



Mobility of Pb in *Sphagnum*-derived peat

MELANIE A. VILE^{1,3,*}, R. KELMAN WIEDER¹ & MARTIN NOVÁK²

¹Department of Biology, Villanova University, Villanova, PA 19085, USA; ²Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic; ³Present address: Department of Biological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA (*Author for correspondence)

Accepted 22 June 1998

Key words: *Sphagnum*-peat, ²¹⁰Pb-dating, Pb-mobility

Abstract. One important assumption in applying ²¹⁰Pb-dating is that atmospherically deposited ²¹⁰Pb is immobilized in the peat or sediment column. This assumption has been challenged widely, but has never been evaluated experimentally. We evaluated Pb mobility and the chemical forms in which Pb is stabilized in peat profiles by adding either soluble or particulate Pb to intact peat cores that were maintained under different water level regimes (permanently high, permanently low, fluctuating between high and low) and were subjected to simulated precipitation over a five month period. By analyzing the behavior of stable Pb we made inferences about the expected behavior of ²¹⁰Pb. Results indicate that added soluble Pb²⁺ was retained in the peat through physiochemical binding to organic matter, and as such Pb²⁺ was largely immobile in peat even under conditions of a fluctuating water table. Added particulate Pb was largely (most likely by physical entrapment), but not completely, immobilized in peat. In none of the water table treatments was there evidence to support mobility of Pb by alternating formation and oxidation of sulfides, or by any other mechanism. The binding of Pb²⁺ with organic matter at the peat surface, and the absence of Pb mobility lend credence to ²¹⁰Pb-dating of *Sphagnum*-dominated peat deposits, which are over 90% organic matter throughout, and have high cation exchange capacities.

Introduction

Sphagnum-dominated peatlands have been used extensively for geochemical monitoring (e.g., Oldfield et al. 1978; Madsen 1981; Schell 1987; Cole et al. 1990; Vile et al. 1995). *Sphagnum* mosses grow apically from compact structures called capitula while dying at the base. The dead remains accumulate when the rate of organic matter production exceeds the rate of organic matter decomposition, resulting in a vertically accreting organic deposit that undergoes progressive chemical and structural alteration during long-term decomposition (Clymo & Hayward 1982). *Sphagnum* moss contains substantial amounts of unesterified polyuronic acids in their cell walls, accounting

for 99% of its cation exchange capacity (CEC). Decomposition of *Sphagnum* further contributes to *Sphagnum*'s CEC by creating organics containing a greater number of negatively charged functional groups, which sorb positively charged metals (Clymo 1983). If left undisturbed, peat deposits are capable of recording historical environmental and anthropogenic changes.

^{210}Pb -dating is a popular tool used in reconstructing past environmental conditions in peat (Appleby & Oldfield 1978). Two implicit assumptions of using ^{210}Pb -dating to derive age as a function of depth within a peat or sediment profile are: (1) there is a constant flux of ^{210}Pb from the atmosphere to the surface of a peat or sediment deposit, and (2) atmospherically deposited ^{210}Pb is immobilized in the vertically accreting peat or sediment column. The first assumption generally is regarded as valid, but the second assumption has been challenged widely.

The assumption of Pb immobility has been questioned based on interpretations of depth profiles of Pb concentration in peat. For example, in a study of metal distributions in Swedish raised mires, Damman (1978) found peaks in Pb concentration in adjacent hummock and hollow peat profiles that corresponded to the position of the water table within each profile measured on the day of sampling. Damman (1978) suggested that within the zone of water table fluctuation, Pb is immobilized as PbS when the peat is saturated. When the water table drops, oxidation to slightly soluble PbSO_4 can allow for Pb mobility. Therefore, Damman (1978) attributed peaks in Pb concentration to the remobilization with subsequent accumulation of Pb within the zone of water table fluctuation. In light of this phenomenon, Clymo and Hayward (1982) suggested that the most important process responsible for heavy metal (including Pb) redistribution in peat may be the fluctuation in redox potential associated with water table movements creating aerobic-anaerobic boundaries, which in turn affect metal solubility and mobility. Other descriptive studies also have interpreted patterns in vertical distribution as indicative of at least partial mobility of Pb in peat (e.g., Pakarinen et al. 1983; Pakarinen & Gorham 1983).

The question of Pb immobility in peat or sediment profiles never has been evaluated experimentally, which seems surprising given the centrality of the Pb immobility assumption involved in the application of ^{210}Pb dating. Therefore, we evaluated Pb mobility and the chemical forms in which Pb is stabilized in peat profiles by adding either soluble or particulate Pb to intact peat cores that were maintained under different water level regimes in the laboratory, and were subjected to simulated precipitation over a five month period.

Methods

Study site and peat core collection

In the summer of 1994, 39 peat cores were collected from Bog Lake Bog (47°32'N, 93°28'W; 416 m a.s.l.), in the Chippewa National Forest, adjacent to the Marcell Experimental Forest near Grand Rapids, Minnesota. Peatlands occupy approximately 21% of the land area of the Chippewa National Forest, and the peat deposits can be up to 12 m deep (Wieder & Yavitt 1994). The vegetation of Bog Lake Bog is dominated by a nearly continuous cover of *Sphagnum* mosses. The *Sphagnum* surface exhibits a hummock-hollow microtopography, with hummocks rising ca. 30–50 cm above hollows (pers. obs.). However, several *Carex* species and *Chamaedaphne calyculata* (L.) Moench are abundant locally within some areas of Bog Lake Bog; trees are not an important component of the vegetation. Where trees are present, the species typically consist of black spruce (*Picea mariana*). The pH fluctuates around 4.4; dissolved Ca^{2+} and Mg^{2+} concentrations are 1.7 and 1.1 mg L^{-1} , respectively (Wieder & Yavitt 1994). The region has a continental climate with temperatures ranging from -40°C to $+40^{\circ}\text{C}$; mean annual temperature is 4°C . Mean annual precipitation is 770 mm, and snow covers the ground from late November through mid-April (Urban et al. 1989; Kim & Verma 1992).

