

DIVISION S-10—WETLAND SOILS

Carbon Accumulation and Storage in Mineral Subsoil beneath Peat

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ABSTRACT

We showed that sandy subsoils beneath peat near Ramsey Lake, MI, contained 7.5 to 8.0 kg organic C (OC) m^{-2} to a depth of 70 cm, compared with 1.6 to 3.6 kg m^{-2} in adjacent forest soils, from which the peatland had evolved through paludification. Compared with the soils beneath the forest, those beneath the peat contained similar amounts of oxalate-extractable Al (Al_o) and less Fe, owing to loss of Fe under reduced leached conditions beneath the peat. Most of the extractable Al in the mineral horizons beneath peat was organically bound. Atomic pyrophosphate-extractable ($Fe_p + Al_p$) Fe + Al/C ratios were smaller ($<0.2:1$) in the mineral horizons beneath peat than in the forest mineral subsoils (generally $>0.2:1$), indicating larger inputs and retention in the mineral subsoils beneath peat. Concentration of OC in subsoil samples was strongly ($r^2 = 0.58$, $p < 0.001$) related to the subsoil Al, null-point dissolved organic C (DOC) and clay concentrations. A DOC sorption study using peat pore water ranging from 0 to 117 mg DOC L^{-1} revealed null-point DOC (DOC_{np}) concentrations (at which there is neither gain nor loss of OC by the soil) varied from <1 to 417 mg DOC L^{-1} and was primarily related to Fe_o (negatively), Al_o (negatively), and C (positively). We suggest that the increase in mineral subsoil OC beneath peat is related to the sorption of DOC carried by pore water percolating through the mineral subsoil, combined with slow rates of mineralization of sorbed DOC under anoxic conditions.

IN THEIR SURFACE ORGANIC HORIZONS, northern peatlands (Histosols) contain between 5 and 250 kg OC m^{-2} , amounting to 250 to 450 Pg C globally and an annual accumulation of 10 to 30 g OC $m^{-2} yr^{-1}$ (Gorham, 1991; Turunen et al., 2001, 2002). This accumulation has developed in response to the slow rates of decomposition of peatland plant tissues and the anoxic conditions associated with high water tables in peatlands. Many northern peatlands have developed from the paludification of adjacent upland forest soils, commonly Spodosols and Inceptisols (Huikari, 1956; Walter, 1977; Turunen et al., 1999).

Based on studies in Finland, Turunen et al. (1999) showed that the mineral soil beneath peatlands could contain substantial amounts of OC, 3.9 to 10.7 kg m^{-2} , larger than that in the adjacent upland forest soils, from which the peatland had developed by paludification. Turunen et al. (1999) suggested that this subsoil OC pool could be 10 Pg globally. The analysis of four soil profiles in the Lakkasuo mire in central Finland showed

a strong relationship between OC and extractable Al in the mineral subsoil (Turunen and Moore, 2003). They suggested that this subsoil OC was derived from the sorption of DOC in the subsoil and preserved under anoxic conditions beneath the peat.

In this paper, we examine mineral subsoil properties in four sandy soils from Michigan, two under upland forest and two developed beneath peatland. We tested whether the amount of OC stored in the mineral subsoils was larger beneath the peatland than the forest. We hypothesized that there would be a relationship between OC and extractable Al and Fe in the subsoils. To test whether the subsoils differed in their ability to sorb OC, we conducted a sorption experiment with DOC-rich water derived from a peat sample and relate sorption parameters to soil properties. Finally, we compare the results from Michigan with those obtained from the Lakkasuo study.

MATERIALS AND METHODS

Study Area

The soils were collected from near Ramsay Lake, upper Michigan (45°59' N, 86°45' W, 230 m above sea level). The area was part of glacial Lake Algonquin and the surface soils are sand derived primarily from the Precambrian sandstone bedrock (Futyma, 1981). The topography is generally flat. Mean annual temperature and precipitation are 5.1°C and 788 mm yr^{-1} , respectively (Golden Gate Weather Services, 2001).

Four profiles were collected from a transect from upland forest to peatland (Fig. 1). The two upland soils were characterized by a closed canopy of *Pinus resinosa* Aiton, *Pinus banksiana* Lamb., *Pinus strobus* L., and *Populus grandidentata* Michx. The profiles contained eluvial and illuvial podzolic horizons and were classified as Spodosols (Soil Taxonomy, 1999, p. 871). The peatland was developed from the paludification of forest soils and the vegetation was characterized by an open canopy of *Picea mariana* (Mill.) Britton et al., with a few *P. banksiana* and *Larix laricina* (Du Roi) K. Koch. Hummocks were dominated by *Sphagnum fuscum* and *Chamaedaphne calyculata* (L.) Moench, and hollows by *Sphagnum capillifolium* and *Carex oligosperma*. The two peatland sites, classified as Histosols (Sphagnofibrists), comprised 93 and 63 cm of weakly decomposed peat (H1–H4 in the von Post scale [von Post, 1922]) over the mineral subsoil, which con-

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Abbreviations: DOC, dissolved organic C; DOC_{np} , null-point concentration of DOC in sorption regression; LORCA, long-term rate of organic C accumulation; OC, organic C; subscript o, oxalate-extractable; subscript p, sodium pyrophosphate-extractable; TOC, total organic C.

