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THE BUFFER CAPACITY OF ORGANIC SOILS OF THE BLUFF MOUNTAIN FEN, NORTH CAROLINA

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Acid deposition can have significant ecological effects on peatlands, especially in fens near the limit of their buffering capacity. This study addresses the impact of exogenous acid on the highly organic peat soils of a Southern Appalachian fen. Soil samples were collected and analyzed for bulk density, percentage of organic matter, cation exchange capacity, base saturation, mineralogy, cations, anions, and buffering capacity, as determined by soil titration. Water samples were collected monthly for 10 mo and analyzed for pH, cations, and anions. The surface soils of the fen were well buffered, requiring about 8.5 cmol of H^+ kg^{-1} to change the pH one unit, an amount much higher than values reported for forest soils. The buffer capacity is concentrated in the top few centimeters of the peat, with the deeper soils being much more susceptible to change. Buffer capacity is significantly correlated to the percentage of organic matter and cation exchange capacity. Almost all buffering of acid additions up to 2.0 cmol H^+ kg^{-1} is the result of the organic matter, with the mineral fraction contributing only at much higher levels of acid addition (10.0 cmol H^+ kg^{-1}). Increased acidification of soils by the addition of H_2SO_4 results in the accumulation of SO_4^{2-}. Sulfate retention is negatively correlated with percentage of organic matter and can be reversed by the addition of a strong base (NaOH). Field data corroborate the laboratory findings and indicate a negative correlation between SO_4^{2-} and Ca^{2+} in surface water. This relationship suggests that the fen soils have not yet reached critical levels of pH for SO_4^{2-} adsorption.

Many peatlands may be highly vulnerable to rapid acidification by acid deposition. Of particular concern are certain types of fen, whose surface waters have low alkalinities and pH values of about 6.0 and whose peats are highly organic (Gorham 1967; Gorham et al. 1984). Such peatlands, which are at or near the limits of their buffering capacity, are subject to major declines of pH and other chemical changes as a result of even small inputs of strong acid (Glass and Loucks 1980). Acidification can occur rather suddenly once minerotrophic inputs either cease, owing to peat accumulation above the normal groundwater level, or are overwhelmed by anthropogenic acid deposition. In either case, the changes can have rapid and adverse consequences leading to the development of ombrotrophic conditions (Heinselman 1970). Gorham et al. (1984) proposed a major research effort to study the chemical and biological responses of such peatlands to both natural and anthropogenic acidification.

This study examined the potential effects of exogenous acidification on the organic soils of a North Carolina fen. The Bluff Mountain fen is the only recorded fen in the southern Appalachians (Weakley 1979). It is a floristically rich, sedge-dominated community with a pH of about 6.0 in surface waters. It contains numerous plant species that are rare in North Carolina; one that is unique to Bluff Mountain, *Cladonia psoromica* (Dey 1973); four northern species that reach their southern limits in the fen, *Calliergon cordifolium, Campylium stellatum, Isopterygium pulchellum,* and *Sphagnum subsecundum* (Crum and Anderson 1981); and four species that are endangered in North Carolina, *Carex buxbaumii, Carex conoidea, Muhlenbergia glomerata,* and *Rhychospora alba* (Radford 1978).

The buffer capacity of a soil is used as an index of the potential effect of acid precipitation. Buffer capacity is defined as the number of moles of H^+ or OH^- that must be added to raise or lower the pH of 1 kg of soil by 1 pH unit. Buffer capacity is, therefore, the reciprocal of the slope of the titration curve for the soil. Such titrations have been made for many years on agricultural soils (Buckman and Brady 1969) and have recently been employed to determine the effects of acidification on forest soils (Mag-

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doff and Barlett 1984; Federer and Hornbeck 1985). To our knowledge titration curves have not been measured for highly organic fen soils. The objectives of this study were to determine the buffer capacity of the organic soils of the Bluff Mountain fen and to evaluate the potential for acid rain to affect the soils of this unique wetland habitat.

