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Spatial and temporal variation of soil chemical characteristics in pine sites in southern Finland

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TIIVISTELMÄ: MAAN KEMIALLISTEN OMINAISUUKSIEN AJALLINEN JA PAIKALLINEN VAIHTELU ETELÄSUOMALAISISSA MÄNNIKÖISSÄ

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In producing time series of soil properties, there are many technical and statistical problems which need to be taken carefully into account when sampling and analysing the measurement data. In field the reliable localization of sample plots and the precise distinction of different soil layers are important to reduce the variance caused by the sampling procedure. In laboratory the use of same extraction salt, sample pretreatment procedure and filter paper throughout a measurement series is important. The remarkable small scale variation within a sampling plot leads to a need of a large number of samples to be collected.

In this study, no trends attributable to soil acidification in the contents of exchangeable base cations could be found among the years 1982, 1985 and 1988. However, in eluvial and illuvial layers the pH decreased and the content of extractable H^+ increased during this period. In illuvial layer also the content of extractable aluminium increased.

Maan ominaisuuksien muutoksia kuvaavia aikasarjoja laadittaessa erityistä huomiota on kiinnitettävä käytettävien menetelmien samankaltaisuuteen eri näytteenotto- ja analysointikerroilla. Huomionarvoisia seikkoja ovat eri maahorisonttien erottelu ja näytteenottopaikan tarkka merkitseminen maastossa ja yhdenmukainen näytteiden esikäsittely, suodatus sekä saman uuttoliuoksen käyttö laboratoriossa. Tutkittavien ominaisuuksien vaihtelu on usein hyvin suuri koealan sisällä, mistä johtuen suuri osanäytteiden lukumäärä on välttämätön.

Tässä tutkimuksessa vuosien 1982, 1985 ja 1988 välillä ei havaittu säännönmukaisia maan happamoitumiseksi tulkittavissa olevia muutoksia vaihtuvien emäskationien määrässä. Huuhtoutumis- ja rikastumiskerroksissa vaihtuvan vedyn määrä lisääntyi sekä pH-arvo aleni. Rikastumiskerroksessa myös vaihtuvan alumiinin määrä lisääntyi.

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1 Introduction

The cations retained on soil particles are in dynamic equilibrium with the cations in soil solution (eg. Gaines and Thomas 1953). Both the biological processes in the soil and the chemistry of incoming precipitation produce changes in the ratios of different cations retained on exchange sites in the soil.

In the boreal forest ecosystems prevailing in Finland, plant biomass accumulation occurs during stand succession, and cation uptake is accompanied by increased H^+ production in the rhizosphere (Hesselman 1937, Troedsson and Nilsson 1984, Tamm and Hallbäcken 1988, Tamm 1989). Many of the products of needle litter decomposition (humic and fulvic substances) are very stable, and being weak organic acids, they have a decreasing effect on soil pH (Waksman 1936, Berg et. al 1982, Staaf and Berg 1982, de Vries and Breeuwsma 1987). The increase in the H^+ concentration in precipitation combined with the uptake of cations by the roots results in the release of exchangeable cations from the soil particles. In the case that the incoming anions are not retained on exchange sites or taken up by plants and the total amount of anions leached from the system increases, increased leaching of base cations follows. Due to the decrease in solution pH, increased dissolution of Al compounds in the mineral soil occurs (Reuss 1977, Johnson and Cole 1980, Ulrich 1983, de Vries and Breeuwsma 1987). However, only a few studies have been carried out, where the long term changes in soil properties under natural conditions are studied and there is little field evidence about the phenomena described above. In Sweden Hallbäcken and Tamm (1986) have presented the results of soil analyses carried out on the same sites in 1927 and again in 1982/84, and detected an apparent decrease in the pH of different soil horizons. Falkengren-Grerup et al. (1987) have reported a considerable decrease in both pH and the amounts of exchangeable cations between 1949/53 and 1984, also in Sweden. Evidence of a decrease in soil pH in southern Finland has been shown by Huttunen (1988).