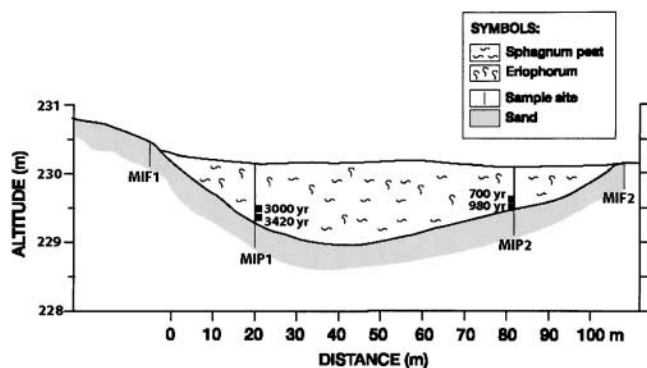


Fig. 1. Transect of the four Ramsay Lake profiles, showing topography, position and basal date.

tained remnants of eluvial and illuvial podzolized horizons inherited from the upland soils.

Soil Sampling and Laboratory Analyses

Samples were taken manually using a box sampler (8.5 by 8.5 by 100 cm), and a Russian pattern peat sampler (5 by 50 cm). The cores were divided into A, E, B, and C horizons. Mineral subsoil samples were taken to a depth of 70 cm from the bottom of the A horizon and subsampled with extreme care to avoid contamination. Core samples of 5-cm increments were sealed in plastic bags and stored at +5°C until dried at 70°C to a constant mass, passed through a 2-mm sieve, and weighed for dry bulk density.

We used a LECO CHN-600 analyzer (LECO Instruments, Mississauga, ON, Canada) to determine OC concentration and OC density, the mass of OC per unit of surface area (g m^{-2}) in a given soil layer, was calculated by multiplying the OC concentration in the unit volume of soil by the thickness of the layer. The OC density of the sampled 70-cm deep mineral soil layer was then calculated by summing of all OC densities of the sublayers. A total of four samples of the basal peat at the two peatland coring sites were taken for ^{14}C dating in the University of Helsinki Dating Laboratory. All results were corrected for isotopic fractionation based on the $\delta^{13}\text{C}$ values. Radiocarbon ages were converted to calendar years using CALIB 3.0.3 (Stuiver and Reimer, 1993).

Oxalate- and pyrophosphate-extractable Fe, Al, and C concentrations in the <2-mm fraction were determined following McKeague (1978, p. 98–104). Iron and Al were determined by atomic adsorption and C by a Shimadzu 5000 TOC analyzer (Shimadzu Corp., Columbia, MD). Particle-size analysis was performed by the hydrometer method (Gee and Bauder, 1986).

The methods in Moore et al. (1992) were used to examine the ability of the soil samples to sorb DOC from a peatwater-derived solution. A solution rich in DOC was produced by soaking a mixture of surface and subsurface peat from the Mer Bleue Bog, ON, in water for 3 d and filtering. The resulting solution was then diluted with distilled water to produce a series of five solutions ranging in DOC from 0 to 117 mg L^{-1} , similar to the range of DOC concentrations in forest soils and peat, reported by Kalbitz et al. (2000). Ten milliliters of the solution was shaken gently with 1 g of the soil sample, left overnight, and then filtered through Gelman A/E 1- μm paper. Dissolved OC concentration was determined on a Shimadzu 5000 TOC Analyzer. Sorption characteristics were determined by regressing the change in DOC concentration in the supernatant against the original DOC concentration, determining the coefficient of determination (r^2), slope (m), and intercept (b). Functionally, m and b can be viewed as measures of soil's ability to sorb DOC (Nodvin et al., 1986).

Table 1. Particle-size analysis of mineral subsoil samples with the standard deviation in parentheses.

Site	Sand	Silt	Clay
	2 to 0.05 mm	0.05 to 0.002 mm	<0.002 mm
	%		
Forest 1 ($n = 13$)	93.42 (2.98)	3.31 (2.56)	3.28 (1.05)
Forest 2 ($n = 12$)	92.41 (2.45)	4.41 (2.78)	3.27 (1.59)
Peat 1 ($n = 14$)	93.93 (3.24)	2.23 (2.20)	3.71 (1.37)
Peat 2 ($n = 11$)	91.12 (2.72)	3.63 (2.82)	5.11 (1.31)

The regression was inverted to calculate the null point DOC concentration (DOC_{np}). This is the original DOC concentration at which there is neither adsorption nor desorption of DOC by the soil, and thus represents, under these laboratory conditions, the DOC concentration in equilibrium with the soil.

SPSS for Windows 10.0 statistical software was used to analyze the relationships between different measured variables. The tests of normal distribution and the homogeneity of variances were tested using the Kolmogorov-Smirnov, Levene statistical tests and partial regression plots. To compare the differences in the soil characteristics between study sites, we performed an analysis of variance (ANOVA). Stepwise, ordinary least squares regression was used to examine which soil properties were related to the subsoil OC and DOC_{np} concentrations.

