Extractable aluminium, iron and manganese in mineral soils III Comparison of extraction methods

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Abstract. The extractability of soil Al, Fe and Mn were studied in 102 mineral soil samples. The extractants were 0.05 M oxalate (pH 2.9), 0.05 M $K_4P_2O_7$ (pH 10), 0.02 M EDTA (pH 5.3) and 1 M CH_3COONH_4 (pH 4.8). In the group of clay and silt soils (n = 51), the Al extracted by the four extractants correlated closely; the r values ranged from 0.91*** to 0.96***; in coarser soils (n = 51) the r values ranged from 0.42* to 0.82***. In clay and silt soils, the organic carbon content and soil pH together explained 50 % of the variation in oxalate-extractable Al, 70 % of the variation in pyrophosphate-extractable Al, 53 % of the variation in pyrophosphate-extractable Fe and 56 % of the variation in acetate-extractable Al. The clay and organic carbon contents together with soil pH explained 77 % of the variation in EDTA-extractable Al in clay and silt soils. In coarse soils, the extractable metals were not closely related to the soil characteristics.

Index words: acetate-extractable Al, EDTA-extractable metals, oxalate-extractable metals, pyrophosphate-extractable metals, organic carbon content, clay content, soil pH

Introduction

Non-crystalline inorganic components of soil are often termed "active" to indicate their importance in soil processes (MITCHELL et al. 1964). The principal forms of these components are oxides and hydrous oxides of Al, Fe, Mn, Si and Ti which may be adsorbed on mineral surfaces, or they exist as discrete particles (HUANG and LEE 1969, HUANG and KOZAK 1970, WADA and HARWARD 1974). Extraction methods have been used to differentiate various forms of soil oxides. Ammoni-um oxalate (TAMM 1922, SCHWERTMANN 1964, McKEAGUE and DAY 1966) and pyrophosphate (ALEKSANDROVA 1960, McKEAGUE 1967), for instance, have been used to extract iron and aluminium in oxides and complexed by organic matter. The purpose of this paper was to compare the release of soil aluminium, iron and manganese by different extraction methods and to study the relationship of metals to soil particle-size distribution, organic carbon content and pH.

Material and methods

The material of 102 mineral soil samples was collected in 15 localities mainly in southern Finland (Table 1). The 53 sampling sites represented principally agricultural soils (9 of them were virgin). The surface layer was sampled from 0 to the depth of 20—30 cm; at 48 sites the deeper layer was sampled to the depth of 40—60 cm. The material included 36 clay soil samples with a clay fraction content ($\varnothing$ < 2 µm) of 30—72 %, and 15 were silt soil samples. Because of the high clay content in the silt soils, they were examined in the same group with clay soils.

The samples were air-dried at room temperature and ground to pass through a 2-mm sieve. The pH of the soil was measured in a soil-0.01 M $CaCl_2$ suspension (1:2.5 v/v) (RYTI 1965). The particle-size distribution of inorganic matter was determined by the pipette method (ELONEN 1971), the organic carbon content by the ALTEN wet combustion method (GRAHAM 1948).

Soil aluminium, iron and manganese were extracted by the methods presented in Table 2. The extractions were carried out in duplicate or triplicate. Aluminium, iron and manganese in filtrates were determined by atomic absorption spectrophotometry, Fe and Mn with air-acetylene flame and Al with N_2O-acetylene flame.

Results

Of the extractants studied, 0.05 M oxalate (Table 3) released metals most effectively. In the group of clay and silt soils, the oxalate-extractable aluminium correlated closely with the aluminium extracted by 0.05 M $K_4P_2O_7$, 0.02 M EDTA and 1 M ammonium acetate (Tables 4—7). In coarse soils, the oxalate-extractable aluminium did not correlate very closely with the aluminium extracted by the other methods (Table 7). The oxalate-extractable iron and manganese (Table 3) did not correlate closely with the metals extracted by pyrophosphate (Table 4) and EDTA (Table 5).

