present pot experiments and field experiments by Urvas (1992) showed that at least in strongly acid coarse mineral soils and peat soils Zn concentration of grass can be elevated beyond the recommended level (50 mg kg$^{-1}$) by application of maximum recommended Zn doses. However, in unpolluted cultivated soils Zn concentration of grass fertilized at that Zn rate is likely to remain below 100 mg kg$^{-1}$. It seems thus evident that a Zn concentration toxic to plants or animals cannot be reached when field crops are fertilized with the recommended rates of Zn.

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## SELOSTUS

# Viljelymaan sinkkivarojen ja lannoitteena annetun sinkin käyttökelpoisuus kasveille

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Suomen viljelymaiden Zn-varojen suuruutta, liukoisuutta ja käyttökelpoisuutta kasveille tutkittiin maa-analyysein ja astiakokein. Erilaisten Zn-lannoitteiden vaikutusta raiheinän, timotein ja ohran satoon ja Zn-pitoisuuteen tutkittiin astia- ja kenttäkokein. Sinkin kokonaispitoisuus ($Zn_{tot}$) 106 pintamaanäytteen aineistossa oli 10 - 202 mg $kg^{-1}$. Kivennäismaissa $Zn_{tot}$ oli positiivisessa korrelaatiossa savespitoisuuden kanssa (r = $0,81^{***}$) ja eloperäisissä maissa $Zn_{tot}$ korreloi negatiivisesti maan orgaanisen hiilen pitoisuuden kanssa (r = $-0,53^{**}$). Useiden savimaiden $Zn_{tot}$ oli yli 150 mg $kg^{-1}$, kun taas muutamien runsaimmin orgaanista hiiltä sisältävien turvemaiden $Zn_{tot}$-varat olivat jopa alle 10 mg $kg^{-1}$. Vesiliukoista ja vaihtuvaa sinkkiä ($Zn_{ex}$) uutettiin 0,5 M $MgCl_2$-liuoksella. $Zn_{ex}$ korreloi negatiivisesti maan pH:n kanssa. Pääosin orgaanisen aineksen sitomaksi oletettua sinkkiä uutettiin 0,1 M $K_4P_2O_7$-liuoksella ($Zn_{py}$) ja sen jälkeen samasta näytteestä 0,05 M oksalaattiliuoksella (pH 2,9) ($Zn_{ox}$) Fe- ja Al-oksidien sitomaksi arveltua sinkiä. Summan $Zn_{py}$ + $Zn_{ox}$ katsottiin kuvastavan maan sekundaaristen Zn-varojen suuruutta vastakohtana rapautumattomien mineraalien sisältämälle sinkille. Sekundaarisen sinkin määrä (mediaani 5,9 mg $dm^{-3}$, n = 106) oli kaikissa maalajeissa samaa suuruusluokkaa. Sen sijaan sekundaarisen sinkin osuus (%) $Zn_{tot}$:sta oli pienin savimaissa (mediaani 5 %) ja suurin turvemaissa (mediaani 49 %), mikä kuvastaa maan $Zn_{tot}$:n määrissä olevia eroja. Maan sinkkiä uutettiin myös viljavuusanalyysissä käytettävällä happamalla ammoniumasetaatti - EDTA -liuoksella (0,5 M $CH_3COOH$, 0,5 M $CH_3COONH_4$, 0,02 M $Na_2$-EDTA, pH 4,65). Menetelmällä saadut tulokset ($Zn_{Ac}$, mediaani 2,9 mg $dm^{-3}$, vaihteluväli 0,6 - 29,9 mg $dm^{-3}$, n = 106) olivat kiinteässä vuorosuhteessa $Zn_{py}$:n kanssa. Voidaankin arvella $Zn_{Ac}$:n sisältävän vesiliukoista, vaihtuvaa, orgaanisen aineksen ja Fe- ja Al-oksidien sitomaa sinkkiä. $Zn_{Ac}$:n pitoisuus oli muokkauskerroksessa lähes poikkeuksetta suurempi kuin jankossa.

Astiakokeessa, jossa kasvatettiin neljä satoa raiheinää, ei maan Zn-varoja saatu ehdytetyiksi, vaikka raiheinän sinkinsaanti vähenikin muutamista turvemaista kokeen loppua kohti. Kasvit ottivat 2 - 68 % (mediaani 26 %, n = 107) sekundaarisen sinkin ($Zn_{py}$ + $Zn_{ox}$) varoista. Suhteellisesti runsaimmin Zn-varat ehtyivät happamista, niukasti sinkkiä sisältävistä turvemaista ja muutamista karkeimmista kivennäismaista. Suhteellisesti vähiten Zn-varat ehtyivät runsaasti $Zn_{Ac}$ sisältävistä maista sekä niukemmin $Zn_{Ac}$ sisältävistä neutraaleista maista. $Zn_{Ac}$ kuvasti melko hyvin raiheinän Zn-ottoa, joskin menetelmä näyttää hieman yliarvioivan kasvin sinkinsaantia maista, joissa oli kesimääräistä korkeampi pH. Kivennäismaissa pH sääteli selvimmin sitä, kuinka tehokkaasti sinkkisulfaattina maahan lisätty Zn (10 mg $dm^{-3}$) kohotti raiheinän Zn-pitoisuutta. Maan pH:n kohotessa Zn-lannoituksen teho heikkeni. $Zn_{Ac}$:n niukkuus maassa lisäsi Zn-lannoituksen tehoa. Zn-lannoitus kohotti raiheinän Zn-pitoisuutta eniten niissä eloperäisissä maissa, joiden Zn-varoilla oli taipumus ehtyä suhteellisesti voimakkaimmin.

Sinkkilannoituksen vaikutusta timotein Zn-pitoisuuteen tutkittiin kahdessa kaksivuotisessa kenttäkokeessa savi- ja hietamaalla. Ilman Zn-lannoitusta kasvaneen timoitein keskimääräinen Zn-pitoisuus oli savimaalla 28 mg $kg^{-1}$ ja hietamaalla 35 mg $kg^{-1}$. Sinkkisulfaattina tai rakeisen kipsin ja sinkkisulfaatin seoksena kokeen alussa annettu 3 ja 6 kg Zn $ha^{-1}$ lannoitus nosti timotein sinkkipitoisuutta 3 ja 7 mg $kg^{-1}$. Kun näitä lannoitteita levitettiin nurmen pintaan ensimmäisen sadonkorjuuvuoden keväällä, oli vaikutus sama kuin nurmen kylvön yhteydessä maahan muokatulla lannoituksella. Nurmen pintaan levitettyjen sinkkiä sisältävien NPK-lannoitteiden Zn-lannoitusvaikutus oli vähäinen. Kolmivuotisissa kenttäkokeissa ilman Zn-lannoitusta viljellyn ohran jyvien Zn-pitoisuus oli savimaalla 29 mg $kg^{-1}$, hietamaalla 18 mg $kg^{-1}$ ja multamaalla 39 mg $kg^{-1}$. Zn-lannoitus (5,4 kg $ha^{-1}$ kerralla kokeen alussa tai yhteensä 4,8 - 5,4 kg $ha^{-1}$ kolmessa osassa) kohotti jyvän Zn-pitoisuutta savimaalla (pH 5,8) 5 mg $kg^{-1}$, mutta sillä ei ollut vaikutusta hietamaalla (pH 7,1) eikä multamaalla (pH 5,3), jonka jankko sisälsi runsaasti sinkkiä ($Zn_{Ac}$ 17,2 mg $dm^{-3}$). Lehtilannoitteena annettu $Na_2Zn$-EDTA (1,8 kg Zn $ha^{-1}$ vuosittain) kohotti jyvän Zn-pitoisuutta kaikissa kokeissa 3 - 4 mg $kg^{-1}$. Hietamaahan sinkkisulfaattina annettu runsaampi lannoitus (15 ja 30 kg Zn $ha^{-1}$) kohotti jyvän Zn-pitoisuutta 5 tai 7 mg $kg^{-1}$, mutta vaikutusta ei havaittu enää seuraavana vuonna, mikä osoittaa sinkin heikkoa käyttökelpoisuutta kyseisellä neutraalilla maalla. Sinkkilannoitus ei vaikuttanut timotein tai ohran sadon määrään.

