Water Quality

Diel Changes in Iron(III)/Iron(II) in Effluent from Constructed Acid Mine Drainage Treatment Wetlands

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ABSTRACT

Within the past decade, over 400 wetlands have been constructed to treat acid coal mine drainage (AMD). This study was undertaken to examine whether the efficiency with which constructed wetlands retain Fe present in AMD changes on a day–night basis. In each of five AMD treatment wetlands, constructed with a different organic substrate (*Sphagnum* peat with limestone and fertilizer, *Sphagnum* peat, sawdust, straw–manure, or mushroom compost), hourly sampling of inflow and outflow waters was conducted over a 19-h (July 1990) and 24-h period (May 1991). The chemical composition of the influent AMD was relatively stable over the duration of either sampling period. However, a striking diel pattern of shifts in the relative abundances of Fe^{2+} and Fe^{3+} in outflow waters was observed for both *Sphagnum* peat wetlands on both sampling dates, and for the straw–manure and mushroom compost wetlands on the May 1991 sampling date. Prior to sunrise, 75 to 100% of the soluble Fe in outflow waters was Fe^{2+}; prior to sunset, 62 to 88% of the soluble Fe was Fe^{3+}. The documented diel shifts in Fe^{3+} vs. Fe^{2+} abundance in outflow waters are greater in magnitude than any previously reported for a natural system and suggest that the cycling of Fe in AMD treatment wetlands is more dynamic than previously recognized and that standard daytime only sampling protocols are inadequate for assessing Fe retention–release in AMD treatment wetlands.

EXPOSURE of pyrite or other sulfide minerals to oxygen and water during coal or metal mining can result in the formation of acid mine drainage (AMD). Although the chemistry of AMD is highly variable, it is generally characterized by low pH and elevated concentrations of dissolved Fe, SO_4^{2-}, and often other dissolved metal cations (Barton, 1978). Prior to the enactment of the Federal Surface Mining Control and Reclamation Act (SMCRA) of 1977 (Public Law 95-87), uncontrolled discharges of AMD had impacted 9120 km of streams in the Appalachian Coal Mining Region alone (Appalachian Regional Commission, 1969). However, regulations established pursuant to the passage of SMCRA require all water discharged from active surface coal mines in the USA to meet water quality criteria specified by either federal or state regulatory agencies. Typical effluent limitations are: pH between 6 and 9; dissolved Fe <7 mg L^{-1} (125 μmol L^{-1}) for any individual sample and <4 mg L^{-1} (72 μmol L^{-1}) for a monthly average; dissolved Mn <4 mg L^{-1} (73 μmol L^{-1}) for an individual sample and <2 mg L^{-1} (36 μmol L^{-1}) for a monthly average; suspended solids <70 mg L^{-1} for any individual sample and <35 mg L^{-1} for a monthly average. Despite inspection and enforcement powers of federal and/or state regulatory agencies and substantial penalties for failure to comply with effluent limitations, AMD continues to be a widespread environmental problem (Herlihy et al., 1990).

Treatment of AMD by the addition of chemical neutralizing agents to raise the solution pH of the AMD, often coupled with aeration, is effective in causing the precipitation of metals in insoluble forms; these precipitates are collected in settling ponds prior to discharging water of acceptable quality. Although technologically feasible, conventional chemical treatment of AMD often is quite costly (Kim et al., 1982; Baker et al., 1991). Field observations of the improvement of AMD upon passage through naturally occurring wetlands led to the suggestion that constructed wetlands could provide a *low cost, low maintenance* alternative to conventional chemical treatment (Wieder and Lang, 1982; Kleinmann et al., 1983). Although over 400 wetlands have been constructed to treat AMD, treatment effectiveness has been quite variable (Hellier, 1989; Wieder, 1989; Brodie, 1991; Kleinmann et al., 1991).

The most common approach toward evaluating the effectiveness of a constructed wetland for treating AMD involves the periodic collection of inflow and outflow waters for chemical analysis. In particular, lower concentrations of metals in outflow waters than in inflow waters have been used as indices of effectiveness (Girts and Kleinmann, 1986; Wieder, 1989). Less commonly, either continuous or occasional measurement of water fluxes entering and exiting wetlands has been combined with water chemical composition analyses to estimate the total quantity of metals retained in wetlands receiving AMD (Hedin and Nairn, 1990; Stark et al., 1990; Wildeman et al., 1990; Wieder, 1993). Regardless of which approach is used to evaluate wetland treatment effectiveness, it is typically the case that samples of inflow and outflow water are collected on some regular schedule, which is often weekly or biweekly, but rarely more frequently. An inherent assumption of this approach is that short-term variability in water chemical composition is minimal so that a single water sample can be considered as representative of water chemical conditions for a week or more. This assumption may be reasonable for dissolved constituents like Ca^{2+}, Mg^{2+}, or Na^+ that do not participate in oxidation/reduction reactions and that may not be substantially retained in wetlands (Wieder, 1993). However, the assumption may be considerably less reasonable for Fe, which typically enters a wetland as soluble Fe and for which the near-surface precipitation of Fe(III) oxyhydroxides represents an important retention mechanism within the wetland (Wieder et al., 1985, 1990; Henrot and Wieder, 1990).

For Fe concentrations in waters exiting AMD treatment wetlands, at least two potentially important sources of vari-

ability can be identified: (i) diel changes in the relative abundance of Fe^{2+} vs. Fe^{3+} in inflow and outflow waters because of daytime Fe(III) photoreduction, and (ii) flushing of surface accumulated Fe oxyhydroxides in response to precipitation events, the former of which is considered in this article.

