

Fe, Al, Mn, AND S CHEMISTRY OF *SPHAGNUM* PEAT IN FOUR PEATLANDS WITH DIFFERENT METAL AND SULFUR INPUT

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(Received September 19, 1985; revised February 17, 1986)

Abstract. Comparisons among 4 peatland sites representing a gradient of increasing Fe, Al, Mn, and S loading revealed significant accumulation of total Fe, Al, and S, but not Mn, in surface (0 to 20 cm deep) peat along the gradient. Iron and Al accumulation were contributed mainly by organically bound fractions, with oxides contributing to a lesser extent. Although SO_4^{2-} and Fe sulfides showed significant increases in concentration along the gradient, most of the accumulation of total S was contributed by organic, rather than inorganic S. Laboratory studies of Fe^{2+} adsorption by peat indicated that increasing the pH of added Fe^{2+} solutions (pH values of 3, 4, 5, and 6) did not significantly affect Langmuir equation estimates of either maximum Fe^{2+} adsorption capacity or the affinity of peat for Fe^{2+} . Regardless of the pH of the added Fe^{2+} solutions, final solution pH values were relatively uniform, averaging about 3.4, reflecting a considerable buffering capacity of *Sphagnum* peat. Factors affecting the accumulation of metals and S in peat remain topics for further investigation.

1. Introduction

Peatland ecosystems have been classified as either ombrotrophic, i.e., receiving their water and nutrients from precipitation only, or minerotrophic, i.e., receiving water and nutrients in runoff from upland mineral soils or from groundwater as well as in precipitation (Moore and Bellamy, 1974). Two types of anthropogenic pollution are currently having an impact on peatlands. First, in both North America and Europe, the phenomenon of acid precipitation is resulting in high loading of acidity, S, and N to peatlands. Acid precipitation may negatively affect the growth of *Sphagnum* species in ombrotrophic peatland ecosystems (Ferguson *et al.*, 1978; Ferguson and Lee, 1980, 1984), but relatively little is known about the effects of acid precipitation on the structure and function of minerotrophic peatlands (Gorham *et al.*, 1984). Second, in the Appalachian Mountains of eastern North America, some minerotrophic peatland ecosystems receive a high loading of heavy metals and S in runoff from coal surface mines. When subjected to large volumes of coal mine drainage waters, peatland ecosystems are often decimated, but when the volume of mine drainage is relatively low, peatland ecosystems may be effective in removing certain metals and S from inputs of coal mine drainage (Wieder and Lang, 1982, 1984; Kleinmann *et al.*, 1983; Burris, 1984).

The purpose of this study was to evaluate the extent to which Fe, Al, Mn, and S are retained in both ombrotrophic and minerotrophic peatlands subjected to anthropogenic pollution. We compare Fe, Al, Mn, and S chemistry in surface *Sphagnum* peat from 4 different peatland sites, each of which has a different long-term history of metal and S loading. At one end of the metal and S loading gradient is a peatland that has been ombrotrophic for thousands of years and which has been relatively unaffected by regional pollution. At the other end of the loading gradient is a minerotrophic peatland that has been receiving low volume inputs of acid coal mine drainage for the past 40 to 45 yr. In addition, laboratory Fe^{2+} loading studies were conducted to determine the capacity for ombrotrophic and minerotrophic peats to further retain Fe^{2+} and to evaluate the effects of solution pH on Fe^{2+} adsorption by peat.

2. Study Sites

Each of the 4 study sites is characterized by an organic peat deposit derived mainly from *Sphagnum* species which form an almost continuous cover across the peatland surface. In the Red Lake peatland region of Minnesota, peat samples were collected in a *Sphagnum*-ericaceous shrub-dwarf *Picea mariana* community, a vegetation type characteristic of ombrotrophic areas (Heinselman, 1963). Hummocks were avoided in sampling. Mean annual precipitation is 80 cm; SO_4^{2-} concentration in precipitation (wetfall only) averages $13.3 \mu\text{mol L}^{-1}$ (NADP, 1983, Itasca County, Minnesota).

Buckle's Bog is a 27 ha peatland located in western Maryland at an elevation of about 815 m above sea level. The peatland is surrounded by 68 ha of mostly forested watershed. A small stream leaves Buckle's Bog and flows to the northeast where it eventually drains into the North Fork of the Casselman River. The physiographic setting of Buckle's Bog suggests a small degree of minerotrophy, so that metal and S loading are higher than at the ombrotrophic Red Lake peatland.

