Temperature and Microbial Activity Effects on Trace Element Leaching from Metalliferous Peats

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ABSTRACT

Due to geochemical processes, peat soils often have elevated concentrations of trace elements, which are gradually released following drainage for agriculture. Our objectives were to use incubation temperatures to vary microbial activity in two metalliferous peats (M7 acidic peat and M3 neutral peat) from the Elba, New York region, and to use periodic leaching to assess the extent of trace element release from these soils. Dried soils were mixed with glass beads to maintain aeration, moistened, and incubated at 4, 16, 28, and 37°C in 10-cm-diameter × 8-cm-tall columns. Five incubation–leaching cycles were performed, each consisting of 7.3 d of incubation (28 d for the final cycle) followed by 16 h of leaching with synthetic acid rain at 2.5 mm h^{-1}. Microbial activity was determined initially and after the final leaching by measuring C mineralization following glucose stimulation. Cumulative respiration results were ranked 28 > 16 > 4 > 37°C, with M7 acidic peat respiration values greater than M3 neutral peat at each temperature. Initial leachate pH levels were between 2 and 4, with acidification less pronounced and shorter-lived for the M3 peat. Leachate S, dissolved organic carbon (DOC), NO$_3$–N, and trace elements declined with successive leachings (rebounding slightly in the final M3 leachate), with concentrations typically greater in the M7 leachate. Elemental losses followed the same general ranking (28 > 16 > 4 > 37°C); losses at 28°C were 15 to 22% for As, Cd, Ni, and Zn from the M7 peat; losses from M3 were comparable only for Cu (1%) and Ni (19%). The correlation of respiration with S, DOC, and trace elements losses indicates that microbial processes mediated the release of trace elements in both peat soils. Neutral M3 peat pH levels limited losses of most analytes.

PEAT LANDS are ubiquitous throughout the world, many of which have elevated levels of heavy metals and other trace elements compared with the surrounding mineral soils (Damman, 1978; Hvatum et al., 1983; Pakarinen et al., 1983; Gignac and Beckett, 1986; Glooschenko and Arafat, 1988; Glooschenko, 1989). Especially high concentrations for Cu, Zn, Pb, Ni, and Cd were found in the acidic peat profiles of Quebec (Canada), with Cu concentrations in nonacidic cupriferous peats of New Brunswick ranging from 1.0 to 68 g kg^{-1} (Kendrick, 1962). Some peat bogs of western New York, developed on Silurian dolomites rich in Zn, have Zn concentrations as high as 70 g kg^{-1} (Cannon, 1955); a small fraction is water soluble, ranging from 39 to 195 mg L^{-1} (Staker, 1942).

Many of the New York peat soils have been drained for agriculture. In areas rich with Zn, trace metal concentrations in surface water increased, seemingly as a direct consequence of drainage and oxidation of Zn sulfides (Cannon, 1955). The maximum Zn concentration in drainage water was 11 mg L^{-1}, with concentrations in aboveground plants as high as 10 g kg^{-1}. The high concentration of Zn in drainage water is a threat to surface and ground water quality, and has raised concern about other toxic trace elements (e.g., Cd) that may be present in the peat and released in soluble forms.

Acidification, oxidation–reduction shifts, and preferential attachment to dissolved organic matter (facilitated transport) have been associated with the release of trace elements from soils into drainage water. Acidification of soils can occur as a result of microbial processes (oxidation of organic sulfur and sulfide minerals, nitrification, nitrogen fixation, and decomposition of organic matter) as well as by depletion of bases by leaching (Martin and Bullock, 1994). Tipping et al. (2003) measured and simulated the release of metals from industrially contaminated peats following drought-induced aeration and acidification.

Olivie-Lauquet et al. (2001) suggested that the soil microbial population may play a dominant role in controlling the release of trace elements into water, with greater concentrations of trace elements found in summer months. Among the few studies devoted specifically to the role of microorganisms in metal mobilization, Chanmugathas and Bollag (1987, 1988) concluded that soil microorganisms were responsible for the transformation and subsequent mobilization of Cd in soil. Peterson et al. (1997) found that 2% of particulate-bound Cd, Cu, and Zn were remobilized from polluted anoxic sediments and that biological activity had a significant effect on the release. Dissolved organic carbon (DOC) has been shown to significantly influence the mobility of heavy and transition metals in soil and subsurface environments (Kuiters and Mulder, 1989; McBride et al., 1997). Production and release of DOC from soils is complex, dependent both on microbial as well as abiotic factors (Kalbitz et al., 2000), and is typically greater following dry periods (Zsolnay and Gorlitz, 1994; Kalbitz et al., 2000).

In recent studies, Qureshi et al. (2003) showed that microbial acidification enabled substantial leaching of trace elements from wastewater sludge when the conditions for microbial growth were favorable and where no soil matrix was present for readsorption of the released metals. The extent of acidification and leaching in these studies was correlated with the level of microbial activity, which was manipulated via incubation temperature and the presence of biocides. In this present study, we

Abbreviations: DOC, dissolved organic carbon; ICP, inductively coupled plasma.

sought to repeat this approach to observe the effect of microbial activity on metal release from metalliferous peats under aerobic conditions. Our specific objectives were to (i) use incubation temperatures to achieve varying levels of microbial activity in two metalliferous peats and (ii) use periodic leaching to assess the extent of trace element release from these soils.