In July 1994, peat cores were collected in a 10 cm diameter, 40 cm long PVC pipe; all cores were collected from hollow sections of the bog. The water table was approximately 5 cm below the surface of the *Sphagnum* carpet. Care was taken to ensure that compaction of the peat was minimal. If in any case compaction was more than 2 cm, the core was abandoned. The underlying peat in each core was primarily *Sphagnum*-derived to a depth of at least 20 cm; the peat became increasingly more decomposed with depth. All peat core manipulations occurred while the cores were housed inside the PVC cylinders for the duration of the study.

Experimental manipulations

Upon return to the laboratory, each core was assigned randomly to one of six treatment groups in a $3 \times 3 \times 11$ factorially-arranged design (i.e., 3 Pb treatments, 3 water table treatments, and 11 depth sections). Lead was added in one of three ways: (1) as soluble Pb (dissolved ultra-pure PbCl_2) to simulate Pb present in wet precipitation, (2) as insoluble particulate-Pb (National Institute of Standards and Technology reference material #1633b coal fly ash; certified Pb concentration is $68.2 \mu\text{g g}^{-1}$) to simulate Pb deposition from coal-fired power plants, or (3) not at all; control cores received no Pb.

In addition to Pb treatments, three water table treatments were employed: (1) fixed at 3 cm below the top of currently growing *Sphagnum* (at the time of collection); (2) fixed at 15 cm below the top of currently growing *Sphagnum*; and (3) fluctuating between 3 and 15 cm (6 days at 3 cm alternating with 6 days at 15 cm). Each combination of water table treatment and Pb-amendment treatment was replicated in five cores. Control cores, subjected to water level treatments but no added Pb, were replicated three times. To ensure proper placement of the water level, drain holes were drilled in the PVC pipe at 3 and 15 cm below the top of the *Sphagnum* (at the time of collection) so that the water level could be controlled easily. Before any water table amendments, we determined that water would flow through the peat to depths of at least 15 cm below the *Sphagnum* surface (the lowest experimental water table).

All 39 cores were placed into a CONVIRON CMP 3023 growth chamber, programmed to mimic field temperature and sunlight regimes for northern Minnesota during the month of July. These conditions were maintained throughout the 5 month duration of the study. Before beginning the Pb and water table treatments, all cores were preconditioned, using a 125 mL squeeze bottle to add 50 mL of distilled, deionized water every 2 days for 2 weeks, a rainfall regime that is consistent with rainfall in northern Minnesota. We note, however, that each 50 mL rainfall addition took about 1 min., for an exceptionally high rainfall intensity of 38 cm hr^{-1} . During the preconditioning phase, a drain hole maintained water table levels at 3 cm below the original peat surface for all cores.

After the preconditioning period, we added 50 mL of synthetic rain that was prepared in the laboratory to approximate precipitation chemistry for the Bog Lake Bog Region in Minnesota (cf. Verry 1983) to all 39 cores every other day for the 17 week duration of the study. Concentrations of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , SO_4^{2-} , NO_3^- , PO_4^{3-} , and Cl^- in the synthetic rain were approximately 0.5, 0.09, 0.09, 0.63, 0.44, 2.09, 1.89, 0.09, and 0.23 mg L^{-1} , respectively; pH of the synthetic rain was adjusted to 4.7 (Verry 1983). Every fourth day, over a 36 day period, the Pb additions took place. Individual cores received either no Pb, or Pb as either 0.49 g of coal fly ash or 50 mL of $0.708 \text{ mg L}^{-1} \text{ PbCl}_2$ (in the synthetic rain base solution) on 10 separate occasions (total Pb additions of $354 \mu\text{g}$ per core). The total quantity of Pb added to each core was equivalent to three times the annual Pb deposition in the Czech Republic (approximately $15 \text{ mg m}^{-2}\text{yr}^{-1}$; Moldan 1991), one of the most air-polluted countries in the world. This high deposition rate was used to ensure measurable increases in Pb concentrations in the peat. The coal fly ash was sprinkled over each core prior to adding 50 mL of Pb-free synthetic rainfall, the soluble Pb-amended cores received 50 mL of synthetic

rain containing dissolved PbCl_2 , and control cores received 50 mL of Pb-free synthetic rain. For the 12 weeks following the final Pb addition, all cores received 50 mL of Pb-free synthetic rain every 2 days.

Prior to the first Pb additions, for the high, fluctuating and low water table treatment cores, water table levels were set at 3, 3 and 15 cm, respectively, below the original peat surface by removing drain hole plugs. The water table level in the fluctuating water table treatment cores was lowered to 15 cm (by removing a drain hole plug) for the first time 6 days after the first Pb addition. Subsequently, the water table alternately was raised to 3 cm (by addition of Pb-free synthetic rain), or lowered to 15 cm every 6 days throughout the duration of the study. If at any time the water level dropped below or rose above the designated level, water was either added (as synthetic Pb-free rain water) or drained out of the cores through drain holes, respectively. At the end of the experiment, the water table for the fluctuating water table treatment cores was at 3 cm below the original top of the *Sphagnum*.

Peat processing

Upon completion of the study, the cores were removed from the growth chamber and frozen. Each frozen, intact peat core was extruded from its PVC cylinder and sectioned at 2 cm depth intervals using a band saw. Individual sections were freeze-dried (to avoid sulfide oxidation; Wieder et al. 1996), weighed, and homogenized by grinding to pass a 2 mm-mesh screen in a Tecator Cyclotec sample mill. For each core, the deepest section sliced and analyzed was 2 depth sections below the lowest drain hole, i.e., the 18–20 cm section for the low and fluctuating water table treatment cores, and the 6–8 cm section for the high water table treatment cores. Peat extending above the original peat surface represented new growth and was contained in a single section (referred to as “top”).

Control and soluble-Pb amended cores

For each 2 cm section, two separate subsamples were extracted, one with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ to obtain the organically-bound Pb fraction (Miller & McFee 1983; Miller et al. 1983; Stevenson 1994). Water-soluble Pb is also extracted with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$, but is assumed to be negligible. The other subsample was extracted with 16 M Trace Metal Grade HNO_3 to obtain total Pb (Livett et al. 1979). Lead present as PbS was estimated by subtracting organically-bound Pb from total Pb (Livett et al. 1979).

