Copper in cultivated soils of Finland

MARKKU YLI-HALLA

YLI-HALLA, M. 1994. Copper in cultivated soils of Finland. Agricultural Science in Finland 3: 487-495. (Department of Applied Chemistry and Microbiology, P.O. Box 27, FIN-00014 University of Helsinki, Finland.)

Soil samples from the plough layers of 105 fields in different parts of Finland were analyzed for Cu fractions. Vertical distribution of Cu was also studied in a smaller material. Total Cu (Cu_{tot}), HNO_{3}-HClO_{4}-HF-H_{2}SO_{4} digestion) in the surface soil ranged 6.9-97.4 mg kg^{-1} (mean 37.1 mg kg^{-1}) and was highest in clay soils (mean 59.0 mg kg^{-1}) and lowest in fine sand and moraine soils (mean 18.3 mg kg^{-1}). Copper in the water-soluble, exchangeable and mainly organically bound fraction was extracted with 0.1 M K_{2}P_{2}O_{7} (Cu_{py}), and Cu bound by poorly crystalline Fe, Al and Mn oxides (Cu_{org}) was dissolved subsequently with 0.05 M oxalate (pH 2.9). The average percentages of Cu_{py} and Cu_{org} were 18% and 12% of Cu_{tot} in mineral soils and 34% and 19% of Cu_{tot} in organogenic soils, respectively. Residual Cu (Cu_{res}) incorporated in mineral lattices was calculated to constitute 70% and 47% of Cu_{tot} in mineral and organogenic soils, respectively. In two thirds of the soils the potentially plant-available reserves of Cu (Cu_{py}+Cu_{org}) were more plentiful than those of Zn (Zn_{py}+Zn_{org}). An acetic acid–ammonium acetate – Na_{2}EDTA solution used in routine soil testing extracted 56% and 71% of the sum of Cu_{py}+Cu_{org} in mineral and organogenic soils, respectively. In soil profiles, Cu_{EDTA} was higher in the plough layer than in the subsoil but a few soils rich in Cu_{be} had abundant reserves of Cu_{EDTA} below the rooting depth of annual field crops.

Key words: total analysis, sequential extractions, pyrophosphate extraction, oxalate extraction, ammonium acetate-acetic acid-EDTA extraction, vertical distribution of Cu, zinc

Introduction

Soil Cu is commonly divided into fractions with different extractants applied sequentially (McLAREN and CRAWFORD 1973, SHUMAN 1979, 1985, LIANG et al. 1991). It is assumed that each solution dissolves a specific fraction retained by a given mechanism or soil constituent: Cu in soil solution, exchangeable, specifically adsorbed, complexed by organic matter or by Fe, Al and Mn oxides and residual Cu incorporated mainly in the lattices of primary minerals (VIETS 1962). The residual fraction is considered unavailable to plants, while the other ones, collectively called secondary fractions, are, at least to some extent, sources of plant-available Cu (GALLARDO-LARA and TORRES-MARTIN 1990, LIANG et al. 1991). A few sediment samples mainly from polluted industrial areas of Finland have been analyzed for the fractions of Cu (RAISÄNEN and HÄMALÄINEN 1991) but the fractional distribution of Cu in cultivated soils of the country is unknown.

An ammonium acetate – acetic acid – Na_{2}EDTA solution (AAAc-EDTA, pH 4.65) is used to extract Cu in soil testing in Finland. Recently, JOKI-NEN et al. (1993) found that this extractant dis-
solved 40% of total Cu in organogenic soils. However, it is not known, either in organogenic or mineral soils, to what extent the secondary reserves, the potential source of plant-available Cu, are extracted by this solution. This information would be important in order to be able to translate the soil testing results into a quantitative estimate of plant-available Cu.

The purpose of the present study is to examine the distribution of soil Cu into different fractions using a simplified procedure of McLAREN and CRAWFORD (1973). The extraction power of AAAC – EDTA was studied and the results obtained by this method were related to the secondary fractions. The fractions of soil Cu were also compared to those of Zn obtained in a previous study (YLI-HALLA 1993).

Material and methods

The distribution of Cu into various fractions was studied in 105 soil samples collected from the plough layers (A<sub>p</sub> horizons) of cultivated fields in Finland. The material consisted of 25 clay soils, 20 silt and very fine sand soils, 26 fine sand and moraine soils, 14 mull soils and 20 peat soils. The vertical distribution of Cu was studied on seven soil profiles of cultivated fields as well as on 15 pairs of samples from the plough layer (A<sub>p</sub> horizon) and from the respective subsoil (30–35 cm). All the samples have been described in detail in an earlier study (YLI-HALLA 1993). However, a moraine (soil 53) and a fine sand soil (soil 71) of the surface soil material of the previous study were not included in the present investigation.