MATERIALS AND METHODS

Two high-Zn peats from the Elba, NY region were incubated at four different temperatures (4, 16, 28, and 37°C). The peat was mixed with glass beads as a support matrix to assure sufficient aeration. The release of trace elements was determined by periodic leaching with synthetic acid rainfall. Microbial activity was assessed with short-term glucose stimulation tests.

Peat Description

Neutral (pH 7) peat, designated "Manning 3" in Martinez et al. (2002) and abbreviated as M3 here, was collected from the surface soil (plow layer) in an agricultural area. The second peat, designated "Manning 7" in Martinez et al. (2002) and abbreviated as M7 here, had a pH of 5 and was from an area that had been abandoned for agriculture because of low yields. Martinez et al. (2002) reported that the soils were drained for agriculture circa 1940. Samples were collected, air-dried, and stored for several years before use. Table 1 shows the total concentration of selected trace elements analyzed including very high Zn concentrations. The Zn concentrations are attributable to the underlying mineralized beds of the Lockport dolomite of the Niagaran age, rich in sphalerite (Cannon, 1955). The soils tested here were characterized extensively by Martinez et al. (2002), including the fraction of total S in varying oxidation states shown in Table 1. Only a small fraction of total S was found in the most oxidized state (sulfate), with the balance of total S divided between the most reduced (sulfide, thiol) and intermediate (sulfoxide, sulfonate) forms.

Incubation and Leaching

Approximately 35 g of dry peat was weighed and mixed thoroughly with 600 g of 1.2-mm-diameter glass beads. The mixture was placed as a 5-cm-thick layer, at the top of a 3-cm layer of 2-mm-sized glass beads in a 10-cm-diameter × 8-cm-tall column. Glass beads were used to maintain aerated conditions, as an inert substrate to avoid adsorption, and to simulate field conditions where peat can be applied as a source of organic mater in coarse-textured soil. For each peat, three

replicate columns were incubated at each temperature (4, 16, 28, and 37°C).

Each column leaching experiment consisted of four cycles of 7.3 d of incubation, then 16 h of leaching with rain at an intensity of 2.5 mm h^{-1}, followed by a final incubation of 28 d and leaching of 16 h with the same rain intensity. Incubation was done in constant temperature chambers. Rain was applied with a rainmaker apparatus using synthetic acid rain at 16°C. Synthetic acid rainfall was prepared by adding acid and salts (Table 2; Richards et al., 2000) to tap water. Leachate was collected for two 8-h periods. After free drainage had ceased, the columns were returned immediately to the temperature chambers for the next incubation cycle. During incubation, moisture in the columns was kept constant by weighing the columns and spraying the same amount of water that had evaporated from the columns every other day. At 37°C, water application was performed daily because of the high evaporation rate.

Leachate pH was determined immediately after collection using a standardized pH meter. The percolate was then filtered through acid-washed cellulose filters (0.45-μm pore size). Dissolved organic carbon (DOC) analysis of the percolate was performed by using an OI Analytical (College Station, TX) Model 1010 wet oxidation total organic carbon analyzer using persulfate oxidation. The complexation capacity of DOC was expressed as moles of charge per liter, calculated using the fulvic acid charge density of 11.2 mol of charge kg^{-1} (Sposito, 1989).

As Zn was the most mobile element in previous work, a preliminary screening analysis of all percolates collected over the eight weeks was performed by flame atomic absorption (AA) spectroscopy. The screening analysis was used to save costs by allowing us to composite samples before analysis by inductively coupled plasma (ICP) spectroscopy. For the first, second, and eighth week, samples of the first 8 h and last 8 h of each leaching episode were combined into volume-weighted composites before analysis. Furthermore, all leachate samples from Weeks 3 and 4 were composited for a single sample because Zn concentrations from Week 3 onward were essentially unchanged. The composited leachate samples were filtered (0.45-μm porosity) and analyzed by ICP spectroscopy (Thermo Jarrell Ash IRIS Advantage ICP with a duoview torch; Thermo Elemental, Franklin, MA). The ICP analysis of leachate S yields total dissolved sulfur only, with no discrimination between sulfate, elemental, or organic forms of S. Because of a bias in AA results for Zn (which were in good agreement with ICP results up to 5 mg L^{-1}), ICP Zn results were used.

Table 1. Peat analysis by inductively coupled plasma (ICP).

Analyte	M3 neutral peat	M7 acidic peat
pH	7	5
Soil organic matter†, %	78	82
Ca, mg kg^{-1}	64 920	25 770
Mg, mg kg^{-1}	2 190	1 663
Zn, mg kg^{-1}	5 350	3 582
Cu, mg kg^{-1}	80	131
Ni, mg kg^{-1}	16.5	19
Cd, mg kg^{-1}	4.5	3.7
As, mg kg^{-1}	28	16
S (total), mg kg^{-1}	8 346	8 470
Forms of S (oxidation states)†, % of total S		
Most reduced (+0.02–0.9)	43.5	35.5
Intermediate (+1.2–5)	51.8	61.3
Most oxidized (+6)	4.6	3.2

† Soil organic matter and sulfur state data are from Martinez et al. (2002).

Table 2. Synthetic acid rain preparation and analysis.