The phenomenon of Fe photoreduction in natural waters is fairly widespread (McMahon, 1969; Miles and Brezonik, 1981; Francko and Heath, 1982; Collienne, 1983; Waite and Morel, 1984; Madsen et al., 1986). Two different AMD-impacted streams in Colorado exhibited daytime dissolution and photoreduction of colloidal hydrous Fe(III) oxides to Fe^{2+}, whereas at night there was a net oxidation of Fe^{2+} (McKnight and Bencala, 1988; McKnight et al., 1988). In constructed wetlands, if daytime photoreduction of surface-accumulated Fe(III) oxyhydroxides were to occur to any substantial extent, Fe retention would be greater at night than in the daytime, and as such the typical daytime sampling regime used by researchers, coal mine operators, and federal and state inspectors would underestimate the effectiveness of the wetland for Fe retention. Thus, this study was undertaken to examine whether the efficiency with which constructed wetlands retain Fe present in AMD changes on a day–night basis.

METHODS

During the summer of 1989, five wetlands were constructed at the Earle C. Clements Job Corps Satellite Facility in Greenville, KY (Wieder, 1993). Each wetland was 6 m wide and 30 m long and contained 30 cm of one of five organic substrates (Sphagnum peat to which 75 kg of pelleted limestone and 70 kg of 10-10-10 fertilizer were surface-applied on a quarterly basis, Sphagnum peat, sawdust, straw-manure (composted horse barn cleanings), or spent mushroom compost). The wetlands were underlain by plastic liners (4–6 mil thickness) to prevent loss of wetland water by seepage and to prevent groundwater from entering the wetlands. Beginning in late June 1989, each wetland received inputs of AMD (pH 2.9; soluble Fe, 2.13 mmol L^{-1}; SO_4^{2-}, 32.6 mmol L^{-1}) at a mean flow rate of 8510 L d^{-1}. Diel changes in the pH and in the concentrations of Fe^{2+}, Fe^{3+}, and particulate Fe in inflow and outflow waters of each of the five wetlands were evaluated on 17 July 1990 and again on 14 May 1991.

Water entered and exited each wetland through 0.4 H-S weirs; hydrologic fluxes into and leaving each wetland were measured continuously using ISCO Model 2870 flowmeters powered by 12-V deep cycle marine batteries. The flowmeters record instantaneous and totalized flows. On each sampling date, the quantity of water that entered and left each wetland was recorded at hourly intervals. Differences between the maximum and minimum water level depths in any of the weirs over the duration

Table 1. Mean values for water flow, pH, and concentrations of forms of Fe during the 19-h and 24-h sampling of inflows and outflows at the five constructed wetlands. The mean pH value was calculated as the mean H^+ concentration and has been reconverted to pH.

Parameter	Location	Peat with limestone and fertilizer	Peat	Sawdust	Straw-manure	Mushroom compost
				Wetland		
19-hour sampling on 17 July 1990						
Flow (L h^{-1})	In	203[a]*	71[c]	126[b]	113[b]	64[c]
	Out	94[w]	32[y]	65[x]	34[y]	40[y]
pH	In	2.80[a]	2.80[a]	2.81[a,b]	2.82[b]	2.82[b]
	Out	3.16[y]	2.76[w]	2.83[x]	5.40[z]	6.92[z]
Fe^{2+} (mmol L^{-1})	In	0.15[a,b]	0.16[a]	0.12[c]	0.12[c]	0.13[b,c]
	Out	0.94[w]	0.99[w]	0.21[x]	0.03[x]	0.01[x]
Fe^{3+} (mmol L^{-1})	In	1.16[a-c]	1.13[c]	1.20[a]	1.17[a,b]	1.14[b,c]
	Out	0.88[w]	0.43[y]	0.76[x]	0.03[y]	0.04[y]
Soluble Fe (mmol L^{-1})	In	1.31[a]	1.29[a,b]	1.31[a]	1.29[a,b]	1.27[b]
	Out	1.82[w]	1.43[x]	0.98[y]	0.06[z]	0.05[z]
Partic. Fe (mmol L^{-1})	In	0.08[c]	0.08[c]	0.10[b]	0.10[b]	0.13[a]
	Out	0.07[w]	0.05[x]	0.04[y]	0.08[w]	0.07[w]
Total Fe (mmol L^{-1})	In	1.39[a]	1.37[a]	1.42[a]	1.39[a]	1.40[a]
	Out	1.89[w]	1.48[x]	1.02[y]	0.14[z]	0.12[z]
24-hour sampling on 14 May 1991						
Flow (L h^{-1})	In	512[a]	377[b]	383[b]	393[b]	377[b]
	Out	349[x,y]	170[z]	485[w]	458[w,x]	257[y,z]
pH	In	2.89[a]	2.89[a]	2.89[a,b]	2.90[b,c]	2.91[c]
	Out	2.85[y]	2.71[w]	2.80[x]	2.89[z]	3.23[y]
Fe^{2+} (mmol L^{-1})	In	0.33[d]	0.39[c]	0.41[b,c]	0.44[b]	0.55[a]
	Out	0.80[w]	0.72[w,x]	0.22[y]	0.69[w,x]	0.59[x]
Fe^{3+} (mmol L^{-1})	In	1.36[a]	1.33[a,b]	1.34[a,b]	1.31[b]	1.24[c]
	Out	0.57[x]	0.60[x]	0.83[w]	0.46[y]	0.13[z]
Soluble Fe (mmol L^{-1})	In	1.69[c]	1.72[b,c]	1.75[a,b]	1.75[a,b]	1.78[a]
	Out	1.37[w]	1.32[w]	1.06[y]	1.16[x]	0.72[z]
Partic. Fe (mmol L^{-1})	In	0.22[b]	0.26[a,b]	0.30[a]	0.26[a,b]	0.28[a]
	Out	0.08[w]	0.06[x]	0.07[w]	0.05[x]	0.06[x]
Total Fe (mmol L^{-1})	In	1.92[c]	1.98[b]	2.05[a]	2.01[a,b]	2.06[a]
	Out	1.45[w]	1.38[w]	1.12[x]	1.21[x]	0.78[y]