To determine total Cu, the soil was digested with a mixture of HNO<sub>3</sub>, HClO<sub>4</sub>, HF and H<sub>2</sub>SO<sub>4</sub> (YLI-HALLA 1993). Water-soluble and exchangeable Cu as well as Cu bound mostly by organic matter were extracted as one fraction with 0.1 M K<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (pH 10), and Cu bound by poorly crystalline Fe, Al and Mn oxides was extracted by a 0.05 M oxalate solution (0.026 M ammonium oxalate, 0.024 M oxalic acid, pH 2.9) sequentially after the pyrophosphate extraction (YLI-HALLA 1993). In 16 representative soil samples, the residue remaining after the sequential pyrophosphate and oxalate extraction was further digested with a mixture of HNO<sub>3</sub>, HClO<sub>4</sub>, HF and H<sub>2</sub>SO<sub>4</sub> to determine the residual Cu (Cu<sub>res</sub>) but in most soil samples Cu<sub>res</sub> was calculated as total Cu minus the sum of Cu extracted with pyrophosphate and oxalate, i.e. Cu<sub>tot</sub> = (Cu<sub>py</sub> + Cu<sub>ox</sub>). All the digestions and extractions were carried out in duplicate. The Cu concentration of the extracts was determined by atomic absorption spectrophotometry. In order to allow a relevant comparison of Cu<sub>tot</sub>, Cu<sub>py</sub>, Cu<sub>ox</sub> and Cu<sub>res</sub> between the mineral and organogenic soils, the results, originally expressed as milligrams per kilogram of soil, were in some instances transformed into milligrams per dm<sup>3</sup> of soil by multiplying them with the bulk density. Copper was also extracted with a solution containing 0.5 M CH<sub>3</sub>COONH<sub>4</sub>, 0.5 M CH<sub>3</sub>COOH and 0.02 M Na<sub>2</sub>-EDTA at pH 4.65 (LAKANEN and ERVIÖ 1971), which is the method used in soil testing in Finland.

Results

Total copper

In mineral soils, total Cu (Cu<sub>tot</sub>, mg kg<sup>-1</sup>) increased with increasing clay content (r = 0.87**) In a few heavy clay soils, Cu<sub>tot</sub> approached 100 mg kg<sup>-1</sup>, while in some fine sand soils it was very low (< 10 mg kg<sup>-1</sup>) (Table 1). Mull and peat soils had a similar concentration of Cu<sub>tot</sub> but the number of very low contents of Cu<sub>tot</sub> was higher among the peat soils. When expressing the results as milligrams per dm<sup>3</sup> of soil, the averages were 26.8 and 14.7 mg dm<sup>-3</sup> in mull and peat soils, respectively, being of the same level as the fine sand and moraine soils. In organogenic soils, Cu<sub>tot</sub> (mg dm<sup>-3</sup>) decreased with increasing organic C (r = -0.52**).

Fractions of soil copper

In the 16 representative soil samples, Cu<sub>tot</sub> and the sum of the fractions (Cu<sub>py</sub> + Cu<sub>ox</sub> + Cu<sub>res</sub>)...
Table 1. Total Cu (Cu\textsubscript{tot}) and Cu in fractions extracted with pyrophosphate (Cu\textsubscript{py}) and oxalate (Cu\textsubscript{ox}) and in the residual fraction (Cu\textsubscript{res}), and Cu extracted with AAAC-EDTA (Cu\textsubscript{EDTA}) as well as the bulk density of the plough layer soil samples.\textsuperscript{1}

| Soil class and number of samples | Bulk density\textsuperscript{2} (kg dm\textsuperscript{-3}) | Cu\textsubscript{tot} (mg kg\textsuperscript{-1}) | Cu\textsubscript{py} (mg kg\textsuperscript{-1}) | Cu\textsubscript{ox} (mg kg\textsuperscript{-1}) | Cu\textsubscript{res} (mg kg\textsuperscript{-1}) | Cu\textsubscript{EDTA} (mg kg\textsuperscript{-1}) |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Clay n = 25                     | mean 0.96\textsuperscript{b}   | 59.0\textsuperscript{a}        | 9.2\textsuperscript{a}        | 6.2\textsuperscript{a}        | 43.8\textsuperscript{a}        | 7.7\textsuperscript{a}        |
|                                 | range 0.76–1.14                 | 31.6–97.4                      | 2.9–26.9                       | 2.4–20.8                       | 12.4–77.8                      | 2.5–26.0                       |
| Silt, very fine sand, n = 20    | mean 1.00\textsuperscript{b}   | 30.7\textsuperscript{b}       | 4.3\textsuperscript{b}       | 3.1\textsuperscript{b}       | 23.4\textsuperscript{b}       | 4.2\textsuperscript{b}       |
|                                 | range 0.77–1.16                 | 20.6–45.9                      | 0.4–11.9                       | 1.3–5.0                        | 7.7–36.8                       | 1.5–10.6                       |
| Fine sand, moraine, n = 26      | mean 1.14\textsuperscript{a}   | 16.3\textsuperscript{a}       | 3.3\textsuperscript{a}       | 2.1\textsuperscript{a}       | 10.8\textsuperscript{a}       | 3.7\textsuperscript{a}       |
|                                 | range 0.89–1.43                 | 8.4–31.0                       | 1.1–8.4                        | 0.7–5.4                        | 3.5–21.5                       | 1.3–9.1                        |
| Mull n = 14                     | mean 0.65\textsuperscript{c}   | 41.4\textsuperscript{b}       | 15.3\textsuperscript{a}      | 7.8\textsuperscript{a}       | 18.3\textsuperscript{bc}      | 8.1\textsuperscript{a}       |
|                                 | range 0.53–0.77                 | 21.0–80.5                      | 3.9–26.2                       | 2.8–14.9                       | 4.9–40.2                       | 3.0–14.1                       |
| Peat n = 20                     | mean 0.37\textsuperscript{d}   | 38.5\textsuperscript{b}       | 12.9\textsuperscript{a}      | 7.7\textsuperscript{a}       | 17.9\textsuperscript{bc}      | 5.9\textsuperscript{ab}      |
|                                 | range 0.25–0.55                 | 6.9–73.6                       | 0.8–34.3                       | 0.6–17.4                       | 4.6–38.6                       | 0.9–14.9                       |

\textsuperscript{1} The means in each column have been tested separately. Means marked with the same superscript within a column do not differ at P = 0.05.

