

A comparison of nitrogen and carbon reserves in acid sulphate and non acid sulphate soils in western Finland

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Previous studies suggest that nitrogen (N) loads from acid sulphate soil (AS soil) catchments in Finland are higher than those from other agricultural catchments. This study seeks to explain this difference by measuring carbon (C) and N profiles in both an AS soil and a neighbouring non AS soil. In Lapua, western Finland, two adjacent fields (Dystric Cambisols), subjected to similar agricultural practices, were analysed to the depth of 240 cm for pH, total C (C_{tot}), total N (N_{tot}), NH_4^+ -N, NO_3^- -N, sulphur and bulk density. Field A, an AS soil, contained sulfidic materials and 0.9% C_{tot} below 170 cm, while Field B, not an AS soil, had 0.3% C_{tot} in the subsoil and no sulfides. In these soils, the groundwater level declined below 200 cm in summer, subjecting the subsoil to oxidation. This study revealed large stocks of C_{tot} , N_{tot} and mineral N in the subsoil, particularly in the AS soil. At 20–240 cm, Field A contained 292 tons of C_{tot} ha⁻¹ and 25 tons of N_{tot} ha⁻¹, while Field B had 152 tons of C_{tot} ha⁻¹ and 11 tons of N_{tot} ha⁻¹. Field A contained up to 435 kg of mineral N ha⁻¹ in autumn, while in Field B there was only up to 137 kg of mineral N ha⁻¹. In Field A, NH_4^+ -N dominated strongly, while NO_3^- -N dominated in Field B. It is suggested that the greater concentration of mineral N in the AS soil is due to 1) a greater stock of total (mineralizable) N and 2) the slower rate of nitrification resulting in substantial NH_4^+ -N retention on cation exchange sites.

Key words: carbon, nitrogen, nitrification, mineralization, organic matter, acid sulphate soils, subsoil, drainage

Introduction

Soils developed in materials sedimented in lakes and small bays of the sea often contain plenty of

organic matter in the subsoil. Organic matter originates from the biota of the water and has been thoroughly mixed with the mineral matter, mostly fine or medium textured. In the Nordic countries, these mud materials are traditionally called gytja

(e.g., Wiklander et al. 1950) and they closely resemble the limnic materials of Soil Taxonomy (Hansen 1959). They often contain substantial amounts of sulphur (S), accumulated as iron sulfides in the sediment under reducing conditions. The parent material of acid sulphate soils (AS soils), which was deposited predominantly during the Litorina period (7500–3000 BP) in the Baltic basin, is a typical example of these soils, occurring particularly on the western coast of Finland (Purokoski 1958, Erviö 1975). These former sediments have been brought into an oxidized environment by the isostatic land uplift and agricultural drainage. Small shallow lakes and wetlands have also been drained to serve as agricultural land. According to the FAO system (FAO 1988), these soils are commonly classified as Gleysols (Öborn 1989, Yli-Halla 1997, Joukainen and Yli-Halla 2003), while the best-drained ones are also classified as Cambisols (Öborn 1989).

Inventories of carbon (C) in soil and lake sediments have recently been carried out in Finland, resulting in estimates of that element in forest soils (Kauppi et al. 1997, Liski and Westman 1997), in peatlands (Minkkinen 1999) and lake sediments (Kortelainen and Pajunen 2000). For agricultural lands, there are plenty of data on the C content in the plough layer but fewer dealing with the subsoil. Inaccurate information about the areas of the different soil types also contributes to the fact that a detailed inventory of C in Finnish agricultural soils is still missing.

In organic forms, C and nitrogen (N) are intimately linked. In mineral soils, over 95% of the total nitrogen (N_{tot}) is generally contained in soil organic matter. The major part of these N reserves is usually in the top layer due to accumulation of crop residues and humus. Investigations of AS soils (Wiklander et al. 1950, Öborn 1989, Yli-Halla 1997, Bärlund et al. 2004) have indicated a high content of N_{tot} in the subsoil also. This N stock is potentially subjected to mineralization, which is controlled by several factors, such as composition of the substrates, soil temperature, moisture and pH. Mineral N fractions, ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and especially nitrate nitrogen ($\text{NO}_3^-\text{-N}$) are liable to leaching via subsurface drainage flow

or deep percolation of groundwater. Indeed, within the Finnish network of small representative catchments, the N load from catchments with AS soils has been observed to be higher than the loads from other agricultural catchments in Finland (Rekolainen 1989, Vuorenmaa et al. 2002).

This study seeks to explore the origins of this increased N load by comparing soil profile concentrations of C and N to depths of 240 cm in an AS soil and a neighbouring non AS soil, both under crops, in western Finland. The aims of the study were (1) to investigate the vertical distribution of C and N_{tot} and mineral nitrogen (N_{min}) reserves in an AS soil compared with a non AS soil and (2) to evaluate the role of native organic matter as a source of N_{min} . Concentrations of N_{min} in AS soils have not been published before; this is the first study to monitor N_{min} below 120 cm in any Finnish agricultural soil. This study contributes to our knowledge of the stock and distribution of N and C in AS soils. This basic information is needed for a more detailed understanding of the observed net transport of N to watercourses and to develop sound management practices for AS soils, as well as to assess the impacts of different practices involving these soils.