Property	Value
	mg L^{-1}
Additions made to tap water (Richards et al., 2000)	
Na$^+$	0.15
NH$_4^+$	0.32
K$^+$	0.09
SO$_4^{2-}$	3.96
Ca^{2+}	0.83
NO$_3^-$	2.88
Mg^{2+}	0.08
Cl$^-$	0.47
Analysis results of synthetic acid rain	
Total S	78.9
Ca	50.4
Cu	0.022
Ni	0.011
Zn	0.073
Rain pH (pH units)	4.0–4.5

All leachate samples analyzed for trace elements were also analyzed for nitrate using a method modified from that of Vendrell and Zupancic (1990). Leachate samples (200 μL) were placed into empty color development tubes, and 1 mL of 6% salicylic acid in concentrated H_2SO_4 was added to each tube. After 20 min, 20 mL of 2.2 M NaOH was added to neutralize the acid. After all reagents were mixed, the sample tubes were allowed to cool for approximately 45 min, and nitrate in the samples was quantified by absorbance (wavelength = 410 nm) measured using a Milton Roy (Ivyland, PA) Spectronic Model 1001 Plus spectrophotometer.

The synthetic acid rain was analyzed by ICP so that mass balances could be compensated for elements present therein. Substantial Ca and S were present in tap water, so those elements were in excess of typical acid rainfall levels (Table 2). Trace levels of Ni (0.011 mg L^{-1}), Cu (0.022 mg L^{-1}), and Zn (0.073 mg L^{-1}) were also observed; other analytes (Cd, As) were not detected. Leachate data presented here represent net concentrations (i.e., after subtracting rainfall input concentrations).

Peat Analysis

To measure the pH of the peat, 5 g (dry weight) was mixed with 10 mL of distilled water in a 50-mL beaker. After 24 h, the pH of the soil suspension was measured with a standardized pH meter. Trace elements were analyzed following nitric–perchloric digestion using a Thermo Jarrell Ash IRIS Advantage ICP with a duoview torch.

Microbial Respiration

As an indicator of microbial activity, respiration following stimulation with glucose was measured at all temperatures for both fresh (before leaching) and aged (after eight weeks of incubation–leaching cycles) samples of the M3 and M7 peat soils. The amounts of CO_2 released from the peat were measured following stimulation with glucose addition. Five grams of peat (dry weight) was added to a 250-mL flask followed by 5 mL of a solution containing 1 g L^{-1} glucose and 20 mg L^{-1} yeast extract. The rate of glucose C amendment was 400 μg C per gram of dry peat, similar to that proposed by Dahlin et al. (1997). A 10-mL glass tube containing 8 mL of NaOH was placed in the flask to trap and measure the evolved CO_2. The flasks were closed hermetically, placed on a rotary shaker set at 120 rpm, and incubated in triplicate for 28 h at each temperature. After each 4-h interval, the NaOH solution was removed and replaced with a fresh solution without opening the flask by using a needle-sampling system. The amount of CO_2 released was measured by determining the quantity of NaOH that had not reacted with CO_2 in the samples compared with that of the control. The NaOH was neutralized with HCl using a pH-controlled dispenser in the presence of excess $BaCl_2$ added to precipitate carbonate ion as insoluble $BaCO_3$ (Stotzky, 1997). Error caused by HCO_3^- remaining in solution was considered in these experiments, but previous measurements of evolved CO_2 after identical incubation times in flasks acidified just before the NaOH removal showed this error to be negligible (Dumestre et al., 1999).

Statistical Analysis

The effects of three factors (temperature, time, and treatment) were analyzed using SAS/Proc to compute orthogonal polynomials and SAS/GLM to run the analyses (SAS Institute, 1996). The three-factor interaction has been used as an error term, but it is not appropriate here as some parameters of the three-factor interaction represent real effects. We used treatment by linear and quadratic effects of time and temperature. An exploratory model procedure presented by Bozivich et al. (1956) and applied by Federer (1998) was used to determine which of these three-factor interaction parameters to retain in the model. Treatment means were compared for statistical difference with Duncan's Multiple Range test (SAS Institute, 1996).

RESULTS

Microbial Respiration

Mineralization of glucose started immediately after the addition of substrate, reaching its maximum rate after 25 h and subsequently stabilizing. For both peat types, the greatest microbial respiration was at 28°C and decreased with temperature (Fig. 1). However, microbial respiration was lowest at 37°C, consistent with trends observed in our previous work (Qureshi et al., 2003). The M7 acidic peat had a significantly greater cumulative respiration ($P < 0.0001$) than the M3 neutral peat at all temperatures. Moreover, at 28°C cumulative respiration was significantly greater ($P < 0.0001$) for the initial peat compared with the leached samples.

Leachate pH, Sulfur, Nitrate Nitrogen, and Dissolved Organic Carbon

Following one week of incubation, the first cycle leachates had pH values of 2.0 to 2.4 for the acidic M7 peat (Fig. 2), gradually rising to 4.4 at the end of the experiment, approximately equal to the pH of the rainwater. The pattern for the M3 neutral peat was similar although at less acidic levels, with first-week leachate values of 2.6 to 4, increasing to the pH of the peat itself in subsequent leaching cycles. For both soils the 28°C treatment produced the most acidic leachates.