\textsuperscript{2} Determined by YLI-HALLA (1993).

The concentration of Cu extracted with pyrophosphate (Cu\textsubscript{py}, Table 1) was highest in mull and peat soils, but when expressing the results as mg dm\textsuperscript{-3} of soil, the mean of 9.8 mg dm\textsuperscript{-3} places the mull soils at the same level as clay soils. The mean of 5.1 mg dm\textsuperscript{-3} in peat soils equals that in silt and very fine sand soils. In most soils the concentration of Cu extracted with oxalate (Cu\textsubscript{ox}, Table 1) was smaller than Cu\textsubscript{py}; only in 13 soils was Cu\textsubscript{ox} equal to or higher than Cu\textsubscript{py}. Cu\textsubscript{ox} was at the same level in peat, mull and clay soils and substantially lower in coarse mineral soils. Both in mineral and organogenic soils, Cu\textsubscript{py} and Cu\textsubscript{ox} correlated highly with each other. In mineral soils, Cu\textsubscript{py} correlated highly significantly (P = 0.001) also with clay and Cu\textsubscript{tot} (Table 2), while Cu\textsubscript{ox} correlated with Cu\textsubscript{tot}, Cu\textsubscript{res}, clay and poorly crystalline Fe oxide (Fe\textsubscript{ox}). However, the partial correlation between Cu\textsubscript{ox} and Fe\textsubscript{ox}, after the elimination of the effect of clay, was not significant (P = 0.05). In organogenic soils, both Cu\textsubscript{py} and Cu\textsubscript{ox} correlated most closely (P = 0.001) with Cu\textsubscript{res} and Cu\textsubscript{tot}.

Table 2. Correlation coefficients between copper extracted with pyrophosphate (Cu\textsubscript{py}) and oxalate (Cu\textsubscript{ox}) and soil properties in mineral and organogenic soils. The calculations have been carried out with the logarithmic (log\textsubscript{10}) transformations of the concentrations of Cu (mg dm\textsuperscript{-3}) and Fe and Al (g dm\textsuperscript{-3}).

| Soil characteristic | Mineral soils | Organogenic soils |
|---------------------|--------------|------------------|
|                     | Cu\textsubscript{py} | Cu\textsubscript{ox} | Cu\textsubscript{py} | Cu\textsubscript{ox} |
| Clay                | 0.52\textsuperscript{***} | 0.68\textsuperscript{***} | –                  | –                  |
| Organic C           | 0.32\textsuperscript{**} | 0.09\textsuperscript{***} | -0.52\textsuperscript{*} | -0.45\textsuperscript{**} |
| Fe\textsuperscript{1} | 0.35\textsuperscript{**} | 0.44\textsuperscript{***} | 0.50\textsuperscript{**} | 0.48\textsuperscript{**} |
| Al\textsuperscript{1} | 0.24\textsuperscript{***} | 0.23\textsuperscript{***} | 0.47\textsuperscript{**} | 0.22\textsuperscript{***} |
| Cu\textsubscript{res} | 0.38\textsuperscript{***} | 0.62\textsuperscript{***} | 0.61\textsuperscript{***} | 0.67\textsuperscript{***} |
| Cu\textsubscript{tot} | 0.57\textsuperscript{***} | 0.80\textsuperscript{***} | 0.95\textsuperscript{***} | 0.91\textsuperscript{***} |
| Cu\textsubscript{ox} | 0.87\textsuperscript{***} | –                  | 0.90\textsuperscript{***} | –                  |

\textsuperscript{1} Extracted with 0.05 M oxalate (0.029 M ammonium oxalate, 0.021 M oxalic acid) at pH 3.3 (NISSANEN 1989).

\textsuperscript{*} *, ** Significant at P=0.05, 0.01 and 0.001, respectively.

\textsuperscript{a} Not significant (P > 0.05).
Table 3. Copper extracted with pyrophosphate (Cu\textsubscript{py}) and oxalate (Cu\textsubscript{ox}) as well as residual Cu (Cu\textsubscript{res}) as percentages of total Cu.\(^1\)

| Soil class     | Cu\textsubscript{py} | Cu\textsubscript{ox} | Cu\textsubscript{res} | % of total Cu |
|----------------|----------------------|----------------------|----------------------|---------------|
| Clay n = 25    | mean 16.5\(^{b}\)   | 10.5\(^{b}\)         | 73.0\(^{a}\)         |               |
|                | range 6.3-51.3       | 5.3-22.1             | 33.3-88.1            |               |
| Silt, very fine sand n = 20 | mean 14.8\(^{b}\)   | 10.6\(^{b}\)         | 75.4\(^{a}\)         |               |
|                | range 1.1-32.0       | 3.7-24.0             | 44.0-95.2            |               |
| Fine sand, moraine n = 26 | mean 20.3\(^{b}\)   | 13.1\(^{b}\)         | 66.6\(^{a}\)         |               |
|                | range 9.0-37.6       | 9.7-25.4             | 37.1-81.6            |               |
| Mull n = 14    | mean 37.0\(^{a}\)   | 19.0\(^{a}\)         | 44.0\(^{b}\)         |               |
|                | range 18.6-62.5      | 12.6-24.8            | 14.1-63.5            |               |
| Peat n = 20    | mean 31.1\(^{a}\)   | 19.6\(^{a}\)         | 49.3\(^{b}\)         |               |
|                | range 11.6-50.1      | 8.7-35.8             | 16.0-68.7            |               |

\(^1\) The means in each column have been tested separately. Means marked with the same superscript within a column do not differ at P = 0.05.