Material and methods

Study site

The experimental site is located at Lapua (62°51'N, 23°15' E) in Ostrobothnia, western Finland (Fig. 1). The site is 60–62 m above the sea level and the surface slope is about 1%. The study was carried out for two field sections (Fields A and B), which have separate subsurface drainage systems. The distance between the experimental areas is about 100 m. The area of Field A is 2.47 ha and that of Field B is 0.59 ha. The soil texture is fine sand to a depth of about 0.5 m, while deeper horizons consist of silt. The clay content of the top layer (0–30 cm) is 11–15%, increasing downwards to 27–29% at the depth of 50–100 cm.



Fig. 1. Location of the Lapua study area in western Finland.

Drainage of the fields was accomplished with open ditches in the 1960s and with subsurface drainage pipes in the early 1970s. The drain depth in Field A varies from 1.0 to 1.5 m. The field drains discharge into a main collector pipe having an outlet to a main ditch flowing between the fields. In Field B, the drain depth is about 1 m and the drains discharge directly to the main ditch. The initial drain spacing was 20 m, but the spacing was halved to 10 m in spring 1993 for a controlled drainage experiment.

The crop was mainly starch potato (*Solanum tuberosum*, L.) several years before and during the study period. The annual N fertilizer rate was 70–83 kg ha⁻¹. No manure or other types of organic fertilizers were applied. Agricultural practices in the two fields were the same and representative of those employed in the region.

Soil sampling and groundwater observations

Soil sampling and monitoring of groundwater level were carried out during the period 1994–1996. The soils were sampled down to 240 cm taking samples at 20–40 cm increments with a 25 mm diameter manual drill. Upon sampling, the soil was

sealed in airtight plastic containers, which were stored in cool boxes. The sampling dates were 1) after snowmelt and before fertilization in May and 2) after harvest in November. The number of sampled profiles was 1–3 per field and date. The total number of profiles sampled was 10 for Field A and 7 for Field B.

The depth of the water table was recorded in observation wells in each field in the middle of two drain lines. There were twelve wells in total, with depths ranging from 1.6 to 2.5 m. The wells were made of 30 mm diameter PVC pipe surrounded by a filter. Manual observations using a graded water-detecting gauge were carried out on a two-to-four-week basis. Furthermore, automatic pressure sensors (Jensen Ltd. Type PSL) with a 15-min measurement interval were installed in three wells in Field A. Due to technical problems, continuous water table data series were not achieved. The field site and measurements have been described in more detail by Paasonen-Kivekäs et al. (1997).

Soil analyses

Mineral N was determined from all sampled profiles. The soil samples, stored at +4°C, were analyzed within 3–4 days after sampling. Ten grams of fresh soil was extracted by shaking with 50 ml of 2 M KCl for 1 h. The suspension was centrifuged for 5 min and then filtered using a Schleicher & Schuell 595 filter. The concentrations of NO₃⁻-N and NH₄⁺-N in the extract were measured by a flow injection analyser (Tecator, FIAstar 5010 Analyzer) according to the Tecator Application Notes ASN 65-31/84 and ASN 65-32/84 (Emteryd 1989). The contents of NO₃⁻-N and NH₄⁺-N were calculated as mg g⁻¹ of dry soil. Water content in the fresh soil samples was determined gravimetrically by drying at 105°C. The soil samples were analysed for pH(H₂O) in the field immediately after sampling (MacLean 1984; pH meter ORION SA 520).

Total S (S_{tot}), C_{tot} and N_{tot} were determined using air dry samples taken in May 1994. These concentrations were assumed to be so stable that they were determined only once from three soil profiles from Field A and two from Field B. A Leco CN

2000 dry combustion analyzer was used for the determination of C_{tot} and N_{tot} . The detection limit (blank mean + $3 \times$ standard deviation of the blanks), calculated on the basis of the results over a long time, is 0.12% and 0.09% for C_{tot} and N_{tot} , respectively. Mean deviation between the two replicates of each sample was on average 1.5% for C_{tot} and 3.2% for N_{tot} . All C was assumed to be organic. Total S was digested with concentrated HNO_3 (SFS 3044) and determined by plasma emission spectroscopy. Subsoil samples (110–240 cm) were tested for the presence of sulfidic materials by the method of Soil Survey Staff (1999) using an aerobic incubation of 8 weeks. After incubation, the $\text{pH}(\text{H}_2\text{O})$ was determined and sulphate sulphur ($\text{SO}_4^{2-}\text{-S}$) was extracted from the soil samples with 0.01 M CaCl_2 and determined by plasma emission spectroscopy. Mean deviation between the two replicates was on average 1.5% for $\text{SO}_4^{2-}\text{-S}$ and 1.8% for S_{tot} .