RESULTS

The accumulation of OC was 0.1 and 0.08 kg m^{-2} in the organic horizons of the forest soils and 48 and 21 kg m^{-2} in those of the peat. The long-term OC accumulation rate, based on ^{14}C basal dates of 3420 and 980 calibrated years BP, in the two peat deposits was 14.0 and 22.0 $\text{g m}^{-2} \text{yr}^{-1}$. The four mineral profiles had a similar texture, with average sand, silt, and clay concentrations of 92.0, 4.1, and 3.9%, respectively (Table 1). Concentration of OC of the mineral subsoil samples ranged from 0.05 to 6.22% and generally decreased with depth within each of the profiles (Table 2). Density of OC for the 5-cm increments ranged from 20 to 1594 g m^{-2} and also decreased with depth. Over the 70-cm thickness, the forest mineral subsoils contained 1.6 and 3.6 kg OC m^{-2} and the mineral subsoils beneath peat contained 7.5 and 8.0 kg OC m^{-2} . The difference in OC density between the forest soil and mineral soil beneath the peat was primarily caused by larger amounts of OC in the upper part of the mineral soil beneath the peat (Fig. 2).

Oxalate-extractable Fe and Al concentrations ranged from 0.02 to 14.00 mg g^{-1} , with the largest concentrations generally in the B horizons (Table 2). Concentrations of Al_o were similar in the Forest 1, Forest 2, and Peat 2 soil profiles, with means of 3.50 ± 1.84 , 4.00 ± 1.84 , and $5.04 \pm 2.52 \text{ mg g}^{-1}$, respectively, but smaller in the Peat 1 profile with $0.78 \pm 0.27 \text{ mg g}^{-1}$. There was much less Fe_o in the mineral soil samples beneath the peat than in the forest subsoils, with means of 0.09 ± 0.08 and $1.52 \pm 1.26 \text{ mg g}^{-1}$, respectively. Over the 70-cm thickness, the forest subsoils contained 14.2 and 2.8 $\text{g Fe}_o \text{ m}^{-2}$ compared with 0.02 and 0.83 $\text{g Fe}_o \text{ m}^{-2}$ in the mineral subsoil beneath the peat. Concentrations of