In mineral soils, 29\% of Cu\textsubscript{tot} occurred in the secondary fractions (Cu\textsubscript{py}, Cu\textsubscript{ox}), while these fractions constituted 53\% of Cu\textsubscript{tot} in the organogenic soils (Table 3). Even though some organogenic soils more than half of soil Cu was in the form of Cu\textsubscript{py}, Cu\textsubscript{ox} was usually relatively the most abundant fraction in both soil groups. In mineral soils, the percentage of Cu\textsubscript{py} correlated weakly (r = 0.39\(*\)) with organic C content.

**Copper extracted with AAAC-EDTA**

Copper extracted with AAAC-EDTA (Cu\textsubscript{EDTA} mg dm\(^{-3}\)) was highest in clay and mull soils (Table 1). The lowest result (0.9 mg dm\(^{-3}\)) occurred in a Sphagnum peat soil which had been cultivated for five years. Cu\textsubscript{EDTA} constituted on average 16\% of Cu\textsubscript{tot} in mineral soils and 42\% in organogenic soils. In mineral and organogenic soils, AAAC-EDTA extracted 56\% and 71\% of the secondary Cu (Cu\textsubscript{py} + Cu\textsubscript{ox}, mg dm\(^{-3}\)), respectively. Cu\textsubscript{EDTA} correlated most strongly with Cu\textsubscript{py} and Cu\textsubscript{ox} in organogenic soils also with Cu\textsubscript{tot} (Table 4). According to the regression analysis, Cu\textsubscript{EDTA} (mg dm\(^{-3}\)) increased with increasing Cu\textsubscript{py} (mg dm\(^{-3}\)) and Cu\textsubscript{ox} (mg dm\(^{-3}\)) and with decreasing poorly crystalline Al oxide (Al\textsubscript{ox} g dm\(^{-3}\)). The equations, calculated with the logarithms (log\(_{10}\)) of the results, were as follows:

**Mineral soils:**

\[
\log \text{Cu}_{\text{EDTA}} = 0.66 \log \text{Cu}_{\text{py}} + 0.23 \log \text{Cu}_{\text{ox}} - 0.24 \log \text{Al}_{\text{ox}} + 0.14 \\
R^2 = 0.82^{***}
\]

**Organogenic soils:**

\[
\log \text{Cu}_{\text{EDTA}} = 0.43 \log \text{Cu}_{\text{py}} + 0.34 \log \text{Cu}_{\text{ox}} - 0.31 \log \text{Al}_{\text{ox}} + 0.28 \\
R^2 = 0.86^{***}
\]

According to the β coefficients (Table 5), Cu\textsubscript{py} was the dominant soil factor explaining the variation of Cu\textsubscript{EDTA} in both soil groups. In organogenic soils, Cu\textsubscript{ox} and Al\textsubscript{ox} appeared to be slightly

**Table 4. Correlation coefficients (r) between AAAC-EDTA-extractable Cu and other indices of soil Cu. The correlation coefficients have been calculated using the logarithms (log\(_{10}\)) of the results (mg dm\(^{-3}\) of soil).**

| Mineral soils | Organogenic soils |
|---------------|-------------------|
| Cu\textsubscript{py} | 0.88*** | 0.78*** |
| Cu\textsubscript{ox} | 0.81*** | 0.87*** |
| Cu\textsubscript{tot} | 0.56*** | 0.76*** |
| Cu\textsubscript{res} | 0.35**  | 0.45**  |

\(*, **, ***\) Significant at P = 0.01 and 0.001, respectively.

**Table 5. t-Values of the regression coefficients and beta coefficients (β) of the independent variables explaining the variation of log Cu\textsubscript{EDTA} in mineral and organogenic soils.**

| Independent variable | Mineral soils | Organogenic soils |
|----------------------|--------------|------------------|
|                      | t  | β  | t  | β  |
| log Cu\textsubscript{py} | 6.88*** | 0.73 | 2.88**  | 0.61 |
| log Cu\textsubscript{ox} | 2.05*  | 0.22 | 2.18*  | 0.42 |
| log Al                | -3.83*** | -0.21 | -4.51*** | -0.43 |

\(*, **, ***\) Significant at P = 0.05, 0.01 and 0.001, respectively.
more important variables than in mineral soils, but this conclusion becomes less reliable due to the small number of organogenic soils in the material. Poorly crystalline Fe oxide (Fe$_{ox}$) correlated with the secondary Cu fractions (Cu$_{py}$, Cu$_{ox}$) and therefore Fe$_{ox}$ was not a statistically significant variable with Cu$_{py}$ and Cu$_{ox}$, whether or not Al$_{ox}$ was in the equation. In organogenic soils there was a negative correlation ($r = -0.45^{**}$) between log Al$_{ox}$ and organic C. The appearance of Al$_{ox}$ in the above regression equation thus means that the extractability of Cu with AAAc-EDTA increases with increasing organic C and decreases with increasing mineral material.