Table 1. Soil characteristics.

| | n | pH($CaCl_2$) | | | Org.C, % | | | Particle-size distribution (µm), % | | | | | | | | |
| | | | | | | | | < 2 | | | 2—20 | | | > 20 | | |
		$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:																
Surface soils	27	5.4	0.9	3.9—7.2	4.6	3.0	1.1—14.6	37	14	15—70	33	12	8—55	30	15	9—61
Subsoils	24	5.4	0.6	4.1—6.9	3.2	2.3	0.8—11.5	43	13	19—72	32	15	6—61	25	13	7—55
All	51	5.4	0.8	3.9—7.2	3.7	2.8	0.8—14.6	40	14	15—72	33	13	6—61	28	14	7—61
Coarse soils:																
Surface soils	26	5.2	1.0	3.5—7.3	4.0	2.5	1.5—12.3	9	7	2—28	12	6	2—23	80	11	56—95
Subsoils	25	5.3	0.9	4.1—7.2	1.6	0.9	0.6—3.7	7	8	1—28	11	8	1—29	82	13	51—98
All	51	5.2	1.0	3.5—7.3	2.8	2.2	0.6—12.3	8	8	1—28	12	7	1—29	81	12	51—98
All soils:																
Surface soils	53	5.3	1.0	3.5—7.3	4.3	2.7	1.1—14.6	23	18	2—70	23	14	2—55	55	28	9—95
Subsoils	49	5.3	0.8	4.1—7.2	2.1	1.8	0.6—11.5	25	21	1—72	22	16	1—61	54	31	7—98

Table 2. Extraction methods.

Extractant	pH	Extraction ratio, w/v	Shaking time, h	Reference
0.05 M oxalate (0.026 M ammonium oxalate, 0.024 M oxalic acid)	2.9	1:20	2	NISKANEN 1989a
0.05 M $K_4P_2O_7$	10	1:100	3	NISKANEN 1989a
0.02 M Na_2-EDTA	5.3	1:50	3	
1 M ammonium acetate	4.8	1:10	2	McLEAN et al. 1958

Table 3. 0.05 M oxalate-extractable Al, Fe and Mn.

		Al, mmol/kg soil			Fe, mmol/kg soil			Mn, µmol/kg soil		
	n	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:										
Surface soils	27	78	41	32—210	96	38	43—191	2 610	1 730	230—6 240
Subsoils	24	64	39	29—222	108	46	32—202	2 020	1 520	160—4 870
All	51	71	41	29—222	102	42	32—202	2 330	1 650	160—6 240
Coarse soils:										
Surface soils	26	79	49	16—186	60	29	7—144	1 460	1 070	120—4 640
Subsoils	25	82	63	11—249	44	32	3—135	730	900	20—3 990
All	51	81	55	11—249	53	31	3—144	1 100	1 050	20—4 640
All soils:										
Surface soils	53	78	45	16—210	79	38	7—191	2 050	1 540	120—6 240
Subsoils	49	73	52	11—249	76	50	3—202	1 360	1 400	20—4 870

Table 4. 0.05 M $K_4P_2O_7$-extractable Al, Fe and Mn.

		Al, mmol/kg soil			Fe, mmol/kg soil			Mn, µmol/kg soil		
	n	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:										
Surface soils	27	46	51	6—243	33	22	7—111	790	480	240—1 910
Subsoils	24	29	47	4—233	24	21	5—76	430	290	120—1 050
All	51	38	50	4—243	29	22	5—111	620	440	120—1 910
Coarse soils:										
Surface soils	26	46	28	12—104	24	15	7—77	800	500	120—1 940
Subsoils	25	39	28	4—93	14	15	4—53	300	480	0—1 800
All	51	43	28	4—104	19	15	4—77	550	550	0—1 940
All soils:										
Surface soils	53	46	41	6—243	28	19	7—111	800	490	120—1 940
Subsoils	49	34	39	4—243	19	19	4—76	360	400	0—1 800

The pyrophosphate-extractable aluminium (Table 4) correlated closely (Table 7) with the EDTA-extractable (Table 5) and acetate-extractable aluminium (Table 6). The correlation between the EDTA-extractable and acetate-extractable aluminium was also close (Table 7). The pyrophosphate-extractable iron (Table 4) correlated with the EDTA-extractable iron (Table 5). In clay and silt soils, the correlation between the pyrophosphate-extractable and EDTA-extractable manganese was weaker than in coarse soils (Table 7).