Maan pH vaikuttaa ratkaisevasti sekä luontaisen että varsinkin lannoitteena annetun sinkin käyttökelpoisuuteen. Tästä syystä maan sinkkianalyysin ($Zn_{Ac}$) tulkinnassa ja lannoitussuosituksia annettaessa olisi otettava huomioon myös maan pH. Neutraaleilla mailla on turha antaa Zn-lannoitusta maahan sen vähäisen vaikutuksen takia; niillä on mieluummin käytettävä lehtilannoitusta. Happamammissa oloissa myös maahan annettu lannoitus kohottaa kasvien Zn-pitoisuutta.

Soils used in the methodological studies

| Number and location | Soil class | Particle size composition µm, % | | | Organic C % | pH |
|---|---|---|---|---|---|---|
| | | <2 | 2-20 | 20-60 | | |
| 201 Kirkkonummi | Heavy clay | 65 | 28 | 6 | 6.6 | 5.4 |
| 202 Mäntsälä | Silty clay | 54 | 31 | 5 | 4.0 | 5.6 |
| 203 Liljendahl | Silty clay | 52 | 25 | 6 | 2.5 | 5.5 |
| 204 Tarvasjoki | Silty clay | 40 | 41 | 14 | 2.5 | 5.7 |
| 205 Tammisaari | Sandy clay | 39 | 22 | 18 | 5.1 | 6.8 |
| 206 Lapinjärvi | Very fine sand | 28 | 26 | 23 | 2.7 | 5.4 |
| 207 Pälkäne | Very fine sand | 23 | 31 | 31 | 3.1 | 5.8 |
| 208 Siuntio | Very fine sand | 20 | 28 | 17 | 1.5 | 5.7 |
| 209 Helsinki | Very fine sand | 20 | 20 | 34 | 2.7 | 4.9 |
| 210 Koski Hl | Silt | 17 | 43 | 21 | 3.7 | 5.2 |
| 211 Vihti | Fine sand | 10 | 6 | 8 | 1.5 | 4.5 |
| 212 Pälkäne | Mull | 34 | 41 | 15 | 27.0 | 5.3 |
| 213 Koski Hl | Mull | 22 | 48 | 18 | 28.0 | 6.8 |

Characteristics of the soils of surface soil material. $Fe_{ox}$ and $Al_{ox}$ stand for oxalate-extractable Fe and Al, respectively.

| Number and location | Soil class | pH | Organic C % | Particle size composition µm, % | | | | $Fe_{ox}$ | $Al_{ox}$ | Bulk density |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | <2 | 2-20 | 20-60 | >60 | mmol $kg^{-1}$ | | kg $dm^{-3}$ |
| *Clay soils:* | | | | | | | | | | |
| 1 Somero | Heavy clay | 6.8 | 2.9 | 74 | 17 | 3 | 6 | 106 | 71 | 0.98 |
| 2 Somero | Heavy clay | 5.3 | 7.7 | 67 | 24 | 4 | 5 | 134 | 172 | 0.76 |
| 3 Somero | Heavy clay | 6.1 | 3.0 | 67 | 18 | 5 | 10 | 126 | 75 | 0.98 |
| 4 Kylmäkoski | Heavy clay | 5.9 | 4.7 | 66 | 19 | 9 | 6 | 93 | 141 | 0.94 |
| 5 Somero | Heavy clay | 6.4 | 2.2 | 66 | 8 | 4 | 22 | 118 | 73 | 1.03 |
| 6 Jokioinen | Heavy clay | 7.0 | 2.0 | 64 | 10 | 5 | 21 | 80 | 70 | 1.04 |
| 7 Ypäjä | Heavy clay | 6.0 | 2.3 | 63 | 22 | 6 | 9 | 100 | 55 | 1.00 |
| 8 Kirkkonummi | Gyttja clay | 5.7 | 4.1 | 58 | 34 | 5 | 3 | 76 | 124 | 0.88 |
| 9 Loimaa | Clay loam | 5.8 | 2.9 | 56 | 23 | 7 | 14 | 70 | 69 | 1.05 |
| 10 Kirkkonummi | Gyttja clay | 4.6 | 3.7 | 56 | 30 | 11 | 3 | 121 | 84 | 0.85 |
| 11 Vehkalahti | Clay loam | 6.0 | 1.9 | 55 | 24 | 13 | 8 | 87 | 57 | 1.10 |
| 12 Vihti | Gyttja clay | 5.4 | 9.5 | 51 | 41 | 7 | 1 | 79 | 133 | 0.76 |
| 13 Perniö | Silty clay | 6.7 | 3.2 | 51 | 31 | 11 | 7 | 172 | 66 | 0.88 |
| 14 Loimaa mlk | Silty clay | 5.9 | 2.4 | 49 | 44 | 3 | 4 | 92 | 69 | 1.03 |
| 16 Koski TL | Clay loam | 5.7 | 2.0 | 45 | 31 | 15 | 9 | 79 | 57 | 1.14 |
| 17 Helsinki | Clay loam | 6.4 | 3.5 | 43 | 22 | 21 | 14 | 102 | 57 | 1.05 |
| 18 Valkeala | Clay loam | 6.2 | 2.5 | 42 | 37 | 17 | 4 | 55 | 49 | 1.12 |
| 19 Valkeala | Clay loam | 6.5 | 2.4 | 42 | 36 | 18 | 4 | 60 | 47 | 1.12 |
| 20 Mustasaari | Silty clay | 5.2 | 6.1 | 40 | 43 | 14 | 3 | 166 | 96 | 0.69 |
| 21 Kuhmoinen | Clay loam | 6.4 | 3.2 | 39 | 37 | 12 | 12 | 80 | 74 | 0.85 |
| 22 Vehkalahti | Clay loam | 6.1 | 1.2 | 39 | 32 | 19 | 10 | 90 | 55 | 1.08 |
| 23 Tampere | Silty clay | 6.2 | 2.2 | 37 | 54 | 5 | 4 | 83 | 85 | 0.90 |
| 24 Valkeala | Silty clay | 5.7 | 2.6 | 35 | 31 | 14 | 20 | 69 | 57 | 1.01 |
| 25 Valkeala | Silty clay | 5.9 | 1.4 | 35 | 31 | 15 | 19 | 87 | 51 | 1.14 |
| 26 Ylihärmä | Silty clay | 5.0 | 7.0 | 32 | 45 | 18 | 5 | 144 | 86 | 0.72 |
| *Coarse mineral soils and moraines:* | | | | | | | | | | |
| 27 Vihti | Loam | 6.3 | 2.0 | 29 | 34 | 22 | 15 | 60 | 56 | 1.18 |
| 28 Korpilahti | Silt | 6.6 | 0.8 | 27 | 51 | 17 | 5 | 65 | 34 | 1.05 |
| 29 Vihti | Loam | 5.7 | 2.0 | 27 | 27 | 11 | 35 | 58 | 52 | 1.16 |
| 30 Laihia | Loam | 6.2 | 3.1 | 25 | 37 | 32 | 6 | 91 | 50 | 1.00 |
| 31 Tarvasjoki | Loam | 5.2 | 2.2 | 25 | 32 | 28 | 15 | 90 | 46 | 1.13 |
| 32 Luumäki | Loam | 6.4 | 2.4 | 24 | 45 | 19 | 12 | 59 | 33 | 1.00 |
| 33 Ylistaro | Loam | 6.3 | 2.3 | 24 | 46 | 16 | 14 | 94 | 49 | 1.01 |
| 34 Pyhäselkä | Loam | 5.0 | 2.7 | 23 | 41 | 23 | 13 | 88 | 57 | 0.94 |
| 35 Isokyrö | Silt | 6.8 | 2.1 | 23 | 52 | 21 | 4 | 128 | 36 | 1.00 |
| 36 Ylivieska | Loam | 5.8 | 2.7 | 22 | 44 | 27 | 7 | 80 | 37 | 0.97 |
| 37 Huittinen | Loam | 6.2 | 2.0 | 22 | 36 | 23 | 19 | 77 | 43 | 1.01 |
| 38 Hollola | Silt | 6.4 | 4.8 | 21 | 64 | 12 | 3 | 87 | 96 | 0.77 |
| 39 Luumäki | Silt | 6.1 | 3.1 | 20 | 50 | 19 | 11 | 57 | 26 | 0.95 |
| 40 Tervola | Loam | 4.2 | 5.3 | 16 | 45 | 27 | 12 | 210 | 29 | 0.84 |
| 41 Alavieska | Sandy moraine | 6.0 | 4.0 | 16 | 24 | 10 | 50 | 103 | 48 | 1.04 |
| 42 Maalahti | Very fine sand | 5.0 | 3.1 | 16 | 27 | 48 | 9 | 56 | 56 | 0.96 |
| 43 Vihti | Loam | 6.2 | 1.9 | 15 | 39 | 33 | 13 | 51 | 41 | 1.08 |
| 44 Lammi | Loam | 6.0 | 2.7 | 12 | 42 | 37 | 9 | 59 | 137 | 0.87 |
| 45 Alavieska | Sandy moraine | 6.2 | 3.0 | 11 | 21 | 28 | 40 | 115 | 39 | 1.07 |
| 46 Lapinlahti | Sandy moraine | 6.1 | 1.9 | 11 | 17 | 10 | 62 | 50 | 40 | 1.18 |
| 47 Sonkajärvi | Fine sand | 5.6 | 2.9 | 9 | 18 | 21 | 52 | 62 | 57 | 1.08 |
| 48 Kitee | Very fine sand | 5.9 | 2.5 | 9 | 35 | 41 | 15 | 63 | 133 | 1.03 |
| 49 Maaninka | Fine sand | 5.8 | 1.8 | 8 | 19 | 29 | 44 | 66 | 49 | 1.09 |
| 50 Sotkamo | Silt | 6.3 | 1.3 | 8 | 59 | 17 | 16 | 72 | 55 | 0.99 |
| 51 Vihti | Sandy moraine | 6.4 | 2.4 | 8 | 9 | 7 | 76 | 45 | 70 | 1.21 |
| 52 Ylivieska | Sandy moraine | 5.2 | 3.1 | 7 | 13 | 23 | 57 | 31 | 45 | 1.10 |
| 53 Siikajoki | Sandy moraine | 6.3 | 2.6 | 7 | 9 | 16 | 68 | 85 | 32 | 1.31 |
| 54 Saari | Sandy moraine | 6.4 | 3.3 | 6 | 15 | 30 | 49 | 231 | 28 | 1.14 |