Big Run Bog, West Virginia, is a 15 ha minerotrophic poor fen located at an elevation of about 980 m above sea level. Peat and water chemical characteristics are similar to ombrotrophic bogs (Wieder, 1985). The upland soils in the 276 ha of forested watershed surrounding Big Run Bog are predominantly Typic Dystrochrepts. Concentrations of Fe and SO_4^{2-} in forest soil water averaged 35 and $175 \mu\text{mol L}^{-1}$, respectively (Wieder, 1982). Since the area of watershed with mineral soil surrounding Big Run Bog is over 18 times the area of the peatland itself, the input of minerotrophic drainage is considerably greater than at Buckle's Bog where the watershed area to wetland area ratio is only 2.5. Thus, metal and S loading at Big Run Bog are greater than at Buckle's Bog.

Tub Run Bog, West Virginia, is a 23 ha minerotrophic fen located 10 km east of Big Run Bog at an elevation of about 950 m above sea level. Tub Run Bog is bordered along its eastern edge by an abandoned, unreclaimed coal surface mine which is a source of acid mine drainage input to the peatland. The chemistry and volume of the acid mine drainage entering Tub Run Bog are spatially and temporally variable; we have measured pH values as low as 2.2 and Fe, Al, Mn, and SO_4^{2-} concentrations as high as 1323, 778, 53, and $2875 \mu\text{mol L}^{-1}$. The volume of acid mine drainage entering Tub Run Bog

as runoff is low and is generally observable as small rivulets during and immediately following rain events (Wieder and Lang, 1982, 1984).

Buckle's Bog, Big Run Bog, and Tub Run Bog are all within 50 km of Parsons, WV where mean annual precipitation is about 130 cm and SO_4^{2-} concentration in precipitation (wetfall only) averages $36.5 \mu\text{mol L}^{-1}$ (NADP, 1983).

Because it is technically difficult to measure the volume of minerotrophic runoff and groundwater entering minerotrophic peatlands, we have not tried to quantitatively estimate metal and S loadings to each of the 4 peatland sites. Nonetheless, Red Lake, Buckle's Bog, Big Run Bog, and Tub Run Bog represent a qualitatively distinct gradient of increasing loading of Fe, Al, Mn, and S. We recognize that superimposed over this loading gradient are considerable differences in hydrology, especially between ombrotrophic and minerotrophic peatland sites, and that hydrologic factors can affect both metal and S chemistry (cf. Damman, 1978). Our approach in this study was to first examine broad-scale differences among peatland sites with regard to metal and S chemistry. Subsequent to finding any such differences, additional studies would be needed to more clearly elucidate the role of hydrology in affecting metal and S chemistry in *Sphagnum* peat.

3. Methods

Bulk peat samples were collected to a depth of 20 cm from each site. We chose a depth limit of 20 cm because most of the horizontal water movement in a peatland occurs near the peat surface (Boelter, 1965; Korpijaakko and Radforth, 1972). Since our intent was to compare the 4 sites with regard to metal and S concentrations in surface peat, we collected the top 20 cm of peat as a single unit. This sampling procedure did not allow us to consider possible site differences in the depth distributions of metals and S that may have resulted from site differences in water table level and water table fluctuation.

The bulk peat samples were returned to the laboratory, oven-dried at 50°C to a constant mass, and ground to pass a 2 mm mesh screen. Organic matter concentration in peat was determined by dry-ashing subsamples at 600°C for 6 hr. The ash resulting from this combustion was extracted with hot HCl and the extract solutions were analyzed for total Fe, total Al, and total Mn concentrations on a Varian AA6 atomic absorption spectrophotometer (Likens and Bormann, 1970). An air-acetylene flame was used for the Fe and Mn determinations and a nitrous oxide-acetylene flame for the Al determinations.