* Values with the same letter superscript (a–d for inflows; w–z for outflows) do not differ significantly based on an analysis of variance, randomized complete design, with hour as the blocked effect ($P < 0.05$).

of each sampling period was less than 1 cm, indicating that both water levels within each wetland and hydrologic fluxes (L h⁻¹) into and out from each wetland remained fairly constant on both sampling dates.

Also at hourly intervals beginning at just before sunrise and continuing until well after sunset, influent and effluent water samples were collected from each wetland. Sample pH was determined immediately on an aliquot of each unfiltered sample using a battery-operated Beckman Model Φ44 pH meter. Particulate Fe was determined by filtering a 50-mL portion of each sample through a 0.45-μm pore size nitrocellulose filter (Micron Separations, Westborough, MA); the filters were retained for later determination of total Fe by dry ashing, hot HCl digestion of the resulting ash, and analysis of the digest solution for Fe concentration by atomic absorption spectrometry. An aliquot of the filtrate from each collected water sample was immediately analyzed for Fe^{2+} concentration using the Ferrozine method (Stookey, 1970). A separate 20-mL aliquot of the filtrate was acidified with concentrated HNO_3 and returned to the laboratory for total soluble Fe determination by atomic absorption spectrometry using an air-acetylene flame. The concentration of Fe^{3+} was calculated as total soluble Fe minus Fe^{2+}.

Both 17 July 1990 and 14 May 1991 were bright, sunny days; mean daytime air temperature was 23.3 and 25.8°C, respectively; mean nighttime air temperature was 14.1 and 18.1°C, respectively; mean daytime inflow water temperature was 28.2 and 25.9°C, respectively; and mean nighttime inflow water temperature was 26.2 and 23.6°C, respectively.

RESULTS

On both sampling dates, differences between wetlands regarding the chemical composition of the influent AMD generally were small in magnitude (Table 1). For the 19-h sampling in July 1990, the influent AMD had a mean pH of 2.8 and a mean total Fe concentration of 1.39 mmol L^{-1}; on average, 93% of the total Fe was soluble Fe and 90% of the soluble Fe was Fe^{3+}. For the 24-h sampling in May 1991, the influent AMD had a mean pH of 2.9 and a mean total Fe concentration of 2.01 mmol L^{-1}; on average, 87% of the total Fe was soluble Fe and 76% of the soluble Fe was Fe^{3+}. For both dates, neither pH nor concentrations of the various Fe fractions in the influent AMD varied substantially over the duration of the sampling periods (Fig. 1–5).

In contrast, the chemical composition of the outflow waters not only differed substantially between wetlands, but also changed, sometimes dramatically, over the duration of the sampling periods. More specifically, a striking diel pattern in outflow Fe^{2+} and Fe^{3+} concentrations was
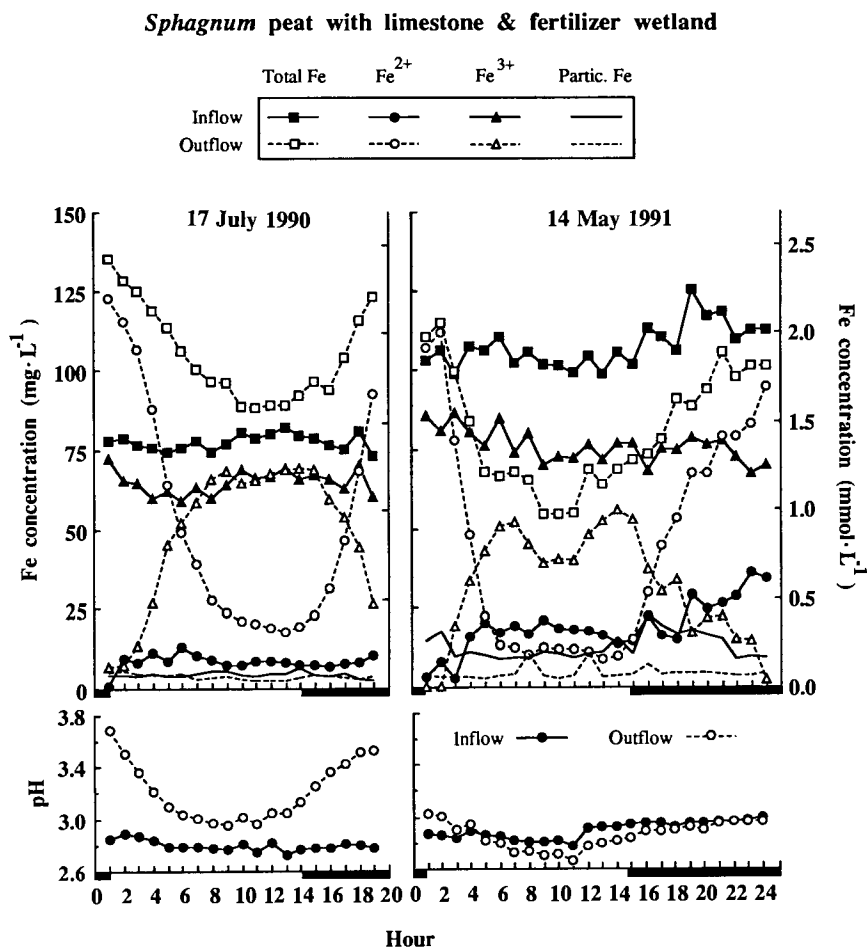