In clay and silt soils, the organic carbon content and soil pH together explained (P = 0.001) 50 % of the variation in the oxalate-extractable aluminium, the regression equa-

Table 5. 0.02 M Na$_2$-EDTA-extractable Al, Fe and Mn.

		Al, mmol/kg soil			Fe, mmol/kg soil			Mn, μmol/kg soil		
	n	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:										
Surface soils	27	21	18	7—81	18	11	4—46	1 230	820	210—3 720
Subsoils	24	17	18	4—85	16	11	2—42	1 040	920	130—3 380
All	51	19	18	4—85	17	11	2—46	1 140	870	130—3 720
Coarse soils:										
Surface soils	26	17	9	5—34	9	7	3—32	830	530	110—1 590
Subsoils	25	14	13	2—61	4	5	1—23	230	250	20—1 110
All	51	16	11	2—61	6	7	1—32	540	510	20—1 590
All soils:										
Surface soils	53	19	14	5—81	13	10	3—46	1 040	720	110—3 720
Subsoils	49	15	15	2—85	10	10	1—42	630	780	20—3 380

Table 6. 1 M ammonium acetate-extractable Al.

		Al, mmol/kg soil		
	n	$\bar{x}$	s	range
Clay and silt soils:				
Surface soils	27	8.8	11.0	0.2—48.2
Subsoils	24	8.0	10.1	1.4—48.9
All	51	8.4	10.5	0.2—48.9
Coarse soils:				
Surface soils	26	7.8	5.5	1.2—22.5
Subsoils	25	9.4	7.6	0.9—34.8
All	51	8.6	6.6	0.9—34.8
All soils:				
Surface soils	53	8.3	8.7	0.2—48.2
Subsoils	49	8.7	8.8	0.9—48.9

tion being: Al(oxal.) (mmol/kg) = 118.75 + 10.35org.C-% — 15.96pH. The partial correlation coefficients for the relation between the oxalate-extractable Al (1), the organic carbon content (4) and soil pH (5) were:

$r_{14.5}$ 0.67***

$r_{15.4}$ —0.36*

Soil properties did not significantly explain the variation in the oxalate-extractable aluminium in coarse soils and the oxalate-extractable iron and manganese in clay and silt soils. In coarse soils, the clay content weakly correlated with iron (r = 0.40*) and manganese (r = 0.54***).

The organic carbon content and soil pH together explained (P = 0.001) 70 % of the variation in the pyrophosphate-extractable aluminium in clay and silt soils, the regression equation being: Al(K$_4$P$_2$O$_7$) (mmol/kg) = 79.56 + 13.59org.C-% — 17.06pH. The par-

Table 7. Linear correlation coefficients between extractable metals.

	Clay and silt soils (n = 51)			Coarse soils (n = 51)		
	Al(K$_4$P$_2$O$_7$)	Al(EDTA)	Al(acet.)	Al(K$_4$P$_2$O$_7$)	Al(EDTA)	Al(acet.)
Al(oxal.)	0.96***	0.94***	0.91***	0.76***	0.42*	0.68***
Al(K$_4$P$_2$O$_7$)		0.95***	0.95***		0.74***	0.80***
Al(EDTA)			0.92***			0.82***
	Fe(K$_4$P$_2$O$_7$)	Fe(EDTA)		Fe(K$_4$P$_2$O$_7$)	Fe(EDTA)	
Fe(oxal.)	0.43**	0.63***		0.68***	0.55***	
Fe(K$_4$P$_2$O$_7$)		0.72***			0.72***	
	Mn(K$_4$P$_2$O$_7$)	Mn(EDTA)		Mn(K$_4$P$_2$O$_7$)	Mn(EDTA)	
Mn(oxal.)	0.53***	0.69***		0.70***	0.75***	
Mn(K$_4$P$_2$O$_7$)		0.32*			0.72***	

tial correlation coefficients for the relationship between the pyrophosphate-extractable Al (1), the organic carbon content (4) and soil pH (5) were:

$$r_{14.5} \qquad 0.82***$$
$$r_{15.4} \qquad -0.44**$$

Soil properties did not significantly explain the variation in the pyrophosphate-extractable aluminium in coarse soils.