Table 2. Analytical properties of the four mineral subsoil profiles.†

Profile	Depth	Horizon	Bulk density	OC	Fe _o	Al _o	Fe _p	Al _p	C _p	DOC _{np}	<i>m</i>	
	cm		g cm ⁻³	%	mg g ⁻¹					mg L ⁻¹		
Forest 1	6-11	E	0.59	0.34	0.15	1.32	0.12	1.18	2.3	178.5	0.11	
	11-16	E	0.77	0.26	0.24	0.40	0.18	0.22	1.3	120.2	0.14	
	16-21	E	1.16	0.40	1.53	0.88	0.61	1.91	1.5	84.7	0.25	
	21-26	B	0.85	0.70	2.39	3.04	0.60	1.32	3.2	52.2	0.37	
	26-31	B	0.98	0.52	2.97	5.52	0.30	1.97	2.5	21.7	0.46	
	31-36	B	0.99	0.30	2.64	6.60	0.20	2.62	1.8	10.7	0.45	
	36-41	B	1.02	0.10	2.14	5.08	0.14	2.13	0.9	0.9	0.39	
	41-46	C	0.95	0.16	1.85	4.00	0.09	1.72	0.6	2.2	0.39	
	45-50	C	1.09	0.17	1.74	3.08	0.10	1.80	0.6	6.7	0.32	
	50-55	C	0.91	0.21	3.57	4.04	0.19	1.83	0.6	4.6	0.52	
	55-60	C	0.95	0.14	3.54	4.76	0.15	2.28	0.3	0.3	0.56	
	60-65	C	0.91	0.28	3.40	3.96	0.14	0.75	0.2	1.4	0.52	
	65-70	C	0.95	0.10	3.47	2.84	0.13	0.63	0.1	1.1	0.46	
	Forest 2	5-10	A	0.35	6.22	2.12	0.32	1.31	0.47	11.4	417.0	0.28
10-15		E	0.38	0.99	1.69	0.08	0.94	0.12	4.5	239.9	0.19	
15-20		E	0.73	0.19	0.20	0.08	0.79	0.81	1.2	101.1	0.12	
20-25		E	0.79	0.14	0.13	0.24	0.11	0.10	0.5	103.5	0.06	
25-30		E	0.81	0.05	0.10	0.12	0.12	1.64	0.3	84.3	0.05	
30-38		E	0.87	0.09	0.20	0.24	0.15	0.92	0.5	41.6	0.16	
38-43		B	0.89	1.67	1.81	7.20	1.29	4.38	7.0	42.8	0.27	
43-50		B	0.89	1.30	1.20	14.00	0.90	4.54	7.5	39.5	0.32	
50-55		B	0.93	0.52	0.39	10.00	0.13	1.99	1.9	20.2	0.34	
55-60		C	1.00	0.35	0.25	7.60	0.09	3.39	1.6	16.8	0.29	
60-65		C	0.93	0.23	0.22	4.72	0.10	1.86	1.3	18.5	0.29	
65-70		C	0.93	0.18	0.18	3.44	0.09	1.91	1.4	20.4	0.23	
Beneath Peat 1		0-5	E	0.67	4.75	0.05	0.72	0.06	0.96	11.1	98.8	0.16
		5-10	E	0.66	1.84	0.04	1.12	0.05	1.85	13.2	136.8	0.11
	10-15	B	0.79	2.28	0.03	1.08	0.04	2.38	9.6	94.4	0.23	
	15-20	B	0.80	1.52	0.03	1.32	0.06	2.33	11.3	106.8	0.18	
	20-25	B	0.77	2.21	0.03	0.96	0.04	1.49	10.0	119.2	0.17	
	25-30	B	0.78	3.60	0.03	1.04	0.04	2.01	12.5	98.3	0.23	
	30-35	B	0.84	0.94	0.02	0.72	0.03	1.68	5.7	95.9	0.27	
	35-40	C	0.86	0.43	0.03	0.60	0.02	1.18	3.8	99.7	0.20	
	40-45	C	0.72	0.34	0.02	0.48	0.03	0.92	3.6	140.7	0.15	
	45-50	C	0.95	0.60	0.02	0.56	0.07	1.44	3.6	113.0	0.19	
	50-55	C	0.96	0.34	0.02	0.68	0.03	0.51	3.2	135.7	0.15	
	55-60	C	0.88	0.20	0.03	0.48	0.03	0.51	3.5	146.2	0.12	
	60-65	C	0.85	0.34	0.04	0.60	0.03	1.61	3.3	151.4	0.12	
	65-70	C	0.89	0.30	0.06	0.56	0.04	1.42	3.5	171.2	0.09	
Beneath Peat 2	0-5	E	0.70	1.35	0.07	0.36	0.06	1.63	4.3	123.7	0.20	
	5-10	E	0.66	2.91	0.08	1.68	0.09	1.69	11.9	103.1	0.26	
	10-15	E	0.50	3.03	0.09	3.76	0.09	4.93	18.4	60.6	0.34	
	15-20	E	0.69	2.12	0.12	6.48	0.15	4.59	17.7	61.3	0.34	
	20-25	B	0.76	1.76	0.15	6.96	0.13	4.51	14.1	43.7	0.30	
	25-30	B	0.85	1.04	0.10	1.60	0.06	1.55	7.2	57.8	0.22	
	30-35	B	0.84	1.39	0.05	2.88	0.07	2.61	11.2	61.5	0.28	
	35-40	B	0.90	1.03	0.22	6.68	0.06	2.12	9.2	68.5	0.28	
	40-45	B	0.84	2.71	0.20	7.36	0.21	4.98	20.3	56.5	0.25	
	45-50	B	0.93	1.78	0.24	8.08	0.17	4.82	15.8	49.1	0.23	
	50-55	C	0.97	1.11	0.27	7.00	0.11	3.54	10.0	46.1	0.20	
	55-60	C	0.68	0.68	0.23	5.36	0.09	3.01	7.8	40.7	0.22	
	60-65	C	0.55	0.48	0.20	7.04	0.08	4.55	9.8	44.8	0.25	
	65-70	C	0.64	0.43	0.16	5.32	0.10	3.84	10.0	41.0	0.22	

† OC, organic carbon; Fe_o and Al_o, oxalate-extractable Fe and Al; Fe_p, Al_p and C_p, pyrophosphate-extractable Fe, Al and C; DOC_{np}, null-point concentration of dissolved organic carbon in sorption regression; *m*, slope of sorption regression.

Al_o were 21.7 and 22.0 g m⁻² in forest subsoils and 4.4 and 27.1 g m⁻² in the mineral soil beneath the peat.

Pyrophosphate-extractable Fe and Al concentrations ranged from 0.02 to 4.93 mg g⁻¹ (Table 2). There was more Al_p in the mineral subsoil beneath peat than forest (means of 2.45 ± 1.44 and 1.70 ± 1.16 mg g⁻¹, respectively), but there was less Fe_p in the mineral soil beneath peat than in the forest subsoils (means of 0.07 ± 0.04 and 0.33 ± 0.38 mg g⁻¹, respectively). Pyrophosphate-extractable Al/Fe ratios ranged from 10:1 to 60:1 in the mineral subsoil samples beneath the peat, whereas in the forest soils this ratio was generally <20:1. In the forest subsoils, oxalate-extractable Fe and Al were an average of 4.6 and 2.2 times that of Fe_p and Al_p, respectively, but in the mineral subsoil beneath the peat the averages were 1.3 and 1.2 times, respectively. Pyrophos-

phate-extractable C concentrations ranged from 0.1 to 20.3 mg g⁻¹, an average of 56% of the total OC. Pyrophosphate-extractable C/Fe and C/Al ratios were generally in the range 1:1 to 10:1 beneath the forest, but were larger in the mineral subsoil beneath the peat, where the ratio was about 100:1 (Fig. 3).