Vertical distribution of soil Cu

Except for profile 7 (P 7), Cu$_{tot}$ was highest in all the profiles at the bottom (Table 6). The heavy clay layers in P 3 and the Carex peat sample taken from the bottom of P 5 had the highest Cu$_{tot}$ (> 100 mg kg$^{-1}$) of the entire material. Within the fine-textured mineral soil profiles P 1, P 2 and P 3, Cu$_{tot}$ increased with increasing clay content towards the deeper layers. In P 7 generally poor in Cu$_{tot}$, the highest Cu$_{tot}$ in the plough layer may originate from Cu fertilization. In the profiles 1, 3, 5 and 6, Cu$_{EDTA}$ was highest in the deepest layers, two-to-four times that in the plough layer while in the three remaining profiles, Cu$_{EDTA}$ was highest in the plough layer.

In 14 sample pairs consisting of the plough layer (A$_p$) and the subsoil (B) sample, Cu$_{EDTA}$ was significantly higher ($t = 3.375^{* *}$ in the t test for paired measurements) in the plough layer. The means and ranges were as follows:

|        | Mean | Range   |
|--------|------|---------|
| A$_p$  | 5.0  | 2.2–8.9 |
| B      | 2.7  | 0.6–6.2 |

There were three pairs in which Cu$_{EDTA}$ in the subsoil was equal to or slightly lower (0.3–1.0 mg dm$^{-3}$) than in the plough layer. Of 15 sample pairs one pair not included in the above means had a heavy clay subsoil richer in Cu$_{EDTA}$ (18.4 mg dm$^{-3}$) than the organogenic plough layer (8.4 mg dm$^{-3}$).

Comparison of soil Cu and Zn

In mineral soils, the reserves of Cu$_{tot}$ (36 mg kg$^{-1}$) were substantially smaller than those of Zn$_{tot}$ (94 mg kg$^{-1}$, for detailed results see YLI-HALLA 1993), but in organogenic soils the two elements occurred in the same quantities (Cu$_{tot}$ 40 mg kg$^{-1}$, Zn$_{tot}$ 41 mg kg$^{-1}$). In two thirds of the soils the reserves of Cu in the secondary fractions (Cu$_{py}$ + Cu$_{ox}$) were larger than those of Zn. There were only 3 clay soils and 5 silt soils but as many as 16 coarse mineral soils and 8 peat soils where the secondary reserves of Zn exceeded those of Cu. Accordingly, Cu$_{EDTA}$ was lower than Zn$_{EDTA}$ only in 21 soils. The correlation coefficients between the various indices of soil Cu with those of Zn were poorer in the organogenic soils than in the mineral soils (Table 7). It should be pointed out that in organogenic soils the correlation coefficients between Cu$_{py}$ and Zn$_{py}$ as well as between Cu$_{EDTA}$ and Zn$_{EDTA}$ were not statistically significant.

Discussion

In total Cu (Cu$_{tot}$), the present soils corresponded to other soil materials from Finland (BAGHDADY and SIPPOLA 1983, KOLJONEN and MALISA 1991, JOKINEN et al. 1993). They contained more Cu$_{tot}$ than the silty and sandy soils of England (mean 20.3 mg kg$^{-1}$, range 5.2–63.5 mg kg$^{-1}$, McLAREN and CRAWFORD 1973) and clay and silt soils of Saskatchewan, Canada (mean 20.9 mg kg$^{-1}$, range 6.5–39.0 mg kg$^{-1}$, LIANG et al. 1991). Values of Cu$_{tot}$ as high as those commonly found for the heavy clay soils in the present study are seldom reported in unpolluted cultivated soils elsewhere.

The mineral soils studied were richer in Cu$_{EDTA}$ than those of JOKINEN and TÄHTINEN (1987) who deliberately included soils where plants had shown symptoms of Cu deficiency. The mean Cu$_{EDTA}$ was also higher than in some other research materials (2.8 mg dm$^{-3}$, SIPPOLA and TARES 1978, SILLANPÄÄ 1982). Like in SIPPOLA and TARES (1978), Cu$_{EDTA}$ was higher in clay soils than in the other mineral soil classes. In organogenic soils,
Table 6. Total Cu (Cu\textsubscript{tot}) and Cu extracted with AAc-EDTA (Cu\textsubscript{EDTA}) in samples taken from various depths in seven soil profiles.

| Profile 1: Tarvasjoki loam (0-38 cm)/clay loam (38-120 cm) | Profile 2: Vihti, silt |
|---|---|
| **Depth** | **Clay** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** | **Depth** | **Clay** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** |
| 0-30 | 25 | 25.1 | 2.5 | 0-27 | 17 | 29.5 | 2.9 |
| 32-38 | 29 | 27.0 | 2.4 | 30-40 | 11 | 34.0 | 1.2 |
| 38-46 | 34 | 33.4 | 2.7 | 40-50 | 12 | 37.5 | 1.3 |
| 50-60 | 41 | 40.5 | 3.2 | 50-70 | 17 | 48.5 | 1.6 |
| 65-80 | 51 | 51.2 | 3.8 | 70-90 | 6 | 26.5 | 0.9 |
| 85-100 | 56 | 47.5 | 4.8 | 90-100 | 16 | 48.5 | 1.6 |
| 105-120 | 55 | 48.0 | 9.8 | 110-120 | 27 | 62.6 | 2.0 |
| HSD | 1.63 | 0.61 | | HSD | 7.67 | 0.18 |