The organic carbon content and soil pH together explained (P = 0.001) 53 % of the variation in the pyrophosphate-extractable iron in clay and silt soils, the regression equation being as follows: $Fe(K_4P_2O_7)$ (mmol/kg) = 77.87 + 4.22org.C-% — 12.07pH. The partial correlation coefficients for the relationship between the pyrophosphate-extractable iron (2), the organic carbon content (4) and soil pH (5) were:

$$r_{24.5} \qquad 0.62***$$
$$r_{25.4} \qquad -0.54***$$

In coarse soils, the organic carbon content correlated weakly with the pyrophosphate-extractable iron (r = 0.45**). In clay and silt soils, the pyrophosphate-extractable manganese correlated weakly with the soil silt content (r = 0.47***).

The pyrophosphate-extractable metals are expressed as the percentages of the oxalate-extractable metals in Table 8. In clay and silt soils, the organic carbon content correlated closely with the percentages of aluminium (r = 0.80***), iron (r = 0.80***) and manganese (r = 0.77***). When the whole coarse soil group was examined, the correlation for manganese was weak (r = 0.53***), and that for aluminium and iron was insignificant. In coarse surface soils (n = 26), the organic carbon content correlated with the percentages of aluminium (r = 0.59*), iron (r = 0.73***) and manganese (r = 0.77***).

The clay content, the organic carbon content and soil pH explained (P = 0.001) 77 % of the variation in the EDTA-extractable aluminium in clay and silt soils, the regression equation being: Al(EDTA) (mmol/kg) = 28.87 + 0.26clay-% + 4.49org.C-% — 6.85pH. The partial correlation coefficients for the relation between the EDTA-extractable Al (1), the clay content (3), the organic carbon content (4) and soil pH (5) were:

$$r_{13.45} \qquad 0.39**$$
$$r_{14.35} \qquad 0.83***$$
$$r_{15.34} \qquad -0.53***$$

In coarse soils, only soil pH correlated significantly with the EDTA-extractable aluminium (r = —0.49***).

The organic carbon content correlated weakly with the EDTA-extractable iron in clay and silt soils (r = 0.46**). In coarse soils, the clay and organic carbon content together explained (P = 0.001) 40 % of the variation in the EDTA-extractable iron. The partial corre-

Table 8. 0.05 M $K_4P_2O_7$-extractable Al, Fe and Mn as the percentage of oxalate-extractable.

		Al, %			Fe, %			Mn, %		
	n	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:										
Surface soils	27	48	25	13—116	35	19	12—74	50	39	6—157
Subsoils	24	34	24	9—105	22	18	5—86	36	37	6—169
All	51	42	25	9—116	29	19	5—86	43	38	6—169
Coarse soils:										
Surface soils	26	62	22	28—105	44	22	17—97	73	36	12—194
Subsoils	25	53	28	17—110	42	32	6—113	51	48	0—180
All	51	58	25	17—110	43	27	6—113	62	43	0—194
All soils:										
Surface soils	53	55	25	13—116	39	21	12—97	61	39	6—194
Subsoils	49	44	28	9—110	32	28	5—113	44	43	0—180

Table 9. 0.02 M Na$_2$EDTA-extractable Al, Fe and Mn as the percentage of oxalate-extractable.

	n	Al, %			Fe, %			Mn, %		
		$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Clay and silt soils:										
Surface soils	27	25	7	11—39	19	12	5—47	61	35	12—189
Subsoils	24	23	8	13—45	14	8	2—36	58	30	11—138
All	51	24	8	11—45	17	11	2—47	60	32	11—189
Coarse soils:										
Surface soils	26	27	14	1—59	17	16	4—71	72	41	16—222
Subsoils	25	22	16	2—72	16	19	1—59	52	43	6—190
All	51	24	15	1—72	17	17	1—71	62	43	6—222
All soils:										
Surface soils	53	26	11	1—59	18	14	4—71	66	38	12—222
Subsoils	49	23	13	2—72	15	14	1—59	55	37	6—190

lation coefficients for the relation between the EDTA-extractable Fe (2), the clay content (3) and the organic carbon content (4) were:

$r_{23.4}$ 0.37**
$r_{24.3}$ 0.60***

In clay and silt soils, the EDTA-extractable manganese correlated weakly with soil pH (r = 0.39*) and in coarse soils with the clay content (r = 0.45***).