Fig. 1. Inflow and outflow concentrations of total Fe, Fe^{3+}, Fe^{2+}, and particulate Fe, as well as inflow pH and outflow pH values for the *Sphagnum* peat with limestone and fertilizer wetland on both sampling dates. Solid bars beneath each x axis indicate samples that were collected during nighttime (prior to sunrise and after sunset). On 17 July 1990, sunrise was at 0700 h and sampling began at 0700 h; sunset was at 2008 h. On 14 May 1991, sunrise was at 0542 h and sampling began at 0600 h; sunset was at 1949 h.

observed in both *Sphagnum* peat wetlands on both sampling dates, and for the straw–manure and mushroom compost wetlands on the May 1991 sampling date (Fig. 1, 2, 4, 5). In all of these instances, prior to sunrise, in the outflow waters Fe^{2+} represented 75 to 100% of the soluble Fe, but with the onset of daylight Fe^{2+} concentrations began to decrease along with a corresponding increase in Fe^{3+}. After sunset, outflow Fe^{3+} concentrations began to decrease along with an attendant increase in Fe^{2+} concentrations until Fe^{2+} again comprised 78 to 100% of soluble Fe after several hours of darkness (final hour of each sampling date). Associated with these shifts in the relative abundance of Fe^{2+} and Fe^{3+} in the outflows was a diel pattern in total Fe concentration, reaching maximum values at night and minimum values during the daylight. For the two *Sphagnum* peat wetlands in July 1990, outflow total Fe concentrations were substantially greater than inflow total Fe concentrations at night, but slightly less than or similar to inflow total Fe concentrations during the day (Fig. 1 and 2). These diel patterns in Fe^{2+}, Fe^{3+}, and total Fe concentrations were either less striking or not evident in the outflow from the sawdust wetland on either sampling date (Fig. 3), or in the outflows from the straw–manure and mushroom compost wetlands in July 1990 (Fig. 4 and 5).

Over the course of the 19-h sampling in July 1990, outflow pH values were consistently greater than inflow pH values for the *Sphagnum* peat with limestone and fertilizer, straw–manure, and mushroom compost wetlands, although the magnitude of the difference between inflow and outflow pH values was much greater for the latter two wetlands (Fig. 1, 4, 5). Neither the *Sphagnum* peat nor the sawdust wetland was effective in raising the pH of the influent AMD (Fig. 2 and 3). In contrast, throughout the duration of the May 1991 sampling, outflow pH values were less than or similar to inflow pH values for all except the mushroom compost wetland (Fig. 1–5). On both sampling dates, outflow pH was greater than inflow pH for the mushroom compost wetland, but magnitude of the difference was much greater in July 1990 than in May 1991 (Fig. 5).

DISCUSSION

Diel changes in the relative abundance of Fe^{2+} and Fe^{3+} were expected because the low pH and high concentrations of Fe^{3+} in the influent mine drainage provide conditions that are conducive to Fe(III) photoreduction (cf. Collienne, 1983; Waite and Morel, 1984). Moreover, independent of the present study (see Wieder, 1992), we determined that after 13 mo of exposure to mine drainage
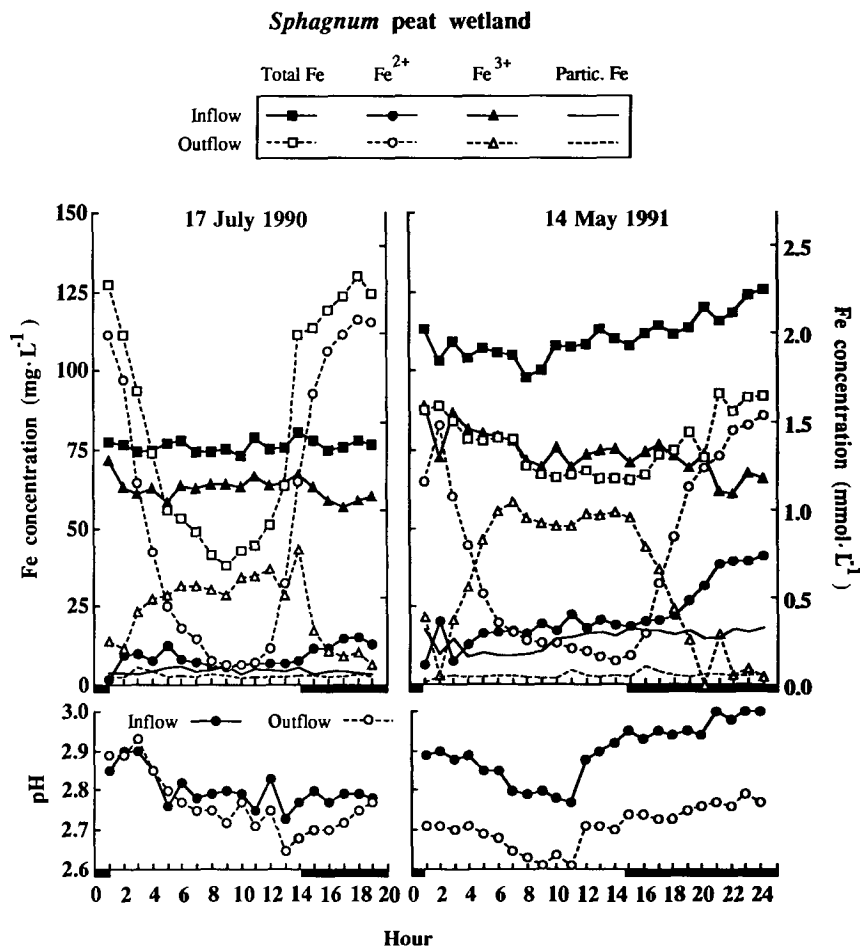