Determination of soil exchangeable cations is based on the extraction of soil samples with salt solutions. Numerous methods have been presented (Bache 1976, Page 1982), which differ from each other as regards the form and molarity of the salt used, the duration of the extraction process and the number of successive extractions. Either unbuffered salts or salts buffered to various pH values have been used, as well as different chelating compounds (Lakanen and Erviö 1971, Nömmik 1974).

The cation exchange capacity (CEC) of soils is frequently determined as the sum of exchangeable cations and titratable acidity, according to the so-called summation method (Juo et al. 1976, Stuanes 1984). Another widely used method is the replacement method, in which the exchange sites are first saturated with a specific salt and this salt is then displaced by another salt. The equivalent amount of cations from the first salt that are retained on the exchange sites is the CEC value.

When giving the value of the total amount of CEC and base saturation (BS), it is crucially important to state whether the measurements are done near the original pH of the soil (effective CEC) or near the neutral point (potential CEC) (Westman 1990), because the latter gives significantly higher CEC and lower BS values, especially in soils where a large number of variable charge exchange sites exist (Gillman 1979). Effective CEC is recommended for acidic soils rich in humus and sesquioxides (Kalisz and Stone 1980). As an extractant, Hendershot and Duquette (1986) recommend 0.1 M $BaCl_2$ extract (summation method), because $BaCl_2$ has a high exchange capacity without being preferentially adsorbed on the soil particles.

Varying the extraction period from 0.5 to 16 hours does not seem to have very much effect on the yield of exchangeable cations apart from aluminium (Lee et al. 1985, Truby and Aldinger 1989). The amount of Al extracted increases as the extraction period increases. The amount of exchangeable Al has also been found to be affected by the ion concentration of the extractant (Truby and Aldinger 1989). If the extractions are repeated, the cation exchange reactions will continue. In the study of Truby and Aldinger using unbuffered NH_4Cl most of the exchangeable Ca^{2+}, Mg^{2+}, Mn^{2+}, K^+ and even Fe^{3+} came out in the first extraction, the amount of Al was considerable also in the second extraction. In the study of Niskanen (1986), 57–79 % of the total amount of ions obtained in 4 successive extractions were in the first extract.

The aim of this study was to produce a time series of changes in soil chemical properties in 1980´s and to develop methods for more accurate comparisons between different sampling events. The pH and the contents of exchangeable cations in different horizons of podzol soils are compared based on samples taken from 9 permanent sample plots in 1982, -85 and -88. The sources of variance are discussed and the properties of three different extractants are compared with respect to their exchange capacity. The correlations between soil organic matter content and the silt fraction with the amount of exchangeable cations are also presented.

2 Material and methods

Soil samples were collected in June–August 1982 and in September 1985 and 1988 from 9 permanent plots in southern Finland (Fig. 1). The plots represented the infertile Calluna site type Scots pine forests. The age of the stands on the plots was between 80 and 105 years. Only plots with no visible signs of human interference (recent cuttings, fertilizer applications etc.) were selected. In 1982 four or five samples were taken from each plot using a soil auger (diameter 8 cm). In 1985 four samples were taken from each plot and the location of the sampling points marked with plastic sticks so that the 1988 sampling could be done at exactly the same points. The samples were taken from the edge of a pit dug with a spade and the volume of the sample varied between 0.3–1.0 l in different horizons. The soil profile was divided into humus, eluvial and illuvial layers. The illuvial layer sample was divided into two parts: the uppermost 5–7 cm and the 20–30 cm layer measured from the top of the mineral soil (not analysed here). In some cases the sample of the layer was divided into two subsamples, which were analysed separately. The depth of each layer was measured. The samples were dried in an oven within a couple of days after collection at 80–100 °C. The mineral soil samples were sieved to give the < 2 mm fraction, which was used in the analyses. Clearly detectable roots were removed from the humus samples, after which the samples were milled. The samples were stored for further analysis at room temperature and analysed in 1989/90. Two replicates of each sample of the humus and eluvial layers and the uppermost 5–7 cm of the illuvial layer were prepared.