METHODS

The study area, Bluff Mountain, is located on the eastern slope of the Blue Ridge Mountains in Ashe County, North Carolina. The fen is near the top of the mountain at 1340-m elevation in a shallow bowl-shaped plateau. Several springs at the base of the surrounding slope, near the southwestern end of the fen, are a source of minerotrophic water. The water moves through the fen in many small channels and exits in a single small stream in the northeastern corner. The fen is 1.3 ha in area, contains 140 species of plants, and consists of several different vegetation types (Weakley 1979). The main portion of the fen is dominated by four vegetationally similar, yet compositionally distinct, sedge/rush communities; *Cladium mariscoides* community; *Cladium mariscoides-Carex stricta* community; *Carex stricta* community; and a *Rhynchospora alba* community. All soil and water samples were collected in these areas of the fen.

The soils of the fen are classified as Cryaquents (Weakley 1979). Soil samples were collected from two depths, 0 to 5 cm (surface) and 10 to 20 cm (subsurface), at each of six sampling stations in the fen on 23 November 1984. At each sampling site two small "pits" were excavated, and soil was collected with a trowel. The samples were combined into a single surface and subsurface sample for each site. The soils were transported to the laboratory and immediately oven-dried at 90°C for 24 h. After drying, they were sieved through a 2-mm sieve and stored in paper containers. Percentage of organic matter was determined as loss on ignition from subsamples maintained at 550°C for 4 h. Cation exchange capacity and base saturation were determined on subsamples following Rhoades (1982, p. 152) and Thomas (1982, p. 160), respectively. Although the CEC method of Rhoades (1982) was developed for use in arid soils, it may also be used to determine permanent charge in acid soils (p. 154). At each of the six sampling stations a separate volumetric sample of undisturbed soil was collected from the surface and subsurface depths for determination of bulk density. The soil was transported to the laboratory in closed containers, oven-dried at 105°C for 48 h and weighed. At two sites, surface and subsurface samples were air-dried, cleared of organic matter by incremental additions of H_2O_2, ground, and examined for sesquioxide minerals using a Philips x-ray diffraction unit with Cu-Kα radiation.

To determine buffer capacity, titration curves for the soil samples were produced by a modification of the procedure described by Federer and Hornbeck (1985). A 5-g soil sample was weighed into each of nine 50-ml beakers. A 10-ml aliquot of water was added to one beaker for the standard 1:2 pH measurement (ambient pH). Aliquots of 0.01 N or 0.1 N H_2SO_4 in amounts equal to 1.0, 2.0, 5.0, and 10.0 cmol of H^+ kg^{-1} of soil were added to four beakers, and the solutions were made up to 10 ml. This procedure was repeated with additions of the same number of cmol of OH^- as NaOH to the remaining four beakers. After the solutions were added, the slurry was stirred and allowed to stand for 24 h. The pH was then determined in the supernatant with an Orion Model 701-A pH meter. A second set of samples was prepared identically, and the supernatant from these samples was analyzed for SO_4^{2-} by ion chromatography (Dionex Model 2010i).

In a separate experiment a 5-g soil sample was weighed into each of eight 50-ml beakers, and aliquots of 0.1 N H_2SO_4 equal to 2.0 and 10.0 cmol of H^+ kg^{-1} were added to duplicate samples. The solutions were stirred and allowed to stand for 24 h. A 2-ml sample was withdrawn for SO_4^{2-} analysis, and a sufficient quantity of NaOH was added to the remaining soil-acid solution to neutralize the added acid and bring the solution volume back to 10 ml. Again the slurry was stirred and allowed to stand for 24 h. The supernatants from these samples were then analyzed for SO_4^{2-} by ion chromatography.

Surface water samples were collected at eight sampling sites in the fen (three inlet sites, four sites in channels within the fen, and one site in the outlet stream). Samples were collected in 100-ml polyethylene containers on nine monthly dates between 11 October 1984 and 9 July 1985. Samples were cooled immediately and transported to the laboratory within 3 h. The samples were analyzed immediately or frozen until they

Mean soil values for s

	pH	Bulk d g c
Surface (0–5 cm)	4.89 ± 0.28	0.24 ±
Deep (10–20 cm)	4.82 ± 0.19	0.80 ±

[a] * = significant at 0.05; ** = signific

could be analyzed. All samples wer
Ca^{2+}, Mg^{2+}, K^+, and Na^+, by atom
spectrophotometry (Perkin-Elmer
SO_4^{2-}, Cl^-, and NO_3^- by ion chr
and pH.

