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THE EFFECTS OF CARBON SUPPLEMENTATION AND PLANT SPECIES ON IRON RETENTION IN MESOCOSM TREATMENT WETLANDS

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Abstract: Oxides of Fe were dominant in composite sediment samples from the upper region of simulated compost wetlands exposed to acidic mine water, accounting for nearly half of substrate iron among the three sampling stations. In the middle and lower wetland regions, however, 65% of all Fe was retained as oxidizable Fe. Inferential evidence suggests that sulfate reduction was likely to be a critical process in Fe retention over at least half of the wetland length. However, overall, oxides of Fe (including amorphous and crystalline oxides) constituted the dominant phase of Fe in the wetland. The addition of a supplemental carbon source significantly stimulated both the formation of oxidizable Fe and reducible Fe in the middle and lower wetland regions, but not near the inlet. The use of effective carbon supplements is therefore recommended in field tests at acidic sites. Over the short term, the presence or species of vegetation had no effect on the partitioning of Fe phases.

Key Words: wetlands, iron, sequential metal extractions, sulfate reduction, iron oxidation, wetland plants

INTRODUCTION

Acidic mine drainage is a serious water pollution problem across the nation and especially in the Appalachian region. If not treated, coal mine drainage can adversely affect aquatic vascular plants, fish, and benthic invertebrates (Letterman and Mitsch 1978). Conventional water treatment involves the application of chemical bases to elevate pH, causing iron and manganese to precipitate from solution due to the pH-dependent solubility of these metals upon exposure to oxygen. Attendant problems of this mode of treatment include the high costs of chemicals and associated labor and the large amounts of sludge generated, which create disposal concerns. The application of strong bases to acid mine drainage is a perpetual situation that is vulnerable to human error.

In the last decade, over 500 wetlands have been constructed to treat mine water as passive, low maintenance biological systems (Kleinmann and Hedin 1993). In some instances, mining companies and utilities have saved thousands of dollars in treatment costs by installing a wetland. However, the U.S. Office of Surface Mining (OSM) views treatment wetlands as temporary solutions to the treatment of mine water. Predictability and the effective life span of constructed wetlands are largely unknown. Because of this, the current OSM policy is to deny bond release on sites employing wetland treatment systems. In order to better understand these crucial issues of predictability and longevity, data are needed in the area of metal retention with an eye toward longevity.

A number of studies carried out by Wieder and his associates, beginning in 1988, indicated that constructed wetlands have a finite life span with respect to metal retention and will eventually fail (Wieder 1988, Wieder 1989, Wieder et al. 1990, Wieder 1992). Laboratory and field studies chronicled by the foregoing papers concluded that a wetland's capacity to retain iron (primarily as an oxide) will eventually be exhausted, and the acidity of the mine water will overcome the capability of the wetland to neutralize the water. Despite these predictions, some wetlands are approaching ten years of age and have exceeded expectations for metal retention (e.g., Brodie 1993, Stark et al. 1994).

The phase of the metal that is retained and stored in a treatment wetland is critical to its long-term effectiveness. When iron and manganese occur in the water-soluble, exchangeable, or amorphous oxide phases, they may eventually become unstable and enter the water column again as dissolved divalent ions. However, when these metals occur as a sulfide or in a crystalline form, stability, while not assured, is more likely, provided that the substrate remains flooded.

A few studies have employed sequential extraction techniques to determine the phase of metal occurring in constructed wetlands receiving coal mine drainage. Tarutis and Unz (1990) found that in two constructed wetlands in Pennsylvania, oxides of iron and manganese were the most common form of metal retained. Furthermore, in the reducing zone, dissolved iron concentrations in the interstitial water increased with depth. Presumably, the iron oxides precipitated in the shallower wetland depths were chemically reduced at depth in the wetland, forming ferrous iron in the pore water. Sulfate reduction was not a major process in either wetland. Evaluations of the phase of iron in a mushroom compost wetland in Kentucky revealed that a single, dominant phase was absent (Wieder 1992). Iron occurred in roughly similar amounts across the depth profile of the wetland as an oxide, carbonate, organically-bound, and as residual iron. However, oxides of iron were more common within the compost wetland at the greatest depths, indicating that a reducing zone was not well-established. Wieder therefore regarded sulfate reduction as insignificant, and estimated that the wetland would ultimately fail to sustain iron retention. In mesocosm peat wetlands with living vegetation, iron oxides were again the dominant form of retained iron, accounting for 73-86% of the total. These treatment systems were also estimated to lose their capacity to retain iron after a finite period (Wieder et al. 1990). Similarly, in surface-flow constructed and experimental treatment wetlands in Kentucky, the dominant phase of iron was found to be crystalline oxides (Faulkner and Richardson 1990).