| Profile 3: Vihti silty clay (0-60 cm)/heavy clay (60-120 cm) | Profile 4: Sotkamo, fine sand |
|---|---|
| **Depth** | **Clay** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** | **Depth** | **FS\textsuperscript{2}** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** |
| 0-30 | 50 | 46.9 | 5.7 | 0-30 | 55 | 13.1 | 3.5 |
| 30-40 | 53 | 55.5 | 5.7 | 30-40 | 63 | 4.7 | 1.0 |
| 40-60 | 54 | 61.0 | 4.1 | 40-45 | 52 | 5.8 | 1.4 |
| 60-80 | 72 | 67.7 | 6.4 | 45-60 | 67 | 6.7 | 0.9 |
| 80-100 | 88 | 108.9 | 9.3 | 60-80 | 75 | 8.0 | 0.7 |
| 100-120 | 76 | 109.2 | 10.5 | 80-110 | 82 | 12.6 | 1.3 |
| HSD | 5.13 | 0.79 | | 110-120 | 64 | 15.4 | 1.0 |
| | | | | HSD | 1.43 | 0.31 |

| Profile 5: Sotkamo, Carex peat (20-120 cm), mineral soil mixed in the plough layer | Profile 6: Jokioinen, Carex peat (0-40 cm)/mud (40-50 cm)/heavy clay (50-80 cm) |
|---|---|
| **Depth** | **Organic C** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** | **Depth** | **Organic C** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** |
| 0-20 | 9 | 32.5 | 10.5 | 0-25 | 31 | 51.2 | 6.4 |
| 20-30 | 52 | 23.8 | 2.4 | 30-40 | 30 | 83.2 | 11.5 |
| 30-40 | 49 | 27.6 | 2.7 | 40-45 | 17 | 89.1 | 15.0 |
| 40-60 | 52 | 35.4 | 3.6 | 50-70 | 1 | 79.9 | 17.0 |
| 60-80 | 47 | 46.8 | 5.2 | 70-80 | 1 | 95.3 | 17.5 |
| 80-100 | 40 | 55.7 | 7.4 | HSD | | 1.98 | 4.05 |
| 100-120 | 31 | 65.5 | 9.8 | | | |
| 120-130 | 32 | 107.3 | 20.5 | | | |
| HSD | 2.94 | 0.61 | | | | |

| Profile 7: Muhos Carex peat (0-110 cm)/fine sand (110-125 cm) |
|---|
| **Depth** | **Organic C** | **Cu\textsubscript{tot} mg kg\textsuperscript{-1}** | **Cu\textsubscript{EDTA} mg dm\textsuperscript{-3}** |
| 0-30 | 45 | 41.9 | 23.3 |
| 30-50 | 55 | 2.7 | 0.9 |
| 50-70 | 52 | 1.3 | 0.8 |
| 70-90 | 56 | 4.9 | 1.3 |
| 90-110 | 54 | 11.4 | 1.8 |
| 110-125 | 0.2 | 2.8 | 0.7 |
| HSD | 3.61 | 0.29 |

\footnotetext{1}{Each profile was tested separately for Cu\textsubscript{tot} and Cu\textsubscript{EDTA}. Means marked with the same superscript within a column do not differ at P = 0.05.}

\footnotetext{2}{Fine sand, 0.06-0.2 mm}
Table 7. Correlation coefficients (r) between various indices of soil Cu and Zn, calculated using the logarithms of the results (mg dm⁻³ of soil).

| Correlation coefficients between         | Mineral soils | Organogenic soils |
|------------------------------------------|---------------|------------------|
| Cu₁py and Zn₁py                          | 0.48***       | 0.20 ns          |
| Cu₁ox and Zn₁ox                          | 0.65**        | 0.42*            |
| Cu₁res and Zn₁res                         | 0.89***       | 0.34*            |
| Cu₁tot and Zn₁tot                         | 0.87**        | 0.51**           |
| Cu₁EDTA and Zn₁EDTA                      | 0.49***       | 0.07 ns          |

*, **, *** Significant at P = 0.05, 0.01 and 0.001, respectively.
ns Not significant (P > 0.05).

The mean Cu₁EDTA was similar to that reported by Joakin et al. (1993). The present soils also exhibited nearly the average Cu₁EDTA reported in routine soil testing in 1986–1988 (Viljavuuspalvelu – Soil Testing Service, Ltd., unpublished data) in over 60000 samples of mineral soils coarser than silt (mean 4.2 mg dm⁻³) and in over 25000 organogenic soils (mean 5.2 mg dm⁻³). The material of this study represents fairly well the average cultivated soils of Finland, even though there was only one soil classified as 'poor' in Cu (Cu₁EDTA below 1 mg dm⁻³) according to the interpretation of Sillanpää (1982).