Bulk density (BD) was determined for the depths 0–30 cm, 40–50 cm and 60–70 cm by the core sampling method (Blake 1985a). Bulk density for deeper horizons was calculated on the basis of C content using the formula presented by Howard et al. (1995): $\text{BD} = 1.3 - (0.275 \times \log C\%)$. Particle density was measured employing a pycnometer (Blake 1985b). Porosity was calculated from the BD and particle density (Vomocil 1985). Total porosity of the plough layer was about 55 vol-% in both fields. The porosity of the silty subsoil below the fine sand layer was about 51 vol-% in Field A and about 48 vol-% in Field B.

The concentrations of C_{tot} , N_{tot} , $\text{NO}_3^- \text{-N}$ and $\text{NH}_4^+ \text{-N}$ were converted to quantities, expressed as kg ha^{-1} , for the individual soil layers using the BD values. The measured BD values were used for the upper three layers and the estimated values (Howard et al. 1995) for the deeper ones. The amount of N_{min} was calculated as the sum of $\text{NO}_3^- \text{-N}$ and $\text{NH}_4^+ \text{-N}$ quantities.

Plant sampling and analyses

To estimate the N content of the harvested crop and in the above-ground plant residues, the plants

were also analysed for N. Ten potato plants were collected randomly over each experimental area. The crop density was determined by measuring the number of potato plants per 10 m of ten randomly selected beds in each area. The plants were divided into leaves, stems and tubers. The samples were oven dried (12 h, 105°C) and their dry weight was determined. The nitrogen concentration of each plant organ was determined by using a Leco CHN-900 analyzer (Kleemola and Teittinen 1996).

Results

Soil profiles

The three studied profiles in Area A had sulfidic materials in the subsoil, which started at the depth of 140 cm to 200 cm and had its average upper boundary at 170 cm, see Table 1. According to Soil Taxonomy (Soil Survey Staff 1999), fresh $\text{pH} > 4.0$ and a decrease of soil pH by at least 0.5 units to values below 4.0 indicates the presence of sulfidic materials. The S_{tot} concentration of these horizons was, however, too low ($< 0.75\%$) to qualify as sulfidic materials of the FAO system (FAO 1988). Morphologically, these horizons were grey and massive, indicating predominantly reduced conditions. The oxidized horizons above (80–140 cm) had a pH of between 3.5 and 4.0, no decrease of pH upon incubation and a well developed structure, stabilized by plenty of iron hydroxide. The concentration of $\text{SO}_4^{2-}\text{-S}$ at 140–170 cm was just above 0.05% (Table 1). As the soils were sampled in spring, soon after the snow melt waters had leached the soil profile, higher values of $\text{SO}_4^{2-}\text{-S}$ may have been measured in summer. Area A did not have a sulphuric horizon ($\text{pH} < 3.5$; Table 1), but the criteria of the sulfic attribute of Soil Taxonomy were barely met.

Deviating substantially from Area A, Area B did not have sulfidic materials within the investigated depth (–240 cm). The pH of the incubated subsoil samples remained above 5.2. Also the concentration of $\text{SO}_4^{2-}\text{-S}$ was very low throughout the two profiles sampled, and the concentrations of S_{tot}

Table 1. The pH values and sulphur concentrations of soil samples taken from different depths of the experimental fields in Lapua. The concentrations of $\text{SO}_4^{2-}\text{-S}$ were analysed from incubated samples.

Depth cm	pH fresh	pH incubated	$\text{SO}_4^{2-}\text{-S}$ %	Total S %
<i>Field A</i>				
0–20	5.7	n.d.	n.d.	0.05
20–50	5.3	n.d.	n.d.	0.02
50–80	4.3	n.d.	n.d.	0.03
80–110	3.9	n.d.	n.d.	0.05
110–140	3.9	3.9	0.015	0.12
140–170	4.1	3.7	0.050	0.17
170–200	4.5	3.7	0.082	0.26
200–240	6.2	3.5	0.206	0.41
<i>Field B</i>				
0–20	6.2	n.d.	n.d.	0.04
20–50	4.9	n.d.	n.d.	0.02
50–80	5.0	n.d.	n.d.	0.01
80–110	5.3	n.d.	n.d.	0.01
110–140	5.4	5.2	0.002	0.01
140–170	5.4	5.3	0.002	0.02
170–200	5.4	5.3	0.002	0.01
200–240	6.0	5.2	0.003	0.02

n.d. = not determined

in the subsoil of Area B were only 3–10% and C_{tot} 38–53% of those in the corresponding horizons of Area A.