The coefficient of determination (*r*²) of the regression equation of the sorption study ranged from 0.66 to 0.99, with an average of 0.94 and a standard deviation of 0.07. The regression slope (*m*) ranged from 0.06 to 0.56, generally increasing with depth in the profiles and with an average of 0.25 (± 0.12) (Table 2). The DOC_{np} of the 53 samples ranged from 0.3 to 417 mg L⁻¹ and generally decreased with depth in the four profiles (Fig. 4). The mineral subsoil profiles beneath the peat

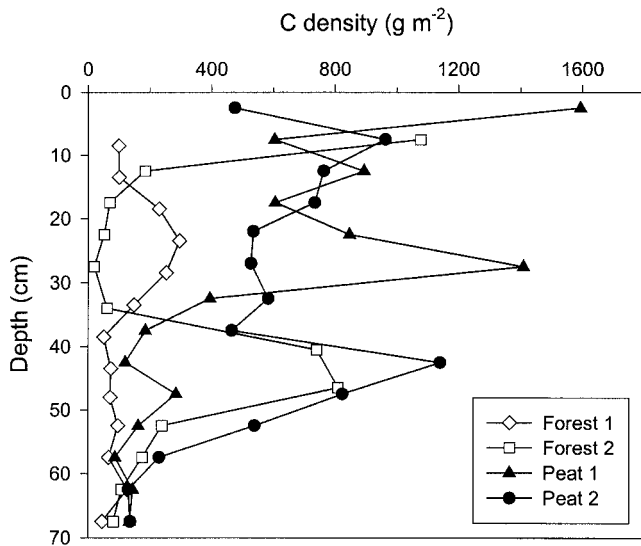


Fig. 2. Organic C density in the four profiles.

had a smaller DOC_{np} at the surface, and larger DOC_{np} at depth, than the forest subsoil profiles.

The log-transformed OC concentration of the mineral soil samples showed a strong positive correlation with C_p , sorption regression intercept (b), clay concentration, and a negative correlation with soil bulk density (Table 3). There was a weak or not significant correlation, however, between OC concentration and extractable Fe and Al (Table 3). Of the extractable Fe and Al, Fe_o was strongly correlated with Fe_p and Al_o , and Al_o with Fe_o and Al_p . A stepwise, ordinary least squares regression indicated a strong relationship ($r^2 = 0.58$, $F = 20.4$, $p < 0.001$) between subsoil organic OC concentration and the subsoil Al_o , DOC_{np} , and clay concentrations (Eq. [1]):

$$\log(\text{OC}) = -1.512 + 0.619\log(\text{Al}_o) + 0.105\sqrt{(\text{DOC}_{\text{np}})} + 0.078(\text{clay}) \quad [1]$$

The slope of the sorption regression (m) was positively correlated with Fe_o and Al_o and negatively with DOC_{np} , but independent of OC concentration (Table 3). Null-point DOC concentration was positively correlated with OC, C_p , and b and negatively with bulk density, Al_p , Fe_o , Al_o , and m (Table 3). A stepwise, ordinary least squares regression indicated a strong relationship ($r^2 = 0.78$, $F = 50.5$, $p < 0.001$) between subsoil DOC_{np} concentration and Fe_o , Al_o , and OC concentrations (Eq. [2]):

$$\sqrt{(\text{DOC}_{\text{np}})} = 8.633 - 1.328\log(\text{Fe}_o) - 4.193\log(\text{Al}_o) + 3.096\log(\text{OC}) \quad [2]$$

DISCUSSION

These results confirm the occurrence of large amounts of OC stored in sandy subsoils beneath peatlands. There was an average of 7.8 kg m^{-2} to 70 cm in the Ramsey Lake subsoils, compared with 6.2 kg m^{-2} at Lakkasuo, Finland and about three times that stored in adjacent well-drained forest soils, compared with 1.5 times reported from Finland (Turunen et al., 1999). The mean amount of OC per unit of surface area in the upland