The fraction of water-soluble and exchangeable Cu is too small to satisfy the needs of the plants (McLaren and Crawford 1973, Liang et al. 1991), and this readily plant-available form is replenished from other secondary fractions, especially from that bound by organic matter (Liang et al. 1991). It was therefore considered appropriate in this study to include water-soluble, exchangeable and specifically adsorbed Cu, together with Cu bound mainly by organic matter, in Cu₁py and not to extract them separately as is commonly done in fractionation procedures. Cu₁py expressed as percentages of Cu₁tot was in mineral soils at the same level as the sum of water-soluble, exchangeable, specifically adsorbed and organically bound Cu in soils of Saskatchewan, Canada (18.4% of Cu₁tot, Liang et al. 1991). Also Cu₁ox and Cu₁res in the soils of Canada (11% and 71% of Cu₁tot, respectively) were equal to those in texturally similar soils of the present study. In other studies (McLaren and Crawford 1973, Shuman 1985), the relative sizes of the secondary fractions have been higher and those of Cu₁res slightly lower (Cu₁res 53% and 65%, respectively) than the relative sizes in the mineral soils of this investigation. In organogenic soils, the lower percentage of Cu₁res and the higher ones of Cu₁py and Cu₁ox as compared to the mineral soils can be explained by the smaller quantity of mineral material, the source of Cu₁res.

Copper extracted with AAAC-EDTA has correlated rather closely with Cu supply to plants in pot experiments (Sillanpää 1982, Ervio and Sipponen 1993). On the basis of the observation that the content of Cu₁py explained a great deal of the variation of Cu₁EDTA especially in mineral soils, it can be concluded that AAAC-EDTA dissolves Cu from the same reserves as does pyrophosphate. Also Cu bound by poorly crystalline oxides (Cu₁ox) can be plant-available (Gallardo-Lara and Torres-Martin 1990, Liang et al. 1991) but according to McLaren and Crawford (1973) Cu₁ox is of minor importance as a source of plant-available Cu. The latter assumption is supported also by the results of the present study where Cu₁ox relatively poorly explained the variation of Cu₁EDTA.

In Finland, Cu deficiency in crop production has been reported especially in peat soils (Tainio 1963, Tähtinen 1971). Even though quite a few peat soils may be low in Cu₁tot, the present results demonstrate that by far all of them are not poor in Cu₁EDTA. Therefore soil testing is necessary to recognize the soils where Cu fertilizers should be applied. In organogenic soils, AAAC-EDTA extracted a higher proportion of the potentially plant-available Cu (Cu₁py + Cu₁ox) than in mineral soils. Thus, low Cu₁EDTA in organogenic soils implies for certain a scarcity of Cu and a probable requirement of Cu fertilization.

A higher Cu₁EDTA in the plough layer, as compared to the B horizon, can partly be attributed to fertilizers, manures, atmospheric deposition and uplift of Cu by plant roots from below the plough layer. The higher content of organic matter may also enhance the solubility of Cu (Sillanpää
1982). On the other hand, investigation of the soil profiles revealed that soils rich in Cu$_{tot}$ had abundant reserves of Cu$_{EDTA}$ also in the layers below the rooting depth of annual field crops. There, Cu released from primary minerals is not within the reach of plant roots and has obviously remained where the mineral was weathered. In the soils poor in Cu$_{tot}$ this phenomenon was not observed, probably owing to the lack of weatherable Cu-containing minerals. A similar vertical distribution of Zn$_{EDTA}$ has earlier been observed in the same soil profiles (Yli-Halla 1993).

In a recent study, carried out with the same soil samples (Yli-Halla 1993), 90% of Zn$_{tot}$ in mineral soils occurred as Zn$_{res}$, while in the present investigation only 71% of Cu$_{tot}$ occurred as Cu$_{res}$. Accordingly, the percentages of the secondary fractions of Cu were higher than those of Zn. Similar conclusions can be drawn also from the results of Shuman (1979, 1985) and Liang et al. (1990, 1991). The difference between the distribution of Cu and Zn was even wider in the mull soils of the present studywhere 47% of Cu$_{tot}$ and as much as 80% of Zn$_{tot}$ occurred in the residual fraction. According to Mullins et al. (1982), fertilizer Cu and Zn are accumulated in forms extractable with pyrophosphate and oxalate. The relative abundance of secondary Cu fractions as compared to those of Zn as well as the poor correlation between the fractions of Cu and Zn in organogenic soils can partly be explained by additions in Cu fertilizers, applied commonly in Finland since the 1950’s. Zinc fertilization, as a rarer and a more recent practice, has probably contributed to a smaller increase in soil Zn content. Ample application of fertilizer Cu may also explain why even Cu$_{tot}$ was equal to Zn$_{tot}$ in organogenic soils, while in mineral soils Cu$_{tot}$ was much lower than Zn$_{tot}$. However, the secondary Cu fractions were more abundant than those of Zn also in mineral soils, and it is very unlikely that clay soils in particular have received either Cu or Zn in chemical fertilizers. The relative abundance of Cu in the secondary fractions therefore suggests that Cu minerals have weathered at a higher rate than those containing Zn.

The sufficiency of plant nutrients in soil can, to some extent, be assessed by comparing the need of a plant for the plant-available reserves. In the study of Yläranta and Sillanpää (1984), the Zn concentration was 5–11 times the concentration of Cu in cereal crops and 3–6 times that in forage crops. However, the size of the secondary Cu fractions in two thirds of the soil samples of the present study was higher than that of Zn. Therefore, the reserves of plant-available Cu in average soils may be more abundant as related to plant uptake than those of Zn.

Acknowledgements. The author wishes to thank Kemira Oy Espoo Research Centre for carrying out the chemical analyses of this investigation.

References

Baghdady, N. H. & Sippola, J. 1983. Total heavy metal recovery by aqua regia in soils of different origin. Annales Agriculturae Fenniae 22: 175–185.