Problems arise with determining the phase of metal accumulating at a constructed wetland without accounting for the metal load and, more importantly, wetland design parameters. At the Frenchville wetland (Tarutis and Unz 1990) and the Kentucky study (Wieder 1992), metal load exceeded recommended design loadings of Brodie et al. (1988). In addition, both of these wetlands were designed with a significant amount of surface free water flow, which further impedes metal retention and favors oxide precipitation.

In this paper, we document the phases of iron present using sequential extraction techniques in the substrate under mesocosm wetland conditions while experimentally varying the parameters carbon supplementation, plant species, and plant biomass. We previously reported the outlet water quality aspects of this experiment (Stark et al. 1991). The principal finding was that supplementing a simulated wetland with dairy whey resulted in increased iron retention and lowered sulfate concentrations. In this report we focus on the phase of iron present in the sediments with respect to the experimental treatments: plant vs. no plant, and supplementation vs. no supplementation. At the conclusion of the experiment, the biomass densities across treatments were roughly equivalent due to rapid growth in the low biomass treatments; therefore biomass as a treatment variable was not addressed here.

METHODS

Wetland Simulation Facility

A series of simulated wetland cells was assembled in early 1990 in a campus greenhouse, based in principle on the apparatus used by Gerber et al. (1985). It was a non-circulating continuous flow system in which a concentrated stock solution of mine water was prepared, stored in a 1600-L fiberglass reservoir, and pumped to a series of chambers where the solution was diluted, mixed, and adjusted to the experimental pH, metal concentration, and flow rate. The solution was then distributed to individual simulated wetland lanes, where it was passed through the wetland, and the water was finally collected at the wetland outlet (Figures 1–2). The stock solution was prepared from ferrous sulfate, sulfuric acid, and tap water. For other details of the experimental setup, see Stark et al. (1991).

Experimental Design

Three wetland plant species were planted at high and low densities in spent mushroom compost and exposed