In the Lapua area, soils have a cryic temperature regime (Yli-Halla and Mokma 1998). In spite of a relatively high content of organic matter, the soils were not very dark (moist colour 7.5YR 4/2, dry colour 7.5YR 6/2) and they consequently had ochric Ap horizons. According to Soil Taxonomy (Soil Survey Staff 1999) and given the requirement that acid sulphate characteristics occur within 150 cm of soil surface, Area A was a *Sulfic Cryaquept* and Area B a *Typic Cryaquept*. According to the FAO system (FAO 1988), both areas represented *Dystric Cambisols*, because the more stringent criteria of acid sulphate characteristics of the FAO system (pH < 3.5 and total S of sulfidic materials > 0.75%) were not met.

Total carbon and nitrogen

The C_{tot} - and N_{tot} -concentrations, shown in each sampling layer in Table 2, indicated clearly that Field A was richer in both elements, the relative

difference being largest below the depth of 50 cm. In both fields, the amount of C_{tot} and N_{tot} varied clearly with the depth (Table 3). The amount of C_{tot} in the plough layer accounted for 40% of the reserves in the whole profile of 0–240 cm in Area A and 53% in Area B. The horizons of 100–240 cm formed 36% of C_{tot} in Area A and 27% in Area B. Concerning N_{tot} the plough layer had only 25%, while the depths below 100 cm had as much as 52% in the profile of the 0–240 cm in Area A. The corresponding proportions in Area B were 38% and 42%, respectively. The mean C/N ratio at 0–20 cm was about 23 in both fields. The ratio decreased sharply below the depth of 50 cm (Table 2).

Mineral nitrogen

On average, N_{min} (NO_3^- -N and NH_4^+ -N) accounted for 1.4% and 0.8% of N_{tot} in the whole profile (0–240 cm) in Area A and in Area B, respectively. The amount of N_{min} and its fractions and their vertical distribution in the soil profile clearly differed between the fields (Table 4). There was over three times more N_{min} in Field A than in Field B. In both

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Table 2. Mean concentration of total carbon (C) and nitrogen (N), C/N ratio and bulk density of soil samples taken from different depths in Fields A and B at the Lapua site.

Depth cm	Total C %	Total N %	C/N ratio	Bulk density g cm ⁻³
<i>Field A</i>				
0–20	6.65	0.29	22.8	1.07
20–50	1.92	0.10	19.5	1.54
50–80	0.56	0.05	11.2	1.35
80–110	0.91	0.09	10.1	1.31
110–140	0.90	0.09	9.9	1.31
140–170	0.86	0.09	9.5	1.32
170–200	0.87	0.09	9.6	1.32
200–240	0.78	0.08	9.8	1.33
<i>Field B</i>				
0–20	5.71	0.25	23.3	1.14
20–50	1.27	0.06	21.1	1.52
50–80	0.22	0.02	11.0	1.66
80–110	0.22	0.02	10.9	1.48
110–140	0.34	0.03	11.3	1.43
140–170	0.45	0.04	11.1	1.40
170–200	0.46	0.04	11.6	1.39
200–240	0.38	0.04	9.4	1.42

Table 3. Mean stock of total carbon (C) and nitrogen (N) in different depth intervals and in a 0–240 cm profile in Fields A and B in Lapua.

Depth, cm	Total C, tn ha ⁻¹	Total N, tn ha ⁻¹
<i>Field A</i>		
0–30	172	7.8
30–50	59	3.0
50–100	46	4.4
100–150	59	6.0
150–200	57	5.9
200–240	42	4.3
0–240	435	31.4
<i>Field B</i>		
0–30	150	6.5
30–50	39	1.8
50–100	17	1.6
100–150	24	2.1
150–200	32	2.8
200–240	21	2.3
0–240	283	17.1

fields, there was a prominent pool of N_{\min} in the deeper soil layers. In Area A, 75% of the N_{\min} reserve was at a depth of 100–240 cm. The corresponding value in Area B was 57%.

At the depth of 0–100 cm, NO_3^- -N formed over 80% of the N_{\min} pool in both fields. In Field A, the

amount of NH_4^+ -N sharply increased and NO_3^- -N decreased below the 100–150 cm layer. The amount of NH_4^+ -N at 150–240 cm was 256 kg ha⁻¹, accounting for 96% of the N_{\min} in this horizon. In Field B, NO_3^- -N remained the dominant fraction at all depth intervals, while the proportion of NH_4^+ -N remained below 17%, even in the deepest layers. The vertical distribution of the N_{\min} fractions within each field gave the same type of pattern at all sampling dates.

The amount of N_{\min} was relatively consistent between the different sampling profiles and dates within each field. The average amount of N_{\min} in spring was 429 kg ha⁻¹ in Field A and 122 kg ha⁻¹ in Field B. In November, there was only 6.1 kg ha⁻¹ more N_{\min} at 0–240 cm in Field A than in May and 14.8 kg ha⁻¹ more in Field B. The change in the quantity of NH_4^+ -N and NO_3^- -N in Field A was 6.7 kg ha⁻¹ and -0.6 kg ha⁻¹, respectively. In Field B, the quantity of NO_3^- -N increased by 23.0 kg ha⁻¹, whereas NH_4^+ -N decreased by 8.2 kg ha⁻¹. The biggest changes from spring to autumn were detected at the depths below 100 cm. The coefficient of variation (CV) of NH_4^+ -N ranged from 19% to 80% within single soil layers. The lowest variation was observed in the deepest layers of Field A. On

Table 4. Content of ammonium, nitrate and mineral nitrogen (NH₄⁺-N, NO₃⁻-N and N_{min}, respectively) in different depth intervals and in a 0–240 cm profile in Fields A and B in Lapua. Mean, minimum (min) and maximum (max) value, standard deviation (std) and number of profiles studied (n).