The exchangeable cations were extracted with 0.1M $BaCl_2$ and for the 1988 samples also with 1N KCl (two different extraction series) and 1N NH_4OAc (pH 4.65). After the extraction period the suspensions were filtered. The pH and the

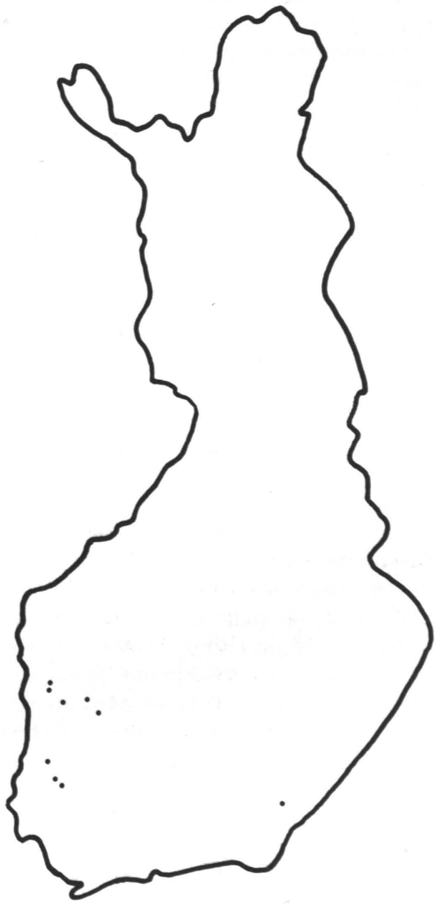

Fig 1. Location of the sample plots in southern Finland: 60°56', 27°36'; 60°59', 22°35'; 61°03', 22°26'; 61°15', 22°11'; 61°54', 23°28'; 61°56', 22°29'; 62°01', 23°08'; 62°09', 22°11'; 62°10', 22°11'.

content of exchangeable cations Al^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, K^+ and H^+ were determined from the extractants (except for K^+ in KCl and H^+ and Mn^{2+} in the NH_4OAc extracts). The extraction solution volume:soil sample weight ratio was 100ml:10g for mineral soil samples and 100 ml:2g for humus samples. Prior to shaking the humus samples were mixed thoroughly with a glass rod. pH was measured with a glass electrode, exchangeable acidity titrated with 0.01 N NaOH to pH 8.2 (phenolphthalein as end-point indicator), Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+} and Fe^{3+} determined by flame atomic absorption spectrometry and K^+ by flame emission spectrometry.

The cation exchange capacity (CEC) was calculated in two different ways: as the equivalent sum of exchangeable Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} (CEC_1) and as the equivalent sum of exchangeable Ca^{2+}, Mg^{2+} and titratable acidity (CEC_2). The base saturation (BS) is the proportion (as %) of the sum of Ca^{2+} and Mg^{2+} equivalents out of CEC. The values of K were not included in the calculation of BS, because the changes in the contents of exchangeable divalent cations is often presented to describe better the effects of acid deposition on soil chemical characteristics.

The amount of organic matter in the 1985 mineral soil samples was estimated as the loss in weight on ignition in a muffle furnace at 550°C for 3 hours. The soil texture of these samples was determined by the sedimentation method (Elonen 1971).

The statistical significance of the differences between sampling years was tested by the analysis of variance and the t-test, the existing variance also being divided into the variance among plots, among samples and among replicate measurements. The significance of correlations between different extraction solutions, mineral soil organic content and CEC, and silt fraction and CEC was tested by correlation analysis.