Fig. 2. Inflow and outflow concentrations of total Fe, Fe^{3+}, Fe^{2+}, and particulate Fe, as well as inflow pH and outflow pH values for the *Sphagnum* peat wetland on both sampling dates. Format is the same as in Fig. 1.
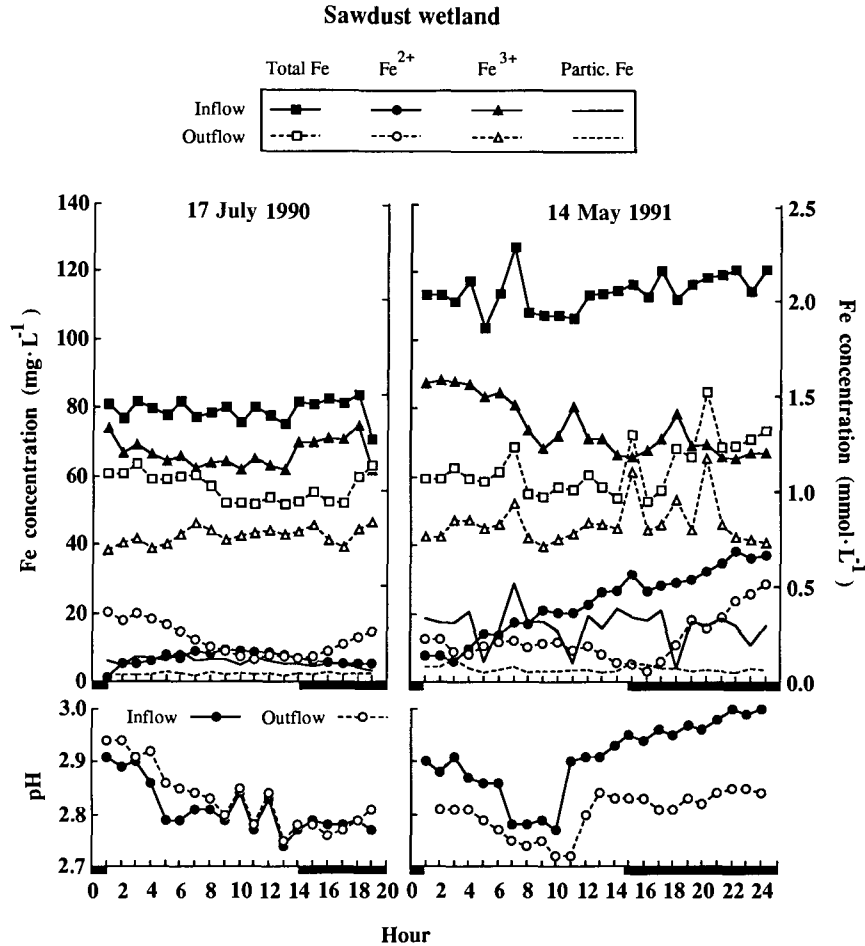
Fig. 3. Inflow and outflow concentrations of total Fe, Fe^{3+}, Fe^{2+}, and particulate Fe, as well as inflow pH and outflow pH values for the sawdust wetland on both sampling dates. Format is the same as in Fig. 1.

(July 1990), the surface substrates of all five wetlands had accumulated considerable quantities of Fe oxyhydroxides. More specifically, in July 1990, the surface substrates of the *Sphagnum* peat with limestone and fertilizer, *Sphagnum* peat, sawdust, straw–manure, and mushroom compost wetlands had Fe oxyhydroxide concentrations (citrate–dithionite–bicarbonate extractable Fe) of 1106 ± 254, 635 ± 217, 180 ± 38, 352 ± 49, and 90 ± 24 mmol Fe kg^{-1} dry mass, respectively (means ± standard errors, $n = 12$) as compared with values of 8 ± 2, 8 ± 2, 8 ± 1, 89 ± 15, and 19 ± 0.3 mmol Fe kg^{-1} dry mass, respectively (means ± standard errors, $n = 5$), prior to exposure to mine drainage. Although there was considerable spatial variability in the depth of the water column within each wetland, on average the wetlands had no more than 5 cm of standing water above the surface of the substrates, so the surface-accumulated Fe oxyhydroxides should have been susceptible to photoreduction.