Fifteen mL of either 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ or 16 M HNO_3 were added to separate 0.15–0.3 g subsamples of dried, ground peat in centrifuge tubes. After 24 hr, the mixtures were centrifuged for 10 min and filtered through

Whatman #541 filter paper into 20 mL borosilicate glass vials. Lead concentrations were measured in the final extract solutions using a Perkin-Elmer 4100 graphite furnace atomic absorption spectrophotometer. Pyrolytically coated graphite tubes with integrated platforms were used for all samples. The 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ extraction caused considerable matrix interferences. To minimize matrix interferences and to decrease the high background absorbances observed in the 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ extracts, we added 5 μL of 0.06 M La_2O_3 in 0.22 M HNO_3 to each 25 μL sample injected into the graphite tube (Burau 1982). The standard matrix modifier, 0.2 g $\text{NH}_4\text{H}_2\text{PO}_4$ per 25 μL of injected sample was used for analyzing the 16 M HNO_3 extractions for Pb.

Coal fly ash Pb-amended cores

The nitric acid digestion method used for the control and soluble Pb-amended cores was not sufficiently aggressive to extract all of the Pb in the coal fly ash Pb-amended cores; therefore, a different digestion procedure was used to determine total Pb (Lim & Jackson 1982). Subsamples (0.20–0.50 g) of each 2 cm section were dry-ashed at 450 °C for 4 hr. Five mL of concentrated HF and 0.5 mL of HClO_4 were added to the ashed samples in teflon cups and heated in a sandbath at 200 °C for 2 hr, or until a white smoke appeared. Five mL of concentrated HF were added and the mixture heated to dryness. Once dry, 3 mL of a saturated HBO_3 solution plus 0.5 mL of concentrated HClO_4 were added and the mixtures again were heated to dryness. The resulting ash was dissolved in 20 mL of distilled, deionized water and 3 mL of 8 M HNO_3 , and filled to volume (50 mL). Lead in the resulting solutions was analyzed using flame atomic absorption spectrophotometry. Because we did not expect Pb in coal fly ash (mostly Pb oxides) to be retained by physiochemical binding of Pb^{2+} to organic matter, $\text{Na}_4\text{P}_2\text{O}_7$ extractions of the coal fly ash cores were not performed.

Results

Control cores

For each water level treatment, three cores were set aside to receive water level manipulations without Pb additions. We considered the Pb in the control cores to represent background Pb, i.e., the natural profile of Pb concentrations at Bog Lake Bog, Minnesota. To evaluate whether water table treatment affected the depth distribution of background Pb, we compared the total Pb contents per 2 cm depth section for all three water table treatments, using a 2-way ANOVA, with main effects of water table treatment, depth and the

interaction term. There was a significant water table treatment effect ($p = 0.0356$) and a significant depth effect ($p = 0.0001$), but no significant interaction between water table treatment and depth ($p = 0.9983$). Because the high water table treatment cores had six fewer depth sections than either the fluctuating or low water table treatment cores (shaded bars in Figures 1 and 2), the high water table treatment cores contained significantly less Pb per 2 cm section than either the fluctuating or low water table-treatment cores ($p < 0.05$, Duncan's Multiple range test for *a posteriori* comparisons). Furthermore, both the fluctuating and low water table treatment cores had a greater amount of Pb in the deeper sections of the core (i.e., 8–20 cm) than in the more recently deposited depth sections (i.e., top 8 cm; Figures 1 or 2). Therefore, another 2-way ANOVA was run including only those depth sections common to all three water table treatments (top 8 cm). There was no significant water table treatment effect ($p = 0.0736$), no significant depth effect ($p = 0.0726$), and most importantly, no significant interaction between water level and depth ($p = 0.9963$). Collectively, these results indicate that the water table manipulations did not affect the background or natural profile of Pb over the five month duration of the study.

Soluble-Pb amended cores

By determining the natural profiles of total Pb and organically-bound Pb in the control cores, we were able to separate total Pb and organically-bound Pb in the cores to which Pb^{2+} was added experimentally into background component and excess components. For each depth section of those cores receiving Pb^{2+} amendments, the mean background total and organically-bound Pb components (from the control cores) were subtracted from total and organically-bound Pb, allowing us to evaluate Pb mobility in peat cores by quantifying the final depth distribution of the Pb^{2+} that we added. The profile of excess Pb only (i.e., with the background component subtracted from total Pb) as a function of depth reveals the fate of the added soluble Pb.

The mean total of excess Pb recovered in the low water table treatment cores was $368.7 \pm 21.4 \mu\text{g}$ (mean \pm standard error), which was not significantly different from the amount of Pb that was added ($354 \mu\text{g}$; paired t-test; $t = 0.6861$, $p = 0.5303$). Of the $354 \mu\text{g}$ of added soluble Pb, 74% was retained in the top 3 sections of the peat core (Figure 1A). Of the $354 \mu\text{g}$ of Pb added to the cores, statistically 100% was retained in peat by physiochemical binding to organic matter (Table 1).

For the high water table treatment cores, we recovered a total of $328.6 \pm 14.9 \mu\text{g}$ of excess Pb, which was not significantly different from the amount of soluble Pb that was added ($t = -1.711$, $p = 0.1622$). Of the $328.6 \mu\text{g}$ of excess Pb recovered, 95% was retained in the top 3 sections of the peat core