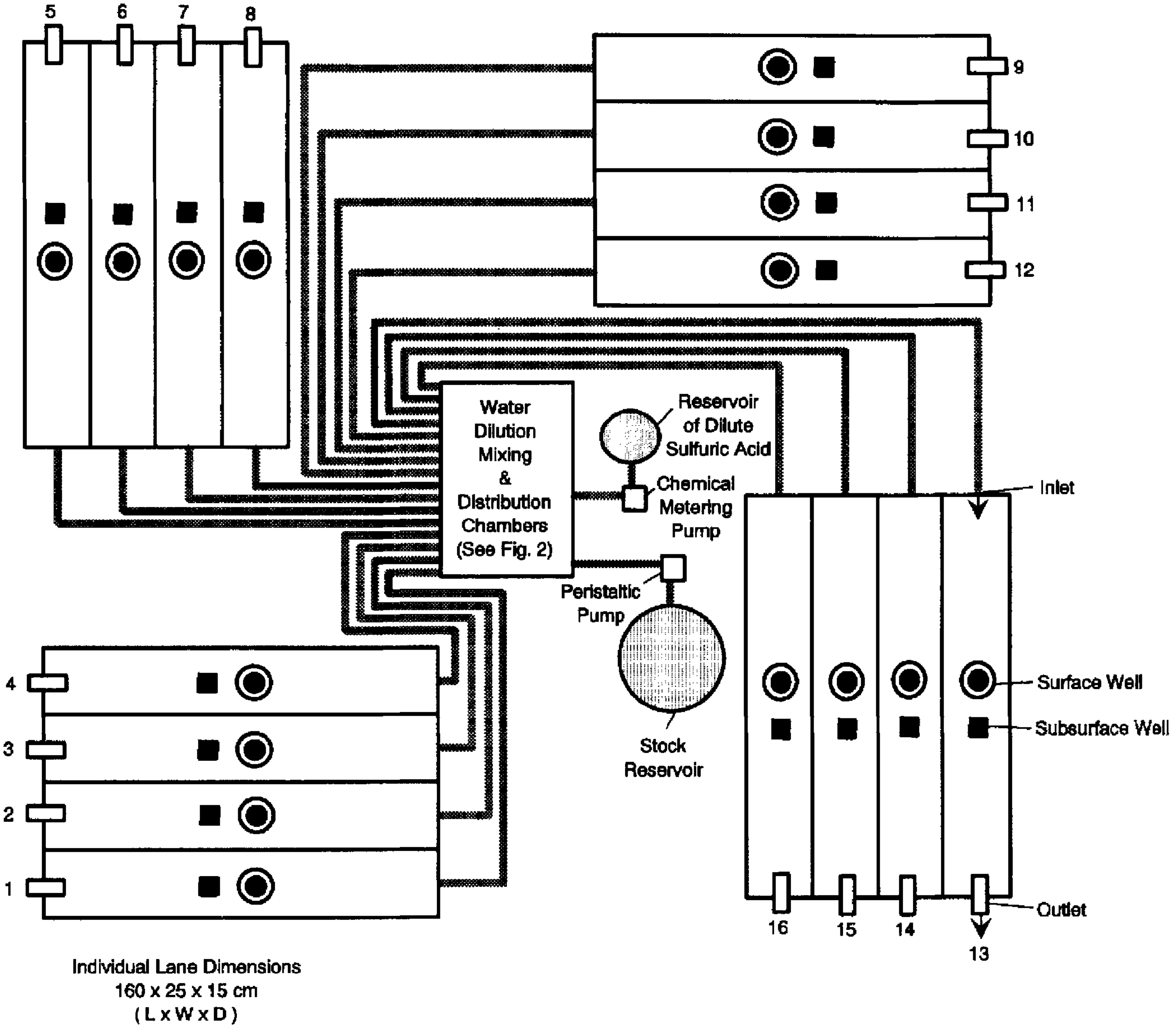
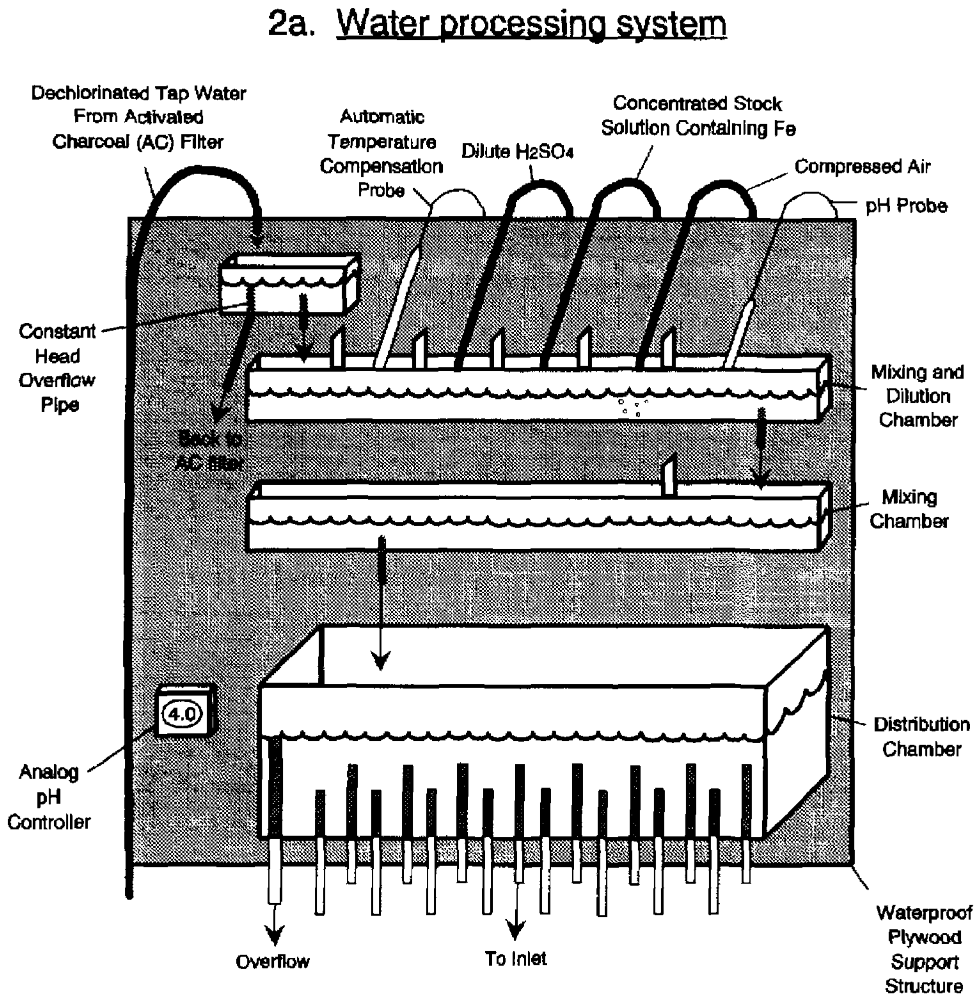


