

Copper in cultivated soils of Finland

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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} , $HNO_3-HClO_4-HF-H_2SO_4$ 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 $K_4P_2O_7$ (Cu_{py}), and Cu bound by poorly crystalline Fe, Al and Mn oxides (Cu_{ox}) was dissolved subsequently with 0.05 M oxalate (pH 2.9). The average percentages of Cu_{py} and Cu_{ox} 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 soils the potentially plant-available reserves of Cu ($Cu_{py} + Cu_{ox}$) were more plentiful than those of Zn ($Zn_{py} + Zn_{ox}$). An acetic acid – ammonium acetate – Na_2EDTA solution used in routine soil testing extracted 56% and 71% of the sum of $Cu_{py} + Cu_{ox}$ 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_{tot} 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 (RÄISÄNEN and HÄMÄLÄINEN 1991) but the fractional distribution of Cu in cultivated soils of the country is unknown.

An ammonium acetate – acetic acid – Na_2EDTA solution (AAAc-EDTA, pH 4.65) is used to extract Cu in soil testing in Finland. Recently, JOKINEN 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_p 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_p 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_3 , $HClO_4$, HF and H_2SO_4 (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 $K_4P_2O_7$ (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_3 , $HClO_4$, HF and H_2SO_4 to determine the residual Cu (Cu_{res}) but in most soil samples Cu_{res} was calculated as total Cu minus the sum of Cu extracted with pyrophosphate and oxalate, i.e. $Cu_{tot} - (Cu_{py} + Cu_{ox})$. 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_{tot} , Cu_{py} , Cu_{ox} and Cu_{res} 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^3 of soil by multiplying them with the bulk density. Copper was also 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), which is the method used in soil testing in Finland.

Results

Total copper

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

Fractions of soil copper

In the 16 representative soil samples, Cu_{tot} and the sum of the fractions ($Cu_{py} + Cu_{ox} + Cu_{res}$)

Table 1. Total Cu (Cu_{tot}) and Cu in fractions extracted with pyrophosphate (Cu_{py}) and oxalate (Cu_{ox}) and in the residual fraction (Cu_{res}), and Cu extracted with AAAC-EDTA (Cu_{EDTA}) as well as the bulk density of the plough layer soil samples.¹

Soil class and number of samples		Bulk density ² kg dm ⁻³	Cu_{tot}	Cu_{py} mg kg ⁻¹	Cu_{ox}	Cu_{res}	Cu_{EDTA} mg dm ⁻³
Clay n = 25	mean	0.96 ^b	59.0 ^a	9.2 ^a	6.2 ^a	43.8 ^a	7.7 ^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 ^b	30.7 ^b	4.3 ^b	3.1 ^b	23.4 ^b	4.2 ^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 ^a	16.3 ^c	3.3 ^b	2.1 ^b	10.8 ^c	3.7 ^b
	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 ^c	41.4 ^b	15.3 ^a	7.8 ^a	18.3 ^{bc}	8.1 ^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 ^d	38.5 ^b	12.9 ^a	7.7 ^a	17.9 ^{bc}	5.9 ^{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

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

² Determined by YLI-HALLA (1993).

were 28.9 mg kg⁻¹ and 33.0 mg kg⁻¹, respectively. The difference between these figures in the individual soils ranged from -0.7 to 13.0 mg kg⁻¹ (median 4.0 mg kg⁻¹). Owing to the satisfactory recovery of Cu in the fractions, the determination of Cu_{res} was discontinued and the rest of the results of Cu_{res} were calculated as the difference $Cu_{tot} - (Cu_{py} + Cu_{ox})$.