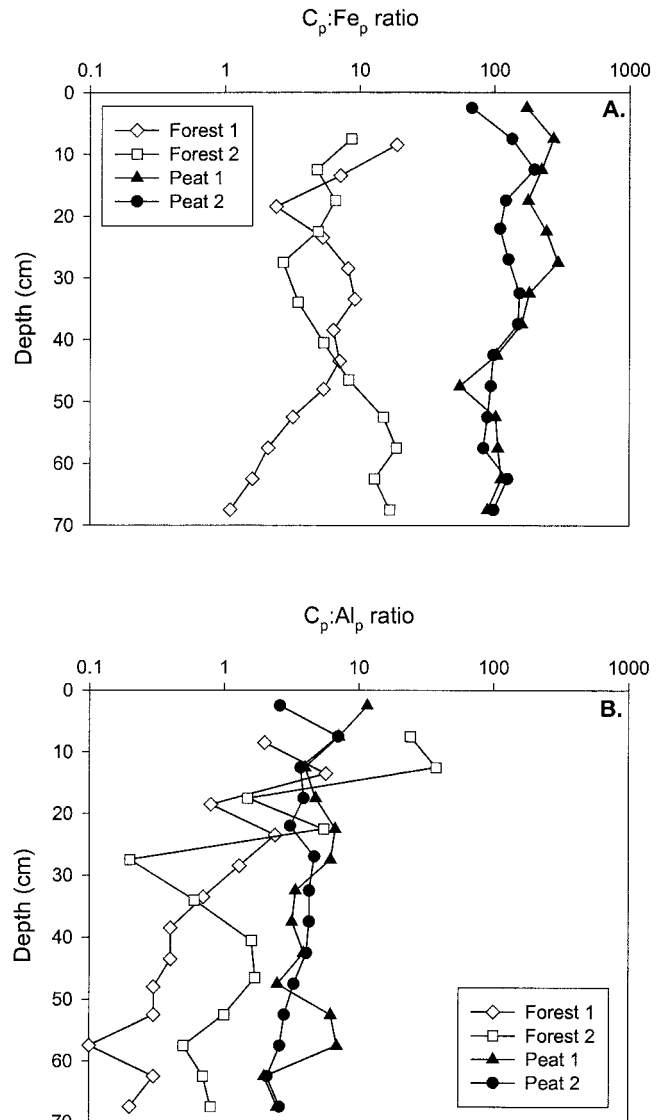


Fig. 3. Ratios of pyrophosphate-extractable C, Fe, and Al in the four mineral soil profiles.

forest sites of Michigan Spodosols fits well within the range studied by Grigal and Ohmann (1992) for mineral soils of *P. banksiana* and *P. resinosa* forest types across Minnesota, Wisconsin, and Michigan. The average long-term rate of OC accumulation (LORCA) in the Ramsey Lake mineral subsoils beneath the peat was $3.5 \text{ g m}^{-2} \text{ yr}^{-1}$, ranging from 1.4 to $5.5 \text{ g m}^{-2} \text{ yr}^{-1}$ depending on the age of paludification. The LORCA estimates of mineral subsoils were of the same magnitude as the values obtained for Spodosols in Finland (Turunen et al., 1999). Also, the LORCA values were higher in younger than in older sites with LORCA decreasing with increasing age of basal peat. The decrease in LORCA in the mineral subsoils beneath the peat is consistent with the saturation of C on the surfaces of soil mineral and oxides. The LORCA of the surface peat accumulation at sites Peat 1 and Peat 2 was 14 and $22 \text{ g m}^{-2} \text{ yr}^{-1}$, respectively. These values are similar to recent average estimates of 17 to $20 \text{ g m}^{-2} \text{ yr}^{-1}$ in Fin-

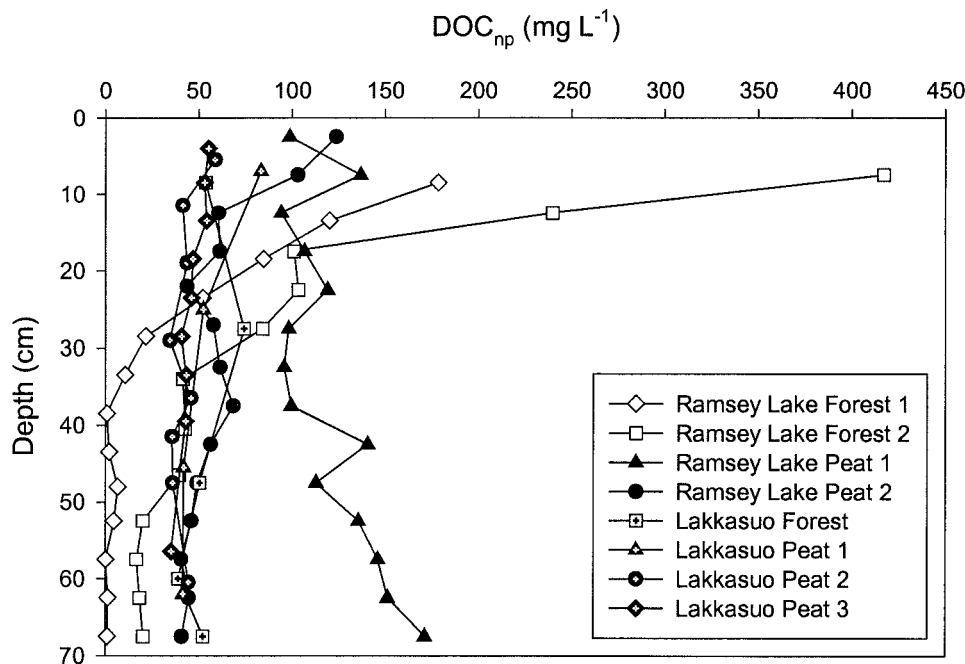


Fig. 4. Null-point DOC concentrations (DOC_{np}) in mineral subsoils from the four Ramsey Lake profiles and three profiles beneath peat and one beneath forest profiles in Lakkasuo mire, Finland (from Turunen and Moore, 2003).

land, Russia, and Canada throughout the Holocene (Turunen et al., 2001, 2002; Vitt et al., 2000).