Figure 1. Overview of greenhouse wetland simulation facility.

to acidic mine water containing iron. Half of the wetland lanes were supplemented with a carbon source (dairy whey; Table 1). Fresh liquid sweet dairy whey (cheddar cheese whey) was obtained locally from the Pennsylvania State University Creamery and refrigerated prior to use. Each week following the normal weekly water sampling regime, a syringe tip was inserted to the bottom of each lane, and 600 mL of whey was injected into the substrate adjacent to the inlet. Whey is the watery part of milk remaining after separation of the curd that results from the coagulation of milk and contains a significant lactose component along with a variety of vitamins, minerals, and proteins (Zadow 1986). The pH of the fresh whey was typically near 6.0, and the dissolved organic carbon was measured at 18,250 mg L^{-1}. On three of the 15 whey-injection dates, fresh whey was unavailable. In these instances, an equivalent amount of whole milk was used.

Water Quality and Metal Loading Regimes

Prior to planting, in order to (i) partially overcome the natural neutralizing capacity of the compost substrate, and (ii) allow the substrate to equilibrate with experimental conditions, the mesocosms were pretreated with 40 mL min^{-1} of acidic (pH 2.0) simulated mine water containing Fe (350 mg L^{-1}) for a period of seven days, followed by near experimental conditions (pH 4.0, 50 mg Fe L^{-1}, 40 mL min^{-1}) for 11 days. Throughout the following experiment, pH and flow rate were maintained at approximately 4.0 and


2a. Water processing system

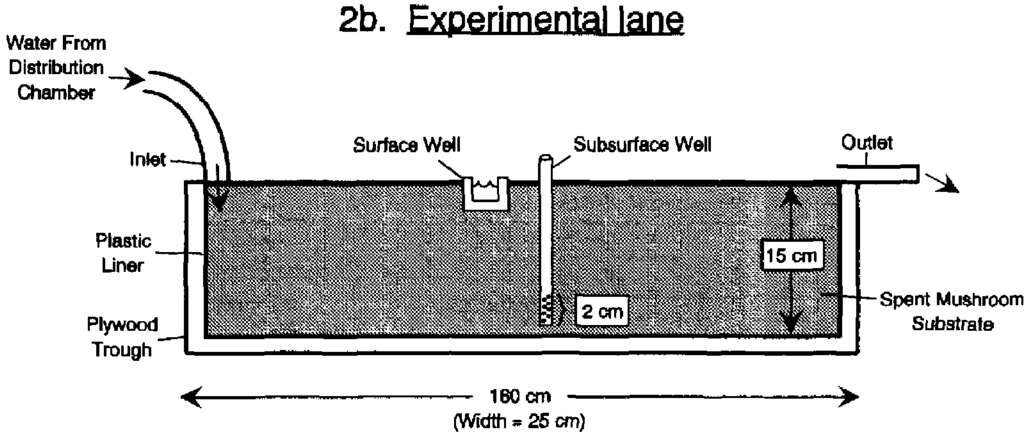

2b. Experimental lane

Figure 2. Water processing system used in the experiment (A), and the length profile of single experimental mesocosm lane (B).

30 mL min^{-1}, respectively. The simulated wetlands received water containing 50 mg L^{-1} iron (or 5.4 g Fe m^{-2} day^{-1}) for 60 days (Phase I), followed by water containing 150 mg L^{-1} iron (or 16.2 g Fe m^{-2} day^{-1}) for 60 days (Phase II).

Extractions

At the conclusion of the experiment (120 days), three composite substrate samples were taken from each of the sixteen simulated wetland lanes. Along the length

Table 1. Experimental design and source water quality for the mesocosm wetlands.