The concentration of Cu extracted with pyrophosphate (Cu_{py} , Table 1) was highest in mull and peat soils, but when expressing the results as mg dm⁻³ of soil, the mean of 9.8 mg dm⁻³ places the mull soils at the same level as clay soils. The mean of 5.1 mg dm⁻³ in peat soils equals that in silt and very fine sand soils. In most soils the concentration of Cu extracted with oxalate (Cu_{ox} , Table 1) was smaller than Cu_{py} ; only in 13 soils was Cu_{ox} equal to or higher than Cu_{py} . Cu_{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_{py} and Cu_{ox} correlated highly with each other. In mineral soils, Cu_{py} correlated highly significantly ($P = 0.001$) also with clay and Cu_{tot} (Table 2), while Cu_{ox} correlated with Cu_{tot} , Cu_{res} , clay and poorly crystalline Fe oxide (Fe_{ox}). However, the partial cor-

relation between Cu_{ox} and Fe_{ox} , after the elimination of the effect of clay, was not significant ($P = 0.05$). In organogenic soils, both Cu_{py} and Cu_{ox} correlated most closely ($P = 0.001$) with Cu_{res} and Cu_{tot} .

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

Soil characteristic	Mineral soils		Organogenic soils	
	Cu_{py}	Cu_{ox}	Cu_{py}	Cu_{ox}
Clay	0.52***	0.68***	—	—
Organic C	0.32**	0.09 ^{n.s.}	-0.52**	-0.45**
Fe ¹	0.35**	0.44***	0.50**	0.48**
Al ^{ox1}	0.24 ^{n.s.}	0.23 ^{n.s.}	0.47**	0.22 ^{n.s.}
Cu_{res}	0.38**	0.62***	0.61***	0.67***
Cu_{tot}	0.57***	0.80***	0.95***	0.91***
Cu_{ox}	0.87***	—	0.90***	—

¹ Extracted with 0.05 M oxalate (0.029 M ammonium oxalate, 0.021 M oxalic acid) at pH 3.3 (NISKANEN 1989). *, **, *** Significant at $P = 0.05$, 0.01 and 0.001, respectively. ^{n.s.} Not significant ($P > 0.05$).

Table 3. Copper extracted with pyrophosphate (Cu_{py}) and oxalate (Cu_{ox}) as well as residual Cu (Cu_{res}) as percentages of total Cu.¹

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

Copper extracted with AAAC-EDTA

Copper extracted with AAAC-EDTA (Cu_{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_{EDTA} constituted on average 16% of Cu_{tot} in mineral soils and 42% in organogenic soils. In mineral and organogenic soils, AAAC-EDTA extracted 56% and 71% of the secondary Cu ($Cu_{py} + Cu_{ox}$, $mg\ dm^{-3}$), respectively. Cu_{EDTA} correlated most strongly with Cu_{py} and Cu_{ox} , in organogenic soils also with Cu_{tot} (Table 4). According to the regression analysis,

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).

	r	
	Mineral soils	Organogenic soils
Cu_{py}	0.88 ^{***}	0.78 ^{***}
Cu_{ox}	0.81 ^{***}	0.87 ^{***}
Cu_{tot}	0.56 ^{***}	0.76 ^{***}
Cu_{res}	0.35 ^{**}	0.45 ^{**}

^{**}, ^{***} Significant at $P = 0.01$ and 0.001 , respectively.

Cu_{EDTA} ($mg\ dm^{-3}$) increased with increasing Cu_{py} ($mg\ dm^{-3}$) and Cu_{ox} ($mg\ dm^{-3}$) and with decreasing poorly crystalline Al oxide (Al_{ox} , $g\ dm^{-3}$). The equations, calculated with the logarithms (\log_{10}) of the results, were as follows:

Mineral soils:

$$\log Cu_{EDTA} = 0.66 \log Cu_{py} + 0.23 \log Cu_{ox} - 0.24 \log Al_{ox} + 0.14$$

$$R^2 = 0.82^{***}$$

Organogenic soils:

$$\log Cu_{EDTA} = 0.43 \log Cu_{py} + 0.34 \log Cu_{ox} - 0.31 \log Al_{ox} + 0.28$$

$$R^2 = 0.86^{***}$$

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

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

Independent variable	Mineral soils		Organogenic soils	
	t	β	t	β
$\log Cu_{py}$	6.88 ^{***}	0.73	2.88 ^{**}	0.61
$\log Cu_{ox}$	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 $\log \text{Al}_{\text{ox}}$ 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} ($> 100 \text{ mg kg}^{-1}$) 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 ($0.3\text{--}1.0 \text{ mg dm}^{-3}$) 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 ($\text{Cu}_{\text{py}} + \text{Cu}_{\text{ox}}$) 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 $5.2\text{--}63.5 \text{ mg kg}^{-1}$, MCLAREN and CRAWFORD 1973) and clay and silt soils of Saskatchewan, Canada (mean 20.9 mg kg^{-1} , range $6.5\text{--}39.0 \text{ mg kg}^{-1}$, 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_{tot}) and Cu extracted with AAAC-EDTA (Cu_{EDTA}) in samples taken from various depths in seven soil profiles.¹