All pairwise comparisons betwee
subsurface samples were made b
tests based on six replicate sam
depth. Correlation coefficients wer
by linear regression (Snedecor
1967). All statistical tests were co
nificant at a 95% confidence interv

RESULTS

The surface samples, which ar
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(CEC) slightly greater than 90.0
and a base saturation (BS) of 24.0
The deep samples have significan
and CEC for the surface samples
than expected, because the samplin
5 cm) often extended below the
"peatlayer" into the mineral soil. L
deviations indicate that the soils
highly variable both within the san
type and between vegetation types

To relate buffering capacity to
organic matter, cation exchange
base saturation, buffer capacity w
the cmol of H^+ necessary to lowe
unit from ambient and expressed
kg^{-1} pH^{-1}. The H^+ increments did
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nearly five times that of the subsur
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boratory within 3 h. The samples
immediately or frozen until they

TABLE 1

Mean soil values for surface (0–5 cm) and subsurface (10–20 cm) fen samples[a]

	pH	Bulk density, g cm^{-3}	Buffer capacity, cmol kg^{-1} pH^{-1}	Organic matter, %	Cation exchange capacity, cmol (+) kg^{-1}	Base saturation, %
Surface (0–5 cm)	4.89 ± 0.28	0.24 ± 0.07*	8.53 ± 4.40**	30.5 ± 8.4**	91.3 ± 36.8*	24.0 ± 2.3*
Deep (10–20 cm)	4.82 ± 0.19	0.80 ± 0.35*	1.99 ± 1.01**	13.0 ± 5.3**	48.7 ± 33.1*	30.6 ± 11.7*

[a] * = significant at 0.05; ** = significant at 0.01.

could be analyzed. All samples were analyzed for Ca^{2+}, Mg^{2+}, K^+, and Na^+, by atomic absorption spectrophotometry (Perkin-Elmer Model 370); SO_4^{2-}, Cl^-, and NO_3^- by ion chromatography; and pH.

All pairwise comparisons between surface and subsurface samples were made by standard t tests based on six replicate samples at each depth. Correlation coefficients were determined by linear regression (Snedecor and Cochran 1967). All statistical tests were considered significant at a 95% confidence interval ($P < 0.05$)

RESULTS

The surface samples, which are highest in organic matter, have a cation exchange capacity (CEC) slightly greater than 90.0 cmol(+) kg^{-1} and a base saturation (BS) of 24.0% (Table 1). The deep samples have significantly less CEC, and CEC for the surface samples may be less than expected, because the sampling depth (0 to 5 cm) often extended below the thin surface "peatlayer" into the mineral soil. Large standard deviations indicate that the soils of the fen are highly variable both within the same vegetation type and between vegetation types (Table 1).

To relate buffering capacity to percentage of organic matter, cation exchange capacity, and base saturation, buffer capacity was defined as the cmol of H^+ necessary to lower the pH one unit from ambient and expressed as cmol H^+ kg^{-1} pH^{-1}. The H^+ increments did not produce exact 1.0-unit pH changes, so buffer capacity was determined by interpolation between points on the titration curves. The mean buffer capacity of the surface samples is 8.53 cmol H^+ kg^{-1}, nearly five times that of the subsurface samples. The titration curve for the surface samples is linear and relatively flat over the pH range of 3.5 to 6.5 (Fig. 1). Preliminary titration curves over a wider range of pH (20.0 cmol H^+ kg^{-1}) showed a continuation of the curve. The curve for the subsurface samples, which is nearly linear and very steep through the pH range 3.5 to 7.5, gradually flattens out at the more extreme pH values (Fig. 1). The subsurface samples have little buffer capacity in the range ±1.5 pH units from ambient. Buffer capacity is strongly correlated with percentage of organic matter ($r = 0.90$) and cation exchange capacity ($r = 0.77$) (Fig. 2).