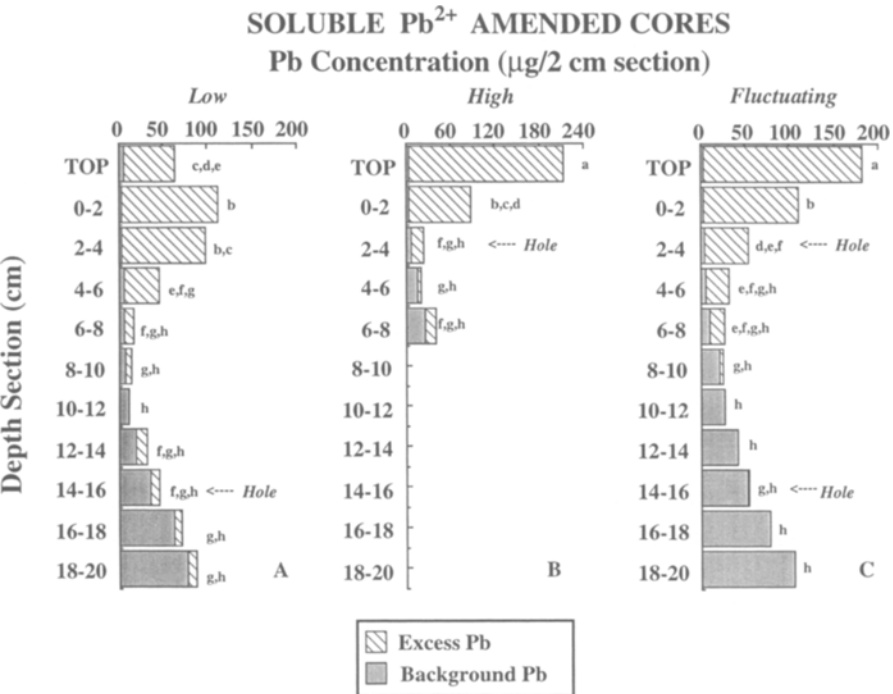


Figure 1. Pb concentration as a function of depth for the background (shaded bars) and excess amounts (hatched bars) of Pb present in the cores for the low, high, and fluctuating water table treatment cores. Shaded bars at each depth represent the mean of three control cores while hatched bars at each depth represent the mean of 5 cores that received soluble Pb additions; letters apply to hatched bars only and bars with the same letter do not differ significantly.

(Figure 1B). Statistically, 100% of the 354 μg of excess Pb added to the cores was retained in the peat by physiochemical binding to organic matter (Table 1).

Lastly, for the fluctuating water table treatment cores, we recovered a total of 385.0 ± 46.2 μg of excess Pb, which was not statistically different from the amount of soluble Pb that was added (t = 0.6725, p = 0.5381). Of the 385.0 μg of Pb recovered, 87% was retained in the top 3 sections of the peat core (Figure 1C). Of the 354 μg of excess Pb added to the cores, statistically, 100% was retained in peat by physiochemical binding to organic matter (Table 1).

To evaluate the patterns of excess content per 2 cm section, we performed a 2-way ANOVA with main effects of water table treatment, depth, and the interaction between water table treatment and depth. There was a significant interaction between depth and water level treatment (p = 0.0001). The nature of the interaction is that there was significantly less Pb retained in the top and 2–4 cm sections of the low water table-treatment core than in the cor-

Table 1. Mean percent \pm standard error of total excess Pb retained as organically bound Pb. Using a paired t test a p value greater than 0.05 indicates that the mean percent of added Pb recovered in the organically bound fraction was not significantly different from 100%.

Water level treatment	Percent of excess Pb organically bound	n	t	p
Low	120.3 \pm 19.7	44	1.031	0.3084
High	117.8 \pm 23.3	19	0.7613	0.4563
Fluctuating	103.1 \pm 15.2	28	0.2019	0.8415
Overall	114.5 \pm 11.6	91	1.249	0.2150

responding sections of the high or fluctuating water table treatment cores. All remaining depth sections for all three water table treatments retained statistically equal amounts of Pb (Figure 1).

For all three water table treatments, all of the added soluble Pb was retained in the peat through physiochemical binding to organic matter, not through the formation of sulfides. As such, Pb was largely immobile in peat, even under conditions of a fluctuating water table.

Coal fly ash Pb-amended cores

The mean total of excess Pb recovered in the low water table treatment cores was $278.7 \pm 43.3 \mu\text{g}$ of Pb, which was not significantly different from the amount of Pb that was added ($354 \mu\text{g}$; $t = -1.558$, $p = 0.1942$). Of the $354 \mu\text{g}$ of added Pb in coal fly ash, 18% was recovered from the top 3 sections of the peat cores, partly because the top section did not exist in any of the replicate cores (Figure 2A). Low recovery of Pb is due, at least partially, to the absence of new growth in all five replicate cores (no top section) and no 0–2 cm sections in four of the five replicate cores. If the top-most three sections of the low water table treatment cores are considered (i.e., the 2–4 cm, 4–6 cm, and 6–8 cm sections in four cores, the 0–2, 2–4, and 4–6 cm sections in the fifth core), 71% of the Pb was recovered in the uppermost 6 cm of peat.

For the high water table treatment cores, a total of $331.3 \pm 60.7 \mu\text{g}$ of Pb was recovered, which was not significantly different from the amount of soluble Pb that we added ($t = -0.3732$, $p = 0.7279$). Of the $354 \mu\text{g}$ of added Pb, 90% was retained in the top three sections of the peat core (Figure 2B). For the fluctuating water table treatment cores, a total of $352.5 \pm 23.6 \mu\text{g}$ of Pb was recovered, which was not significantly different from the amount of