3 Results

3.1 Comparison among years

The variation in soil properties among the samples taken from the same plot was very high. The significances of the differences among sampling years were therefore tested by combining the whole material of nine plots and the four to five samples. Only minor changes were found among years in the humus layer, although the means of the content of exchangeable K^+ and Al^{3+} were somewhat lower in 1988 than in 1982 (Table 1a). In the eluvial layer the content of exchangeable Ca^{2+}, Mg^{2+} and K^+ increased simultaneously with an increase in the content of H^+ and the corresponding decrease in pH. This also led to an increase in CEC (Table 1b). In the illuvial layer the contents of exchangeable Al^{3+}, Fe^{3+} and H^+ increased and the pH decreased. The decrease in BS was also statistically significant (Table 1c).

3.2 Sources of variance

In order to estimate the sources of the variance in the material, the total variance of the analyses of the $BaCl_2$ extraction samples (1988) was divided into three components namely, among plots, within plots and among replicates. Most of the variance consisted of the among plots and within plots variance, the variance among extraction replicates being only a few per cent, apart from exchangeable acidity in the humus layer (Table 2). In most cases the variance was divided equally into variance among plots and among samples.

Proper wetting of the samples during the extraction process seems to be of great importance for humus samples especially. In the first analysis series done on the humus layer samples with KCl, the aggregates formed after addition of the extraction solution were not mixed with a glass rod before shaking. Even after one hour's shaking some of these aggregates were still not completely wetted. The effect of differences in sample wetting can be clearly seen as an increase in the contribution of replicates as a source of variance (Table 2, column "HumusB"). Determination of the end point in the titration of coloured humus samples is difficult when phenolphtalein is used, which increases the proportion of replicate variance in the case of this method. The potentiometric end point titration would probably reduce the variance produced by the measurement procedure.

Table 1a. The pH, the contents of exchangeable cations (me/kg), base saturation (%) and cation exchange capacity (me/kg) of the oven dry humus layer samples in 1982, 1985 and 1988. F denotes the F value in the analysis of variance, * for the significance level and s.e.m. for the standard error of the mean. Significantly different means by t-test are indicated by differing letters. N is the number of samples analysed for the corresponding year.

	1982 n = 32	1985 n = 41	1988 n = 36	F
Ca	80.9a	74.5a	82.4a	1.21
s.e.m.	4.3	3.9	3.7	
Mg	15.9a	14.9a	15.1a	0.55
s.e.m.	4.7	4.3	2.8	
K	19.2a	16.8ab	15.9b	4.08 *
s.e.m.	1.0	0.8	0.6	
Al	35.5a	29b	31.1ab	6.03 **
s.e.m.	1.7	1.2	1.2	
Fe	6.8a	11.6b	9.4c	19.54 ***
s.e.m.	0.3	0.6	0.6	
Mn	10.7a	10.2a	9.6a	0.26
s.e.m.	1.4	1.0	1.0	
H	183.5a	176.9a	174.9a	0.99
s.e.m.	4.9	4.7	3.3	
pH	2.89a	2.89a	2.88a	0.21
s.e.m.	0.02	0.01	0.01	
CEC 1	139.1a	130a	138a	1.33
s.e.m.	4.5	4.6	3.8	
CEC 2	280.3a	266.3a	272.3a	1.13
s.e.m.	6.6	7.6	4.7	
BS 1 %	68.5a	67.6a	70.1a	0.82
s.e.m.	1.7	1.3	1.3	
BS 2 %	34.2a	33.1a	35.6a	1.31
s.e.m.	1.4	1.0	1.1	

Table 1b. Same as Table 1a, but for eluvial layer.