Gallardo-Lara, F. & Torres-Martin, M. 1990. Dynamics of copper fractions in the soil-plant system under conditions of intensive forage cropping. Zeitschrift für Pflanzenernährung und Bodenkunde 153: 291–292.

Erviö, R. & Sippola, J. 1993. Micronutrient concentration of Italian ryegrass (Lolium multiflorum L.) grown on different soils in a pot experiment. Agricultural Science in Finland 2: 141–148.

Jokinen, R. & Tahtinen, H. 1987. Copper content of coarse mineral and peat soils and the growth of oats in a pot experiment. Annales Agriculturae Fenniae 26: 227–237.

Lakanen, E. & Erviö, R. 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. Acta Agraria Fennica 123: 223–232.

Liang, J., Karamanos, R. E. & Stewart, J. W. B. 1990. Distribution of zinc fractions in prairie soils. Canadian Journal of Soil Science 70: 335–342.
Stewart, J. W. B. & Karamanos, R. E. 1991. Distribution and plant-availability of soil copper fractions in Saskatchewan. Canadian Journal of Soil Science 71: 89–99.

Mclaren, R. G. & Crawford, D. V. 1973. Studies on soil copper. I. The fractionation of copper in soils. Journal of Soil Science 24: 172–181.

Mullins, G. L. & Martens, D., Gettier, S. W. & Miller, W. P. 1982. Forms and availability of copper and zinc in a Rhodic Paleudult following long-term CuSO₄ and ZnSO₄ applications. Journal of Environmental Quality 11: 573–577.

Niskanen, R. 1989. Extractable aluminium, iron and manganese in mineral soils. II. Extractability by oxalate and pyrophosphate. Journal of Agricultural Science in Finland 61: 79–87.

Raisanen, M.-L. & Hamäinen, L. 1991. Selective sequential dissolution of polluted and non-polluted sediments. Environmental geochemistry in northern Europe. Geological Survey of Finland. Special Paper 9: 157–162.

Shuman, L. M. 1979. Zinc, manganese, and copper in soil fractions. Soil Science 127: 10–17.

1985. Fractionation method for soil microelements. Soil Science 140: 11–22.

Sillanpää, M. 1982. Micronutrients and the nutrient status of soils: a global study. FAO Soils Bulletin 48: 1–444.

Sippola, J. & Tares, T. 1978. The soluble content of mineral elements in cultivated Finnish soils. Acta Agriculturae Scandinavica, Suppl. 20: 11–25.

Tainio, A. 1963. Kuparinvaloiteista, niiden käytöstä ja merkityksestä. Leipä leveämäksi 1, 2: 12–16.

Tähtinen, H. 1971. Copper content of the soil and the effect of copper fertilization. Acta Agralia Fennica 123: 136–142.

Viets, F. G. Jr. 1962. Chemistry and availability of micronutrients in soils. Journal of Agricultural and Food Chemistry 10: 174–178.

Yli-Halla, M. 1993. Plant-availability of soil and fertilizer zinc in cultivated soils of Finland. Agricultural Science in Finland 3: 197–270.

Yläranta, T. & Sillanpää, M. 1984. Micronutrient contents of different plant species grown by side. Annales Agriculturae Fenniae 23: 158–170.

Manuscript received April 1994

SELOSTUS

Kupari Suomen viljelysmaissa

Markku Yli-Halla

Helsingin yliopisto

Viljelysmaiden muokkauskerroksen kuparivarojen tutkittiin määritetämällä kuparin (Cu) kokonaismäärä sekä eri tavoin maahan sitoutuneita kuparin fraktioita. Kuparin kokonaismäärä (6,9 – 97,4 mg kg⁻¹) oli suurin savimaisissa (keskiarvo 59,0 mg kg⁻¹) ja pienin karkeassa hiedassa ja moreenimaisissa (18,3 mg kg⁻¹). Kivennäismaissa kuparin kokonaismäärä oli vuorosuhteessa savespiitouduksen kanssa. Vesiliukoisen ja vaihtuvan kuparin sekä orgaanisen aineksen ja rauta-alumiini- ja mangaanioksidien sitoman kuparin summa oli kivennäismaissa 30 % ja eloperäisissä maissa 53 % kokonaismäärästä. Näitä osuuksia voidaan pitää potentiaalisesti kasveille käyttökelpoisina. Kummassakin maalajiryhmässä mineraalirakenteisiin sitoutuneen, kasveille käyttökelpottoman kuparin osuu oli suuri (kivennäismaisissa 70 %, eloperäissä maissa 47 %). Viljavuusanalyysissä kupari uuttaan hoppamalla ammoniumasetaattitettakahappo-EDTA-liuoksella, pH 4,65 (CuEDTA). Tämä liuos uutti vaihtuvasta, orgaanisen aineksen ja oksidien sitomasta kuparista kivennäismailla 36 % ja eloperäissillä mailla 71 %.

Muokkauskerroksen CuEDTA-varat olivat lähes poikkeamatta suuremmat kuin jankoon, mutta varsinkin savimailta juuristoyöhykkeen alapuolisissa maakerroksissa oli runsaasti CuEDTA. Perinteisesti turvemaiden on sanottu tarvitsevan kuparilannoitusta. Vaikka tässäkin aineistossa moneessa turvemäessä kuparin kokonaismäärä oli pieni, olemme joissa runsaasti CuEDTA. Tästä syystä kuparilannoitus ei saa millään maalajilla olla automaattinen viljelytoimi vaan sen on perustuttava maa-analyysi.