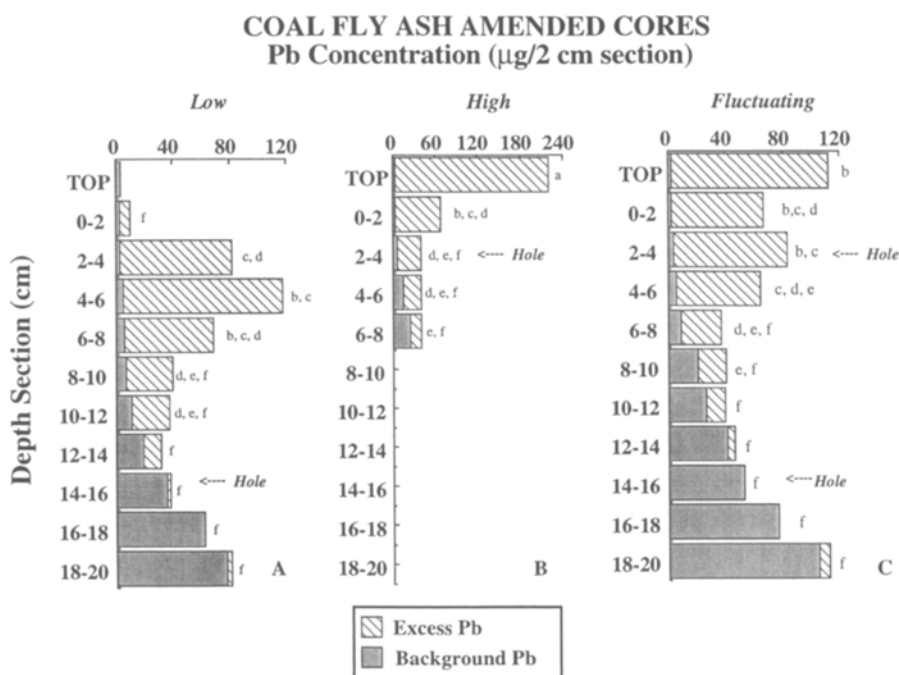


Figure 2. Pb concentration as a function of depth for the background (shaded bars) and excess amounts (hatched bars) of Pb present in the cores for the low, high, and fluctuating water table treatment cores. Shaded bars at each depth represent the mean of three control cores while hatched bars at each depth represent the mean of 5 cores that received coal fly ash Pb additions; letters apply to hatched bars only and bars with the same letter do not differ significantly. Note that there was an absence of new growth in all five replicate cores (no top section) and no 0–2 cm section in four of the five replicate cores.

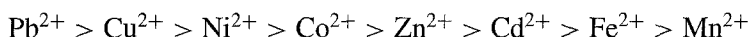
Pb that was added ($t = -0.0640$, $p = 0.9521$). Of the $354\text{ }\mu\text{g}$ of added Pb, 68% was retained in the top three sections of the peat core (Figure 2C).

To evaluate the patterns of excess Pb content per 2 cm section, we performed a 2-way ANOVA with the main effects of water table treatment, depth, and the interaction between water table treatment and depth. There was a significant interaction between depth and water table treatment ($p = 0.0001$; Figure 2). The nature of the interaction is that there was significantly less Pb retained in the top and in the 0–2 cm sections of the low water table treatment cores than in either the high or fluctuating water table treatments, while there was significantly less Pb recovered in the 4–6 cm and 6–8 cm sections of the high water table treatments than in the corresponding sections in the low water table treatments, and significant less Pb in the 2–4 cm section of the high water table treatment than in the 2–4 cm section of the fluctuat-

ing water table treatment. Each remaining depth section retained statistically equal amounts of Pb in the three water table treatments (Figure 2).

Discussion

This study was conducted to evaluate one of the assumptions associated with ^{210}Pb -dating of a peat deposit or sediment column, namely that atmospherically-deposited ^{210}Pb is immobilized at the surface of the peat or sediment column and is retained in the peat as the peat or sediment grows vertically. Lead and other atmospherically deposited metals can be retained in peat by binding to organic matter, by forming sulfides, or by physical entrapment (Schnitzer 1978). In any soil where there is an abundance of organic matter, such as peat, retained metals resulting from organic matter-heavy metal interactions may dominate over metals retained by sulfide formation (Friedland 1990). Peat has a high cation exchange capacity. Heavy metal cations, including Pb^{2+} , Zn^{2+} , and Cu^{2+} , bind preferentially over the base metal cations Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} (Bunzl et al. 1976; Coupal & Lalancette 1976; Wieder 1990). The relative affinities of humic substances for different heavy metals, described by stability constants obtained experimentally, generally are in the order:



(Ruhling & Tyler 1970; Van Dijk 1971; Bunzl et al. 1976; Schnitzer 1982; Friedland 1990). Additionally, new growth of *Sphagnum* at the apex continuously produces new cation exchange sites that are situated at the top of the peat deposit, where atmospherically deposited metals land. Chemical fractionation of Pb in peat (Livett et al. 1979; Jones 1987; Livett 1988), and in different soil types (Benninger et al. 1975; Friedland 1991; Miller & Friedland 1994; Mench et al. 1994) has shown that by far, organically-bound Pb represents the greatest Pb fraction in soil. For these reasons, long-term immobilization of Pb in peat is likely.

Alternatively, both changing redox conditions associated with a fluctuating water table and complexation of Pb with dissolved organic carbon in peat bog waters, may result in ^{210}Pb mobility, and hence minimal (25%) retention of Pb inputs to the bog (Clymo 1970; Damman 1978; Clymo et al. 1990; Urban et al. 1990). The argument for mobility of Pb in peat has been inferred from a commonly seen pattern of maximum Pb concentration in the zone of water table fluctuation in a peat deposit (Damman 1978). Under anaerobic conditions, bacterial sulfate reduction first produces sulfide, which may react with Pb^{2+} to form insoluble PbS . It has been suggested that PbS , formed in

the zone of water table fluctuation under anaerobic conditions when the water table is high, will be oxidized to PbSO_4 under aerobic conditions when the water table drops to a lower position. Because PbSO_4 is slightly soluble, it can be translocated when the water table rises. Therefore, changing redox conditions in peat, driven by fluctuation in the water table may create alternating aerobic and anaerobic conditions, which are thought to be responsible for Pb mobility in peat. Although this scenario seems intuitively reasonable, there is a distinct lack of data that either (1) clearly identifies PbS as an important Pb fraction in soil or peat, (2) directly demonstrates Pb mobility, or (3) definitively implicates changing redox conditions as causing Pb mobility.

In our study, if changing redox conditions associated with a fluctuating water table influenced mobility of Pb, then in the fluctuating water table treatment cores, we should have found a broad Pb peak between the high and low water table positions (i.e., between 3 and 15 cm below the surface of the peat). Instead, 95% and 67% of the 354 μg of soluble Pb and Pb in coal fly ash that was added to the cores over the five month duration of the study was retained in the top three sections of the fluctuating water treatment cores. These three sections are at or above the high water table position, suggesting that atmospherically-deposited Pb^{2+} is effectively retained, even above the high water table level. Through the $\text{Na}_4\text{P}_2\text{O}_7$ extractions, we demonstrated that soluble Pb^{2+} retention occurred wholly by binding to negatively charged functional groups associated with the organic matter of *Sphagnum* plants.

The low water table treatments exhibited the lowest recovery of both soluble Pb and coal fly ash Pb. While the soluble Pb treatment cores recovered 74% of the added Pb, the coal fly ash treatment cores recovered only 18% of the 354 μg of added Pb in the top three sections (Figures 1A and 2A). While the absence of new growth in all five replicate cores (no top section) and no 0–2 cm sections in four of the five replicate cores contributed to low recovery, premature decomposition of already existing peat, and compaction of *Sphagnum* peat from the added mass of the coal fly ash also could have contributed to low Pb recovery. If the top four sections of the low water table treatment cores are considered, approximately 80% of the Pb was recovered in the uppermost 6 cm of peat for the coal fly ash treatment cores.