| Number and location | Soil class | pH | Organic C % | Particle size composition µm, % | | | | $Fe_{ox}$ | $Al_{ox}$ | Bulk density kg $dm^{-3}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | <2 | 2-20 | 20-60 | >60 | mmol $kg^{-1}$ | | |
| 55 Liperi | Sandy moraine | 6.0 | 3.0 | 6 | 14 | 27 | 53 | 29 | 81 | 1.11 |
| 56 Joroinen | Fine sand | 6.3 | 1.7 | 6 | 15 | 16 | 63 | 39 | 64 | 1.16 |
| 57 Jyväskylä mlk | Very fine sand | 5.6 | 1.5 | 6 | 29 | 51 | 14 | 61 | 122 | 1.10 |
| 58 Lapua | Fine sand | 6.1 | 4.2 | 5 | 10 | 25 | 60 | 22 | 51 | 1.00 |
| 59 Ristiina | Sandy moraine | 5.8 | 3.2 | 5 | 12 | 17 | 66 | 47 | 109 | 1.16 |
| 60 Ristiina | Sandy moraine | 6.1 | 2.0 | 5 | 13 | 9 | 73 | 41 | 104 | 1.26 |
| 61 Hammarland | Sandy moraine | 6.9 | 0.7 | 5 | 3 | 3 | 89 | 17 | 9 | 1.43 |
| 62 Kauhava | Sandy moraine | 6.7 | 3.4 | 4 | 8 | 43 | 45 | 19 | 43 | 1.06 |
| 63 Liminka | Sandy moraine | 5.8 | 2.7 | 4 | 8 | 46 | 42 | 55 | 25 | 1.15 |
| 64 Vihti | Fine sand | 6.5 | 1.9 | 4 | 4 | 6 | 86 | 46 | 104 | 1.30 |
| 65 Jalasjärvi | Fine sand | 6.3 | 2.0 | 4 | 7 | 24 | 65 | 25 | 35 | 1.10 |
| 66 Muhos | Fine sand | 5.4 | 6.1 | 3 | 6 | 5 | 86 | 10 | 74 | 0.89 |
| 67 Närpiö | Fine sand | 5.2 | 5.1 | 3 | 4 | 38 | 55 | 33 | 57 | 0.96 |
| 68 Pieksämäki | Sandy moraine | 5.9 | 2.6 | 3 | 11 | 28 | 58 | 19 | 32 | 1.10 |
| 69 Ruovesi | Fine sand | 7.4 | 1.5 | 3 | 4 | 16 | 77 | 48 | 122 | 1.26 |
| 70 Ähtäri | Sandy moraine | 5.8 | 2.2 | 3 | 7 | 10 | 80 | 42 | 178 | 1.22 |
| 71 Harjavalta | Fine sand | 7.1 | 2.1 | 3 | 8 | 21 | 68 | 11 | 16 | 1.10 |
| 72 Hammarland | Fine sand | 4.9 | 2.0 | 2 | 3 | 4 | 91 | 17 | 23 | 1.24 |
| 73 Kuusamo | Sandy moraine | 5.4 | 2.7 | 2 | 8 | 16 | 74 | 95 | 10 | 1.14 |
| 74 Sotkamo | Sandy moraine | 5.3 | 2.3 | 1 | 4 | 5 | 90 | 18 | 51 | 1.26 |
| *Organogenic soils:* | | | | | | | | | | |
| 75 Sotkamo | Mull | 6.2 | 12.4 | 2 | 11 | 43 | 44 | 88 | 40 | 0.77 |
| 76 Sotkamo | Mull | 5.1 | 12.8 | 5 | 24 | 15 | 56 | 94 | 95 | 0.71 |
| 77 Maaninka | Mull | 5.5 | 14.4 | 22 | 44 | 14 | 20 | 120 | 117 | 0.55 |
| 78 Savitaipale | Mull | 5.7 | 14.8 | 10 | 17 | 29 | 44 | 70 | 86 | 0.69 |
| 15 Vihti | Mull | 5.0 | 18.3 | 27 | 56 | 14 | 3 | 93 | 225 | 0.64 |
| 79 Vihti | Mull | 5.1 | 19.0 | 75 | 20 | 3 | 2 | 54 | 266 | 0.76 |
| 80 Muhos | Mull | 5.8 | 20.3 | 4 | 11 | 10 | 75 | 249 | 17 | 0.70 |
| 81 Sievi | Mull | 4.8 | 21.3 | 14 | 57 | 24 | 5 | 131 | 85 | 0.54 |
| 82 Ylivieska | Mull | 5.0 | 21.4 | 25 | 55 | 16 | 4 | 147 | 127 | 0.57 |
| 83 Sotkamo | Mull | 5.6 | 21.5 | 42 | 48 | 10 | 0 | 108 | 120 | 0.61 |
| 84 Eno | Mull | 5.8 | 21.9 | 8 | 20 | 17 | 55 | 235 | 42 | 0.58 |
| 85 Honkajoki | Mull | 5.7 | 22.0 | 9 | 42 | 28 | 21 | 65 | 53 | 0.59 |
| 86 Savitaipale | Mull | 5.8 | 22.5 | 16 | 25 | 28 | 31 | 87 | 72 | 0.60 |
| 87 Forssa | Mull | 5.5 | 22.6 | 68 | 19 | 7 | 6 | 145 | 151 | 0.72 |
| 88 Tammela | Carex peat | 5.6 | 23.9 | n.d. | n.d. | n.d. | n.d. | 102 | 74 | 0.55 |
| 89 Sotkamo | Carex peat | 5.0 | 24.3 | n.d. | n.d. | n.d. | n.d. | 135 | 67 | 0.46 |
| 90 Närpiö | Carex peat | 4.7 | 25.1 | n.d. | n.d. | n.d. | n.d. | 252 | 26 | 0.54 |
| 91 Jokioinen | Carex peat | 6.2 | 28.7 | n.d. | n.d. | n.d. | n.d. | 122 | 97 | 0.52 |
| 92 Joroinen | Carex peat | 5.0 | 29.9 | n.d. | n.d. | n.d. | n.d. | 107 | 222 | 0.48 |
| 93 Sonkajärvi | Carex peat | 4.5 | 30.2 | n.d. | n.d. | n.d. | n.d. | 100 | 100 | 0.29 |
| 94 Längelmäki | Carex peat | 5.2 | 32.3 | n.d. | n.d. | n.d. | n.d. | 82 | 249 | 0.44 |
| 95 Pyhäselkä | Ligno Carex peat | 5.5 | 34.0 | n.d. | n.d. | n.d. | n.d. | 232 | 28 | 0.44 |
| 96 Sotkamo | Ligno Carex peat | 4.6 | 38.0 | n.d. | n.d. | n.d. | n.d. | 90 | 94 | 0.35 |
| 97 Sotkamo | Carex peat | 5.5 | 38.8 | n.d. | n.d. | n.d. | n.d. | 132 | 154 | 0.31 |
| 98 Pudasjärvi | Ligno Carex peat | 4.9 | 39.8 | n.d. | n.d. | n.d. | n.d. | 223 | 76 | 0.27 |
| 99 Yli-Ii | Ligno Carex peat | 5.5 | 40.5 | n.d. | n.d. | n.d. | n.d. | 202 | 29 | 0.26 |
| 100 Rantsila | Ligno Carex peat | 3.8 | 40.5 | n.d. | n.d. | n.d. | n.d. | 147 | 83 | 0.36 |
| 101 Vaala | Ligno Carex peat | 6.0 | 45.0 | n.d. | n.d. | n.d. | n.d. | 165 | 48 | 0.31 |
| 102 Kuusamo | Sphagnum Carex peat | 5.5 | 45.0 | n.d. | n.d. | n.d. | n.d. | 95 | 10 | 0.27 |
| 103 Valtimo | Ligno Carex peat | 4.8 | 47.3 | n.d. | n.d. | n.d. | n.d. | 70 | 94 | 0.30 |
| 104 Säkylä | Carex peat | 4.7 | 48.0 | n.d. | n.d. | n.d. | n.d. | 29 | 64 | 0.27 |
| 105 Suomussalmi | Ligno Carex peat | 4.1 | 49.2 | n.d. | n.d. | n.d. | n.d. | 44 | 53 | 0.25 |
| 106 Muhos | Ligno Carex peat | 5.1 | 49.8 | n.d. | n.d. | n.d. | n.d. | 196 | 52 | 0.34 |
| 107 Mikkeli | Carex peat | 4.4 | 50.4 | n.d. | n.d. | n.d. | n.d. | 62 | 205 | 0.39 |