There are two main processes whereby the mineral subsoil beneath peatlands could accumulate more OC than that beneath adjacent forests, from which the peatland has developed by paludification. One process is the penetration of peatland plant roots into the subsoil, their death and preservation under anoxic conditions, which retard the rate of organic matter decomposition. Root growth in the catotelm (anoxic zone) of peatlands can be significant, especially where the vegetation is sedges (*Carex* and other genera), up to $20 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Wallén, 1986; Saarinen, 1996; Moore et al., 2002). This could have occurred in the initial development of the peatland at Ramsey Lake, though there were no visible macrofragments of roots in the two mineral subsoil sites beneath the peat.

A second mechanism is the percolation of DOC-rich

water from the peatland through the mineral soil, its adsorption and preservation under the anoxic conditions. Most peat pore water contains large concentrations of DOC, commonly between 20 and 100 mg L^{-1} (e.g., Dalva and Moore, 1991; Kalbitz et al., 2000). It is well established that DOC can be adsorbed on to the mineral surfaces in subsoils, such as clay minerals and oxides and hydroxides of Fe and Al (e.g., Jardine et al., 1989; Greenland, 1971; Tipping and Woolf, 1990; Moore et al., 1992; Vance and David, 1992; Mulder et al., 1992; Mayer, 1994a, 1994b; Kaiser and Zech, 1998; Kalbitz et al., 2000). This is one of the mechanisms by which organic matter accumulates in the B horizon of Spodosols and other soil orders (e.g., Wilding et al., 1983). Farmer et al. (1983) suggested that humus accumulation in mineral hydromorphic soils could arise from the interaction of downward-percolating DOC and Al-rich groundwater at the water table surface, but in the Michigan soils,

Table 3. Pearson's correlation coefficient between properties of Ramsey Lake mineral soil samples, $n = 53$.†

	Bulk density	Log(OC)	Log(Fe_p)	Log(Al_p)	Log(Fe_o)	Log(Al_o)	Log(C_p)	$\sqrt{\text{DOC}_{\text{np}}}$	m	b	Clay	Sand	Silt
Bulk density	1.000												
Log(OC)	-.471**	1.000											
Log(Fe_p)	-.091	.070	1.000										
Log(Al_p)	.209	.302*	-.023	1.000									
Log(Fe_o)	.228	-.287*	.763**	-.003	1.000								
Log(Al_o)	.341*	.152	.162	.727**	.380**	1.000							
Log(C_p)	-.458**	.872**	-.102	.415**	-.489**	.163	1.000						
$\sqrt{\text{DOC}_{\text{np}}}$	-.527**	.352*	-.287*	-.368**	-.707**	-.680**	.477**	1.000					
m	.314*	-.070	.341*	.306*	.718**	.638**	-.296*	-.821**	1.000				
b	-.610**	.539**	.265	-.276*	-.088	-.380**	.421**	.816**	-.197	1.000			
Clay	-.424**	.573**	.128	.148	-.121	.076	.607**	.280*	-.010	.434**	1.000		
Sand	-.157	-.071	-.207	-.190	.058	-.143	-.201	-.140	.167	-.016	-.362*	1.000	
Silt	.365**	-.193	.203	.170	.034	.124	-.096	-.015	-.160	-.206	-.134	-.852**	1.000

* Significant at the 0.05 probability level (2-tailed).

** Significant at the 0.01 probability level (2-tailed).

† OC, organic carbon; Fe_o and Al_o , oxalate-extractable Fe and Al; Fe_p , Al_p and C_p , pyrophosphate-extractable Fe, Al and C; DOC_{np} , null-point concentration of dissolved organic carbon in sorption regression; m , slope of sorption regression; b , intercept of sorption regression.

the water table is within the organic surface layer. Part of the sorbed organic matter may be mineralized from the subsoil profile under oxic conditions (Kalbitz et al., 2000; McCracken et al., 2002). Under anoxic conditions, the rate of mineralization of organic matter is reduced by 5 to 40 times, compared with oxic conditions (Scanlon and Moore, 2000; Moore and Dalva, 2001), preserving the organic matter stored in the subsoils beneath peatlands.

The sandy Ramsey Lake forest soils contain Fe and Al oxides and hydroxides released by weathering and concentrations of the noncrystalline, Fe_o and Al_o forms are greater than those of the organically bound pyrophosphate forms (McKeague et al., 1971). In the mineral subsoil beneath the peat, most of the Fe has been lost by reduction and leaching. In Finnish forested catchments, Kortelainen and Saukkonen (1998) observed total OC (TOC) exports ranging from 2.6 to 8.8 g m⁻² yr⁻¹ and Fe export rates from 0.14 to 0.98 g m⁻² yr⁻¹, with the higher values in catchments with a large peatland coverage. Their results suggest that catchments with no peatland export 3.9 and 0.17 g m⁻² yr⁻¹ of TOC and Fe, whereas those wholly occupied by peatlands export 8.4 and 0.82 g m⁻² yr⁻¹, respectively.