As noted earlier, leachate concentrations shown have been corrected for any elements present in the synthetic acid rainwater. Dissolved total S concentration in the M7 acidic peat leachate was significantly greater than in the M3 leachate ($P < 0.0001$) at comparable times
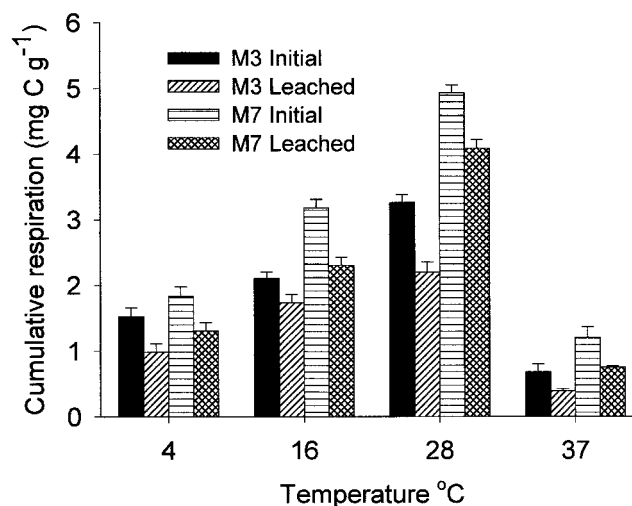

Fig. 1. Cumulative respiration (mg carbon mineralized per gram peat solids) for both initial and leached M3 and M7 peat soils. Error bars represent ±1 standard deviation.
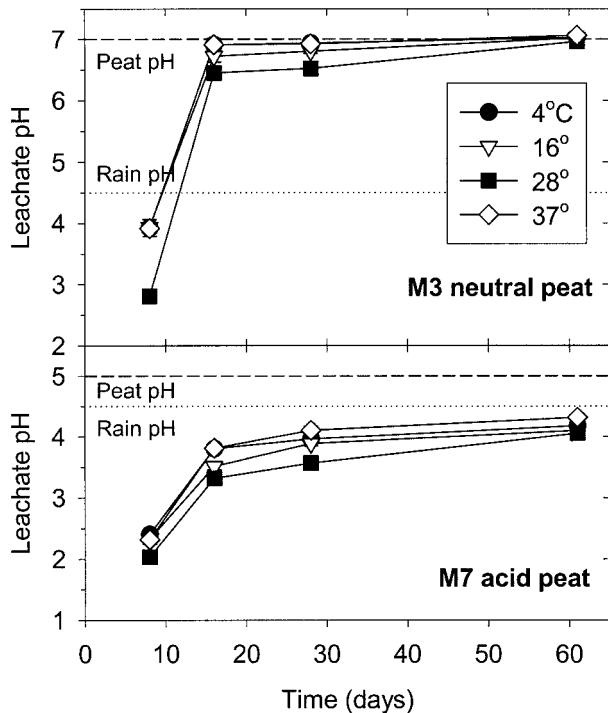
Fig. 2. Leachate pH as a function of time and incubation temperature. Dashed lines indicate peat soil pH, dotted lines indicate rainfall pH. For this and similar figures, cumulative time (incubation plus leaching) is plotted on the *x* axis, with the composited Week 3 + 4 sample plotted midway between the Week 3 and 4 leachings.

Table 3. Percent loss of elements in the leachate at different temperatures in low and neutral pH peat.

Element	Temperature (°C)			
	28	16	4	37
	M7 acidic peat			
As	21.5a†	16.2b	12.0c	9.6c
Ca	37.2a	14.8b	8.4c	6.2d
Cd	15.0a	12.2b	7.0c	5.9c
Cu	0.9a	0.6b	0.4b	0.2c
Ni	17.2a	15.5a	11.8b	9.7b
S	31.3a	27.0b	14.9c	10.4d
Zn	14.9a	14.6a	10.7b	9.0c
	M3 neutral peat			
As	5.6a	5.2ab	4.0bc	3.5c
Ca	21.0a	6.3b	3.3c	2.8c
Cd	0.6a	0.4ab	0.3b	0.2b
Cu	1.0a	0.7b	0.4c	0.2d
Ni	19.0a	12.0b	9.8bc	7.5c
S	14.7a	8.8b	5.7c	3.3d
Zn	1.7a	1.0b	1.0b	0.8b

† Numbers followed by similar letters are not significantly different between temperature treatments (α = 0.05).

throughout the experiment except for the final leachate (Fig. 3). In the first week's M7 leachate, the S concentrations were significantly greater at 28 and 16°C than other
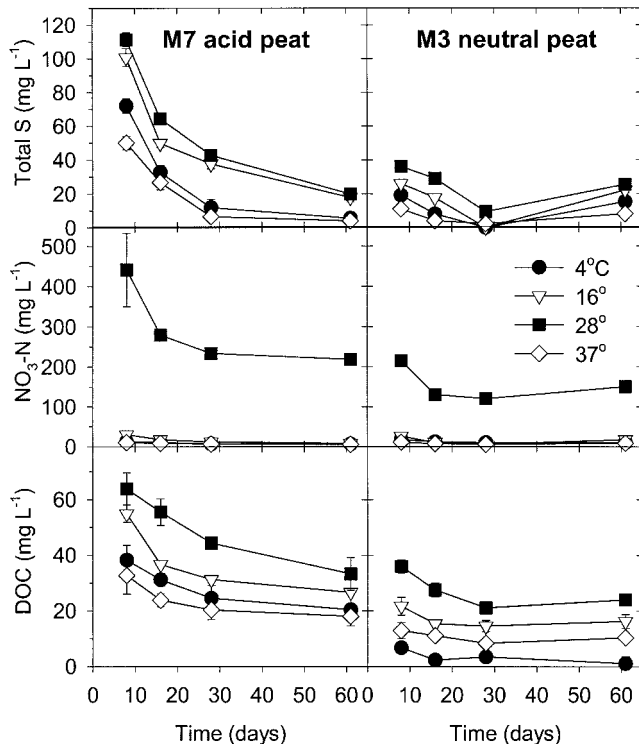

Fig. 3. Leachate total S, NO$_3$–N, and dissolved organic carbon (DOC) concentrations as a function of time and incubation temperature.

treatments ($P = 0.0025$). The lowest concentrations were observed at 37°C during all incubation–leaching cycles. A similar response to temperature was observed in the M3 neutral peat, but mean concentrations were approximately one-third of that in the M7 peat. The lower S concentrations at 37 and 4°C were consistent with our wastewater sludge leaching work (Qureshi et al., 2003). The cumulative S recovery in the leachate after five incubation–leaching cycles was 28 and 14% at 28°C for the M7 and M3 peats, respectively (Table 3).