n.d. = Not determined

Some physical and chemical characteristics of soil profile samples.

*Profile 1:* Tarvasjoki, loam (0-38 cm), clay loam (38-120 cm)

| Depth<br>cm | Clay<br>% | Org. C<br>% | pH |
|---|---|---|---|
| 0-30 | 25 | 1.8 | 5.5 |
| 32-38 | 29 | 0.4 | 6.2 |
| 38-46 | 34 | 0.2 | 6.4 |
| 50-60 | 41 | 0.2 | 6.8 |
| 65-80 | 51 | 0.2 | 6.8 |
| 85-100 | 56 | 0.4 | 7.0 |
| 105-120 | 55 | 0.6 | 7.0 |

*Profile 2:* Vihti, strongly layered silt

| Depth<br>cm | Clay<br>% | Org. C<br>% | pH |
|---|---|---|---|
| 0-27 | 17 | 3.2 | 6.0 |
| 30-40 | 11 | 0.2 | 6.8 |
| 40-50 | 12 | 0.2 | 6.6 |
| 50-70 | 17 | 0.2 | 6.6 |
| 70-90 | 6 | 0.1 | 6.6 |
| 90-100 | 16 | 0.1 | 6.7 |
| 110-120 | 27 | 0.2 | 6.9 |

*Profile 3:* Vihti, silty clay (0-60 cm), heavy clay (60-120 cm)

| Depth<br>cm | Clay<br>% | Org. C<br>% | pH |
|---|---|---|---|
| 0-30 | 50 | 2.6 | 6.3 |
| 30-40 | 53 | 0.5 | 6.7 |
| 40-60 | 54 | 0.4 | 6.8 |
| 60-80 | 72 | 0.5 | 7.0 |
| 80-100 | 88 | 0.5 | 7.1 |
| 100-120 | 86 | 0.6 | 7.1 |