Given that most previous studies of Fe(III) photoreduction have been conducted in waters with soluble Fe concentrations of 10 μmol L^{-1} or less (e.g., McMahon, 1969; Miles and Brezonik, 1981; Francko and Heath, 1982; Collienne, 1983; Waite and Morel, 1984; Madsen et al., 1986; McKnight and Bencala, 1988; McKnight et al., 1988), it is useful to calculate whether the magnitude of

potential photoreduction-induced changes in Fe^{2+} concentrations would have been detectable against the much higher soluble Fe concentrations present in the inflows and some of the outflows of the constructed wetlands (cf. Table 1). The theoretical range in the change in Fe^{2+} concentrations that could have resulted from Fe(III) photoreduction in the constructed wetlands was calculated using an apparent quantum yield approach (McKnight et al., 1988). We did not measure incident UV-radiation (250–400 nm) intensity, but estimate it as 10% of incident photosynthetically active radiation (PAR), taken as 60 mol m^{-2} d^{-1} (a typical maximum for a sunny, midsummer day at mid-latitudes; Salisbury and Ross, 1992). Given an apparent quantum yield of 10^{-4} moles of Fe^{2+} produced per mole of incident UV radiation (the quantum yield for photoreduction of goethite has been estimated as 10^{-5} moles of Fe^{2+} per mole of UV irradiation — amorphous hydrous Fe(III) oxides are more reactive; Waite and Morel, 1984; Cunningham et al., 1987), a surface area of the wetland of 180 m^2, and mean discharges of 53 and 344 L h^{-1} (Table 1), the estimated potential changes in Fe^{2+} concentrations resulting from Fe(III) photoreduction are 84.5 μmol L^{-1} for the July 1990 sampling date and from 13.1 μmol L^{-1} for the May 1991 sampling date. Given the mean inflow Fe^{2+} concentrations for these two sampling days of 136
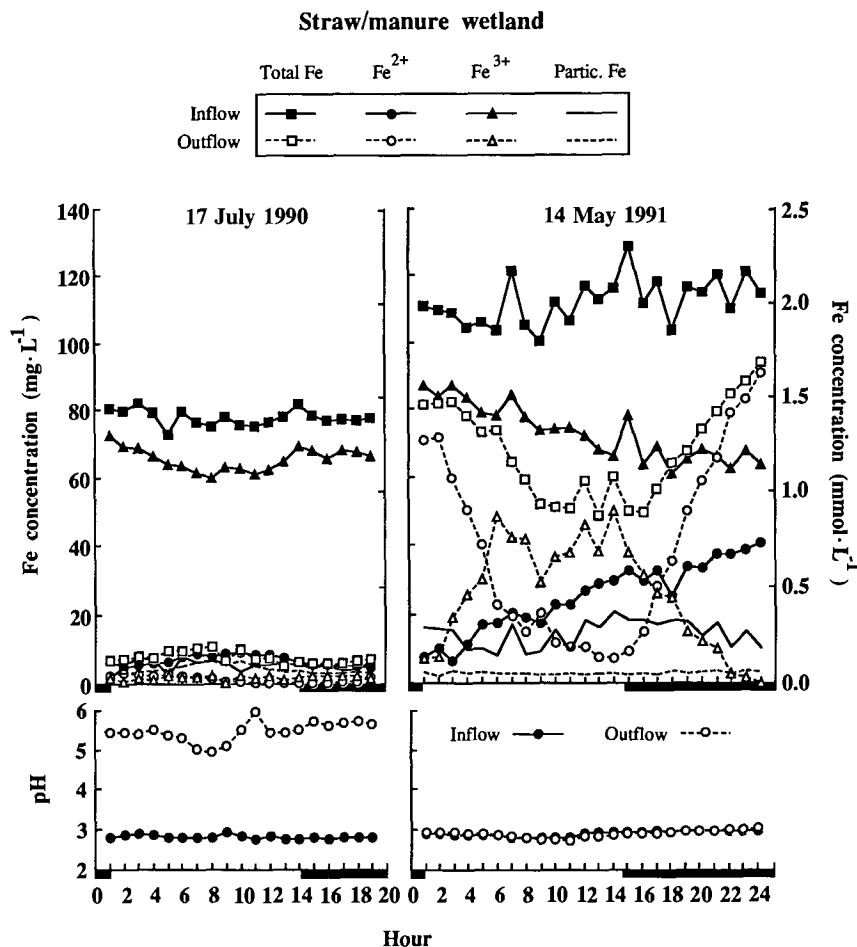
Straw/manure wetland

Fig. 4. Inflow and outflow concentrations of total Fe, Fe^{3+}, Fe^{2+}, and particulate Fe, as well as inflow pH and outflow pH values for the straw–manure wetland on both sampling dates. Format is the same as in Fig. 1.

and 424 μmol L^{-1}, increases in Fe^{2+} concentration in the water as it passed through the wetlands resulting from photoreduction should have been easily detectable.

Surprisingly, the data from this study provided no evidence for Fe(III) photoreduction within any of the wetlands (Fig. 1–5), despite what would seem to be optimal conditions for photoreduction. If Fe(III) photoreduction did occur, its impact on the relative abundance of Fe^{2+} vs. Fe^{3+} in the water discharged from these wetlands was overwhelmed by other processes that had an even greater effect on the forms of Fe in the wetland effluents. More specifically, the shape of the diel responses obtained for the wetland outflows in most instances (maximum Fe^{2+} concentrations at night; maximum Fe^{3+} during the day) is precisely opposed to what would be expected if Fe(III) photoreduction were affecting substantially the relative abundance of Fe^{2+} vs. Fe^{3+} in these waters. The results obtained from this study raise two questions: what is the source of the Fe^{2+} in the water leaving the wetlands, and what is the cause of the striking diel patterns?