	1982 n = 41	1985 n = 38	1988 n = 37	F
Ca	0.89a	0.87a	1.55b	4.83 **
s.e.m.	0.1	0.12	0.27	
Mg	0.34a	0.4a	0.53b	7.81 ***
s.e.m.	0.02	0.03	0.05	
K	0.38ab	0.35b	0.46a	3.3 *
s.e.m.	0.22	0.03	0.05	
Al	9.43a	10.21a	9.81a	0.5
s.e.m.	0.52	0.60	0.53	
Fe	1.04a	1.54b	1.61b	9.96 ***
s.e.m.	0.06	0.09	0.14	
Mn	0.09a	0.14a	0.13a	0.73
s.e.m.	0.01	0.01	0.02	
H	17.2a	18.6ab	20.1b	3.84 *
s.e.m.	0.65	0.78	0.83	
pH	3.55a	3.42b	3.26c	25.67 ***
s.e.m.	0.04	0.03	0.02	
CEC 1	11.7a	13.0a	13.5a	1.91
s.e.m.	0.1	0.1	0.1	
CEC 2	18.4a	19.8ab	22.2b	4.70 *
s.e.m.	0.1	0.1	0.1	
BS 1 %	10.7a	9.5a	14.5b	5.73 **
s.e.m.	0.1	0.1	0.1	
BS 2 %	6.4ab	6.1b	8.4a	4.22
s.e.m.	0.0	0.1	0.1	

Table 1c. Same as Table 1a, but for illuvial layer.

	1982 n = 46	1985 n = 36	1988 n = 36	F
Ca	0.19a	0.15a	0.20a	1.19
s.e.m.	0.03	0.02	0.03	
Mg	0.10a	0.08a	0.12a	2.7
s.e.m.	0.01	0.01	0.01	
K	0.13a	0.08b	0.17a	15.46 ***
s.e.m.	0.01	0.01	0.01	
Al	4.5a	5.12ab	6.61b	5.34 **
s.e.m.	0.51	0.40	0.45	
Fe	0.47a	0.72b	1.00c	23.79 ***
s.e.m.	0.04	0.06	0.07	
Mn	0.10a	0.15a	0.19a	0.62
s.e.m.	0.05	0.04	0.08	
H	7.4a	8.3ab	10.3b	4.45 *
s.e.m.	0.1	0.1	0.1	
pH	4.29a	4.23a	4.13b	9.67 ***
s.e.m.	0.02	0.03	0.03	
CEC 1	5.3a	6.1ab	7.9b	6.44 **
s.e.m.	0.1	0.0	0.1	
CEC 2	7.7a	8.5ab	10.6b	4.32 *
s.e.m.	0.1	0.1	0.1	
BS 1 %	7.0a	3.7a	3.9a	3.36 *
s.e.m.	0.1	0.0	0.0	
BS 2 %	4.2a	2.6a	2.9a	3.39 *
s.e.m.	0.1	0.0	0.0	

The number of samples needed to obtain a statistically significant difference for a 10 % change in the measured value at the 5 % risk level and at 90 % certainty in the humus samples was between 5 to 25 for most of the elements studied, but in the mineral soil markedly higher. The pH and H^+ measurements seem to give statistically significant differences with the smallest number of replicates in all soil layers (Table 3).

3.3 Soil organic content and soil texture

The correlation between loss in weight on ignition and the content of exchangeable ions and pH was studied in the mineral soil layers. In the eluvial layer the correlations were insignificant, except for K^+ and Al^{3+} which had a positive correlation. In the illuvial layer the values of the correlation coefficient were small and in most cases insignificant. When the results of the two sample plots with the highest organic content were omitted, the situation changed markedly. All the measured parameters apart from pH were then positively correlated with the loss in weight on ignition (Table 4).

The proportion of the silt fraction (Ø < 0.02 mm) and the contents of exchangeable cations were not correlated in this material.