Separate peat subsamples were sequentially extracted with pyrophosphate, oxalate, and citrate-bicarbonate-dithionite solutions (USDA, 1972). For Fe, and to a lesser extent for Al, this extraction sequence has been used to quantify organically bound, amorphous oxide, and crystalline oxide metal fractions, respectively, in mineral soils (McKeague *et al.*, 1971). We also analyzed for Mn in the extracts, but the specificity of these extractions for different chemical forms of Mn is not well documented (Blume and Schwertmann, 1969). For all 3 metals, however, it seems reasonable to equate the pyrophosphate extractable fraction with the organically bound form of the metal. FeS

and FeS_2 concentrations were calculated from a sequential determination of acid volatile and Cr^{2+} reducible sulfides in a Johnson–Nishita apparatus (Wieder *et al.*, 1985a). Since Cr^{2+} reduction also recovers elemental S, the values reported here for Fe as FeS_2 may be slight overestimates. The values reported for S as FeS_2 really represent S as FeS_2 plus elemental S.

Total S was determined using a LECO sulfur analyzer. SO_4^{2-} –S values are the sum of the water soluble and PO_4^{3-} extractable SO_4^{2-} fractions (Johnson and Henderson, 1979). Organic S was calculated as the difference between total S and the sum of the inorganic fractions (Wieder *et al.*, 1985a).

To test directly the question of whether metal and sulfur concentrations increased with increasing loading, the nonparametric Jonckheere's Test (Hollander and Wolfe, 1978) was used. This test examines the null hypothesis of equal site medians (H_0 : $\theta_1 = \theta_2 = \theta_3 = \theta_4$) against the alternative hypothesis of ordered medians (H_a : $\theta_1 < \theta_2 < \theta_3 < \theta_4$), where θ_1 through θ_4 correspond to median values for the Red Lake, Buckle's Bog, Big Run Bog, and Tub Run Bog peatlands, respectively.

The incorporation of Fe^{2+} into an organically bound fraction by adsorption onto *Sphagnum* peat was examined in peat samples from Buckle's Bog ($n = 5$), Big Run Bog ($n = 10$), and Tub Run Bog ($n = 32$). Separate 2 g peat samples were placed in a Buchner funnel. The peat was subjected to 2 sequential distilled water rinses followed by sequential addition of 5 Fe^{2+} solutions (40 mL each) with concentrations of 448, 895, 1791, 2686, and 3581 $\mu\text{mol L}^{-1}$. The Fe^{2+} solutions were made using $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ dissolved in distilled, deionized, deoxygenated water, and the pH of these solutions was adjusted to 4.0. After 30 min of contact with each solution, a vacuum was applied to the funnel, the filtrate was collected and analyzed for Fe concentration by atomic absorption spectrophotometry, and Fe adsorption was calculated. For each site, the data from all of the peat samples were pooled, and nonlinear least squares regression (Rubin and Mercer, 1981; SAS, 1982) was used to fit the Langmuir equation:

$$\text{Fe adsorption} = \frac{\text{YMAX} * \text{X}}{\text{K} + \text{X}},$$

where Fe adsorption is the cumulative Fe^{2+} adsorbed by the peat sample in $\mu\text{mol g}^{-1}$ dry peat, YMAX is the maximum Fe^{2+} adsorption capacity in $\mu\text{mol g}^{-1}$ dry peat, K is the Fe^{2+} concentration at which 50% of YMAX is achieved in $\mu\text{mol L}^{-1}$, and X is the Fe^{2+} concentration in the filtrate from each step of the loading sequence. The YMAX and K values were also determined individually for each peat sample and these values were correlated with percent organic matter of the peat and to the organically bound Fe concentration of the peat using Spearman's rho (Conover, 1980).

Finally, to examine the effect of initial solution pH on Fe^{2+} adsorption, 6 peat samples from Big Run Bog were randomly chosen and supplemental Fe^{2+} loading experiments were conducted in which the pH of the added Fe^{2+} solutions was adjusted to either 3.0, 4.0, 5.0, or 6.0. For each of the pH treatments, the data from the 6 peat

samples were pooled and YMAX and K values were determined as described above. In addition, for each peat sample, at each step in the loading sequence the pH of the filtrate was determined. A two-way analysis of variance was performed to determine whether filtrate pH varied as a function of initial solution pH or as a function of the step of the Fe²⁺ loading sequence. Because of nonhomogeneity of the variances associated with the filtrate H⁺ concentration means, the analysis of variance was performed on rank-transformed data.