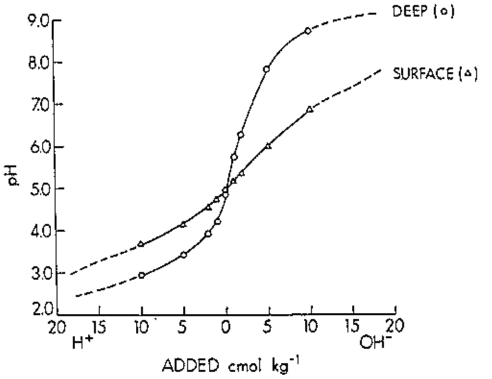

FIG. 1. Titration curves for surface (▲) and deep (●) fen soils. Each curve is obtained from mean values based on six samples.

As the soils were acidified with H_2SO_4, the added SO_4^{2-} was retained (Fig. 3). Retention of SO_4^{2-} in the subsurface samples began close to ambient pH (4.9), whereas the organic surface soils did not retain SO_4^{2-} until pH was lowered below 4.5 by the addition of 10.0 cmol H^+ kg^{-1}. Sulfate retention is negatively correlated with percentage of organic matter ($r = -0.69$) (Fig. 4).

The retention of SO_4^{2-} by acidifying the samples, both surface and subsurface, can be reversed by neutralizing the acid with NaOH, allowing complete recovery of initial SO_4^{2-} (Table

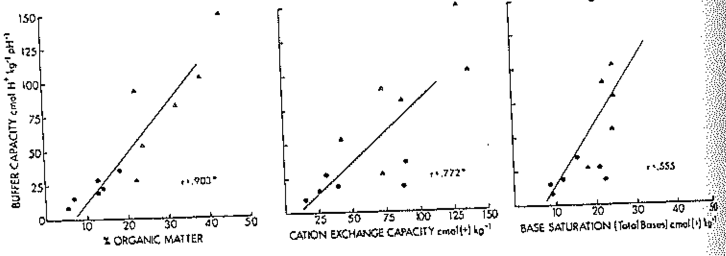

FIG. 2. The relationship of buffer capacity to percentage of organic matter, cation exchange capacity, and base saturation. Points represent the six surface samples (△) and six deep samples (○) *($p < 0.01$).

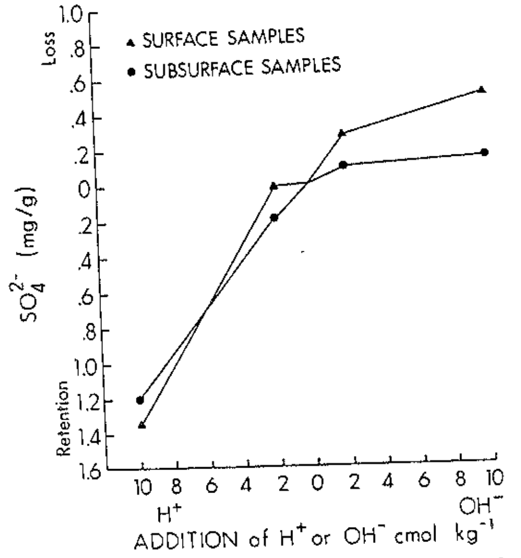

FIG. 3. Sulfate retention or loss by soil with the addition of H^+ (H_2SO_4) or OH^- (NaOH). Points below the 0-line represent soil samples that are accumulating SO_4^{2-}. All sample points are means based on six soil samples.