Plant Species	*Typha latifolia* L.				*Leersia oryzoides* (L.)				*Juncus effusus* L.				No Plant Control			
Initial Plant Biomass	High		Low		High		Low		High		Low		High		Low	
Whey Amendment	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−

Source water quality: pH 4.0; [Fe] = 50 and 150 mg L^{-1}; Flow = 30 mL min^{-1}.

of each lane, samples were taken at the one-quarter, one-half, and three-quarter point and included an evenly distributed composite sample (i.e., a substrate core that included a profile from the surface of the substrate to the bottom of the wetland). Wet substrate samples were removed and placed in air-tight plastic containers that were frozen until they could be oven-dried at 60°C to constant weight. The dried material was sieved (2-mm mesh), separating coarse from fine material. A one-gram composite sample was constituted reflecting the proportion of the coarse and fine elements in the whole sample. Six metal fractions potentially sensitive to changes in environmental conditions were sequentially extracted using the procedure of Tessier et al. (1979), incorporating minor modifications from Tarutis (1989). These extractions were as follows: (1) *water soluble,* (2) *exchangeable,* sensitive to changes in water ionic composition, (3) *carbonate* phases, sensitive to changes in pH, (4) *reducible,* unstable under anoxic conditions, (5) *oxidizable* (organic matter and sulfides), can be degraded under oxidizing conditions, and (6) *residual* (trapped in the crystal lattice of minerals), not expected to be released over a reasonable time span under conditions normally encountered in nature. In addition, compost unexposed to mine water was extracted as above as a control.

Samples were extracted in polycarbonate tubes following centrifugation at 2500 rpm for 12 min using the following reagents: (1) hot deionized water for 1 hr, (2) 1 M magnesium chloride at pH 7.0 for 1 hr, (3) 1 M sodium acetate at pH 5.0 for 12 hr, (4) 0.1 M hydroxylamine hydrochloride in 25% (v/v) acetic acid for 6 hr, and then this step was repeated, (5) 30% hydrogen peroxide at pH 2.0 for 6 hr, followed by 3.2 M ammonium acetate in 20% nitric acid for 30 min, and (6) a mixture of ⅔ nitric acid and ⅓ perchloric acid for 4 hr. In steps (4), (5), and (6) above, samples were submerged in a hot bath (85°C) during the extraction and agitated periodically. Iron in the supernatant was determined by flame atomic absorption spectrophotometry. After each successive extraction, the residue was resuspended in deionized water, centrifuged again, and the supernatant discarded.

The oven-drying phase in preparation of the substrate samples for extractions may promote oxidation of reduced compounds. However, for iron, Saeki et al. (1993) found that drying and exposure to oxygen of lake sediments, if anything, increased the sulfide/organic fraction, while slightly decreasing the reducible fraction. The sequential extraction procedure (adopted in this paper) of Tessier et al. (1979) was developed and tested on inorganic sediments. However, the former authors indicated that possible applications of the procedure included anoxic lacustrine sediments, which are similar to those found in wetlands. Therefore, although precedent is established for using this procedure on organic/wetland sediments receiving mine water (Tarutis and Unz 1990, Tarutis et al. 1992), we caution that interpretations in this paper are under the assumption that the procedure of Tessier et al. (1979) is adaptable for organic sediments.

The interpretation of sequential metal extraction data is not necessarily straightforward and can be frought with errors. A variety of extraction procedures has been developed (e.g., Shuman 1985, Rauret et al. 1988, Rudd et al. 1988), and the operational definition of solid materials does not identify specific mineral phases (Nirel and Morel 1990). Significant variation can be introduced by readsorption during extraction with several reagents (Rendell and Batley 1980), differences in substrate composition and reagent choice (Robinson 1984), the order of the extraction sequence of reagents (Miller et al. 1986), and the possibility of phase changes occurring upon preparatory drying of the sample (Saeki et al. 1993).

RESULTS

Three of the fractions contained relatively little iron: water soluble, exchangeable, and carbonate-bound (Table 2). Therefore, only a small proportion of the iron retained in these compost wetlands was present in these forms. The bulk of the iron occurred in the remaining three fractions, with the proportion dependent on the position within the wetland. These three fractions were residual, reducible, and oxidizable iron.

Upper Wetland

Close to the inlet water source, the predominant form of iron was in the residual and reducible phases, indicative of oxides of iron in crystalline and amor-

Table 2. Mean (± one S.D.) iron levels present in post-experimental spent mushroom substrate that was exposed to simulated mine water (pH 4.0, 50 and 150 mg Fe L^{-1}, and 30 mL min^{-1}). Iron load over the latter half of the experiment was 16.2 g Fe m^{-2} day^{-1}. Values are in mg Fe per gram of compost.