3.4 Comparison of the extractant solutions

It is evident from Table 5 that the values obtained with different leaching solutions were strongly intercorrelated, the only exceptions being NH_4OAc extractable Al^{3+} and Fe^{3+} in the illuvial layer. In all layers the correlation coefficients for Al^{3+} and Fe^{3+} were slightly smaller than those for the other cations. The exchange capacities of the extraction solutions for the base cations Ca^{2+} and Mg^{2+} in the humus and eluvial samples used were rather close to each other (meanX/meanY in Table 5). The contents of Ca^{2+} and Mg^{2+} extracted from the humus samples followed the order $KCl > BaCl_2 > NH_4OAc$, the order being the same for Al in the eluvial layer. As far as Al^{3+} and Fe^{3+} are concerned, the results of the NH_4OAc extraction differed from those obtained with neutral salt solutions, the NH_4OAc values being smaller in the humus and markedly higher in the illuvial layers.

Table 2. The proportion (in %) of individual variance components for the elements studied in different soil layers. A = the variance between sample plots, B = the variance between samples within a plot, C = the variance between replicates. The column "Humus B" refers to the extraction series with KCl, in which the humus aggregates remained unwetted during the shaking period. The values of line pHC correspond to the H^+ concentrations calculated from the pH measurements and H the titratable acidity in the extract.

		Humus A	Humus B	Eluvial	Illuvial
Ca	A	50.9	42.0	46.7	40.6
	B	48.8	43.1	52.6	55.2
	C	0.3	14.9	0.7	4.2
Mg	A	23.0	29.6	58.7	51.1
	B	76.5	49.2	39.0	46.7
	C	0.5	21.1	2.3	2.2
K	A	46.8	–	69.8	15.8
	B	52.7	–	29.0	76.5
	C	0.5	–	1.2	7.8
Al	A	54.7	41.8	59.4	23.3
	B	44.6	32.9	35.1	76.0
	C	0.6	25.4	5.5	0.7
Fe	A	83.4	72.4	83.8	12.7
	B	16.0	6.6	15.9	85.7
	C	0.6	21.1	0.3	1.6
Mn	A	42.5	37.5	14.1	47.8
	B	53.5	54.8	85.6	52.2
	C	4.1	7.7	0.3	0.0
H	A	36.8	16.8	56.1	25.7
	B	36.0	53.0	42.7	73.5
	C	27.2	30.2	1.2	0.8
pHC	A	70.5	71.2	22.3	44.1
	B	29.5	17.8	77.1	54.8
	C	0.05	11.0	0.6	1.1

Table 3. The number of samples needed to demonstrate a statistically significant difference for a 10 % change in the measured value at the 5 % risk level and at 90 % certainty in the material studied. The following equation was used in the calculations, $n = (s^2/d^2) \cdot (1.960 + 1.282)$, where n = number of samples needed, s^2 = variance in the 1988 material ($BaCl_2$ extraction), d = 10 % of the mean value of the element studied.

	Ca	Mg	K	Al	Fe	Mn	H	pH	CEC1	CEC2	BS1	BS2
Humus	24	11	17	16	44	120	5	15	10	4	4	11
Eluvial	376	104	116	36	90	1023	21	33	40	29	125	118
Illuvial	198	106	58	54	55	1919	52	50	54	53	51	46

Table 4. The values and significance of the correlation coefficients between the loss in weight on ignition and the results from the chemical analysis of eluvial and illuvial layer samples. The coefficients in the column "illuvial B", are calculated from the material in which the two sample plots with the highest values for the loss in weight on ignition were omitted.

	Eluvial n = 43	Illuvial A n = 36	Illuvial B n = 28
Ca	0.245	0.433**	0.743***
Mg	0.096	0.043	0.708***
K	0.440**	0.248	0.423*
Al	–0.212	–0.006	0.572**
Fe	0.496***	0.015	0.458*
Mn	0.074	0.060	0.569**
pH	0.383	0.450**	0.280
H	–0.192	0.086	0.635***
CEC1	–0.079	0.016	0.588***
CEC2	–0.141	0.098	0.650***
BS1	0.249	0.503**	0.584**
BS2	0.367	0.446***	0.588***

3.5 Filtration

When studying the soil exchangeable cations the extract and soil have to be separated from each other. This is usually performed by filtering the sample through a paper or membrane filter. Filter paper (here Whatman 5) seems to change the properties of the extraction solution. Especially protons were produced in considerable amounts. The original pH of $BaCl_2$ before filtration was 5.61 but after passing through the filter it was altered to 4.38. Also Ca was released from the filter paper and the Ca concentration measured in 100 ml of extraction solution after filtration was 0.25 mg Ca/l. In the case of Al some retention to the filter may have occurred.