Profile 1: Tarvasjoki loam (0–38 cm)/clay loam (38–120 cm)				Profile 2: Vihti, silt			
Depth cm	Clay %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³	Depth cm	Clay %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³
0–30	25	25.1 ^f	2.5 ^e	0–27	17	29.5 ^d	2.9 ^a
32–38	29	27.0 ^e	2.4 ^e	30–40	11	34.0 ^{cd}	1.2 ^d
38–46	34	33.4 ^d	2.7 ^{de}	40–50	12	37.5 ^c	1.3 ^d
50–60	41	40.5 ^c	3.2 ^d	50–70	17	48.5 ^b	1.6 ^c
65–80	51	51.2 ^a	3.8 ^c	70–90	6	26.5 ^d	0.9 ^e
85–100	56	47.5 ^b	4.8 ^b	90–100	16	48.5 ^b	1.6 ^c
105–120	55	48.0 ^b	9.8 ^a	110–120	27	62.6 ^a	2.0 ^b
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 cm	Clay %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³	Depth cm	FS ² %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³
0–30	50	46.9 ^e	5.7 ^c	0–30	55	13.1 ^b	3.5 ^a
30–40	53	55.5 ^d	5.7 ^c	30–40	63	4.7 ^e	1.0 ^c
40–60	54	61.0 ^c	4.1 ^d	40–45	52	5.8 ^{de}	1.4 ^b
60–80	72	67.7 ^b	6.4 ^c	45–60	67	6.7 ^d	0.9 ^d
80–100	88	108.9 ^a	9.3 ^b	60–80	75	8.0 ^c	0.7 ^d
100–120	76	109.2 ^a	10.5 ^a	80–110	82	12.6 ^b	1.3 ^{bc}
HSD		5.13	0.79	110–120	64	15.4 ^a	1.0 ^{cd}
				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 cm	Org. C %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³	Depth cm	Org. C %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³
0–20	9	32.5 ^e	10.5 ^b	0–25	31	51.2 ^e	6.4 ^c
20–30	52	23.8 ^f	2.4 ^f	30–40	30	83.2 ^c	11.5 ^b
30–40	49	27.6 ^f	2.7 ^f	40–45	17	89.1 ^b	15.0 ^{ab}
40–60	52	35.4 ^e	3.6 ^f	50–70	1	79.9 ^d	17.0 ^a
60–80	47	46.8 ^d	5.2 ^e	70–80	1	95.3 ^a	17.5 ^a
80–100	40	55.7 ^c	7.4 ^d	HSD		1.98	4.05
100–120	31	65.5 ^b	9.8 ^c				
120–130	32	107.3 ^a	20.5 ^a				
HSD		2.94	0.61				
Profile 7: Muhos Carex peat (0–110 cm)/fine sand (110–125 cm)							
Depth cm	Org. C %	Cu_{tot} mg kg ⁻¹	Cu_{EDTA} mg dm ⁻³				
0–30	45	41.9 ^a	23.3 ^a				
30–50	55	2.7 ^c	0.9 ^d				
50–70	52	1.3 ^c	0.8 ^d				
70–90	56	4.9 ^c	1.3 ^c				
90–110	54	11.4 ^b	1.8 ^b				
110–125	0.2	2.8 ^c	0.7 ^d				
HSD		3.61	0.29				

¹ Each profile was tested separately for Cu_{tot} and Cu_{EDTA} . Means marked with the same superscript within a column do not differ at $P = 0.05$.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
Cu_{py} and Zn_{py}	0.48***	0.20 ^{n.s.}
Cu_{ox} and Zn_{ox}	0.65***	0.42*
Cu_{res} and Zn_{res}	0.89***	0.34*
Cu_{tot} and Zn_{tot}	0.87***	0.51**
Cu_{EDTA} and Zn_{EDTA}	0.49***	0.07 ^{n.s.}

*, **, *** Significant at $P = 0.05, 0.01$ and 0.001 , respectively.