Factor	Position	Water Soluble	Exchangeable	Carbonate	Reducible	Oxidizable	Residual	Total
Supplemented[1]	Upper	0.94 ± 0.30	0.49 ± 0.12	0.17 ± 0.04	86.52 ± 42.40	72.47 ± 18.03	110.92 ± 53.73	271.51 ± 49.92
	Middle	0.25 ± 0.10	0.41 ± 0.12	0.20 ± 0.07	25.80 ± 13.56	49.59 ± 32.24	1.92 ± 2.80	78.17 ± 45.82
	Lower	0.02 ± 0.02	0.04 ± 0.06	0.14 ± 0.04	33.23 ± 9.13	66.31 ± 17.26	1.55 ± 2.25	101.27 ± 26.11
Unsupplemented[1]	Upper	1.23 ± 0.36	0.45 ± 0.13	0.13 ± 0.04	137.33 ± 59.66	50.13 ± 28.74	114.42 ± 57.85	303.68 ± 89.93
	Middle	0.34 ± 0.32	0.43 ± 0.29	0.10 ± 0.66	15.26 ± 7.03	27.65 ± 13.54	0.54 ± 0.56	44.33 ± 18.30
	Lower	0.03 ± 0.08	0.05 ± 0.09	0.06 ± 0.06	23.17 ± 5.95	49.17 ± 12.96	0.26 ± 0.13	72.81 ± 18.78
Juncus[2]	Upper	1.30 ± 0.17	0.54 ± 0.07	0.13 ± 0.08	74.36 ± 50.58	67.36 ± 17.55	127.31 ± 80.83	271.05 ± 91.47
	Middle	0.29 ± 0.34	0.47 ± 0.16	0.17 ± 0.10	21.18 ± 16.42	35.93 ± 29.31	1.16 ± 0.98	59.20 ± 45.73
	Lower	0.01 ± 0.02	0.05 ± 0.05	0.08 ± 0.06	29.41 ± 11.55	64.46 ± 22.67	1.73 ± 2.69	95.73 ± 36.61
Leersia[2]	Upper	0.82 ± 0.39	0.44 ± 0.16	0.17 ± 0.03	91.18 ± 54.93	69.80 ± 29.20	89.18 ± 31.16	251.59 ± 47.76
	Middle	0.20 ± 0.14	0.36 ± 0.24	0.12 ± 0.06	20.14 ± 12.99	37.37 ± 22.13	0.87 ± 1.06	59.04 ± 34.75
	Lower	0.02 ± 0.04	0.05 ± 0.08	0.06 ± 0.06	27.43 ± 9.95	54.54 ± 18.43	0.23 ± 0.09	82.32 ± 28.18
Typha[2]	Upper	1.32 ± 0.40	0.55 ± 0.09	0.15 ± 0.01	123.40 ± 52.30	53.56 ± 28.91	112.65 ± 54.34	291.62 ± 76.91
	Middle	0.49 ± 0.17	0.58 ± 0.15	0.21 ± 0.04	18.50 ± 4.77	39.32 ± 31.27	0.49 ± 0.14	59.57 ± 35.25
	Lower	0.01 ± 0.02	0.02 ± 0.03	0.07 ± 0.04	24.97 ± 8.22	52.76 ± 19.56	0.21 ± 0.13	78.03 ± 27.53
No plants[2]	Upper	0.91 ± 0.15	0.35 ± 0.02	0.13 ± 0.03	158.77 ± 45.56	54.49 ± 32.69	121.55 ± 54.56	336.18 ± 65.10
	Middle	0.20 ± 0.21	0.28 ± 0.27	0.11 ± 0.09	22.31 ± 14.86	41.87 ± 33.79	2.42 ± 4.08	67.19 ± 51.03
	Lower	0.06 ± 0.12	0.06 ± 0.12	0.06 ± 0.05	30.97 ± 9.23	59.18 ± 11.52	1.45 ± 2.06	91.97 ± 18.03
Overall means[3]	Upper	1.09 ± 0.36	0.47 ± 0.12	0.15 ± 0.04	111.93 ± 56.47	61.30 ± 25.89	112.67 ± 53.96	287.60 ± 72.20
	Middle	0.30 ± 0.24	0.42 ± 0.21	0.15 ± 0.08	20.53 ± 11.77	38.62 ± 26.44	1.23 ± 2.07	61.25 ± 37.97
	Lower	0.02 ± 0.06	0.04 ± 0.07	0.07 ± 0.05	28.20 ± 9.08	57.74 ± 17.20	0.90 ± 1.68	87.01 ± 26.42
Control[4]		0.03 ± 0.00	0.09 ± 0.06	0.02 ± 0.01	0.46 ± 0.04	6.38 ± 1.68	1.80 ± 1.93	8.72 ± 2.77

[1] n = 8.
[2] n = 4.
[3] n = 16.
[4] Control represents six replicates of pre-experimental compost.