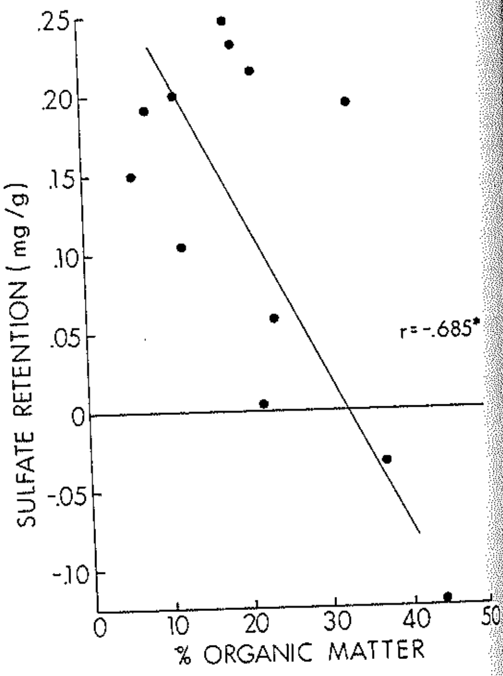

FIG. 4. Dependence of sulfate (SO_4^{2-}) accumulation in the soil on percentage of organic matter. SO_4^{2-} was added in the form of H_2SO_4 at a concentration of 2.0 cmol H^+ kg^{-1}. *($p < 0.05$).

2). Subsurface samples have lower equilibrium concentrations of SO_4^{2-} than surface samples under all experimental conditions, but relative percentages retained after acid additions were similar between depths. Even after neutralization with NaOH, subsurface samples retained 12.3% of SO_4^{2-} added at a concentration of 10.0 cmol kg^{-1}, whereas under similar treatment, SO_4^{2-} was mobilized from surface samples in excess of amounts previously added in acid or measured in ambient conditions.

Surface waters show a negative correlation ($r = -0.61$) between SO_4^{2-} and Ca^{2+} with inflowing minerotrophic waters showing higher Ca^{2+} (Fig. 5). Outflowing waters had higher pH than inflowing waters, and higher SO_4^{2-} concentrations.

DISCUSSION

The linear titration curves for the surface, organic soils of the fen are similar to curves published by Federer and Hornbeck (1985) for organic matter extracted from upland soils. In both studies the curves were linear over the entire range of experimental conditions (10.0 cmol (±) H^+ or OH^- kg^{-1}), but the samples from the fen showed nearly twice the buffer capacity reported by Federer and Hornbeck (1985) when values from both studies were expressed in terms of organic matter.

Subsurface samples from the fen show S-shaped titration curves (Fig. 1), similar to results

obtained from the mineral soils
forests in the eastern United Sta
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Buffer capacity and CEC can be
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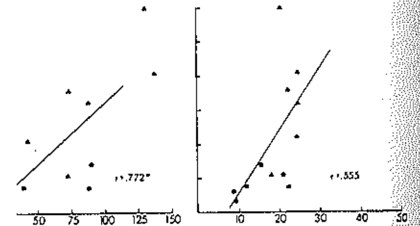

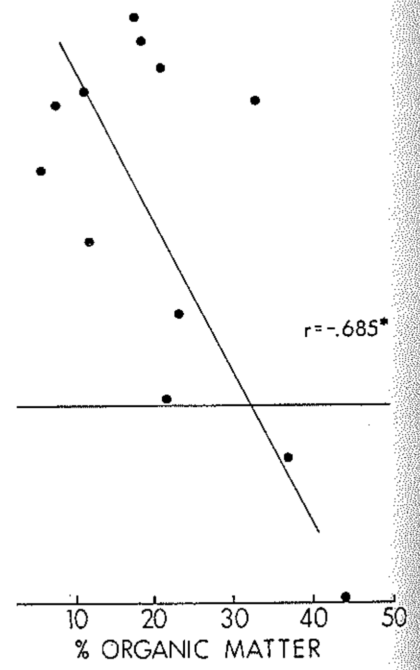

Dependence of sulfate (SO_4^{2-}) accumula-
soil on percentage of organic matter. SO_4^{2-}
in the form of H_2SO_4 at a concentration of
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DISCUSSION

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obtained from the mineral soils of hardwood forests in the eastern United States (Federer and Hornbeck 1985; Laverdiere and Weaver 1977; Wells and Davey 1966). These samples show relatively little buffer capacity within a range of ±1.5 pH units of ambient, but increased buffer capacity at pH < 4.0 and > 7.5.