A likely source of the Fe^{2+} in the water exiting the *Sphagnum* peat wetlands on both dates and in the water exiting the straw–manure and mushroom compost wetlands in May 1991 is bacterially mediated anaerobic Fe(III) reduction. In anaerobic flask incubations (Vile and Wieder,

1993), significant Fe(III) reduction (accumulation of soluble Fe^{2+} over time) was reported for surface substrate samples from all except the mushroom compost wetland [where slurry pH values above 6.0 in the incubation flasks were not conducive to Fe(III) reduction]. Extrapolation of these rates of Fe(III) reduction to a whole wetland basis, and knowing the mean discharge rates on each of our two sampling dates, the potential changes in Fe^{2+} concentrations attributable to Fe(III) reduction can be calculated (Table 2). With the exception of the mushroom compost wetland, the magnitude of these estimated potential changes in Fe^{2+} concentrations are much greater than those actually observed on either the July 1990 or May 1991 sampling dates (Fig. 1–4). Because the flask incubations (Vile and Wieder, 1993) used only surface substrates [which had the highest Fe(III) oxyhydroxide concentrations] and were conducted under strict anaerobic conditions (which may not prevail uniformly throughout the substrates), the approach used in Table 2 provides an upper limit estimate of the extent to which Fe(III) reduction can affect effluent Fe^{2+} concentrations.

A second potential source of Fe^{2+} is the anoxic oxidation of reduced inorganic sulfides (notably FeS_2) in the wetland substrates, using Fe^{3+} as the electron acceptor. Radiotracer studies of sulfate reduction and quantification
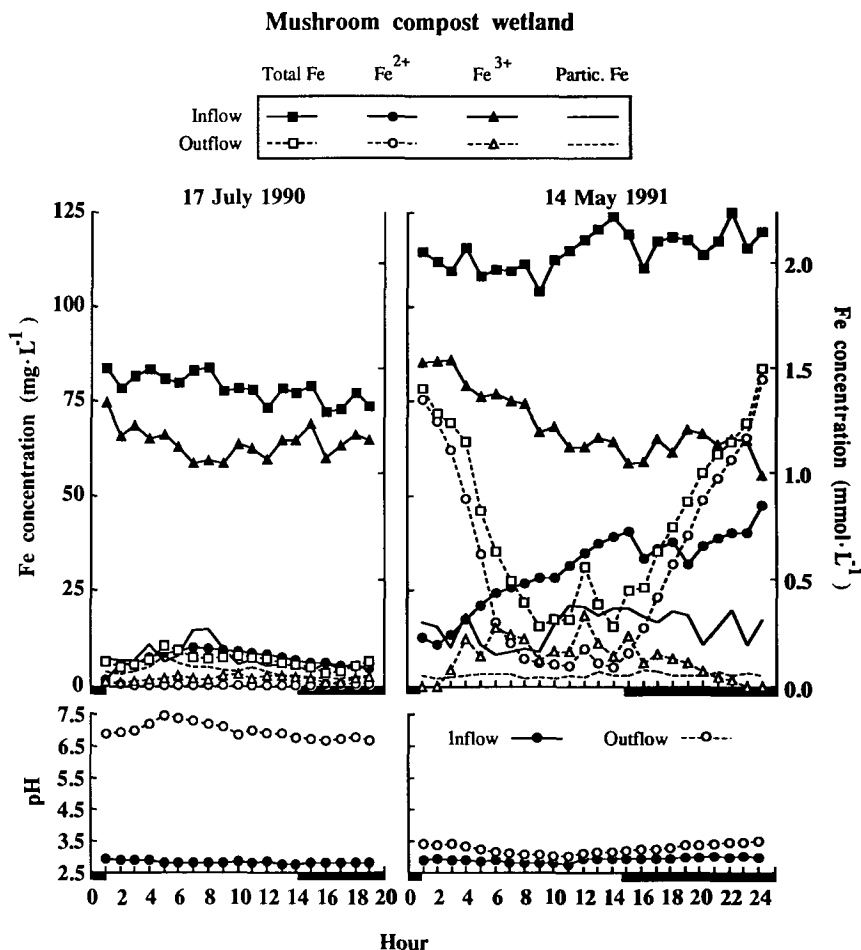
Fig. 5. Inflow and outflow concentrations of total Fe, Fe^{3+}, Fe^{2+}, and particulate Fe, as well as inflow pH and outflow pH values for the mushroom compost wetland on both sampling dates. Format is the same as in Fig. 1.

of the accumulation of reduced S in these substrates (Taddeo, 1991) indicated that reduced inorganic sulfides formed by sulfate reduction do turn over, both in the surface and subsurface substrates, presumably through oxidation by O_2 and Fe^{3+}, respectively. Although in neither the flask incubations nor the field measurements of wetland outflow chemistry was it possible to distinguish Fe(III) reduction vs. anoxic FeS_2 oxidation as the source of the Fe^{2+}, it is likely that both mechanisms contributed to some extent. One important difference between these two mechanisms

of producing Fe^{2+} is that Fe(III) reduction generates alkalinity, consuming 2 moles of H^+ per mole of Fe oxyhydroxide reduced (although the ratio of H^+ consumed per Fe oxyhydroxide reduced depends on the C source being metabolized; Bell, 1988), whereas anoxic FeS_2 oxidation generates acidity, producing 14 moles of H^+ for every mole of FeS_2 oxidized. In both the flask incubations (Vile and Wieder, 1993) and the hourly field sampling of influent and effluent water chemistry (Fig. 1–5), the increases in pH that accompanied the production of Fe^{2+}

Table 2. Estimated potential changes in Fe^{2+} concentrations resulting from biologically mediated Fe(III) reduction within each wetland, calculated from rates of Fe(III) reduction in flask incubations (values are from Vile and Wieder 1993, specifically from the 25°C incubations in flasks that did not receive formalin), substrate bulk densities (values are from Taddeo, 1991), and mean discharges of 53 and 344 L h⁻¹ measured on 17 July 1990 and 14 May 1991, respectively (cf. Table 1).