Unlike metal cations, the behavior of particles, such as pollen and coal fly ash, in peat is poorly understood, especially with regard to particle size, geometry, sculpturing, and surface charge. Clymo and Mackay (1987) demonstrated vertical movement of *Corylus* and *Cedrus* pollen and of *Lycopodium* spores in *Sphagnum* and in *Sphagnum*-derived peat when subjected to manipulated flow regimes over a 36 day period. Given that Pb in coal fly ash consists predominantly of Pb oxides, if retainment of added Pb in coal fly ash occurs, it would most likely be due to physical entrapment. Coal

fly ash particles in this experiment behaved similarly to the pollen particles of Clymo and Mackay (1987) in that some movement occurred, suggesting that immobility of Pb depends on the form in which Pb is deposited in peat.

Atmospherically deposited Pb occurs as both soluble and particulate forms, and the relative abundance of these two broad categories varies spatially and temporally (Schell 1987). Moreover, once deposited onto the peat surface, Pb is subjected to a different biogeochemical environment than in the atmosphere, and may undergo numerous transformations between and among different soluble and insoluble Pb forms (Moldan 1991). In this study, we opted to use Pb^{2+} as a form of soluble Pb and coal fly ash as a form of particulate Pb, under the premise that the behavior of soluble Pb^{2+} and of coal fly ash Pb should provide some insight into the question of atmospherically deposited Pb mobility in peat. Few studies have characterized the exact chemical forms of atmospherically deposited Pb (Rhue et al. 1992). We know that combustion of Pb alkyls (organo Pb compounds) as anti-knocking agents historically have accounted for the greatest source of Pb, constituting 70% of total Pb emissions. Alternatively, coal burning historically has contributed only 3.7% of total Pb emissions (Adriano 1986). Given the disproportionate contribution of alkyl Pb versus coal fly ash Pb, perhaps coal fly ash was not the best Pb treatment to make inferences about the validity of ^{210}Pb dating. Although use of leaded gasoline is no longer global, vehicular traffic using leaded gasoline continues to be the main source of Pb contamination today (Rhue et al. 1992). Both combusted and uncombusted Pb alkyl compounds rapidly undergo photolytic decomposition to Pb^{2+} , which settle out on the ground and become bound to soil organic matter (Rhue et al. 1992). As such, most of the Pb that is atmospherically deposited in peat, most likely is immobilized as organically-bound Pb, despite the results of the coal fly ash treatment cores.

Although less than 100% recovery of the added soluble Pb^{2+} and Pb in coal fly ash, respectively, in the top 3 sections of the low water table treatment cores, could be interpreted as an indication of Pb mobility, other possibilities also could be likely. Other possibilities for a comparatively smaller percentage of the added Pb^{2+} recovered in the top three sections in the low water table treatments than in the high or fluctuating water table treatment cores are: (1) less new growth (length and mass), creating an open, loose structure of the upper sections of peat, and (2) intensity of rainfall events, allowing a more rapid, deeper penetration of Pb^{2+} in rainwater during and immediately following a rain event. For the soluble Pb-amended cores, the physical structure of the living, growing *Sphagnum* was different in the low water table treatment than in the other two treatments. New growth ("top" section) over the duration of the study in the low water treatment cores (receiving Pb) averaged

1.1 cm and 1.5 g versus 6.7 cm and 3.4 g in the high water table treatment and 5.7 cm and 3.1 g in the fluctuating water table treatment. Less growth in the low water table treatment could have affected the structure of the *Sphagnum* and developing peat. In the high and fluctuating water table treatment, the densely packed *Sphagnum* capitula typically formed a continuous, often fairly level, uninterrupted surface upon which synthetic rain fell. In contrast, the low water table treatment cores were more sparsely populated, often with drooping *Sphagnum* plants lacking the physical support provided by water and surrounding plants. The capitula did not form a dense uninterrupted layer and the surface topography was relatively heterogeneous. Many of the *Sphagnum* plants were flaccid and bent over; the bend occurred predominantly between 4–8 cm so that the Pb in the synthetic rainfall came into contact with its first cation exchange site somewhere between 4–8 cm. Without information about the physical structure of the *Sphagnum* plant, accumulation of Pb between 4–8 cm otherwise would be attributed to Pb mobility. Hence, physical structure differences of the *Sphagnum* plants between the low water table treatments may have allowed deeper penetration of the added Pb^{2+} . Additionally, recall that the amount of synthetic rainfall was consistent with the amount the cores would have received in their natural setting, but the rate at which the cores received synthetic rainfall was much more intense (50 mL of synthetic rain were delivered over a one minute period-corresponding to a rainfall rate of 38 cm hr^{-1}). Such an intense rainfall rate increased the likelihood that Pb in the synthetic rainfall came into contact with its first cation exchange site somewhere between 4–8 cm rather than at the top of the *Sphagnum* capitula.

Given that the low water table treatment cores for the coal fly ash amended cores begin with either the 0–2 cm or the 2–4 cm section, it is not surprising that most of the individual depth sections contain significantly different amounts of Pb when compared across water table treatments (cf. Figure 2). If, however, the first existing section in the low water table treatment of the coal fly ash cores (i.e., the 2–4 cm section) is considered analogous to the top section in both the high and fluctuating treatments, then most of the individual depth sections contain similar amounts of Pb when compared across water table treatments (cf. Figure 2).

We acknowledge that the time course (i.e., 5 months) over which this study occurred limits interpretations about the long-term (e.g., 50–100 years) fate of Pb in peat ecosystems. Certainly over 50–100 years there would be much microbial decomposition of the peat itself. However, if Pb^{2+} were to be released from organic matter by mineralization, it could be rapidly and effectively re-immobilized by binding to another cation exchange site. We note that even if all of the $354 \mu\text{g}$ of Pb^{2+} added to the cores in this study were immobilized within one 2 cm depth section ($\sim 3.5 \text{ g}$), the organically-

bound Pb^{2+} would represent less than 0.1% of that section's cation exchange capacity (assuming a cation exchange capacity of $1000 \mu\text{eq g}^{-1}$ dry peat). Furthermore, given the high rainfall intensity of 38 cm hr^{-1} used in this study, it seems reasonable to assume that if Pb potentially were going to be leached from the experimental cores, then it would have done so at least to some extent within the five month duration of the study.