4. Results

Along the gradient of increasing metal and S loading, there were increases in the concentrations of all chemical forms of Fe and Al in surface peat (Table I). At all 4 sites organically bound Fe (pyrophosphate extractable) was the most abundant Fe fraction, contributing between 47 and 90% of the total Fe pool. Similarly, organically bound Al

TABLE I

Fe, Al, Mn, and S chemistry and organic matter concentration in surface (0–20 cm) peat; means \pm standard errors. Jonckheere's *J* values greater than 1.65 indicate a significant trend of increasing concentration with increasing loading ($p \leq 0.05$)

	Red Lake, MN	Buckle's Bog, MD	Big Run Bog, WV	Tub Run Bog, WV	<i>J</i>
Sample size	5	5	10	38	
Fe ($\mu\text{mol g}^{-1}$ dry mass)					
Total (HCl extractable)	45 \pm 8	101 \pm 17	300 \pm 46	869 \pm 96	6.11
Pyrophosphate extractable	23 \pm 6	47 \pm 10	269 \pm 44	484 \pm 44	5.29
Oxalate extractable	8.4 \pm 1.1	17 \pm 2	45 \pm 9	299 \pm 42	6.34
Dithionite extractable	8.7 \pm 1.8	24 \pm 4	17 \pm 2	186 \pm 29	5.55
FeS ₂	2.4 \pm 0.2	2.1 \pm 0.4	6.1 \pm 0.5	7.6 \pm 0.8	3.71
FeS	1.0 \pm 0.3	0.3 \pm 0.04	3.2 \pm 1.0	3.1 \pm 0.3	3.11
Al ($\mu\text{mol g}^{-1}$ dry mass)					
Total (HCl extractable)	65 \pm 11	109 \pm 16	159 \pm 26	243 \pm 12	5.21
Pyrophosphate extractable	35 \pm 5	61 \pm 8	140 \pm 24	109 \pm 12	2.14
Oxalate extractable	6.2 \pm 1.5	11.2 \pm 0.9	12.4 \pm 2.2	31.9 \pm 1.9	6.21
Dithionite extractable	2.9 \pm 1.3	7.4 \pm 2.0	9.3 \pm 0.7	20.4 \pm 1.6	5.49
Mn ($\mu\text{mol g}^{-1}$ dry mass)					
Total (HCl extractable)	1.5 \pm 0.3	5.3 \pm 0.8	2.5 \pm 0.4	4.9 \pm 2.0	-1.46
Pyrophosphate extractable	1.3 \pm 0.2	4.7 \pm 0.7	2.2 \pm 0.3	2.5 \pm 0.8	-2.58
Oxalate extractable	0.4 \pm 0.04	0.7 \pm 0.2	0.2 \pm 0.05	1.2 \pm 0.6	-1.00
Dithionite extractable	0.06 \pm 0.03	0.6 \pm 0.03	0.2 \pm 0.02	1.1 \pm 0.3	4.76
S ($\mu\text{mol g}^{-1}$ dry mass)					
Total	48.6 \pm 2.5	87.2 \pm 5.4	134 \pm 8	108 \pm 6	1.49
Organic	41.2 \pm 2.1	77.2 \pm 5.4	114 \pm 8	83.9 \pm 4.7	1.94
FeS ₂	4.9 \pm 0.5	4.3 \pm 0.8	12.2 \pm 1.0	15.1 \pm 1.5	3.71
FeS	1.0 \pm 0.3	0.3 \pm 0.04	3.2 \pm 1.0	3.1 \pm 0.3	3.11
SO ₄ ²⁻	1.5 \pm 0.3	5.5 \pm 0.6	5.2 \pm 0.5	5.8 \pm 0.5	1.86
Organic matter (%)	84.1 \pm 1.4	86.3 \pm 2.3	89.6 \pm 1.4	55.9 \pm 2.8	-

was the most abundant Al fraction, contributing between 45 and 88% of the total Al pool. Although Fe and Al oxides (oxalate and dithionite extractable fractions reflecting amorphous and crystalline oxides, respectively) were less abundant than the organically bound fractions, significant oxide accumulations resulting from physico-chemical and perhaps biologically-mediated oxidation (cf. Stone, 1984) were observed. The Fe present as mono- and disulfides exhibited significant increases along the loading gradient, but Fe sulfides represented only a minor fraction (between 1.2 and 7.6%) of the Fe pool. Tub Run Bog peat had an average of $936 \mu\text{mol g}^{-1}$ dry mass more Fe than Red Lake peat (calculated as the sum of the site differences for each Fe fraction). Of this accumulation, 49% was contributed by the organically bound fraction, 50% by the oxide fractions, and less than 1% by the sulfide fractions.