*Profile 4:* Sotkamo, strongly podzolized fine sand

| Depth<br>cm | Fine[1]<br>% | FS[2]<br>% | Org. C<br>% | pH |
|---|---|---|---|---|
| 0-30 | 18 | 55 | 5.0 | 6.0 |
| 30-40 | 14 | 63 | 0.3 | 6.0 |
| 40-45 | 3 | 52 | 2.8 | 5.7 |
| 45-60 | 2 | 67 | 0.7 | 5.7 |
| 60-80 | 17 | 75 | 0.2 | 5.6 |
| 80-110 | 11 | 82 | 0.1 | 5.6 |
| 110-120 | 35 | 64 | 0.1 | 5.9 |

*Profile 5:* Sotkamo, Carex peat (20-130 cm), mineral soil mixed in the plough layer

| Depth<br>cm | Clay<br>% | Org. C<br>% | pH |
|---|---|---|---|
| 0-20 | 6 | 9.3 | 5.7 |
| 20-30 | n.d. | 52.2 | 5.4 |
| 30-40 | n.d. | 48.5 | 5.2 |
| 40-60 | n.d. | 51.8 | 5.4 |
| 60-80 | n.d. | 46.8 | 5.5 |
| 80-100 | n.d. | 39.6 | 5.5 |
| 100-120 | n.d. | 30.6 | 5.6 |
| 120-130 | n.d. | 31.5 | 5.6 |

*Profile 6:* Jokioinen, Carex peat (0-40 cm), mud (40-50 cm), heavy clay (50-70 cm)

| Depth<br>cm | Clay<br>% | Org. C<br>% | pH |
|---|---|---|---|
| 0-25 | n.d. | 30.8 | 6.0 |
| 30-40 | n.d. | 30.0 | 5.5 |
| 40-45 | 82 | 16.7 | 5.7 |
| 50-70 | 90 | 1.0 | 6.0 |
| 70-80 | 88 | 0.8 | 6.0 |

*Profile 7:* Muhos, Carex peat (0-110 cm), fine sand (110-125 cm)

| Depth<br>cm | Fine[1]<br>% | FS[2]<br>% | Org. C<br>% | pH |
|---|---|---|---|---|
| 0-30 | n.d. | n.d. | 44.7 | 5.3 |
| 30-50 | n.d. | n.d. | 55.1 | 4.7 |
| 50-70 | n.d. | n.d. | 52.1 | 4.7 |
| 70-90 | n.d. | n.d. | 55.8 | 4.9 |
| 90-110 | n.d. | n.d. | 54.2 | 5.0 |
| 110-125 | 3 | 56 | 0.2 | 5.0 |

n.d. = Not determined

[1] <0.06 mm [2] Fine sand (0.06-0.2 mm)

Characteristics of soil sample pairs consisting of plough layer ($A_p$) and subsoil (B) samples

| Location and number | Horizon | Soil class | Particle size composition µm, % | | | Org. C % | pH | $Zn_{Ac}$ mg dm$^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | | | <2 | 2-20 | 20-60 | | | |
| Somero 1[1] | $A_p$ | Heavy clay | 74 | 17 | 3 | 2.9 | 6.8 | 6.1 |
| | B | Heavy clay | 73 | 12 | 5 | 0.6 | 6.8 | 3.3 |
| Somero 2[1] | $A_p$ | Heavy clay | 67 | 24 | 4 | 7.7 | 5.3 | 3.3 |
| | B | Heavy clay | 66 | 22 | 2 | 1.1 | 5.5 | 0.9 |
| Jokioinen 6[1] | $A_p$ | Heavy clay | 64 | 10 | 5 | 2.0 | 7.0 | 2.8 |
| | B | Heavy clay | 91 | 5 | 2 | 0.6 | 6.5 | 2.1 |
| Somero 3[1] | $A_p$ | Heavy clay | 67 | 18 | 5 | 3.0 | 6.1 | 5.6 |
| | B | Heavy clay | 75 | 14 | 5 | 0.5 | 7.0 | 2.0 |
| Loimaa mlk 14[1] | $A_p$ | Silty clay | 49 | 44 | 3 | 2.4 | 5.9 | 4.9 |
| | B | Heavy clay | 60 | 31 | 4 | 0.5 | 6.5 | 2.1 |
| Koski TL 16[1] | $A_p$ | Silty clay | 45 | 31 | 15 | 2.0 | 5.7 | 3.7 |
| | B | Silty clay | 54 | 27 | 16 | 0.3 | 6.6 | 1.5 |
| Kestilä | $A_p$ | Very fine sand | 6 | 16 | 52 | 2.6 | 5.3 | 1.3 |
| | B | Very fine sand | 5 | 14 | 54 | 2.1 | 5.2 | 0.6 |
| Maaninka 49[1] | $A_p$ | Fine sand | 8 | 19 | 29 | 1.8 | 5.8 | 5.6 |
| | B | Very fine sand | 6 | 21 | 40 | 0.4 | 6.3 | 0.3 |
| Muhos | $A_p$ | Fine sand | 2 | 4 | 4 | 5.8 | 5.5 | 1.5 |
| | B | Fine sand | 2 | 2 | 3 | 0.4 | 4.9 | 0.9 |
| Rantsila | $A_p$ | Loam | 12 | 47 | 36 | 7.3 | 6.4 | 1.3 |
| | B | Carex peat | n.d. | n.d. | n.d. | 35.6 | 4.8 | 1.1 |
| Forssa 87[1] | $A_p$ | Mull | 68 | 19 | 7 | 22.6 | 5.7 | 3.2 |
| | B | Heavy clay | 74 | 14 | 8 | 2.5 | 6.0 | 4.0 |
| Sotkamo 75[1] | $A_p$ | Mull | 2 | 11 | 43 | 12.4 | 6.2 | 2.0 |
| | B | Carex peat | n.d. | n.d. | n.d. | 50.5 | 5.8 | 0.5 |
| Maaninka 77[1] | $A_p$ | Mull | 22 | 44 | 14 | 14.4 | 5.5 | 2.4 |
| | B | Carex peat | n.d. | n.d. | n.d. | 43.8 | 5.4 | 0.5 |
| Sonkajärvi 93[1] | $A_p$ | Carex peat | n.d. | n.d. | n.d. | 30.2 | 4.5 | 3.3 |
| | B | Carex peat | n.d. | n.d. | n.d. | 48.0 | 4.6 | 0.4 |
| Kestilä | $A_p$ | Carex peat | n.d. | n.d. | n.d. | 42.3 | 5.2 | 4.1 |
| | B | Carex peat | n.d. | n.d. | n.d. | 48.5 | 4.7 | 0.8 |

[1] Refers to the number of the $A_p$ horizon sample in the surface soil material (Appendix 2)

n.d. = Not determined

Characteristics of the surface soils: total Zn ($Zn_{tot}$), and Zn extracted with $MgCl_2$ ($Zn_{ex}$), pyrophosphate ($Zn_{py}$), oxalate ($Zn_{ox}$) and acetic acid-ammonium acetate -EDTA ($Zn_{Ac}$). $Zn_{py}$ and $Zn_{ox}$ were extracted sequentially.