Our results (cf. Table 1) are consistent with the hypothesis that Pb-organic matter interactions control the mobility of Pb^{2+} in peat. The behavior of Pb in peat, however, may not be similar to the behavior of Pb in forest soils. Although there can be substantial amounts of organic matter in forest soils, the often thin (compared to a peat deposit) organic layer is at the surface and is underlain by inorganic or mineral soil. Less organic matter coupled with mixing of soil organic matter and deeper mineral soil by soil invertebrates create a situation whereby Pb has a greater potential to move downward in the forest floor profile than it would in a peatland. Swarup et al. (1994) showed that 87–96% of experimentally applied Pb was retained in the organic-rich top 10 cm of a soil profile. Miller and Friedland (1994), through analyses of Pb concentrations in precipitation, cloudwater, and air, demonstrated that Pb is migrating through the mineral soil profile of a high elevation forest in New Hampshire at a rate of approximately $8\text{--}20 \text{ mm y}^{-1}$. At this rate, the Pb that was deposited on northeastern forests from the late 1960's through the present will be redistributed throughout the soil profile by the year 2050. Miller and Friedland (1994) suggested that this migration of Pb is probably the result of passive transport of the soil organic matter to which the Pb is bound, rather than active mobility of the Pb^{2+} ion because of desorption from organic matter. Wang et al. (1995) showed that undisturbed forested ecosystems, such as portions of the Hubbard Brook Experimental Forest, experience little mobility of Pb from the ecosystem. However, Johnson et al. (1995), concluded that the forest floor soils are not as efficient at accumulating Pb as previously reported for the Hubbard Brook Experimental Forest. Conflicting results from descriptive studies such as these illuminate the need for an experimental evaluation of the mobility of Pb.

Collectively, our results indicate that soluble Pb^{2+} is retained in the peat column through physiochemical binding to organic matter, and as such is largely immobile in peat even under conditions of a fluctuating water table and exceptionally high simulated rainfall intensities. In none of the water table treatments was there evidence to support mobility of Pb by alternating formation and oxidation of sulfides. Because we conducted our experiment over a five month period, it is difficult to extrapolate to the mobility of Pb over a time period of 200 years. However, the immobilization of Pb^{2+} at or near the peat surface and the minimal Pb mobility demonstrated in this study, tends to

lend credence to ^{210}Pb -dating of *Sphagnum*-dominated peat deposits, which are over 90% organic matter throughout and have cation exchange capacities several magnitudes greater than those of forest soils.

Acknowledgements

This work has been supported by National Science Foundation grants (BSR-9020583 and DEB-9408043) to RK Wieder and JB Yavitt, a Czech Grant Agency grant (205/96/0370) to M Novák, the Department of Biology and the Office of Research and Sponsored Projects of Villanova University. Suggestions from S. Bridgham on the manuscript were appreciated. We thank Constance Gasda and Daniel T. Lammey for field and lab assistance, respectively.

References

- Adriano DC (1986) Trace elements in the terrestrial environment. Springer-Verlag, New York
- Appleby PG & Oldfield F (1978) The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena* 5: 1–8
- Bureau RG (1982) Lead. In: Page AL (ed) *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties—Agronomy Monograph no. 9* (pp 347–362). American Society of Agronomy, Inc. and Soil Science of Society of America, Inc., Madison
- Benninger LK, Lewis DM & Turekian KK (1975) The use of natural Pb-210 as a heavy metal tracer in the river-estuarine system. In: Church TM (ed) *Marine chemistry in the coastal environment* (pp 202–210). American Chemical Society, New York
- Bunzl K, Schmidt W & Sansoni B. (1976) Kinetics of ion exchange in soil organic matter. IV. Adsorption and desorption of Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Ca^{2+} by peat. *J. Soil Sci.* 27: 32–41
- Clymo RS, Oldfield F, Appleby PG, Pearson GW, Ratnesar P & Richardson N (1990) The record of atmospheric deposition on a rainwater-dependent peatland. *Phil. Trans. R. Soc. Lon., Series B* 327: 331–338
- Clymo RS & Hayward PM (1987) Upwash and downwash of pollen and spores in the unsaturated surface layer of *Sphagnum*-dominated peat. *New Phytol.* 105: 175–183
- Clymo RS (1983) Peat. In: Gore AJP (Ed) *Mires: Swamp, Bog, Fen and Moor, Ecosystems of the World*, 4A (pp 159–224). Elsevier Scientific Publishing Co., New York
- Clymo RS & Hayward PM (1982) The ecology of *Sphagnum*. In: Smith AJE (Ed) *Bryophyte Ecology* (pp 229–289). Chapman and Hall, London
- Clymo RS (1970) Growth of *Sphagnum*: Methods of measurement. *J. Ecol.* 58: 13–49
- Cole KL, Engstrom DR, Futyma RP & Stottlemeyer R (1990) Past atmospheric deposition of metals in northern Indiana measured in a peat core from Cowles Bog. *Environ Sci. Technol.* 24: 543–549
- Coupal B & Lalancette JM (1976) The treatment of waste waters with peat moss. *Water Res.* 10: 1071–1076
- Damman AWH (1978) Distribution and movement of elements in ombrotrophic peat bogs. *Oikos* 30: 480–495