Total Mn did not exhibit a significant accumulation along the loading gradient (Table I). However, a significant increase in dithionite-extractable Mn along the loading gradient was obtained. If dithionite extractable Mn represents a Mn oxide fraction, its increase along the gradient may have resulted from the activity of Mn oxidizing bacteria (cf. Stone, 1984).

A trend of increasing total S concentration with increasing loading is not supported by Jonckheere's test (Table I). Nonetheless, Jonckheere's test does support an increase in each of the S fractions with increasing S loading. In all 4 sites, organic S is the dominant fraction, contributing between 78 and 89% of the total S pool. Thus, organic S is the fraction mainly responsible for the accumulation of S in response to increased input.

Organic matter concentration in Tub Run Bog peat was significantly lower (Kruskal-Wallis test, $p \leq 0.05$) than in peat from the three other sites (Table I). Lower organic matter values for Tub Run Bog peat may be a reflection of the transport of inorganic soil particles from the adjacent abandoned coal surface mine. The low organic matter concentrations in Tub Run Bog peat samples did not affect the chemical results presented in Table I. Statistical analyses were performed after deleting Tub Run Bog peat samples with organic matter concentrations less than 50, 60, 70, or 80%, and the statistical results remained qualitatively unchanged.

The capacity of peat to further retain Fe^{2+} was described by the Langmuir equation (Figure 1). Fe^{2+} adsorption was highest for Buckle's Bog peat and lowest for Tub Run Bog peat. The Langmuir parameters showed no significant site differences in the affinity of the peat for Fe^{2+} (K values), but Buckle's Bog peat had a higher maximum adsorption capacity than either Big Run Bog or Tub Run Bog peat (Table II). It is also noteworthy that 3 sequential distilled, deionized, deoxygenated water rinses following the laboratory loading phase released less than 5% of the total Fe adsorbed during the loading phase. Thus, adsorbed Fe is not readily water-soluble and, therefore, may not be readily susceptible to leaching under field conditions.

When K and YMAX values were estimated individually for each peat sample, K values were negatively correlated with percent organic matter of the peat (Spearman's $\rho = -0.597$, $p \leq 0.0001$) and positively correlated with the initial organically bound Fe fraction in the peat (Spearman's $\rho = 0.755$, $p \leq 0.0001$). Since a high K value

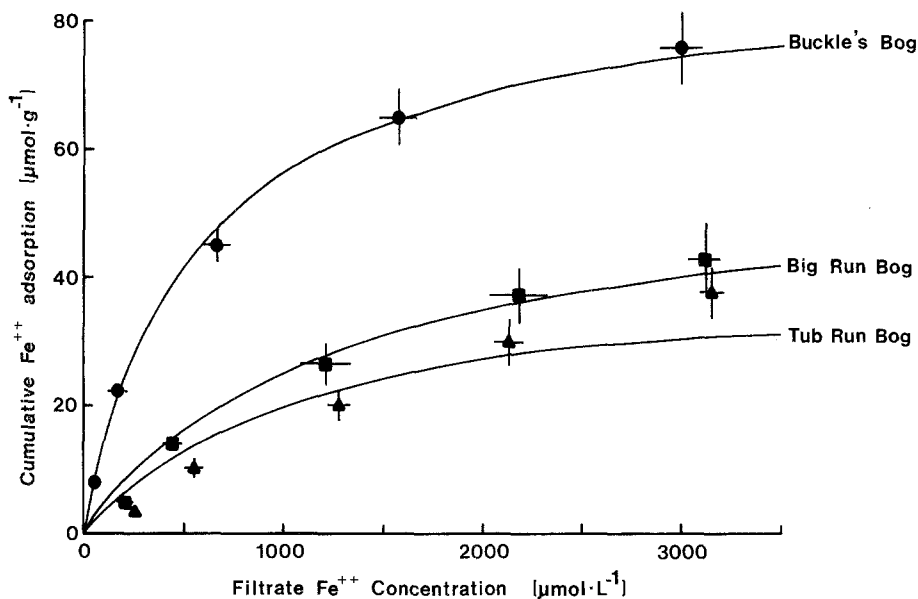


Fig. 1. Fe^{2+} adsorption by Buckle's Bog (\bullet ; $n = 5$), Big Run Bog (\blacksquare ; $n = 10$), and Tub Run Bog (\blacktriangle ; $n = 32$) peat. Plotted points are means \pm standard errors. The Langmuir equation parameter estimates in Table II were used to draw the smooth curves for each of the 3 sites.