| Number and location | $Zn_{tot}$ | $Zn_{ex}$ | $Zn_{py}$ | $Zn_{ox}$ | $Zn_{Ac}$ |
|---|---|---|---|---|---|
| | ---------- | ---------- mg $kg^{-1}$ | ---------- | ---------- | mg $dm^{-3}$ |
| *Clay soils:* | | | | | |
| 1 Somero | 186 | 1.1 | 2.8 | 3.5 | 3.8 |
| 2 Somero | 168 | 3.3 | 8.1 | 2.9 | 3.3 |
| 3 Somero | 171 | 1.0 | 2.4 | 2.3 | 1.7 |
| 4 Kylmäkoski | 122 | 1.0 | 3.4 | 2.2 | 2.3 |
| 5 Somero | 189 | 1.1 | 4.5 | 4.4 | 4.4 |
| 6 Jokioinen | 187 | 0.5 | 2.0 | 4.4 | 2.8 |
| 7 Ypäjä | 150 | 1.2 | 4.1 | 3.7 | 3.7 |
| 8 Kirkkonummi | 157 | 1.3 | 5.2 | 3.4 | 3.0 |
| 9 Loimaa | 146 | 2.3 | 4.8 | 3.1 | 3.7 |
| 10 Kirkkonummi | 108 | 2.6 | 5.4 | 1.9 | 2.8 |
| 11 Vehkalahti | 148 | 1.0 | 1.8 | 2.8 | 2.1 |
| 12 Vihti | 66.4 | 1.5 | 2.6 | 1.2 | 1.5 |
| 13 Perniö | 82.8 | 0.5 | 1.4 | 2.0 | 1.1 |
| 14 Loimaa mlk | 147 | 2.4 | 5.4 | 3.9 | 4.9 |
| 16 Koski TL | 147 | 2.6 | 6.1 | 4.2 | 3.7 |
| 17 Helsinki | 190 | 4.9 | 23.1 | 13.0 | 18.0 |
| 18 Valkeala | 104 | 0.7 | 1.8 | 2.1 | 2.0 |
| 19 Valkeala | 115 | 1.0 | 3.6 | 3.1 | 4.4 |
| 20 Mustasaari | 102 | 3.7 | 7.8 | 3.1 | 3.4 |
| 21 Kuhmoinen | 202 | 0.6 | 3.8 | 5.2 | 2.3 |
| 22 Vehkalahti | 134 | 1.1 | 2.2 | 2.7 | 3.3 |
| 23 Tampere | 146 | 0.7 | 2.1 | 3.1 | 1.6 |
| 24 Valkeala | 140 | 3.7 | 8.6 | 4.8 | 6.3 |
| 25 Valkeala | 137 | 1.3 | 2.6 | 2.7 | 3.4 |
| 26 Ylihärmä | 82.2 | 2.7 | 7.0 | 2.3 | 2.9 |
| *Coarse mineral soils and moraines:* | | | | | |
| 27 Vihti | 128 | 0.7 | 1.6 | 1.9 | 1.0 |
| 28 Korpilahti | 92.0 | 0.5 | 2.6 | 1.7 | 0.8 |
| 29 Vihti | 117 | 1.0 | 1.8 | 1.9 | 1.3 |
| 30 Laihia | 109 | 1.3 | 6.6 | 3.6 | 4.1 |
| 31 Tarvasjoki | 79.8 | 2.2 | 3.6 | 2.4 | 2.3 |
| 32 Luumäki | 81.6 | 0.8 | 1.8 | 1.8 | 1.9 |
| 33 Ylistaro | 114 | 1.2 | 6.7 | 4.6 | 5.7 |
| 34 Pyhäselkä | 106 | 2.6 | 4.3 | 2.4 | 2.5 |
| 35 Isokyrö | 115 | 0.7 | 5.5 | 5.0 | 5.2 |
| 36 Ylivieska | 82.1 | 1.6 | 4.0 | 2.3 | 3.8 |
| 37 Huittinen | 104 | 0.9 | 1.5 | 2.2 | 1.9 |
| 38 Hollola | 201 | 0.6 | 4.2 | 4.4 | 1.4 |
| 39 Luumäki | 62.5 | 1.3 | 4.3 | 2.2 | 4.7 |
| 40 Tervola | 63.8 | 3.5 | 4.1 | 1.9 | 2.9 |
| 41 Alavieska | 55.9 | 0.8 | 1.9 | 1.4 | 1.5 |
| 42 Maalahti | 66.8 | 2.2 | 4.2 | 1.4 | 2.7 |
| 43 Vihti | 92.6 | 0.6 | 2.6 | 2.6 | 1.9 |
| 44 Lammi | 112 | 0.7 | 1.4 | 1.8 | 0.8 |
| 45 Alavieska | 45.7 | 0.6 | 2.0 | 1.4 | 1.5 |
| 46 Lapinlahti | 68.9 | 2.1 | 5.1 | 2.5 | 3.3 |
| 47 Sonkajärvi | 57.1 | 2.2 | 3.8 | 1.5 | 2.4 |
| 48 Kitee | 74.6 | 0.6 | 2.2 | 1.4 | 1.4 |
| 49 Maaninka | 102 | 1.0 | 2.7 | 2.4 | 1.7 |
| 50 Sotkamo | 58.0 | 0.5 | 2.1 | 1.7 | 2.1 |
| 51 Vihti | 57.9 | 0.4 | 1.4 | 1.4 | 1.7 |
| 52 Ylivieska | 26.5 | 1.3 | 2.2 | 0.8 | 1.8 |