Nearly the entire amount of noncrystalline Al appears to be organically bound (Fig. 3). This is reflected in the increase in the OC/Al ratios of the pyrophosphate extract, and suggests that the sorption capacity of the soils may be close to being reached. The atomic Fe + Al/C ratios in the pyrophosphate extract are low in the mineral subsoil beneath the peat: Jansen et al. (2002) suggested that complexation of Fe and Al and OC occurs at ratios >0.03. In addition, the high DOC_{np} in the mineral subsoil beneath the peat (average 61 and 122 mg L⁻¹), compared with those in the forest subsoils (average 26 and 66 mg L⁻¹, excluding A horizons), suggests that little further DOC sorption can occur beneath the peat.

Kaiser et al. (2001) have shown that the intercepts (but not slopes) of DOC sorption experiments are dependent on the methods of soil storage, treatment and soil/solution ratios and Kaiser and Zech (1998) and Moore and Matos (1999) have shown that sorption characteristics vary with the type of organic matter in solution. Thus, interpretation of the DOC_{np} results should be made with caution, as has been noted recently for laboratory experiments by McCracken et al. (2002). Field concentrations of DOC in forest floor and peat pore water generally range from 20 to 100 mg L⁻¹ (e.g., Kalbitz et al., 2000; Dalva and Moore, 1991). Assuming the peat water extract used in this study is similar to that in the field and that the laboratory DOC_{np} values are similar to those encountered in field conditions, little sorption of DOC would occur in the uppermost part of the Ramsey Lake forest soils and mineral subsoils beneath the peat, whereas sorption would be strong in the two forest B and C horizons and weak in the mineral subsoil horizons beneath the peat (Fig. 4).

The results of the Ramsey Lake study can be compared with those from Lakkasuo in Finland, where there was a similar progression from forest to peatland (Turunen and Moore, 2003). Subsoil OC density to 70 cm was similar in the mineral subsoils beneath forest and peat:

Lakkasuo and Ramsey Lake forest subsoils had 1.8 and 1.6 to 3.6 kg m⁻² and mineral subsoils beneath peat contained 3.9 to 8.1 and 7.5 to 8.0 kg m⁻², respectively. For Lakkasuo and Ramsey Lake soils, the ranges were 0.2 to 4.9 and 0.1 to 6.2 mg g⁻¹ C, 0.1 to 0.69 and 0.1 to 3.6 mg g⁻¹ Fe_o, and 0.5 to 14.5 and 0.1 to 14.0 mg g⁻¹ Al_o, respectively. However, the ranges of DOC_{np} (Lakkasuo 35–83 mg L⁻¹ and Ramsey Lake 1–417 mg L⁻¹) were different, even though the extract and methods in the DOC sorption experiment were similar (Fig. 4).

For the combined dataset (*n* = 79) of Ramsey Lake and Lakkasuo subsoil samples, a similar pattern for the relationship between OC and DOC_{np} and soil properties was found. A stepwise, ordinary least squares regression indicated a relatively strong relationship (*r*² = 0.40, *F* = 15.0, *p* < 0.001) between subsoil organic C concentration and the subsoil Al_o, Fe_o, and DOC_{np} concentrations (Eq. [3]):

$$\log(\text{OC}) = -0.912 - 0.252\log(\text{Fe}_o) + 0.422\log(\text{Al}_o) + 0.065\sqrt{(\text{DOC}_{\text{np}})} \quad [3]$$

The DOC_{np} was strongly (*r*² = 0.59, *F* = 26.6, *p* < 0.001) related to the subsoil Fe_o, Al_o, OC, and clay concentrations (Eq. [4]):

$$\sqrt{(\text{DOC}_{\text{np}})} = 7.141 - 0.811\log(\text{Fe}_o) - 0.626\log(\text{Al}_o) + 1.521\log(\text{OC}) + 0.901(\text{clay}) \quad [4]$$

The strength of these relationships suggest that there are fundamental associations between OC and soil properties in forest and paludified mineral soils, with increasing Al and DOC_{np} correlated with increasing OC concentration. Because Fe is lost from the paludified subsoils, it appears to be negatively correlated with OC, and Al assumes an important role (Moore et al., 1992; Kaiser and Zech, 1998; Kalbitz et al., 2000). There is a negative correlation between DOC_{np} and the amount of Fe_o and Al_o and a positive correlations with the OC content.

In summary, we have shown that there can be substantial amounts of OC stored in the sandy subsoils beneath peats, and have suggested that this is related to sorption of DOC from peat pore water by Al oxides and hydroxides combined with slow rates of sorbed organic matter mineralization under anoxic conditions. Two constraints limit this pattern. One is the paludification of upland soils containing Fe and Al oxides released by weathering. A second is the conditions that allow DOC-rich peat water to percolate through the mineral subsoil: coarse texture and/or regional hydrology. Substantial OC accumulation is unlikely to occur in mineral soils which have always been under anoxic conditions (resulting in low Fe and Al concentrations) or those, such as clays, where low hydraulic permeability limits water movement.

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