The greatest concentrations of NO$_3$ (expressed as NO$_3$–N) occurred at 28°C (Fig. 3), with the M7 acidic peat leachate significantly greater ($P < 0.0001$) than the M3 peat, with concentrations in both treatments stabilizing over time and, in fact, slightly increasing in the final M3 leachate. Concentrations at all other temperatures were an order of magnitude lower.

The patterns of leachate DOC concentration were somewhat similar to those for total S (Fig. 3). In the M7 acidic peat, significantly greater concentrations of DOC were observed at 28 and 16°C ($P < 0.0001$), decreasing with time. The DOC concentrations decreased approximately by half as incubation temperature decreased to 4°C. Leachate DOC concentrations for M3 neutral peat were approximately half those of the M7 peat, with concentrations increasing slightly during the final leaching cycle. Assuming the charge density of fulvic acid, DOC concentrations can also be expressed as millimoles of charge; the full scale value of 80 mg L^{-1} DOC in Fig. 3 is equivalent to 0.90 mmol L^{-1}. Peak leachate values were 0.72 (M7 peat) and 0.40 (M3) mmol L^{-1} at 28°C.

Leachate Trace Element Losses

As with other analytes, the leachates from the first incubation–leaching cycle consistently had the greatest concentrations of trace elements, as shown for Zn, Ni, and As in Fig. 4 (M7 acidic peat) and Fig. 5 (M3 neutral peat). Concentrations were typically greater from the M7 peat compared with M3, and all treatments saw
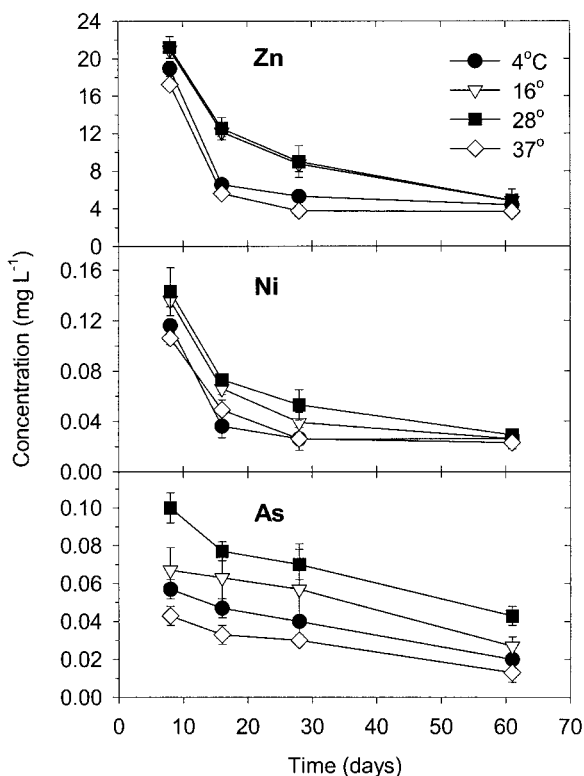
Fig. 4. Leachate Zn, Ni, and As concentrations as a function of time and incubation temperature for M7 acidic peat.
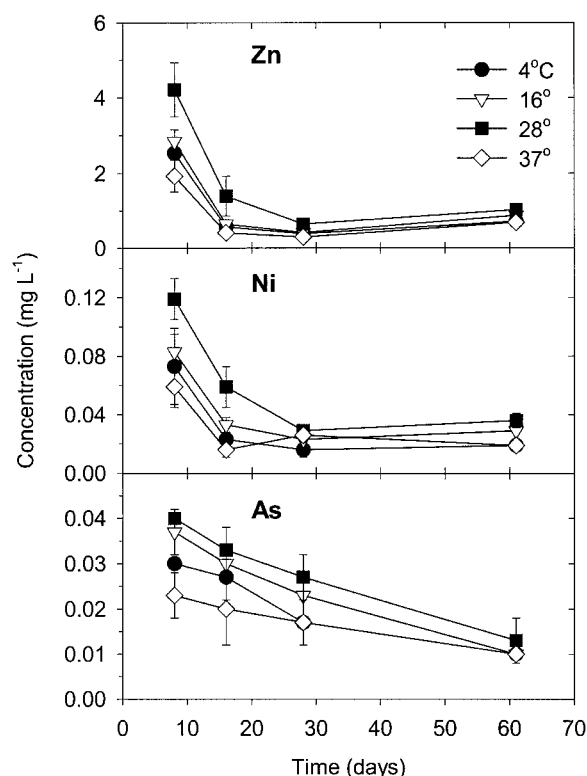

Fig. 5. Leachate Zn, Ni, and As concentrations as a function of time and incubation temperature for M3 neutral peat.

concentrations diminish with time, although concentrations for several analytes rebounded slightly for M3 after the extended final incubation period (Fig. 5). For each peat, leachate concentrations were greatest at 28°C.