| Number and location | $Zn_{tot}$ | $Zn_{ex}$ | $Zn_{py}$ | $Zn_{ox}$ | $Zn_{Ac}$ |
|---|---|---|---|---|---|
| | mg kg$^{-1}$ | | | | mg dm$^{-3}$ |
| 53 Siikajoki | 78.1 | 5.3 | 23.9 | 8.8 | 29.9 |
| 54 Saari | 70.3 | 0.5 | 3.3 | 2.5 | 1.9 |
| 55 Liperi | 45.0 | 1.2 | 4.3 | 1.4 | 2.7 |
| 56 Joroinen | 76.7 | 0.8 | 4.8 | 3.4 | 2.5 |
| 57 Jyväskylä mlk | 68.6 | 1.4 | 3.6 | 1.8 | 2.8 |
| 58 Lapua | 35.2 | 0.8 | 4.0 | 0.9 | 2.3 |
| 59 Ristiina | 62.9 | 2.4 | 7.7 | 3.6 | 5.4 |
| 60 Ristiina | 64.8 | 0.8 | 4.9 | 2.7 | 3.4 |
| 61 Hammarland | 37.4 | 0.4 | 1.4 | 1.2 | 1.5 |
| 62 Kauhava | 37.7 | 0.6 | 3.2 | 0.9 | 2.1 |
| 63 Liminka | 45.1 | 1.6 | 2.2 | 1.1 | 1.6 |
| 64 Vihti | 40.6 | 0.4 | 2.1 | 1.7 | 1.5 |
| 65 Jalasjärvi | 29.2 | 0.5 | 1.8 | 0.6 | 0.9 |
| 66 Muhos | 14.0 | 1.1 | 2.0 | 0.5 | 1.3 |
| 67 Närpiö | 43.3 | 3.1 | 5.6 | 0.9 | 4.2 |
| 68 Pieksämäki | 27.0 | 0.9 | 2.6 | 0.8 | 2.0 |
| 69 Ruovesi | 69.4 | 0.3 | 2.0 | 3.7 | 2.9 |
| 70 Ähtäri | 52.8 | 5.6 | 13.6 | 4.0 | 12.7 |
| 71 Harjavalta | 420 | 22.0 | 227 | 115 | 165 |
| 72 Hammarland | 29.9 | 3.8 | 4.9 | 0.6 | 4.5 |
| 73 Kuusamo | 15.1 | 2.6 | 3.5 | 1.4 | 3.8 |
| 74 Sotkamo | 30.5 | 8.3 | 12.7 | 2.4 | 11.0 |
| *Organogenic soils:* | | | | | |
| 75 Sotkamo | 40.3 | 0.9 | 2.6 | 1.2 | 2.0 |
| 76 Sotkamo | 31.8 | 2.4 | 5.1 | 1.1 | 2.4 |
| 77 Maaninka | 63.8 | 2.5 | 5.1 | 1.2 | 2.4 |
| 78 Savitaipale | 33.1 | 1.3 | 5.8 | 1.4 | 2.9 |
| 15 Vihti | 67.5 | 3.3 | 8.9 | 2.3 | 5.2 |
| 79 Vihti | 59.4 | 1.7 | 5.6 | 2.6 | 3.9 |
| 80 Muhos | 20.0 | 1.5 | 3.3 | 1.0 | 2.2 |
| 81 Sievi | 42.7 | 7.7 | 15.2 | 2.0 | 6.4 |
| 82 Ylivieska | 49.8 | 2.1 | 4.7 | 1.7 | 2.1 |
| 83 Sotkamo | 45.1 | 1.3 | 1.6 | 1.1 | 0.8 |
| 84 Eno | 36.4 | 2.3 | 9.0 | 2.6 | 4.3 |
| 85 Honkajoki | 75.8 | 7.0 | 26.9 | 3.5 | 14.0 |
| 86 Savitaipale | 39.2 | 2.0 | 7.7 | 1.6 | 3.7 |
| 87 Forssa | 80.1 | 1.8 | 7.9 | 2.4 | 3.2 |
| 88 Tammela | 41.7 | 4.2 | 13.8 | 1.9 | 5.6 |
| 89 Sotkamo | 70.8 | 7.6 | 9.3 | 2.0 | 4.9 |
| 90 Närpiö | 42.2 | 5.1 | 12.2 | 1.5 | 5.4 |
| 91 Jokioinen | 63.4 | 1.7 | 8.1 | 2.3 | 3.0 |
| 92 Joroinen | 48.6 | 4.8 | 12.4 | 2.4 | 5.4 |
| 93 Sonkajärvi | 44.3 | 3.8 | 7.7 | 1.5 | 2.9 |
| 94 Längelmäki | 32.2 | 2.4 | 4.4 | 3.1 | 1.7 |
| 95 Pyhäselkä | 85.6 | 10.8 | 53.8 | 10.3 | 19.4 |
| 96 Sotkamo | 27.1 | 8.4 | 13.4 | 1.5 | 3.7 |
| 97 Sotkamo | 10.3 | 1.1 | 2.2 | 0.7 | 1.8 |
| 98 Pudasjärvi | 18.1 | 3.3 | 6.3 | 1.6 | 1.5 |
| 99 Yli-Ii | 24.1 | 3.5 | 14.6 | 2.2 | 3.5 |
| 100 Rantsila | 34.3 | 11.0 | 16.9 | 1.7 | 5.0 |
| 101 Vaala | 41.4 | 5.8 | 28.3 | 3.3 | 8.0 |
| 102 Kuusamo | 32.8 | 6.0 | 26.1 | 2.7 | 6.8 |
| 103 Valtimo | 11.5 | 1.9 | 2.6 | 0.5 | 0.6 |
| 104 Säkylä | 22.0 | 5.6 | 15.8 | 1.6 | 4.0 |
| 105 Suomussalmi | 12.3 | 4.6 | 7.3 | 1.1 | 1.6 |
| 106 Muhos | 15.4 | 4.3 | 9.5 | 1.6 | 2.5 |
| 107 Mikkeli | 25.3 | 8.9 | 17.5 | 1.7 | 5.5 |

# *Appendix 6.*

Some characteristics of the soils of two pot experiments (Sections 4.3 and 5.2.1) and the field experiments. $A_p$ = plough layer, B = subsoil (30-35 cm).

| Soil and crop | | Organic C % | Particle size composition µm, % | | | | pH | $Zn_{Ac}$ mg dm$^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | | | <2 | 2-20 | 20-60 | >60 | | |
| *Pot experiments* | | | | | | | | |
| Clay loam | | 2.3 | 48 | 25 | 18 | 9 | 6.2[1] | 0.9 |
| Fine sand | | 1.0 | 7 | 3 | 46 | 44 | 5.9[1] | 2.8 |
| Carex peat | | 27.2 | n.d. | n.d. | n.d. | n.d. | 6.2[1] | 4.8 |
| Sphagnum peat | | 41.7 | n.d. | n.d. | n.d. | n.d. | 3.6[1] | 3.7 |
| *Field experiments with timothy* | | | | | | | | |
| Clay loam | $A_p$ | 3.4 | 42 | 30 | 13 | 15 | 5.7 | 1.6 |
| | B | 0.8 | 58 | 23 | 8 | 11 | 5.9 | 1.5 |
| Fine sand | $A_p$ | 1.4 | 9 | 4 | 6 | 81 | 5.9 | 3.3 |
| | B | 0.7 | 4 | 1 | 12 | 83 | 6.1 | 0.7 |
| *Field experiments with barley* | | | | | | | | |
| Clay loam | $A_p$ | 2.9 | 33 | 28 | 19 | 20 | 5.8 | 2.1 |
| | B | 0.6 | 35 | 26 | 22 | 17 | 6.1 | 1.0 |
| Fine sand | $A_p$ | 1.3 | 5 | 3 | 6 | 86 | 7.1 | 1.3 |
| | B | 0.8 | 4 | 1 | 5 | 90 | 6.3 | 0.2 |
| Mull | $A_p$ | 22.9 | 38 | 45 | 11 | 6 | 5.3 | 4.7 |
| | B | 32.0 | n.d. | n.d. | n.d. | n.d. | 5.0 | 17.2 |

[1] pH of the unlimed soils of the pot experiments

n.d. = Not determined

**Field experiment: Effect of Zn fertilizers on timothy in the field**

*Sowing:* 1990
*Experimental years:* 1991 and 1992; two crops in each year
*Method:* Randomized blocks
*Plot size:* 2.3 m × 10 m
*Harvested area:* 1.6 × 10 m
*Replicates:* 4
*Soils:* Clay and fine sand
*Crop:* Timothy, cultivar 'Tammisto' (15 kg ha$^{-1}$)
*Application of Zn:* A total of 3 or 6 kg ha$^{-1}$ during the experiment (5.2 kg ha$^{-1}$ in NPK 18-3-12; Control: no Zn applied)
*Application of N, P and K:* at sowing 57, 34 and 37 kg ha$^{-1}$, respectively (NPK 14-9-10 400 kg ha$^{-1}$); in spring and after the first harvest in each year 90-93, 31-33 and 61-65 kg ha$^{-1}$, respectively
*Herbicide* in fine sand in spring 1991: bentazone - MCPA (Basagran MCPA)