Depth cm	NH ₄ ⁺ -N, kg ha ⁻¹				NO ₃ ⁻ -N, kg ha ⁻¹				N _{min} , kg ha ⁻¹				n
	mean	min	max	std	mean	min	max	std	mean	min	max	std	
<i>Field A</i>													
0–30	4	1.4	11	3	34	13.1	56	14	38	17	57	13	10
30–50	2	0.0	3	1	20	10.2	38	11	23	12	40	11	10
50–100	7	1.7	16	5	39	27.5	73	13	45	29	89	17	10
100–150	40	15.7	70	17	22	8.3	33	8	61	48	88	12	10
150–200	106	68.5	160	30	7	2.0	24	6	114	74	165	33	10
200–240	150	98.3	180	29	2	0.2	11	3	152	100	180	29	10
0–240	309	185.6	440		124	61.3	234		433	280	619		
<i>Field B</i>													
0–30	3	1.2	7	2	15	10.9	19	3	18	12	21	3	6 ^a /7 ^b
30–50	2	0.4	5	1	9	4.9	18	5	11	5	20	5	6 ^a /7 ^b
50–100	4	1.1	7	2	23	16.1	35	7	27	19	40	7	6 ^a /7 ^b
100–150	3	0.6	5	2	27	21.4	31	4	29	22	33	4	6 ^a /7 ^b
150–200	2	0.0	4	2	25	19.5	29	5	27	21	33	5	6 ^a /7 ^b
200–240	3	0.1	6	2	15	7.7	20	5	18	14	22	4	6 ^a /7 ^b
0–240	17	3.4	34		114	80.5	152		130	93	169		

^a NO₃⁻-N and N_{min}

^b NH₄⁺-N

average, the amount of NO₃⁻-N showed more consistency at a depth of 0–200 cm. The highest CV (165%) was in the 200–240 cm layer in Field A, where the reserve of NO₃⁻-N was very small.

Nitrogen uptake by crop

The average fertilizer rate and N uptake of crops are presented in Table 5. The N uptake between the samples varied more within Field A (CV 40% on average) than within Field B (CV 24% on average). The N content of potato stems and leaves varied from 22.6 kg ha⁻¹ to 61.9 kg ha⁻¹ one week before harvest depending on the area and year. Potato tubers stored 5–93.6 kg ha⁻¹ more N than the amounts applied as fertilizer N.

Depth to groundwater table

Temporal variation of depth to groundwater table is shown in Fig. 2. Since variation across the fields was found to be small, the mean depths are pre-

Table 5. N fertilizer rate and mean N uptake by crop in Fields A and B in Lapua. Residual N = fertilizer N – N in the tubers.

	Fertilizer rate kg ha ⁻¹	N in tubers kg ha ⁻¹	Residual N kg ha ⁻¹
<i>Field A</i>			
1994	76	106	-30
1995	83	148	-65
<i>Field B</i>			
1994	76	81	-5
1995	83	177	-94

sented for each point of time. The water table in Field A usually remained shallower than in Field B due to the slightly lower topographic position and control drainage measures of Field A. Soil in Field B was also more effectively drained owing to its closer vicinity to the main ditch compared to Field A. Controlled drainage temporarily raised the water table and retarded its decline in Area A.

The water table periodically rose until the drain depth or higher during snow melt and rainy periods in summer and autumn. However, after the