TABLE II

Estimated Langmuir parameters for Fe^{2+} adsorption by Buckle's Bog ($n = 5$), Big Run Bog ($n = 10$), and Tub Run Bog ($n = 32$) peat. K ($\mu\text{mol Fe}^{2+} \text{ L}^{-1}$) and Y_{MAX} ($\mu\text{mol Fe}^{2+} \text{ g}^{-1}$ dry mass) values are means \pm asymptotic standard errors. K and Y_{MAX} values with the same letter superscript do not differ significantly (pairwise t -tests using asymptotic standard errors of the parameter estimates; $p \leq 0.05$). R^2 values indicate the percentage of the uncorrected sum of squares explained by the regression

Site	K	Y_{MAX}	R^2
Buckle's Bog	564 ± 152^a	88.1 ± 7.3^a	96
Big Run Bog	1257 ± 563^a	57.1 ± 10.4^b	85
Tub Run Bog	1115 ± 543^a	42.3 ± 8.1^b	60

indicates a low affinity and visa versa, the affinity of peat for Fe^{2+} is enhanced by high organic matter content (high density of negatively charged sites) and low organically bound Fe concentration (low saturation of available sites by Fe^{2+}). Y_{MAX} values were not significantly correlated with either percent organic matter of the peat (Spearman's $\rho = 0.117$, $p = 0.44$) or the initial organically bound Fe fraction in the peat (Spearman's $\rho = -0.149$, $p = 0.32$).

As initial solution pH increased from 3 to 6, Fe^{2+} adsorption appeared to increase (Figure 2), but the Langmuir parameters were not significantly different between any of

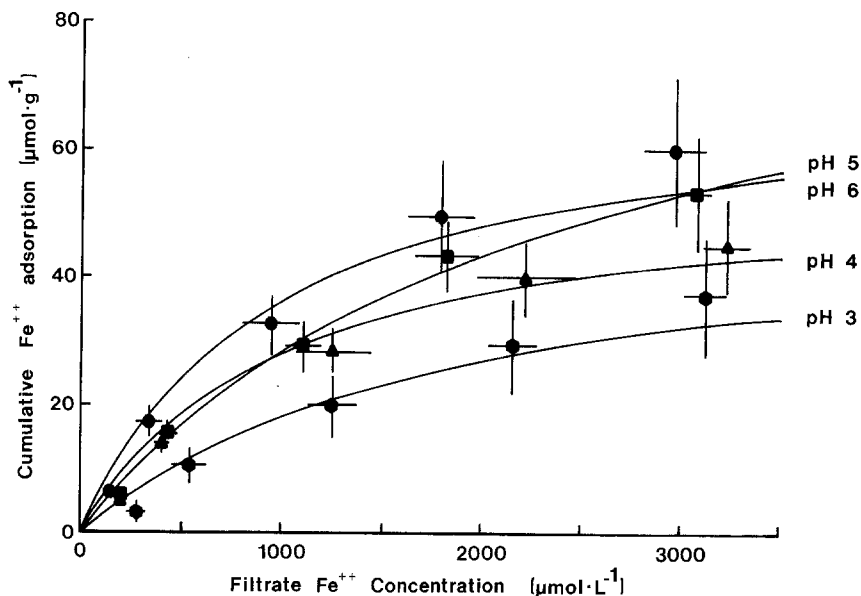


Fig. 2. Fe^{2+} adsorption by Big Run Bog peat ($n = 6$) when subjected to Fe^{2+} solutions with pH values of 3 (●), 4 (▲), 5 (■), and 6 (◐). Plotted points are means \pm standard errors. The Langmuir equation parameter estimates in Table III were used to draw the smooth curves for each of the 4 pH conditions.

the pH treatments (Table III). One reason for the lack of a significant effect of initial solution pH on Fe^{2+} adsorption is that filtrate pH values were relatively uniform (Table IV). Despite a 3 order of magnitude span in initial solution H^+ concentration, mean filtrate H^+ concentrations averaged across the 5 steps in the loading sequence differed by less than a factor of 2. This result indicates that *Sphagnum* peat is an extremely effective buffering agent, capable of either raising or lowering the pH of an added solution to a final value of about 3.4. In addition, regardless of the initial solution