The average buffer capacity of surface soils in the fen was 8.5 cmol kg^{-1} pH^{-1}, and for the subsurface samples it was 2.0 cmol kg^{-1} pH^{-1} (Table 1). Buffer capacity of the soils, with 2.0 cmol H^+ kg^{-1} addition, is directly proportional to percentage of organic matter (Fig. 2). The relationship between buffer capacity and organic matter indicates that the top few centimeters of soil in the fen would be responsible for most of the buffering of exogenous acids. The intercept suggests that most of the buffering in the surface and subsurface samples is the result of the variable charge on the organic matter. In the fen the mineral fraction of the soil does not begin to contribute significantly to buffering until the pH is much lower (10.0 cmol H^+ kg^{-1} addition), and then its greatest contribution occurs in the subsurface soils. Buffer capacity and CEC also showed a strong positive correlation (Fig. 2). Similar results were reported by Federer and Hornbeck (1985).

Buffer capacity and CEC can be used to evaluate the potential for acidification. McFee et al. (1977) used the CEC as an inverse measure of susceptibility and estimated that 100 yr of pH 4.0 rainfall at 1000 mm yr^{-1} would lower soil pH by < 0.6 units in the top 20 cm of soil. Hornbeck and Federer (1984) used buffer capacities to calculate that this amount of pH 4.0 rain would lower O-horizon pH by 1.0 unit in 2 to 10 yr, if the added H^+ remained in that horizon. A decline of 1.0 pH unit would be seen in the entire profile in 30 to 40 yr. Our data suggest that 1500 mm yr^{-1} of pH 4.0 rainfall would lower the pH of the top 5 cm of the fen by 1.0 unit in 30 yr. The same rain would lower the pH by 1.0 unit over the 0- to 20-cm depth in about 200 yr. Although these values are instructive for visualizing the extent of the buffering capacity, they are not realistic for the fen, because the exchange sites on the organic matter are continuously replenished by cations from inflowing waters.

Although most of the concern with the effects of acid deposition has focused on the hydrogen and aluminum ions, the chemical and ecological effects of associated anions may be of more consequence to certain soil processes (Gorham et al. 1984; Johnson and Reuss 1984). The addition of sulfur and nitrogen to ecosystems in quantities in excess of biological requirements may have several important effects, including changes in the leaching of base cations (Johnson and Reuss 1984). Biological transformations may result in neutralization of acid in bog ecosystems (Hemond 1980; Hemond and Eshleman 1984; Kilham 1982).

In the southern Appalachian Mountains, the majority of the acid deposition is associated with sulfate (National Atmospheric Deposition Program 1983). Our experimental simulations of acid deposition showed that SO_4^{2-} accumulation (retention) in the soil was negatively correlated with percentage of organic matter (Fig. 4). The subsurface fen soils, which are lower in organic matter, begin to accumulate SO_4^{2-} near ambient pH. The surface samples, however, do not begin to retain SO_4^{2-} until pH has been lowered significantly from ambient (Fig. 3). The accumulation of SO_4^{2-} in the soil is probably due to adsorption onto Fe and Al sesquioxides, which are eroded into the fen from the highly weathered forest soils on the surrounding slopes. X-ray diffraction showed gibbsite (Al_2O_3) and hercynite ($FeOAl_2O_3$) in several samples. Adsorption of SO_4^{2-} by Al and Fe sesquioxides is well-documented in the literature (Hingston et al. 1967; Wieder and Lang 1986), as is the negative correlation between SO_4^{2-} accumulation and percentage of organic matter (Hemond and Eshleman 1984; Johnson and Reuss 1984; Singh 1984).

The relationship between SO_4^{2-} adsorption and the mineral fraction in the subsurface samples helps explain the buffering relationships recorded for the fen. Based on the negative correlation between SO_4^{2-} adsorption and the percentage of organic matter of the soil, it appears that the high buffer capacity of the surface soil results from the CEC of the organic matter. The peat contains a reservoir of cations that can be exchanged for H^+ added in acid precipitation. In the fen the cation exchange sites are continuously recharged by the minerotrophic water that enters from the surrounding uplands. The buffer capacity is restricted to the top few centimeters of peat, which show linear titration curves over a broad range of acid additions (Fig. 1; Gorham et al. 1984).