The EDTA-extractable metals are expressed as percentages of the oxalate-extractable metals in Table 9. In clay and silt soils, the organic carbon content correlated with the percentages of aluminium (r = 0.61***) and iron (r = 0.64***). In coarse surface soils (n = 26), the organic carbon content correlated weakly with the percentages of aluminium (r = 0.42*) and iron (r = 0.43*).

Table 10. 1 M ammonium acetate-extractable Al as the percentage of oxalate-extractable Al.

	n	Al, %		
		$\bar{x}$	s	range
Clay and silt soils:				
Surface soils	27	9	6	0.4—23
Subsoils	24	10	6	3 —22
All	51	10	6	0.4—23
Coarse soils:				
Surface soils	26	11	6	4 —27
Subsoils	25	13	8	4 —23
All	51	12	7	4 —27
All soils:				
Surface soils	53	10	6	0.4—27
Subsoils	49	11	7	3 —23

The organic carbon content and soil pH explained (P = 0.001) 56 % of the variation in the ammonium acetate-extractable aluminium in clay and silt soils, the regression equation being: Al(acet.) (mmol/kg) = 26.40 + 2.31 org.C-% — 4.95 pH. The partial correlation coefficients for the relation between the acetate-extractable Al (1), the organic carbon content (4) and soil pH (5) were:

$r_{14.5}$ 0.68***
$r_{15.4}$ —0.49***

In coarse soils, the acetate-extractable aluminium correlated weakly with soil pH (r = 0.44*).

In clay and silt soils, the acetate-extractable aluminium, expressed as the percentage of the oxalate-extractable aluminium (Table 10), correlated weakly with the organic carbon content in soil (r = 0.43**).

Discussion

The four extractants to some degree dissolved metals complexed with organic matter in soil. An expression of this was that the organic carbon content of soil together with soil pH explained the variation in the contents of extractable metals.

The conventional oxalate extractant (TAMM 1922, SCHWERTMANN 1964, McKEAGUE and DAY 1966) dissolves iron and aluminium from poorly crystallized oxides as well as from organic matter complexes (SCHNITZER and

SKINNER 1964, SCHWERTMANN 1964, 1973, McKEAGUE and DAY 1966). The iron oxide extracted in darkness is mainly ferrihydrite (SCHWERTMANN 1959); in light and by prolonged extraction, all iron compounds are obviously solubilized (McKEAGUE et al. 1971, PAWLUK 1972, SCHWERTMANN 1973).

In the study of HUANG et al. (1977), the oxalate-extractable aluminium and iron were related to the content of organic matter in soil, but not to acidity or clay content. In the present material, the content of organic carbon in soil together with soil pH explained only the variation in the oxalate-extractable aluminium in clay and silt soils, whereas in coarse soils, the oxalate-extractable iron and manganese were slightly related to the clay content in soil.

The pH of the pyrophosphate solution used as the extractant was about 10. Alkaline pyrophosphate is reasonably specific for the organic iron complexes and somewhat less specific for aluminium complexed with organic matter (McKEAGUE 1967, McKEAGUE et al. 1971). Aluminium may partly be derived from oxides. Little iron is extracted from poorly or well crystallized iron oxides by alkaline pyrophosphate (BASCOMB 1968, BASCOMB and THANINGASALAM 1978, McKEAGUE et al. 1971, ARSHAD et al. 1972), whereas iron is solubilized from oxides as well as from silicate minerals by neutral pyrophosphate (TITOVA 1962, KONONOVA et al. 1964). The manganese extracted by alkaline pyrophosphate is mainly divalent and complexed by organic matter (HEINTZE and MANN 1949). Hydrated manganese oxides are fully soluble in neutral pyrophosphate but are poorly soluble in alkaline extractant (HEINTZE and MANN 1949). Pyrophosphate extracts can also contain manganese derived from oxides of higher oxidation states reduced by organic matter (HEINTZE 1957).