Elemental losses to leachate are summarized as percent loss of the initial peat concentration in Table 3. The general ranking of percent losses observed among temperature treatments was $28 > 16 > 4 > 37$°C. In only four cases (M7 Ni and Zn; M3 As and Cd) was the observed difference between the 28 and 16°C treatment not statistically significant ($P \leq 0.05$). Similarly, in five cases (M7 Cu; M3 As, Cd, Ni, and Zn) the 16°C treatment loss was not significantly greater than 4°C. The losses at 4°C were significantly greater than 37°C ($P \leq 0.05$) in only 6 of 14 cases.

Leachate As concentrations were greatest for the M7 acidic peat (100 μg L^{-1} at 28°C), with somewhat lower leachate As measured from the M3 peat despite higher total As in that soil (Table 1). Maximum As recoveries in leachate were 21.5% for the M7 acidic peat and 5.6% for the M3 neutral peat (Table 3). Leachate concentrations of Ca were approximately the same for both types of peat ($P = 0.058$). Although the M7 acidic peat had much less total Ca, it was presumably more strongly mobilized by the greater H$^+$ activity in the leachate and/or by affinity for the elevated DOC. As a result, the M7 peat lost a larger fraction of its total Ca at all temperatures, with 37% lost at 28°C.

Cadmium concentrations as well as percent loss were significantly greater for the M7 acidic peat ($P < 0.0001$), with maximum losses of 15% from the M7 peat in con-

trast to less than one percent from the M3 neutral peat. Peak Cd concentrations were between 25 and 30 μg L^{-1} from the acidic M7 peat but less than 2 μg L^{-1} from the M3 peat. Leachate concentrations and losses of Cu were similar for both peats, with maximum losses of only 1% observed at 28°C. Leachate Ni concentrations were slightly lower for the neutral M3 peat, but percent losses were similar for both peats due to the differences in initial peat concentrations. Percent S losses were much greater from the M7 acidic peat, with maximum levels of 27 to 31% at 28 and 16°C. Percent losses of Zn recovered in the leachate were up to 15% of the total Zn from the M7 acidic peat in contrast to less than 2% for the M3 neutral peat.

DISCUSSION

Because the soil samples used in this experiment had been air-dried before storage and subsequent use, the results shown here represent effects that would occur during rewetting. This is analogous to summer conditions on drained peats, where the surface usually dries out with periodic wetting by rains. Our experiment shows that the first leachate is likely to be acidic and may contain elevated concentrations of trace elements (especially Zn) and dissolved organic matter. The review of Kalbitz et al. (2000) shows that an increase in DOC after rewetting a dried soil is one of the most consistent findings of both laboratory and field studies. However, under field conditions, the percolate reaching the ground or surface water can be significantly mitigated due to soil readsorption of H$^+$ ions and/or trace elements.

The glucose respiration tests served as a measure of how effective the incubation temperature treatments were at altering overall microbial activity. The greatest respiration rate occurred at 28°C followed by 16 and 4°C. The lower microbial activity at 37°C, consistent with that observed in our earlier experiments (Qureshi et al., 2003), is attributable to fewer bacterial species present that are adapted to that temperature. The reason for generally higher microbial respiration rates in the M7 low pH peat (with the greatest total and soluble Zn concentrations), compared with the M3 neutral pH peat is unclear, although it has been noted. Heavy metal toxicity can actually lead to higher specific microbial respiration, as shown by Brookes and McGrath (1984). It can be hypothesized that toxic levels of soluble Zn and Cd in the low pH peat suppress the growth of many bacterial species, but that acidophiles such as *Thiobacillus thiooxidants* thrive and promote the oxidation of sulfur to sulfate with a concomitant release of Zn, Cd, and other metals from insoluble sulfide forms. The high DOC generated in the low pH peat may reflect the lack of bacterial species able to decompose low molecular weight organic acids in this high Zn environment. Kalbitz et al. (2000) report that the role of pH on DOC release is fragmentary, with some studies showing no effect of decreasing pH on DOC mobilization, and others showing acidic inputs actually enhancing organic matter solubilization.

Our measurements of microbial respiration correlated strongly with many leachate parameters. Figure 6 compared first incubation–leaching cycle leachate concentrations of total S, DOC, and Zn with initial cumulative respiration. Data shown represent both peats at all temperatures (following the temperature treatment order indicated on the first plot). Total dissolved S (which itself correlated with leachate pH) correlated especially strongly for the M3 peat (linear regression $r^2 = 0.99$) as well as for the M7 acidic peat ($r^2 = 0.90$), suggesting microbial mobilization of S via oxidation. Correlations were strong for DOC and for Zn, again indicating microbial processes. While Fig. 6 shows initial leachate parameters vs. initial respiration, Table 4 presents values representing the entire experiment. Linear regressions in this table were calculated using mean (initial and leached) cumulative respiration (Fig. 1) vs. overall percent losses (Table 3). Linear regression slopes were all positive indicating covariance, and the r^2 correlation coefficients were good, ranging from 0.888 to 0.996 (mean 0.95) for the M7 acidic peat and from 0.783 to 0.993 (mean 0.91) for the M3 peat.
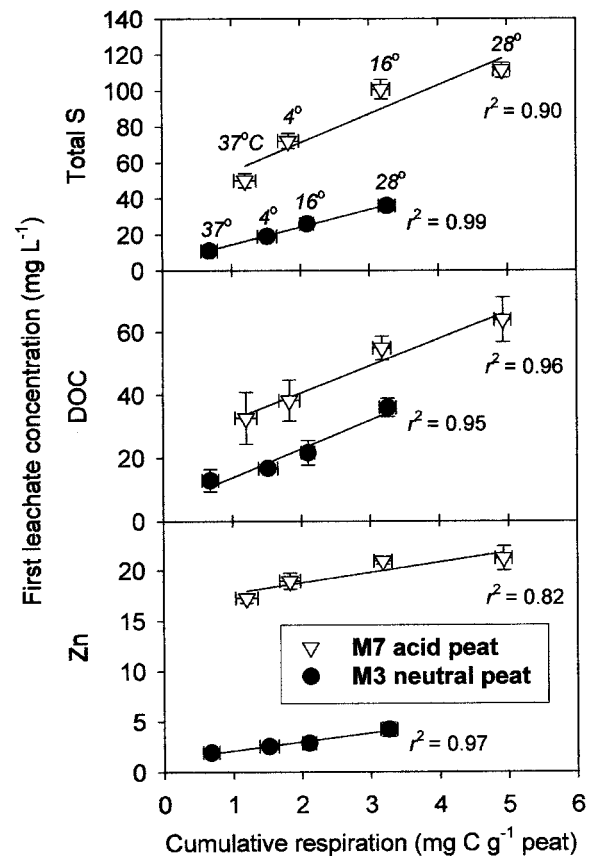