TABLE 2

Quantities of SO_4^{2-}*, mg, in the 10-ml supernatant solution after additions of* H_2SO_4 *and subsequent additions of* NaOH *to 5-g samples; percentage in solution is expressed relative to the total expected in the system from ambient contents plus additions*

	Ambient	After acid 2.0 cmol kg^{-1} (4.80 mg SO_4^{2-} added)	Acid followed by base 2.0 cmol kg^{-1}	After acid 10.0 cmol kg^{-1} (24.00 mg SO_4^{2-} added)	Acid followed by base 10.0 cmol kg^{-1}
Surface					
SO_4^{2-}, mg	1.51 ± 0.07	4.99 ± 0.27	5.83 ± 0.32	17.66 ± 0.88	35.43 ± 1.07
% in supernatant		79.1%	92.4%	69.2%	138.9%
pH	4.69	4.43		3.70	
Deep					
SO_4^{2-}, mg	0.41 ± 0.03	4.44 ± 0.21	5.52 ± 0.28	15.91 ± 0.62	21.42 ± 0.84
% in supernatant		85.2%	105.9%	65.2%	87.7%
pH	4.56	3.78		3.14	

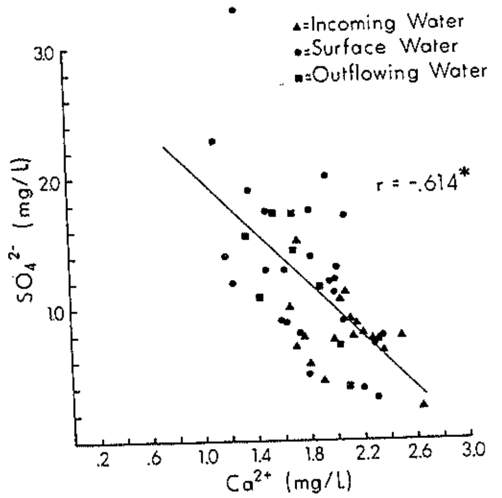

FIG. 5. Relationship between Ca^{2+} and SO_4^{2-} in surface water samples from the fen. Samples were collected on nine sampling dates between October 1984 and July 1985 at inflow sites (▲), surface water sites in the fen (●), and at the site of outflow from the fen (■). *($p < 0.01$).

The buffer capacity of the deep soils, which is limited near ambient pH, may be due to the Al and Fe sesquioxides. As pH is lowered, the adsorption of SO_4^{2-} on sesquioxides increases, which releases OH^- that can neutralize hydrogen ions (Johnson and Reuss 1984). Gorham et al. (1984) noted that Al species contribute to buffering at pH < 5.0, but their importance has not been measured in peatlands. Based on our data, Al and Fe sesquioxides begin to contribute to buffer capacity only at pH below 4.0, and then only to a limited extent.

Although SO_4^{2-} accumulates in the deep soils with the addition of H_2SO_4 in laboratory experiments, and this functions in buffering at low pH, the field data from the fen indicate that retention of SO_4^{2-} is not occurring at this time (Fig. 5). The water samples show a negative correlation ($r = -0.61$) between SO_4^{2-} and Ca^{2+}, with higher SO_4^{2-} at the outflow. Although many peatlands are efficient sinks for sulfate (Braekke 1981), the Bluff Mountain fen does not appear to be stressed by exogenous acid deposition. Correspondingly, the slightly lower Ca^{2+} concentrations at the outflow suggest that the cation exchange sites are being recharged. This is consistent with the findings of Johnson and Reuss (1984), who indicated that the potential for SO_4^{2-} retention in subsoils is reduced by water flowing through surface horizons. It would appear that as long as the flow of minerotrophic water continues, the surface soils in the fen have sufficient buffer capacity to prevent a decrease in pH in the deeper soils that could result in the accumulation of SO_4^{2-}.

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After acid 10.0 cmol kg^{-1} (24.00 mg SO_4^{2-} added)	Acid followed by base 10.0 cmol kg^{-1}
17.66 ± 0.88	35.43 ± 1.07
69.2%	138.9%
3.70	
15.91 ± 0.62	21.42 ± 0.84
65.2%	87.7%
3.14	

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