	Wetland				
	Peat with limestone and fertilizer	Peat	Sawdust	Straw–manure	Mushroom compost
Fe(III) reduction rate (mmol kg⁻¹ d⁻¹)					
25°C (samples collected in May 1991)	13.3	7.6	4.0	15.9	0.2NS†
Substrate bulk density (g cm⁻³)	0.04	0.07	0.21	0.22	0.29
Potential change in Fe^{2+} conc. (mmol L⁻¹)					
July 1990	22.6	22.6	35.7	148.5	−0.5NS
May 1991	3.5	3.5	5.5	22.9	0.1NS

† NS = not significantly different from zero.

were much less than would be expected if all of the Fe^{2+} were derived from Fe(III) reduction alone. Either the Fe^{2+} produced resulted from both Fe(III) reduction and anoxic FeS_2 oxidation with the attendant changes in pH reflecting the relative importance of these two mechanisms, or H^+ consumption by Fe(III) reduction was at least partially offset by other acidity-generating mechanisms, such as the hydrolysis of Al^{3+} or Fe^{3+}, along with the deposition of Al or Fe oxyhydroxides and the release of protons. Although neither the flask incubations nor the hourly field sampling of inflow and outflow waters allows for a quantitative assessment of the relative importance of processes that affect solution pH, it appears that the sources of the Fe^{2+} produced in either the laboratory or the field are both biologically mediated Fe(III) reduction and anoxic oxidation of FeS_2 (cf. Vile and Wieder, 1993).

What, then, was the cause of the striking diel patterns in the relative abundance of Fe^{2+} vs. Fe^{3+} in the water exiting the two *Sphagnum* peat wetlands on both dates, and exiting the straw–manure and mushroom compost wetlands in May 1991? Since most of the soluble Fe entering the wetlands was Fe^{3+}, the pattern is one of a shift from net Fe(III) reduction at night to no net Fe(III) reduction during the daylight hours. A parsimonious explanation of this observed diel pattern is that during the daylight hours oxygenation of surface water by photosynthetic algae and cyanobacteria, typically visible as surface or subsurface scums infused with gas bubbles, created conditions that either inhibited both Fe(III) reduction and anoxic FeS_2 oxidation or enhanced near-surface Fe^{2+} reoxidation, so that most of the Fe^{2+} produced by Fe(III) reduction or anoxic FeS_2 oxidation was oxidized to Fe^{3+} prior to leaving the wetland. In contrast, at night when surface waters became deoxygenated, Fe(III) reduction and anoxic FeS_2 oxidation proceeded relatively uninhibited and/or with minimal oxidation of the Fe^{2+} produced by these processes, so that the dominant form of Fe in the outflow waters was Fe^{2+}.

The *Sphagnum* peat wetlands each exhibited striking diel patterns in the relative abundance of Fe^{3+} vs. Fe^{2+} in outflow waters on both sampling dates (Fig. 1 and 2), the sawdust wetland exhibited relatively weak diel patterns on both sampling dates (Fig. 3), and the straw–manure and mushroom compost wetlands exhibited strong diel patterns only on the second sampling date (Fig. 4 and 5). The absence of striking diel patterns for the straw–manure and mushroom compost wetlands on the first sampling date is most probably related to the relatively high pH of the outflow waters from these two wetlands (Table 1). Although little is known about the microbiology of either Fe(III) reduction or anoxic FeS_2 oxidation in wetlands constructed for AMD treatment, it appears that these processes are inhibited at pH values approaching 6.0. In the flask incubation studies of Vile and Wieder (1993), the slurry pH values of the mushroom compost substrate samples were above 6.0 and there was no evidence of significant Fe(III) reduction. As long as biological and chemical processes in a wetland can act to raise the pH of the influent AMD to values approaching 6.0, metal retention through oxyhydroxide, sulfide, and even carbonate deposition can be quite effective, as manifested by low dissolved metal concentrations in the waters exiting a wetland. However, with continued exposure to AMD over time, a wetland's ability to ameliorate the low pH of AMD may decline, metal retention efficiency may decrease, pH of the outflow waters may decrease (Wieder, 1993), and conditions may begin to favor Fe(III) reduction and anoxic FeS_2 oxidation, which may be manifested as a diel pattern in the relative abundance of Fe^{2+} and Fe^{3+} in outflow waters. These trends are illustrated by comparing the July 1990 and May 1991 effluent water chemical composition data in the straw–manure (Fig. 4) or mushroom compost wetlands (Fig. 5).

In short, this study has documented diel shifts in the relative abundance of Fe^{3+} vs. Fe^{2+} that are much greater in magnitude than any previously reported for a natural system. These shifts were attributed to a dynamic Fe cycle, the components of which change in importance on both short-term (diel) and longer-term time scales. These findings have implications for assessing the effectiveness of constructed wetlands for AMD treatment from both scientific and regulatory standpoints. At least with regard to Fe, the typical sampling scheme of a single inflow and outflow water sample collected during the day on a weekly, biweekly, or less frequent basis clearly is in violation of the inherent assumption that short-term variability in water chemical composition is sufficiently minimal that a single water sample can be considered as representative of water chemical conditions for the entire sample interval. If the results from this study are generalizable to other constructed wetlands receiving AMD, existing and future information on Fe retention effectiveness must be interpreted cautiously. From a regulatory perspective, if an AMD treatment system includes a constructed wetland and if the wetland is not effective in ameliorating the low pH of incoming AMD, effluent Fe concentrations may be much greater at night than during the day. Since sampling by coal mine operators and/or state or federal regulatory personnel is typically a daytime activity, the effectiveness of a wetland treatment system with regard to meeting Fe effluent limitations may be overestimated routinely simply as a result of daytime-only sampling.

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