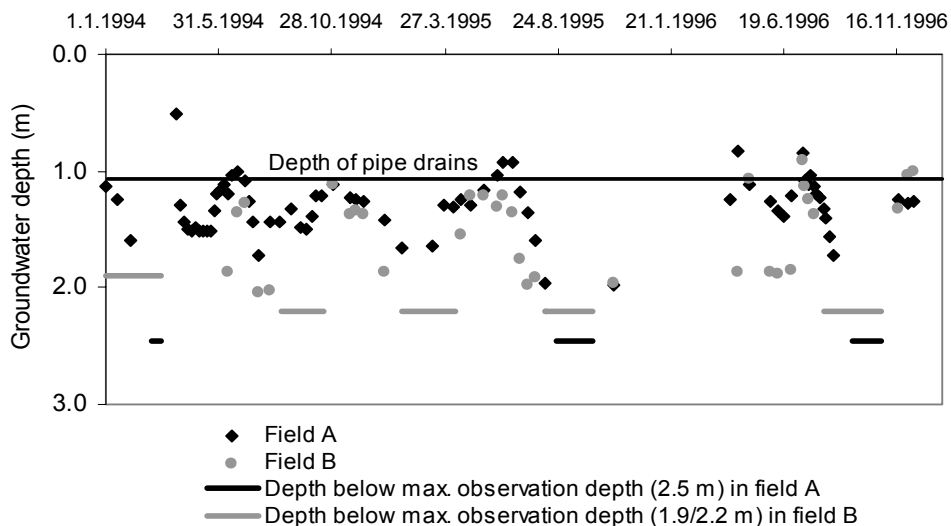


Fig. 2. Groundwater depth in Fields A and B in Lapua. No observations were available from 8 Nov 1995 until 7 April 1996. The depth of pipe drains represents the average depth in the fields.

rainfalls, the water table rapidly declined below the drain depth in both fields. From July to November 1995, the depth to water table remained below 2 m from the soil surface for about 80 days in Field A and about 125 days in Field B. From September to November 1996, the water table was below 2 m for about 65 days in Area A and 88 days in Area B. The water table even dropped to depths exceeding the depth of the deepest observation wells (2.5 m in Field A, 1.9/2.2 m in Field B, see Fig. 2).

Discussion

Field A is a typical example of cultivated Finnish AS soils. Horizons formed of non-sulfidic materials exclusively cover the sulfidic materials, which have been partly oxidized, a process accelerated by increased drainage efficiency. Leaching of water-soluble products of oxidation has resulted in a subsoil rather low in soluble salts and a pH at 3.5–4.0. Often the AS characteristics are not harsh enough or they are too deep to meet the criteria of

international classification systems regarding AS soils (Yli-Halla et al. 1999). On the basis of the surveys by Erviö (1975) and Puustinen et al. (1994), these kinds of soil are typical on the coasts of Finland, the latter giving an estimate of as much as 300,000 ha AS soils in Finland. These soils may not cause problems to agriculture anymore and at the top they may not be distinguished from non-AS soils such as those of Field B, but they may still produce hazardously acidic drainage waters (Joukainen and Yli-Halla 2003). The fact that both soils of the present study have, according to the FAO classification system, the same name while the sulfidic nature of the subsoil A is not recognised, indicates the inadequacy of that system to cope with this environmentally relevant characteristic of effectively drained AS soil.

It is evident that Field B, with its subsoil pH between 4.9 and 6.0, has never contained considerable concentrations of sulfide within the investigated depth. This conclusion is supported by the fact that, after oxidation of sulfide and washing out the solutes, the pH of the soil remains at about 4, which is not raised by leaching with water (Hartikainen and Yli-Halla 1986). Therefore we con-

clude that the difference between the two adjacent fields is caused by the large native heterogeneity indicated clearly in the AS soil material of Puustinen et al. (1994).

The concentration of C_{tot} in the subsoil in Field A was similar to the values observed at corresponding depths in, for example, the soils of Ylistaro (about 1%, Yli-Halla 1997) and Ilmajoki (0.6–1%, Joukainen and Yli-Halla 2003), both AS soils less than 100 km from the present experimental field, and in similar soils of Kungsängen (1.3%, Kirchmann 1991), Ängesby and Ersnäs (0.9–1.3%, Öborn 1989) in Sweden. These concentrations are much lower than in the subsoils of the more severe AS soils of western Finland, such as Laitila (2.5–3%, Yli-Halla 1997) and Mustasaari (1.6–2.2%, Joukainen and Yli-Halla 2003), which probably occupy a relatively small area (Yli-Halla et al. 1999). The much lower concentrations of C_{tot} in Field B resembled the values (0.1–0.5%) measured at similar depths in other soils without any AS characteristics, several examples of which can be found in Yli-Halla et al. (2000).

As compared to other AS soils with similar concentrations of organic matter in their subsoil, the concentrations of N_{tot} at 80–240 cm in Field A (0.08–0.09%) were higher than the values at Liminka (0.04–0.06%) but lower than those in Ylistaro (0.18–0.24% at 50–150 cm, Yli-Halla 1997) and in Ilmajoki (0.23–0.27% at 170–300 cm, Bärlund et al. 2004). Field A had clearly lower concentrations of N_{tot} than more severe AS soils with higher concentrations of organic matter in their subsoil, such as Mustasaari (0.33–0.36% at 50–200 cm, Bärlund et al. 2004) or Laitila (0.32–0.58% at 50–150 cm, Yli-Halla 1997). In Field B, the concentrations of N_{tot} (0.02–0.04%) in the subsoil were in the range of those measured in the agricultural silt and fine sand soils of Finland (0.027–0.068% at 40–100 cm, Sippola and Ylärinta 1985).