Application of Zn and NPK fertilizers in the field experiments with timothy:

| Treatmen | Zn kg ha$^{-1}$ | NPK fertilizer[1] |
|---|---|---|
| 1. Control; no Zn application | 0 | 1 |
| 2. $ZnSO_4 \cdot 7H_2O$ mixed into the soil in fall 1990 | 3 | 1 |
| 3. 'Sinkkilannos' » » | 3 | 1 |
| 4. 'Sinkkilannos' onto the sward in spring 1991 | 3 | 1 |
| 5. Coated NPK II » » | 4×0.75 | 3 |
| 6. $ZnSO_4 \cdot 7H_2O$ mixed into the soil in fall 1990 | 6 | 1 |
| 7. 'Sinkkilannos' » » | 6 | 1 |
| 8. 'Sinkkilannos' onto the sward in spring 1991 | 6 | 1 |
| 9. NPK 18-3-12 onto the sward in spring and summer | 4×1.3 | 2 |
| 10. Coated NPK III » » | 4×1.5 | 4 |

[1] 1 = NPK 17-6-12 530 kg ha$^{-1}$
2 = NPK 18-3-12 500 kg ha$^{-1}$, Triple superphosphate 90 kg ha$^{-1}$
3 = Coated NPK II 360 kg ha$^{-1}$, NPK 17-6-12 170 kg ha$^{-1}$
4 = Coated NPK III 360 kg ha$^{-1}$, NPK 17-6-12 170 kg ha$^{-1}$

| *Dates of farming operations:* | *Clay:* | *Fine sand:* |
|---|---|---|
| Sowing | Aug. 27, 1990 | Aug. 17, 1990 |
| Spring fertilization | May 16, 1991 | May 9, 1991 |
| Harvest I/91 | June 26, 1991 | June 26, 1991 |
| Summer fertilization | June 28, 1991 | June 28, 1991 |
| Harvest II/91 | Aug. 13, 1991 | Aug. 12, 1991 |
| Spring fertilization | May 10, 1992 | May 12, 1992 |
| Harvest I/91 | June 10, 1992 | June 9, 1992 |
| Summer fertilization | June 10, 1992 | June 9, 1992 |
| Harvest II/92 | Sept. 18, 1992 | Sept. 17, 1992 |

**Field experiment: Different fertilizers as Zn sources for barley**

*Experimental years:* 1990, 1991 and 1992
*Method:* Randomized blocks
*Plot size:* 2.3 m × 10 m
*Harvested area:* 1.5 m × 10 m
*Replicates:* 4
*Soils:* Clay, mull and fine sand
*Crop:* Barley, cultivar 'Kymppi' (clay and fine sand soil), cultivar 'Kalle' (mull soil)
*Application of Zn:* A total of 5.4 kg ha$^{-1}$ during three years (4.8 kg ha$^{-1}$ in NPK 18-3-12; Control: no Zn applied)
*Application of N, P and K:* 108-110, 19-20 and 74-76 kg ha$^{-1}$, respectively, to clay and fine sand soil, 110, 39 and 73-78 kg ha$^{-1}$, respectively, to mull soil
*Herbicides:* mixtures of mecoprope, dichlorprope and MCPA (Dipro, Hormoprop, Hormoneste); tribenurone-methyle (Express)
*Fungicide:* propiconazole (Tilt)
*Insecticide* (in 1992 only): dimethoate (Roxion), supermetrine (Ripcord)
*Growth regulators:* chlormequate chloride (CCC), mepiquate chloride, etephone (Terpal)

Application of Zn and NPK fertilizers in the 3-year field experiments with barley:

| Treatment | Zn kg ha$^{-1}$ | NPK fertilizer[1] |
|---|---|---|
| 1. Control; no Zn application | 0 | 1 |
| 2. $ZnSO_4 \cdot 7H_2O$ 24 kg ha$^{-1}$ in the first spring | 5.4 | 1 |
| 3. 'Sinkkilannos' 180 kg ha$^{-1}$ in the first spring | 5.4 | 1 |
| 4. $Na_2Zn$-EDTA 12 kg ha$^{-1}$ sprayed onto the soil annually | 3 × 1.8 | 1 |
| 5. NPK 18-3-12, 610 kg ha$^{-1}$ annually | 3 × 1.6 | 2 |
| 6. Coated NPK I annually | 3 × 1.8 | 3 |
| 7. $Na_2Zn$-EDTA 12 kg ha$^{-1}$ sprayed annually onto the foliage | 3 × 1.8 | 1 |

[1] In clay and fine sand soil:
1 = NPK 25-4-4 440 kg ha$^{-1}$, KCl 110 kg ha$^{-1}$
2 = NPK 18-3-12 610 kg ha$^{-1}$
3 = Coated NPK I 460 kg ha$^{-1}$, KCl 110 kg ha$^{-1}$

In mull soil:
1 = NPK 17-6-12 650 kg ha$^{-1}$
2 = NPK 18-2-12 610 kg ha$^{-1}$, Triple superphosphate 105 kg ha$^{-1}$
3 = Coated NPK I 460 kg ha$^{-1}$, Triple superphosphate 105 kg ha$^{-1}$, KCl 110 kg ha$^{-1}$

Dates of farming operations and length of the growing period:

| | *Clay* | *Mull* | *Fine sand* |
|---|---|---|---|
| *1990:* | | | |
| Sowing | April 30 | May 7 | May 4 |
| Foliar application of $Na_2Zn$-EDTA | June 6 | June 6 | June 6 |
| Harvest | Aug. 16 | Aug. 20 | Aug. 16 |
| Growing period | 109 d | 105 d | 104 d |
| *1991:* | | | |
| Sowing | May 13 | May 27 | May 15 |
| Foliar application of $Na_2Zn$-EDTA | June 28 | July 03 | June 28 |
| Harvest | Aug. 28 | Sept. 2 | Aug. 27 |
| Growing period | 107 d | 98 d | 104 d |
| *1992:* | | | |
| Sowing | May 21 | May 27 | May 21 |
| Foliar application of $Na_2Zn$-EDTA | July 7 | June 30 | July 1 |
| Harvest | Aug. 17 | Aug. 31 | Aug. 26 |
| Growing period | 88 d | 96 d | 97 d |

**Field experiment: Zinc concentration of barley as affected by different Zn rates**

*Experimental years:* 1991 and 1992
*Method:* Randomized blocks
*Plot size:* 2.3 m × 5 m
*Harvested area:* 0.5 $m^2$ (two subsamples of 0.25 $m^2$) four times during the growing period
*Replicates:* 4
*Soils:* Clay and fine sand
*Crop:* Barley, cultivar 'Kymppi' (270 kg $ha^{-1}$)
*Application of Zn:* 15 or 30 kg Zn $ha^{-1}$ as $ZnSO_4 \cdot 7H_2O$ in spring of 1991, (Control: no Zn applied)
*Application of N, P and K:* 110, 22 and 44 kg $ha^{-1}$, respectively (Fertilizer: NPK 20-4-8 550 kg $ha^{-1}$)
*Herbicide:* tribenurone-methyle (Express)
*Insecticide* (in 1992 only): dimethoate (Roxion)
*Growth regulator:* chlormequate chloride (CCC)

Dates of sowing, sampling and harvesting and length of the growing period:

| | 1991 | | 1992 | |
|---|---|---|---|---|
| | Clay | Fine sand | Clay | Fine sand |
| Sowing | May 17 | May 16 | May 21 | May 20 |
| Sampling at Feekes 2 | June 24 | June 24 | June 18 | June 15 |
| Sampling at Feekes 5 | July 8 | July 5 | July 3 | June 29 |
| Sampling at Feekes 10.5 | July 26 | July 24 | July 21 | June 20 |
| Harvest | - | Aug. 28 | Aug. 20 | Aug. 24 |
| Growing period | | 104 d | 91 d | 96 d |