Table 5. The values and significance of the correlation coefficients between the contents of $BaCl_2$, KCl and NH_4OAc extractable cations in the humus, eluvial and illuvial layer samples. In the column "Ratio", A denotes the comparison between $NH_4OAc/BaCl_2$, B the ratio $KCl/BaCl_2$ and C the ratio KCl/NH_4OAc. The ratios of concentrations of the element studied are calculated at the mean value of the divider and are presented in column Y/X. The values of line pHC correspond to the H^+ concentrations calculated from the pH measurements and H the titratable acidity in the extract.

	Ratio	Humus	Y/X	Eluvial	Y/X	Illuvial	Y/X
Ca	A	0.966***	0.70	0.977***	1.06	0.619***	2.16
	B	0.986***	1.13	0.995***	0.96	0.968***	0.95
	C	0.960***	1.62	0.978***	0.91	0.651***	0.44
Mg	A	0.937***	0.87	0.987***	0.93	0.948***	1.30
	B	0.965***	1.04	0.977***	0.90	0.971***	1.01
	C	0.922***	1.19	0.983***	0.96	0.953***	0.78
Al	A	0.585***	0.29	0.627***	0.60	0.252	3.61
	B	0.699***	0.72	0.823***	1.08	0.905***	1.58
	C	0.515***	2.48	0.555***	1.80	0.177	0.44
Fe	A	0.832***	0.12	0.767***	0.56	0.466*	2.18
	B	0.780***	0.57	0.943***	0.62	0.756***	0.70
	C	0.572***	4.89	0.740***	1.10	0.448	0.32
Mn	B	0.890***	0.78	0.992***	0.90	0.990***	1.10
K	A	0.829***	1.02	0.876***	1.26	0.529***	2.37
pH	B	0.986***	1.03	0.890***	1.03	0.874***	1.05
pHC	B	0.988***	0.82	0.802***	0.81	0.896***	0.69
H	B	0.939***	0.88	0.935***	0.97	0.970***	1.29

4 Discussion

In producing time series of soil properties, there are many technical and statistical problems which need to be taken carefully into account when sampling and analysing the measurement data. When the samples are being collected in the field, it is sometimes difficult to make a distinction between different soil layers and this can lead to considerable variation in the amounts of mineral and organic matter in the humus and eluvial layer samples. Furthermore, the distinction between humus and litter is somewhat arbitrary, and causes problems especially when the humus layer is shallow, as was the case in this study. There is considerable variation in vertical direction in the pH of the humus layer. A decrease of 0.6 pH units has been shown within four centimeters down from the top of the litter layer (Skyllberg 1990). This emphasizes the importance of using the same sampling procedure when comparing different cases.

The small scale variation in soil properties was an important source of variance in the material of this study. The spatial variability in pH, especially in the humus layer, has been studied intensively, but less information is available about soil exchangeable cations. In the studies of Aaltonen (1925) the difference between the minimum and maximum pH values within one stand were more than one pH unit. The results of Nykvist and Skyllberg (1989) indicate that the entire variation of pH in the mor layer, to be found in a whole stand, exists within a plot < 2 m², the highest and lowest pH values differing from each other by 0.6 pH units. Riha et al. (1986) have shown that soil cores 1.8 cm in diameter were as effective as larger cores in incorporating the spatial variation in surface mineral soil. They also showed that there was no correlation between soil samples separated by a distance of 20 to 30 cm. This means that even a very precise system for marking the sampling points is ineffective in abolishing the variance when comparing different years, because the sampling from exactly the same point is technically impossible.