Table 3. Reducible and oxidizable iron retention as a function of plant species and whey supplementation; cores taken from the wetland midpoint and ¾ point (n = 4).

Genus	Whey	Mean Reducible Fe (mg/g compost)	Mean Oxidizable Fe (mg/g compost)
Typha	yes	24.6	61.7
	no	18.8	30.4
Leersia	yes	30.4	53.9
	no	17.1	38.0
Juncus	yes	30.2	60.5
	no	20.4	39.9
No plants	yes	32.8	55.7
	no	20.5	45.3

phous phases, respectively. Seventy-eight percent of all sediment iron was present in these two phases, with oxidizable iron making up most of the balance. On a mass basis, about twice as much iron was found in the upper wetland substrates than both of the other wetland stations combined (287.6 vs. 148.3 mg Fe g^{-1}, means, Table 2). About 52% of all the iron retained in all three sampling stations occurred as iron oxides (reducible + residual) in the upper wetland station.

Middle and Lower Wetland

In the middle and lower portion of the wetlands, iron occurred predominantly in oxidizable form (63% and 66% of the total iron retained in the middle and lower portions, respectively), with reducible iron accounting for most of the rest (Table 2). The technique employed for determining oxidizable iron did not allow a separation of the sulfide-bound phase from the organically bound phase. Since our samples were composite in nature, we did not determine the relative amount of iron in a specific form along a depth profile. Residual forms of iron were virtually absent in this region.

Plant Effects

Over the short term of this experiment (essentially a single growing season), the unplanted simulated wetlands accumulated similar levels of reducible iron as the planted wetlands ($p > 0.05$, t-test; middle and lower wetland composite samples). In addition, the presence of plants did not seem to enhance the formation of oxidizable iron. Under conditions of no carbon supplementation, the unplanted wetlands accumulated more iron in the oxidizable phase than the planted wetlands (Table 3), but this was not significant ($p > 0.05$, t-test; middle and lower wetland composite samples).

Supplementation Effects

In the middle and lower regions of the wetlands, supplementation with liquid cheese whey stimulated both reducible iron formation and oxidizable iron formation. In the supplemented wetlands, 53% more reducible and 51% more oxidizable iron were found (significant on both counts, $p < 0.01$, t-test; middle and lower wetland composite samples; Table 3). Carbon supplementation of the wetlands did not affect the ratio of oxidizable to reducible iron; it remained at approximately 2:1 in the middle and lower wetland stations.

In the upper portion of the wetlands, neither reducible iron formation nor oxidizable iron formation was stimulated by supplementation ($p > 0.05$ on both counts, t-test).

DISCUSSION

There is little doubt that well-designed constructed wetlands can effectively remove ferrous iron from mine-water discharges (Wieder 1989). However, because most of the current constructed wetlands are relatively young (< 10 years old), questions remain regarding the expected life span of such wetlands. Recent studies reported that iron is predominantly retained as an amorphous oxide or crystalline oxide, with sulfate reduction playing a minor role in constructed wetlands. However, in constructed wetland treatment systems, metal oxides are less preferred to sulfides as the repository of wetland metals. Amorphous oxides are more unstable and likely to undergo reduction, producing ferrous iron in the pore water that may eventually exit the wetland (unless ferrous iron subsequently forms an iron sulfide). In addition, the reduction of Fe and Mn oxides is energetically favored over sulfate reduction, and oxides occupy more space in wetlands than sulfides and are therefore preferred from the standpoint of longevity of water treatment (Gotoh and Patrick 1972, Tarutis and Unz 1990). Finally, should oxides of Fe build up in the surficial wetland sediments and then become anoxic, sulfate reduction can be suppressed as Fe-reducing bacteria outcompete sulfate-reducers for available carbon sources (Lovley and Phillips 1987).

Based on data from simulated wetlands presented here, we challenge the contention that sulfate reduction is an insignificant process in the retention of iron in wetlands. Clearly, in the upper wetland sampling station nearest the inlet, oxygenated source water interacted with the sediments to form crystalline forms of iron (most likely Fe_2O_3) along with amorphous oxides of iron. At this station, 78% of the iron was in an oxide form, with negligible effects of supplementation. In addition, twice the mass of iron in the substrates was found in the upper wetland station than in the lower two wetland stations combined. These findings mirror those found in a natural Pennsylvania wetland receiving mine drainage (Tarutis and Unz 1992).