Fig. 6. First cycle leachate concentrations of total S, dissolved organic carbon (DOC), and Zn as a function of initial cumulative respiration. Correlation coefficients (r^2) are from linear regressions.

The most likely factors arising from microbial activity that directly can mobilize trace elements are acidification and release of DOC. As shown in the data of Martinez et al. (Table 1), there was a substantial pool of peat S in varying reduced forms available for oxidation. Only a small fraction of total S was found in the most oxidized state (sulfate), with the balance of total S divided between the most reduced (sulfide, thiol) and intermediate (sulfoxide, sulfonate) forms. Reduction in pH is at least partially caused by the microbial oxidation of sulfur and nitrogen (Blais et al., 1993; Couillard et al., 1994). Devito et al. (1998) and Devito and Hill (1999) linked pulses in sulfur release from wetlands to dry summers, when lower water levels allowed aeration of previously anoxic peat. The resulting S oxidation resulted in elevated sulfate concentrations and acidification of both surface and pore water. Thus, the first rain caused the microbial

Table 4. Linear regression results correlating mean cumulative respiration (independent variable) and percent trace element loss (dependent variable) at all temperatures.

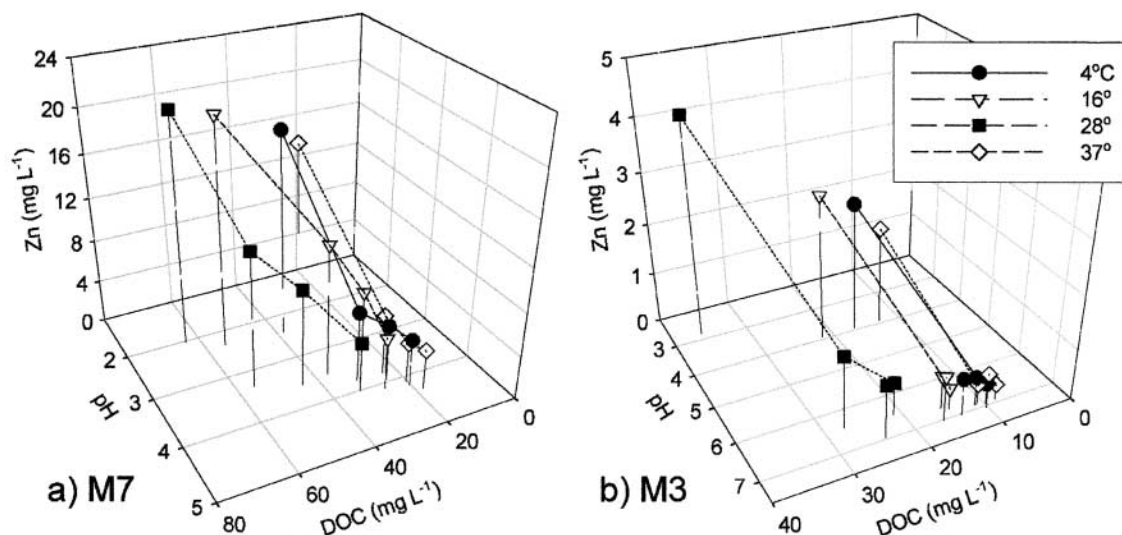| Element	M7 acidic peat			M3 neutral peat		
	Constant	Coefficient	R^2	Constant	Coefficient	R^2
As	5.94	4.29	0.996	2.92	1.00	0.978
Ca	−5.82	10.95	0.888	−4.65	8.09	0.783
Cd	2.51	3.59	0.985	0.04	0.20	0.992
Cu	−0.06	0.29	0.983	−0.02	0.37	0.993
Ni	6.92	2.96	0.976	3.74	5.37	0.889
S	5.60	7.07	0.905	−2.83	5.67	0.881
Zn	7.20	2.42	0.899	0.42	0.42	0.863

Fig. 7. Leachate Zn concentrations as a function of leachate pH and dissolved organic carbon (DOC) concentration for (a) M7 acidic peat and (b) M3 neutral peat.

population to increase, presumably stimulated by the accumulated dissolved compounds in the dry peat (Olivie-Lauquet et al., 2001). In the later leaching cycles, pH increased to 4.0 and 7.0 for low and neutral pH peat, respectively. The pH increase is attributable to the peat buffering capacity, as indicated by the leaching of Ca, a direct consequence of proton adsorption by the organic matter. Much greater Cd and Zn concentrations appeared in the M7 peat leachates compared with the M3 neutral peat; these two metals tend to be most readily desorbed by acidity. In the M3 neutral peat, the limited release of Cd and Zn may be at least partially due to the oxidation of S.