- Friedland AJ (1990) Heavy metal movement in soils and ecosystems. In: Shaw J (Ed) *Evolutionary Aspects of Heavy Metal Tolerance in Plants* (pp 7–17). CRC Press, Boca Raton
- Friedland AJ (1991) The use of organic forest soils as indicators of atmospheric deposition of trace metals. In: Verry ES & Vermette SJ (Eds) *The deposition and fate of trace metals in our environment* (pp 97–104). USDA-Forest Service, North Central Forest Experiment Station, Grand Rapids
- Johnson CE, Siccama TG, Driscoll CT, Likens GE & Moeller RE (1995) Changes in lead biogeochemistry in response to decreasing atmospheric inputs. *Ecol. Appl.* 5: 813–822
- Jones JM (1987) Chemical fractionation of copper, lead, and zinc in ombrotrophic peat. *Environ. Pollut.* 48: 131–144
- Kim J & Verma S (1992) Soil surface CO₂ flux in a Minnesota peatland. *Biogeochem.* 18: 37–51
- Lim CH & Jackson ML (1982) Dissolution for total elemental analysis. In: Page AL (ed) *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties-Agronomy Monograph no. 9* (pp 1–11). American Society of Agronomy, Inc. and Soil Science of Society of America, Inc., Madison
- Livett EA (1988) Geochemical monitoring of atmospheric heavy metal pollution: Theory and application. *Adv. Ecol. Res.* 18: 65–177
- Livett EA, Lee JA & Tallis JH (1979) Lead, zinc and copper analyses of British blanket peats. *J. Ecol.* 67: 865–891
- Madsen PP (1981) Peat bog records of atmospheric mercury deposition. *Nature* 293: 127–130
- Mench M, Vangronsveld V, Didier V & Clijsters H (1994) Evaluation of metal mobility, plant availability, and immobilization by chemical agents in a limed-silty soil. *Environ. Pollut.* 86: 279–286
- Miller EK & Friedland AJ (1994) Lead migration in forest soils: Response to changing atmospheric inputs. *Environ. Sci. Technol.* 28: 662–669
- Miller WP & McFee WW (1983) Distribution of cadmium, zinc, copper, and lead in soils of industrial northwestern Indiana. *J. Environ. Qual.* 12: 29–33
- Miller WP, McFee WW & Kelly JM (1983) Mobility and retention of heavy metals in sandy soils. *J. Environ. Qual.* 12: 579–584
- Moldan B (1991) *Atmospheric Deposition: A Biogeochemical Process*. Academia, Prague
- Novák M (1990). Speciation of sulfur and vertical $\delta^{34}\text{S}$ profiles in *Sphagnum*-dominated wetlands: Indirect evidence for the openness of the system toward buried sulfur. M.S. Thesis, Villanova University, Villanova, Pennsylvania
- Novák M & Wieder RK (1992) Inorganic and organic sulfur profiles in nine *Sphagnum* peat bogs in the United States and Czechoslovakia. *Water, Air, and Soil Pollut.* 65: 343–369
- Oldfield F, Thompson R & Barber K (1978) Changing atmospheric fallout of magnetic particles recorded in recent ombrotrophic peat sections. *Science* 199: 679–680
- Pakarinen P & Gorham E (1983) Mineral element composition of *Sphagnum fuscum* peats collected from Minnesota, Manitoba and Ontario. In: Fuchsman CH & Spigarelli SA (Eds) *Proceedings of the International Symposium on Peat Utilization* (pp 417–429). Bemidji State University, Bemidji
- Pakarinen P, Tolonen K, Heikkinen S & Nurmi A (1983) Accumulation of metals in Finnish raised bogs. *Environ. Biogeochem.* 35: 377–382
- Rhue RD, Mansell RS, Ou LT, Cox R, Tang SR & Ouyang Y (1992) The fate and behavior of lead alkyls in the environment: A Review. *Crit. Rev. Environ. Control* 22: 169–193
- Ruhling A & Tyler G (1970) Sorption and retention of heavy metals in the woodland moss *Hylocomium splendens* (Hedw.) Br. et Sch. *Oikos* 21: 92–97

- Schell WR (1987) A historical perspective of atmospheric chemicals deposited on a mountain top peat bog in Pennsylvania. *Int. J. Coal Geol.* 8: 147–173
- Schnitzer M (1982) Organic matter characterization. In: Page AL (Ed) *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties – Agronomy Monograph 9* (pp 581–593). American Society of Agronomy, Inc. and Soil Science of Society of America, Inc., Madison
- Stevenson FJ (1994) *Humus Chemistry-Genesis, Composition, Reactions*, Second Edition. John Wiley & Sons, New York
- Swarup A, Beese F & Ulrich B (1994) Movement of Zn, Pb, and Cd through an undisturbed community of a soil under forest. *J. Indian Soc. Soil Sci.* 4: 182–184
- Urban NR, Eisenreich SJ & Grigal DF (1989). Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota. *Biogeochem.* 7: 81–109
- Urban NR & Schurr KT (1990) Mobility and diagenesis of Pb and ^{210}Pb in peat. *Geochim. Cosmochim. Acta* 54: 3329–3346
- Van Dijk H (1971) Cation binding of humic acids. *Geoderma* 5: 53–67
- Verry ES (1975) Streamflow chemistry and nutrient yields from upland-peatland watersheds in Minnesota. *Ecol.* 56: 1149–1157
- Verry ES & Timmons DR (1982) Water-borne nutrient flow through an upland-peatland watershed in Minnesota. *Biogeochem.* 7: 1456–1467
- Verry ES (1983) Precipitation chemistry at the Marcell Experimental Forest in North Central Minnesota. *Water Resour. Res.* 19: 454–462
- Vile MA, Novák M, Břízová E, Wieder RK & Schell WR (1995) Historical rates of atmospheric Pb deposition using ^{210}Pb dated peat cores: Corroboration, computation, and interpretation. *Water, Air, Soil Pollut.* 79: 89–106
- Wang EX, Bormann FH & Benoit G (1995) Evidence of complete retention of atmospheric lead in the soils of northern hardwood forested ecosystems. *Environ. Sci. Technol.* 29: 735–739
- Wieder RK (1990) Metal cation binding to *Sphagnum* peat and sawdust: Relation to wetland treatment of metal-polluted waters. *Water, Air, Soil Pollut.* 53: 391–400
- Wieder RK and Yavitt JB (1994) Peatlands and global climate change: Insights from comparative studies of sites situated along a latitudinal gradient. *Wetlands* 14: 229–238
- Wieder RK, Novák M & Rodríguez D (1996) Sample drying, total sulfur and stable sulfur isotopic ratio determination in freshwater wetland peat. *Soil Sci. Soc. Am. J.* 60: 949–952