^{n.s.} Not significant ($P > 0.05$).

mean Cu_{EDTA} was similar to that reported by JOKINEN et al. (1993). The present soils also exhibited nearly the average Cu_{EDTA} 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 (Cu_{EDTA} 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 Cu_{py} and not to extract them separately as is commonly done in fractionation procedures. Cu_{py} , expressed as percentages of Cu_{tot} , 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 Cu_{tot} , LIANG et al. 1991). Also Cu_{ox} and Cu_{res} in the soils of Canada (11% and 71% of Cu_{tot} , 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 Cu_{res} slightly lower (Cu_{res} 53% and 65%, respectively) than the relative sizes in the mineral soils of this investigation. In organogenic soils, the lower percentage of Cu_{res} and the higher ones of Cu_{py} and Cu_{ox} as compared to the mineral soils can be explained by the smaller quantity of mineral material, the source of Cu_{res} .

Copper extracted with AAAC-EDTA has correlated rather closely with Cu supply to plants in pot experiments (SILLANPÄÄ 1982, ERVIÖ and SIPOLA 1993). On the basis of the observation that the content of Cu_{py} explained a great deal of the variation of Cu_{EDTA} 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 (Cu_{ox}) can be plant-available (GALLARDO-LARA and TORRES-MARTIN 1990, LIANG et al. 1991) but according to MCLAREN and CRAWFORD (1973) Cu_{ox} 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 Cu_{ox} relatively poorly explained the variation of Cu_{EDTA} .

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 Cu_{tot} , the present results demonstrate that by far all of them are not poor in Cu_{EDTA} . 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 ($\text{Cu}_{\text{py}} + \text{Cu}_{\text{ox}}$) than in mineral soils. Thus, low Cu_{EDTA} in organogenic soils implies for certain a scarcity of Cu and a probable requirement of Cu fertilization.

A higher Cu_{EDTA} 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 study where 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 addi-

tions 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.

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SELOSTUS

Kupari Suomen viljelysmaissa

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Viljelysmaiden muokkauskerroksen kuparivaroja tutkittiin määrittämällä kuparin (Cu) kokonaismäärä sekä eri tavoin maahan sitoutuneita kuparin fraktioita. Kuparin kokonaismäärä (6,9 – 97,4 mg kg⁻¹) oli suurin savimaissa (keskiarvo 59,0 mg kg⁻¹) ja pienin karkeassa hiedassa ja moreeni- maissa (18,3 mg kg⁻¹). Kivennäismaissa kuparin kokonaismäärä oli vuorosuhteessa savespitoisuuden kanssa. Vesiliukoisien 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 käyttökeltvottoman kuparin osuus oli suuri (kivennäismaissa 70 %, eloperäisissä maissa 47 %). Viljavuusana-

lyysissä kupari uutetaan happamalla ammoniumasetaatti-etikkahappo-EDTA-liuoksella, pH 4,65 (Cu_{EDTA}). Tämä liuos uutti vaihtuvasta, orgaanisen aineksen ja oksidien sitomasta kuparista kivennäismailla 56 % ja eloperäisillä mailla 71 %.

Muokkauskerroksen Cu_{EDTA} -varat olivat lähes poikkeuksetta suuremmat kuin jankon, mutta varsinkin savimailla juuristovyöhykkeen alapuolisissa maakerroksissa oli runsaasti Cu_{EDTA} . Perinteisesti turvemaiden on sanottu tarvitsevan kuparilannoitusta. Vaikka tässäkin aineistossa monessa turvemaassa kuparin kokonaismäärä oli pieni, oli useimmissa turvemaissa melko runsaasti Cu_{EDTA} . Tästä syystä kuparilannoitus ei saa millään maalajilla olla automaattinen viljelytoimi vaan sen on perustuttava maa-analyysiin.