The presence of DOC provides a mobile ligand that has been shown to facilitate mobility of trace elements (Camobreco et al., 1996; McBride et al., 1997; Richards et al., 1997). The comparable leaching loss of Ni from the M3 neutral pH peat can be explained as a result of the action of DOC in complexing Ni at a higher pH. Some peat soils are known for high levels of Ni in easily soluble organic complexes (Kabata-Pendias and Pendias, 1991). The M3 leachate DOC, expressed as millimoles of charge, ranged between 0.24 and 0.40 mmol L^{-1} at 28°C, in contrast to peak Ni concentrations of 0.002 mmol L^{-1}, indicating more than adequate complexation capacity.

Figures 7a and 7b show the interplay of acidification and DOC concentration on leachate Zn at all temperatures. Decreases in either or both of these factors over time were accompanied by corresponding decreases in leachate Zn. In fact, this interplay is also seen in the slight upturn in M3 Zn in the final 28°C leachate (Fig. 7b), which corresponded to an increase in DOC despite an increase in pH.

Leachates from both peats contained substantial concentrations of As (up to 100 μg L^{-1}) despite relatively low total As in the soils (<30 mg kg^{-1}). This suggests the potential for As contamination of shallow ground water in peaty soils. The ICP analysis of total dissolved

As could not distinguish between species of As (e.g., arsenite, arsenate, or organo–arsenic). Correlation of As release to microbial activity, most likely S oxidation, may suggest that As in the peat soil may have been in a reduced form bound to sulfides. For neutral pH peats, As has a tendency to bind with DOC and, hence, can be highly mobile (Kalbitz and Wennrich, 1998). It may therefore be important to monitor arsenic levels in wells in peat soil areas.

Finally, previously unpublished drainage water data from the Elba peatlands (Table 5) indicates that the leaching of trace elements observed in this experiment occurs to some extent in the field. Data from both 1977 and 2001 show drainage water Zn concentrations ranging from 0.9 to 2.0 mg L^{-1}, with Cd concentrations an order of magnitude lower at 0.2 to 1.2 μg L^{-1}. These concentrations are an order of magnitude lower than the *peak* (first leachate) concentrations observed in our study, but it should be remembered that the drainage samples represent longer-term integrated samples. A stream flowing into and out of the peatlands experienced a substantial (12-fold) increase in soluble Zn with a smaller twofold increase in Cd (Table 5), reflecting a proportionately greater mobilization of Zn. This was consistent with the findings of Martinez et al. (2002), who found that Cd in these soils was preferentially immobilized by sulfides and organic matter. Sundstrom

Table 5. Dissolved Zn and Cd concentrations measured in 1977 and 2001 in water samples from the Elba, NY peatlands (McBride, unpublished data, 2002).

Site	Zn	Cd
	mg L^{-1}	μg L^{-1}
	Sampled in 1977	
Peatland Drainage Ditch 1	2.0	1.2
Peatland Drainage Ditch 2	1.9	0.8
Stream above peatland	0.05	0.3
Stream after peatland	0.60	0.7
	Sampled in 2001	
Farm Field Drainage Cistern 1	0.90	0.6
Farm Field Drainage Cistern 2	1.42	0.2

et al. (2002) observed substantial streamwater metal loadings resulting from aeration and acidification of soils.

The fact that substantial concentrations of labile trace elements as well as reduced S remain in these soils some 60 years after initial drainage for agricultural use deserves consideration. This experiment did not simulate the complete annual cycle of temperatures and moisture status that soils in this setting experience, nor did it simulate more than the surface soil layer. Soils are commonly allowed to saturate between growing seasons, which would result both in upward translocation of leached elements as water levels rise as well as S reduction and reimmobilization of trace elements due to the onset of anoxia in the resaturated peat. A degree of immobilization could also be expected to occur during the growing season if leached metals are transported into the saturated anoxic subsoil horizons. The total system thus needs to be considered to assess net mobilization and loss of trace elements from these soils.

CONCLUSIONS

Our results suggest the importance of microbial activity in the release and leaching of trace elements from metalliferous peat soils. The incubation temperature treatments resulted in cumulative respiration measurements with relative rankings of $28 > 16 > 4 > 37°C$, with M7 acidic peat respiration values greater than M3 neutral peat at each temperature. The extent of acidification after the initial rewetting followed the same pattern; initial leachate pH levels for all treatments were between pH 2 and 4, with acidification less pronounced and shorter-lived for the M3 neutral peat. Leachate S, DOC, NO_3–N, and trace elements all declined with successive leachings (although concentrations rebounded somewhat in the final M3 neutral peat leaching cycle), with concentrations typically greater in the M7 acidic peat leachate. Trace elemental losses tended to follow the same ranking pattern ($28 > 16 > 4 > 37°C$) with losses at 28°C ranging between 15 and 22% for As, Cd, Ni, and Zn from the M7 acidic peat; losses from the M3 neutral peat were generally lower, comparable with M7 only for Cu (1%) and Ni (19%). The correlation of respiration with losses of S, DOC, and trace elements is a strong indication that microbial processes facilitate and mediate the release and leaching of trace elements in both neutral and acidic peat soils. The near-neutral M3 soil pH levels limited the potential leaching losses of most analytes.

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