TABLE III

Estimated Langmuir parameters for Fe^{2+} adsorption by 6 Big Run Bog peat samples subjected to Fe^{2+} solutions of different pH values. K ($\mu\text{mol Fe}^{2+} \text{ L}^{-1}$) and YMAX ($\mu\text{mol Fe}^{2+} \text{ g}^{-1}$ dry mass) values are means \pm asymptotic standard errors. K and YMAX values with the same letter superscript do not differ significantly (pairwise t -tests using asymptotic standard errors of the parameter estimates; $p \leq 0.05$). R^2 values indicate the percentage of the uncorrected sum of squares explained by the regression

Treatment	K	YMAX	R^2
pH 6	1827 \pm 1980 ^a	51.9 \pm 26.1 ^a	68
pH 5	1053 \pm 575 ^a	57.2 \pm 11.8 ^a	86
pH 4	2400 \pm 1388 ^a	96.4 \pm 30.3 ^a	89
pH 3	935 \pm 642 ^a	71.4 \pm 18.7 ^a	82

TABLE IV

Mean filtrate pH values ($n = 6$), calculated from H^+ concentrations, for each step of the Fe^{2+} loading sequence under conditions of different initial solution pH. A two-way analysis of variance on the rank-transformed data indicated significant main effects of initial solution pH and of step in the loading sequence ($p \leq 0.0001$), with a nonsignificant interaction ($p = 0.996$). Filtrate pH means for each of the initial solution pH treatments, averaged across the steps in the loading sequence, with the same letter superscript do not differ significantly ($p \leq 0.05$). Filtrate pH means for each step in the loading sequence, averaged across the 4 initial solution pH treatments, with the same number superscript do not differ significantly ($p \leq 0.05$)

Initial solution pH	Step in the Fe^{2+} loading sequence					Row mean
	1	2	3	4	5	
pH 3	3.42	3.31	3.22	3.16	3.13	3.24 ^a
pH 4	3.61	3.51	3.40	3.37	3.38	3.45 ^b
pH 5	3.64	3.55	3.46	3.41	3.40	3.48 ^b
pH 6	3.63	3.51	3.35	3.28	3.27	3.39 ^b
Column mean	3.56 ¹	3.46 ¹	3.35 ²	3.30 ²	3.28 ²	

pH, the filtrate pH values were higher in the first two steps of the loading sequence when Fe^{2+} adsorption was relatively high than in the last three steps of the Fe^{2+} loading sequence when Fe^{2+} adsorption was tapering off (see Figure 2). Although Fe^{2+} adsorption may in fact contribute hydrogen ions to a solution by displacing them from exchange sites on the peat matrix, the results in Figure 2 and Table IV suggest that the mechanisms controlling solution pH and Fe^{2+} adsorption in *Sphagnum* peat are complex and potentially interrelated.

5. Discussion

The ability of living *Sphagnum* moss and of *Sphagnum*-derived peat to remove cations from solution has long been recognized (Skene, 1915). Our result that Fe and Al, but not Mn, accumulate in an organically bound form in response to increased loading is consistent with the findings of Bell (1959) and Clymo (1963) that Al^{3+} , Fe^{3+} , and Fe^{2+} bind more strongly to peat than Mn^{2+} . Thus, in the presence of high Fe and Al concentrations, Mn should be displaced from exchange sites on the peat matrix.

Numerous studies have evaluated peat as a medium for removing heavy metals from industrial wastewaters (e.g., Bunzl *et al.*, 1976; Coupal and Lalancette, 1976; Smith *et al.*, 1977; Chaney and Hundemann, 1979), but these studies have considered exchange (and/or adsorption) to be the dominant process involved in metal removal. Our results indicate that in addition to adsorption, oxide formation is an important mechanism for metal removal from solution and retention in peat under natural conditions. In a laboratory study of Fe removal from acid coal mine drainage and retention in *Sphagnum* peat, Tarleton *et al.* (1984) obtained a maximum Fe accumulation of $72 \mu\text{mol g}^{-1}$ dry peat, with organically bound Fe contributing 62 to 72%, and oxides