In the study of SHOJI and FUJIWARA (1984), soil total carbon correlated with the sum of the pyrophosphate-extractable aluminium and iron. In the present material, both the aluminium and iron extracted by pyrophosphate correlated with the soil organic carbon, especially in clay and silt soils. If the concentration of metals was expressed as percentages of the oxalate-extractable metal, also manganese correlated with the organic carbon content.

EDTA is a widely used extractant for organically-bound metal ions. At pHs from 4 to 7, crystalline iron oxides are not soluble in EDTA (AGUILERA and JACKSON 1953, RUBIO and MATIJEVIC 1979). Very long extraction (90 days) by EDTA at pH 4.4—6.0, proposed for the extraction of ferrihydrite (BORGGAARD 1976, 1979), does not dissolve more iron than does acid oxalate (pH 3.0) during 4—5 hours (BORGGAARD 1976). Instead, 0.05 M EDTA at pH 9 is an effective extractant of aluminium and iron (VIRO 1955). In Finland, micronutrients are extracted by acid ammonium acetate-EDTA (0.5 M CH_3COONH_4, 0.5 M CH_3COOH, 0.02 M Na_2-EDTA, pH 4.65) (LAKANEN and ERVIÖ 1971), the EDTA concentration of which was used in the present study. However, the pH was adjusted to 5.3 because the solubilities of aluminium and iron seemed to be relatively constant at pH 5.3—6.8 in a previous paper (NISKANEN 1989b).

In clay and silt soils, the clay content, together with organic carbon content and soil pH, explained the variation in the content of EDTA-extractable aluminium. This result may mean that EDTA extracts aluminium hydroxide polymers from clay surfaces. Aluminium hydroxide polymers have a tendency to form films over larger surface areas than iron hydroxide, which appears to precipitate at specific hydroxyl sites on the clay surface (EL SWAIFY and EMERSON 1975, RENGASAMY and OADES 1977).

The acetate-extractable aluminium, which consisted of exchangeable aluminium ions, hydroxy aluminium polymers as well as organic aluminium complexes (JACKSON 1963, McLEAN et al. 1964), aluminium phosphates (YUAN and FISKELL 1959) and newly precipitated aluminium hydroxide (PRATT and BAIR 1961), correlated closely with the EDTA-extractable aluminium. The correla-

tion between the acetate-extractable aluminium in clay and silt soils and the soil organic carbon content is in agreement with the opinion of Pionke and Corey (1967), who contended that acetate-extractable aluminium is largely complexed by organic matter. In coarse soils, the acetate-extractable aluminium was not related to the organic carbon content. In coarse soils, the view of Hargrove and Thomas (1984), who proposed that acetate poorly identifies reactive aluminium associated with organic matter, may be valid. In any case, acetate extracts a rather small fraction of the soil aluminium. It seems to be more advantageous to use pyrophosphate to extract metals complexed by organic matter. Another disadvantage of acetate is that it is a poor iron extractant (Paasikallio and Häkkinen 1977).

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SELOSTUS

Kivennäismaiden uuttuva alumiini, rauta ja mangaani
III Uuttomenetelmien vertailu

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Kivennäismaiden (n = 102) alumiinia, rautaa ja mangaania uutettiin 0,05 M oksalaatilla (pH 2,9), 0,05 M $K_4P_2O_7$:lla, 0,02 M EDTA:lla (pH 5,3) ja 1 M ammoniumasetaatilla (pH 4,8). Savi- ja hiesumaissa (n = 51) eri menetelmillä uuttuvan alumiinin pitoisuudet olivat kiinteässä korrelaatiossa keskenään, karkeammissa maissa (n = 51) korrelaatio ei ollut kovin kiinteä. Savi- ja hiesumaissa orgaanisen hiilen pitoisuus ja maan pH yhdessä selittivät 50 % oksalaattiuuttoisen alumiinin, 70 % pyrofosfaattiuuttoisen alumiinin, 53 % pyrofosfaattiuuttoisen raudan ja 56 % asetaattiuuttoisen alumiinin vaihtelusta. Saveksen ja orgaanisen hiilen pitoisuudet yhdessä maan pH:n kanssa selittivät 77 % EDTA-uuttoisen alumiinin vaihtelusta savi- ja hiesumaissa. Karkeammissa maissa maan ominaisuudet selittivät heikosti uuttuvien metallien pitoisuuksien vaihtelua.