The reserves of N_{tot} in the 0–100 cm layer in both fields were similar to reserves determined in other agricultural soils in Finland. The values commonly range from 6300 to 10 900 kg ha⁻¹ at 0–60 cm (Sippola 1981) or up to 13 300 kg ha⁻¹ at 0–100 cm (Linden et al. 1992), usually being higher in

clay soils than in coarse mineral soils. Indeed, the marked differences between the two soils of the present study were below 100 cm, where the stock of N_{tot} of the AS soil was much greater.

The N_{min} amount at 0–100 cm in both fields was equivalent to that of other Finnish soils. The N_{min} in agricultural mineral soils in spring before fertilization has generally varied from 7 to 150 kg ha⁻¹ at 0–60 cm or 0–100 cm profiles (Sippola and Ylärinta 1985, Leppänen and Esala 1995, Kuisma 2002), but N_{min} amounts up to 290 kg ha⁻¹ at 0–60 cm or 0–90 cm in spring and autumn have also been observed in some fields (Leppänen and Esala 1995, 1999). The highest values were connected with animal manure application and cultivation of grass and vegetable crops.

Even though the N_{tot} concentrations in the subsoil samples were generally small, they seem to be quite accurate. This conclusion can be drawn from the small mean deviation of the replicates and the small variation of the C/N ratio in the subsoil samples. The biggest inaccuracy of this study is probably the estimation of the BD values of the subsoil with the help of the Howard et al. (1995) equation. Indeed, that equation gave much lower BD values than were actually measured for the soil samples taken from 40–50 cm, probably compacted by agricultural operations. However, the close match between the calculated and measured BD values of the soil samples taken from 0–30 cm and 60–70 cm gives us confidence in the calculated values of the deeper layers, which are not affected by compaction. We therefore think that the estimates of the C_{tot} and N_{tot} in the deeper layers are reasonable.

In both years of the experiment, the N uptake by potato tubers was higher than the amount of N fertilizers applied, an observation also made in other experiments (Kuisma 2002). Consequently, fertilization does not explain the substantial pool of N_{min} in the subsoil. Moreover, the fields were managed similarly. We therefore conclude that the fact that there was a higher N_{min} pool in Field A than in Field B is explained by the larger amount of organic matter and organic N. The fact that the C/N ratio was clearly below 20 at 50–240 cm in both fields indicates a net mineralization tendency

leading to an accumulation of N_{\min} (Stevenson and Cole 1999). These horizons have been continuously waterlogged before agricultural drainage, which probably enhances the present N mineralization by providing aeration of subsoil. The decline of the water table well below the drains for several weeks in summer and autumn has also been observed in other studies of AS soils of the region (Joukainen and Yli-Halla 2003). The decline at the Lapua site is attributed to low precipitation, evapotranspiration and deep percolation to the neighbouring open channel. The oxidised horizons in the fields have prominent iron-hydroxide-lined cracks and remnant root channels that substantially increase hydraulic conductivity of the fine textured soils. A rough estimate of annual N mineralization is 1.5–3.5% of the amount of organic or total N (Brady and Weil 1999). In Finland, N mineralization at 0–100 cm was about 0.6% of N_{tot} in silty clay soil during the growing season of barley (Sippola 1986). These results correspond well with ours in terms of the ratio of the stocks of N_{\min} and N_{tot} .

NO_3^- -N is usually the dominant N_{\min} fraction in well-drained neutral-to-slightly-acid mineral soils. The predominance of NO_3^- -N at 0–100 cm in Field A and at 0–240 cm in Field B reflects favourable conditions for the nitrifying micro-organisms. The abundant accumulation of NH_4^+ -N below 100 cm in Field A indicates retarded nitrification. It can be attributed to 1) the higher water table, 2) a higher content of organic matter consuming oxygen during decomposition, 3) the strongly acidic conditions in the aerobic subsoil and, consequently, high concentrations of dissolved metals such as Al, 4) the incidence of H_2S in the reduced subsoil and 5) low soil temperature (e.g., Paul and Clark 1989, Scheffer and Schachtschabel 2002).

In spite of the periodically deep groundwater table, the diffusion rate of oxygen into the deepest horizons studied is assumed to be slow due to the massive soil structure and high water retention capacity of the silt soil. Nitrification is one of the most pH-sensitive soil reactions; the minimum pH for the reaction to occur is about 4.5. However, in acid soils (pH < 4), production of NO_3^- -N has been reported to occur probably due to heterotrophic ni-

trifiers (Paul and Clark 1989). They are more acid tolerant than autotrophic organisms, but the rate of nitrification is much lower. The impact of the low pH alone on nitrification in Field A was not clear because high amounts of NO_3^- -N also occurred in horizons which had a pH < 4.5.

Conversion of soil organic N to NH_4^+ -N has been observed even at 2°C, whereas very little NO_3^- -N is formed below +5°C. The rates clearly increase above +15–20°C (Karvonen 1992, Stevenson and Cole 1999). In Ylistaro, less than 100 km from the present experimental site, the average monthly soil temperature in the period 1971–1990 at 100 cm in summer was > 10°C in only three months and never at 200 cm (Heikinheimo and Fougstedt 1992). At both depths, the soil temperature was < 5.0°C for six months with minimum monthly values of 0.4°C at 100 cm and 2.8°C at 200 cm. The temperature conditions indicate that release of mineral N probably proceeds in the bottom layers of the studied soils at relatively low rates throughout the year.