contributing 24 to 37% to the total Fe accumulation. In contrast, in a *Sphagnum* peatland constructed for the purpose of removing Fe from a series of springs and seeps on an active coal surface mine, of a total Fe accumulation of $555 \mu\text{mol g}^{-1}$ dry peat, only 10% was contributed by the organically bound Fe fraction and 90% by Fe oxides (Wieder *et al.*, 1985b). While laboratory loading experiments suggest that there is an upper limit to the Fe^{2+} adsorption capacity of peat, it is not known whether Fe oxide accumulation is also limited. It is conceivable that as Fe adsorption approaches its maximum capacity, the relative dominance of the oxide fractions may progressively increase with time as the peat continues to be exposed to Fe containing waters. To date, the highest values that we have obtained for amorphous and crystalline Fe oxide concentrations are 1125 and $642 \mu\text{mol g}^{-1}$ dry mass, respectively, in a peat sample from Tub Run Bog. In this one sample, total Fe concentration of $2693 \mu\text{mol g}^{-1}$ dry mass accounted for 15% of the dry mass of the peat sample. In peatland ecosystems, both pH and redox conditions change with a fluctuating water table, affecting not only Fe^{2+} adsorption (Figure 3), but also the stability of different Fe compounds (Krauskopf, 1979). The factor or factors affecting the relative importance of the organically bound versus the oxide fractions to metal accumulation in peat remain obscure, not only for Fe but for other metals as well.

Our result of an increase in S concentration in peat in response to increasing loading is in agreement with other recent findings. Ferguson *et al.* (1984) reported higher S concentrations in ombrotrophic peat receiving high SO_4^{2-} input in precipitation than in ombrotrophic peat from a relatively unpolluted site. When live shoots of 5 ombrotrophic *Sphagnum* species were transplanted from the unpolluted site to the polluted site, their tissue S concentration increased over an 18 mo period. In addition, Brown (1985) suggested that minerotrophic peat tends to have higher total S concentrations than ombrotrophic peat. Organic S is the dominant S fraction in freshwater peat and it is the organic S fraction that contributes mainly to S accumulation (Table I). At Big Run Bog, 73.5% of the organic S is carbon bonded S and the remainder is ester sulfate S (Wieder *et al.*, 1985a). Although some of the organic S in peat may be formed through assimilatory metabolism by microbes and plants, it has been suggested that carbon bonded S can be formed by a reaction of H_2S with organic matter (Casagrande *et al.*, 1979; Aizenshtat *et al.*, 1984; Brown, 1985). If H_2S is a product of dissimilatory sulfate reduction (Brown, 1985; Wieder and Lang, 1985), then anaerobic conditions are required for the formation of carbon bonded S via this pathway. Iron sulfides are also formed as an end product of dissimilatory sulfate reduction in freshwater *Sphagnum* peat (Brown, 1985; Wieder and Lang, 1985), but the relatively small pool sizes of Fe sulfides in freshwater peat suggest that these compounds are not stable in the long term. The predominance of carbon bonded S in freshwater peat (Wieder *et al.*, 1985a) suggests that reduced S in organic compounds is less susceptible to reoxidation than reduced S in inorganic compounds.

Peatland ecosystems may directly affect the chemistry of their drainage streams (Crisp, 1966; Verry and Timmons, 1982; Wieder and Lang, 1984). Several studies have suggested that the cyclic oxidation and reduction of S compounds in peatland eco-

systems may play a role in regulating sulfate concentrations in stream water (Odelein *et al.*, 1975; Christophersen and Wright, 1981; Braekke, 1981). Previous work in the Big Run and Tub Run watersheds has indicated that with increasing stream discharge Big Run Bog is a source for SO_4^{2-} and a sink for Fe^{2+} , while Tub Run Bog appears to be a sink for SO_4^{2-} , Fe^{2+} , and possibly other heavy metals as well (Wieder and Lang, 1984). The data presented in this paper indicate that a variety of processes are involved in the retention of metals and S in surface *Sphagnum* peat. The factor or factors controlling the relative importance of each process remain topics for further investigation.

Acknowledgments

We thank V. Granus for laboratory assistance and J. B. Yavitt for his comments on the manuscript. This work was supported by a U.S. Environmental Protection Agency grant (R810082-01-0) to G. E. Lang and R. K. Wieder.

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