The only way to reduce the standard error of the mean seems to be to take a large number of samples, but it is also necessary to accept reasonably high standard error, otherwise the field work will come unduly laborious (Troedsson and Tamm 1969). In studies on the total amount of elements in the forest floor, Carter et al. (1986) showed that a large number of samples are needed to obtain an accurate estimate of the mean. They concluded that for most purposes composite samples appear to provide an adequate estimate of the mean. On the other hand, in the studies of Lundell (1987) considerable variation was found even within composite samples taken from the same sample plot (5 × 20 cores pooled, area of sample plot 25 × 80 m).

The number of samples taken in this study within one plot was very small compared to the number of samples required to show a 10 % change in the amounts of exchangeable ions. When the material from different sample plots is combined, the number of samples was high enough to enable such changes to be detected.

In addition to spatial variation, seasonal variation also occures in soil properties (Runge 1974, Lehtonen et al. 1976, Lundell 1987, Skyllberg 1991), but no clear trends have been found. An attempt was made in this study to minimize the effects of seasonal variation by collecting the 1985 and 1988 samples in September.

The drying temperature used in the laboratory has been shown to have an effect on the pH of organic soil samples. The pH decreases when the drying temperature is increased from 40 °C to 105 °C, but no clear trends were found on the amounts of Ca^{2+}, Mg^{2+}, K^+ and Al^{3+} (Saarinen 1989). The samples in this study were dried in similar conditions throughout the course of the experiment, and relative changes produced by the drying procedure should be negligible.

If the chemical analyses are not performed using exactly the same methodology, artificial changes may occur, filter paper, extraction solutions and measurement calibration being important sources of error. Jardine et al. (1986) have studied 23 different types of paper and membrane filters and found that many of them are sources of contamination, especially with dilute solutions. They showed a considerable proton leaching and cation exchange capacity for certain papers (e.g. Whatman alike the one used in this study). Large discrepancies also exist between boxes of the same type of filter. These problems can be partly controlled by performing all the analyses used in comparisons at the same time, as was done in this study. However, if the analyses of the time series are to be done in as similar conditions as possible, then the samples have to be stored. The results of Aaltonen (1937) concerning the effects of long storage on pH were not consistent, the pH values being somewhat higher in strongly podzolized soils after four years storage, but the opposite in less extensively podzolized soils.

Tamm and Hallbäcken (1988) have studied in detail the possible causes of the pH changes detected in Swedish soils. They found that the acidity of the upper soil horizons, i.e. the humus layer and the leached horizon of podzol profiles, is strongly affected by the dominating tree species and the age of the stand, the pH decreasing with age. The pH of the subsoil, and also the illuvial horizon, are not affected by stand age. The pH decrease detected in deeper soil layers in a sampling area in southern Sweden was concluded to be of anthropogenic origin. No corresponding changes in deeper soil horizons have been found in northern Sweden. The hydrogen and sulphate ion deposition during the 1980's in the areas studied here fell between the values for the two locations studied in Sweden (Järvinen and Vänni 1990). The period of time covered in this study was short for drawing conclusions about the importance of atmospheric deposition causing changes in soil properties. However, the changes detected in the illuvial layer samples were of the kind that might be attributable to acid precipitation.

The sample plots used in this study were chosen according to the assumption that infertile sandy soils are most susceptible to the effects of acid precipitation. However, when we take into account the dynamic features of the cation exchange reactions, it would appear probable that the most profound changes in the total amounts of soil exchangeable base cations (Ca^{2+}, Mg^{2+}) would occur in soils where the initial base saturation is high and the H^+/base cation ratio on the soil exchange sites differs considerably from that of precipitation (Holmberg et al. 1989). Field observations also indicate, that the most profound changes in pH and exchangeable cations have occurred in soils, whose original pH and base saturation have been the highest (Falkengren-Grerup 1987).

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