In spite of the fact that NH_4^+ -N occurred in the subsoil of Field A in larger quantities than found usually, it represented less than 0.2 cmol kg⁻¹. That is a negligible amount when compared to the estimated cation exchange capacity of about 14 cmol kg⁻¹ (see the Ylistaro soil in Yli-Halla 1997). This calculation thus shows that the subsoil of Field A was in no way saturated with NH_4^+ -N, suggesting that NH_4^+ -N can to a large extent be retained by soil. In contrast to NH_4^+ , NO_3^- ions are highly mobile and move readily via drainage water and deep percolation. A major part of NO_3^- -N leached below the drain depth in Field A may be reduced to gaseous N forms (N_2O and N_2) by denitrification. In the deeper horizons, low aeration and an ample supply of soluble organic C form favourable conditions for the reaction (Firestone 1982).

Conclusions

This study dealt with C_{tot} , N_{tot} and N_{\min} reserves in an agricultural AS soil in western Finland as com-

pared to a non AS soil. Despite the small amount of research material, C_{tot} and N_{tot} of the experimental site were in the ranges commonly found in AS soils in Finland. We therefore believe that we can also make meaningful conclusions and generalizations on the basis of the N_{min} results of this study.

A large stock of N_{min} occurred below the depth of 100 cm particularly in the AS soil, but also in the non AS soil. These depths are usually ignored in soil N investigations. This storage may be insignificant for crops, but can have an environmental impact releasing soluble N into drain pipes and deep groundwater. The release of N_{min} from the deeper soil layers is expected to contribute much more to the N_{min} load of watercourses than losses from fertilization. Significant amounts of N_{min} seem to be released from the large reserves of organic matter, particularly in previously poorly drained AS soils, due to their high organic N content and low C/N ratio. The persistence and transport of $\text{NH}_4^+\text{-N}$, the dominant form of N_{min} in the subsoil of AS soil, need to be examined in further studies. Measurements of N_{min} in different types of non AS soils are needed to further explain the differences in N losses between AS soils and non AS soils.

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SELOSTUS

Happaman sulfaattimaan typpi- ja hiilivarat

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Tavanomaisten viljelymaiden hiilestä ja typestä valtaosa on sitoutuneena muokkauskerroksen orgaaniseen ainekseen. Happamissa sulfaattimaissa on melko runsaasti orgaanista ainesta myös muokkauskerroksen alapuolella. Tehokkaasti kuivatetuissa maissa näistä varoista voi mineraloitua melkoisesti typpeä maan toistuvan kuivumisen ja kostumisen seurauksena. Tässä tutkimuksessa verrattiin Lapualla sijaitsevan happaman sulfaattimaan ja vieressä sijainneen lajitekoostumukseltaan samanlaisen tavanomaisen maan hiili- ja typpivarojen määrää ja mineraalitypen (ammonium- ja nitraattityppi) esiintymistä. Molemmilla pelloilla oli viljelty pitkään perunaa, ja satojen typen otto oli poikkeuksetta runsaampaa kuin typpilannoitus. Maaprofiilit tutkittiin kerroksittain 240 cm:n syvyyteen saakka. Sulfaattimaalla 20–240 cm:n välisissä maakerroksissa oli 292 tonnia hiiltä ja 25 tonnia typpeä hehtaaria kohti, kun tavanomaisessa maassa vastaavalla syvyydellä oli hiiltä 152 tonnia ja typpeä 11 tonnia hehtaaria kohti. Syksyllä sulfaattimaassa oli mi-

neraalityppeä 435 kg/ha ja tavanomaisessa maassa 137 kg/ha. Typen arveltiin mineraloituneen pääasiassa maan orgaanisesta aineksesta. Valtaosa sulfaattimaan mineraalitypestä oli ammoniummuodossa, kun taas tavanomaisessa maassa vapautunut typpi oli nitrifioitunut nitraattitypeksi. Ammoniumtypen runsauden sulfaattimaassa arvellaan olevan seurausta ainakin maan suuremmasta vesipitoisuudesta ja heikommasta ilmanvaihdosta, alhaisemmasta pH:sta ja runsaammasta liukoisten metallien pitoisuudesta. Tutkimuksen päätulos oli havainto siitä, että etenkin sulfaattimaan syvemmissä kerroksissa, ja myös tavanomaisella maalla, voi esiintyä suuria mineraalityppimääriä, jotka voivat kuormittaa pinta- ja pohjavesiä tai haihtua kaasumaisina typpiyhdisteinä. Nämä mineraalitypen varat ovat tähän asti jääneet huomaamatta, koska maanäytteet typpimäärityksiä varten otetaan yleensä korkeintaan metrin syvyyteen saakka.