Nevertheless, there may be valid reasons to place more emphasis on the results from the midpoint and lower wetland stations than results from the station nearest the wetland inlet. First, a greater portion of the wetland is represented from the midpoint and lower wetland stations (over half of the wetland length). Second, at these stations, reducing conditions prevailed (mean pore water Eh was < -100 mV), thus simulating conditions normally found in field wetlands. Third, the finding that supplementation only stimulated reducible Fe and oxidizable Fe formation in the middle and lower wetland zones indicated that oxidizing and reducing bacteria were not present or inactive nearest the inlet. If true, then that portion of a wetland nearest the inlet was subject to the abiotic partitioning of iron and can be considered an anomaly restricted to the uppermost reaches of the wetland (or perhaps including wetland surfaces, cf. Tarutis and Unz 1994a). Thus, excluding the extraction data nearest the wetland inlet, more than 65% of all retained iron was bound as oxidizable Fe, which presumably identifies sulfides and/or organic compounds. Furthermore, this figure is significant because the substrate samples taken at the end of the experiment were composite samples, including the surface of the substrate in addition to the remainder of the profile. The substrate surface is expected to encourage the formation of oxides due to the presence of atmospheric oxygen.

It was not possible, using the technique of Tessier et al. (1979), to separate phases of iron bound to organic matter (including humic acids) from iron sulfides. However, water quality data from this experiment strongly suggested that sulfate reduction was occurring: sulfate concentrations were significantly lowered after passage through the wetlands; sulfide production occurred in the pore water; and the hydrogen sulfide odor was so pervasive during the experiment that other greenhouse scientists lodged official complaints (Stark et al. 1991). As others have demonstrated (e.g., McIntire and Edenborn 1990, Devorak et al. 1992), hydrogen sulfide vigorously reacts with ferrous Fe to form iron sulfides, and the sulfur that escapes is less than that combining as a sulfide in reducing systems (at a circumneutral pH, reactions leading to Fe sulfide formation are favored over the protonation reaction in which H_2S gas is formed; Lindsay 1979). Nevertheless, we acknowledge that data regarding sulfate reduction in this study are inferential.

In his Kentucky project, Wieder (1992) found that spent mushroom compost wetlands retained only 14.4% of the iron as a sulfide. In addition, Tarutis and Unz (1990) and Faulkner and Richardson (1990) found little iron bound as a sulfide. Each of the above studies were conducted in constructed or experimental wetlands where oxidizing conditions prevailed and oxides of iron were the dominant phase of iron in the sediments. The significant amount of iron found in the oxidizable phase in our simulated wetland experiment reflected the reducing environment present in the sediments and the slow, subsurface flow patterns present. It is probable that many constructed wetlands in operation today were not designed to encourage reducing conditions by encouraging long retention times and subsurface flows.

When dairy whey was added to the simulated wetlands as a carbon/nutrient supplement, the positive effects on mine-water treatment were represented in the extraction results. Iron oxidation and sulfate reduction processes were equally stimulated in the supplemented wetlands. These results indicate that (1) carbon supplementation should be seriously considered as a wetland design criterion for the removal of iron (see Tarutis and Unz 1994b), and (2) supplementation can improve iron retention processes at the surface of the wetland (oxidation) and at depth in the wetland sediments (sulfate reduction). It should be noted, however, that this may not apply in the upper reaches of a wetland.

Thus, we can conclude that iron retention can be accomplished using a constructed wetland (1) designed to encourage reducing conditions below the surface of the wetland substrate and (2) supplemented with labile carbon. This validates the hypothesis of Tarutis et al. (1992) that organic matter and the lack of reducing conditions limit sulfate reduction, and these should be encouraged in constructed wetlands by altering wetland designs. In the spent mushroom compost, iron will ultimately accumulate (predominantly) as sulfides or crystalline iron oxides, which are stable provided that the wetland remains intact. The longevity of a wetland treating mine water containing iron is enhanced when iron is deposited in forms that resist diagenesis in the wetland sediments. Phases of iron resistant to change include iron sulfides and crystalline forms of iron. Both of these iron phases commonly formed in the simulated wetlands.

Typha latifolia L. is the plant of choice in most constructed wetlands treating mine water, and evidence exists indicating that it is superior to other wetland species in radial oxygen loss (Michaud and Richardson 1989). However, simulated wetlands planted with the common broad-leaved cattail did not accumulate more reducible iron than wetlands planted with other species. These findings and others suggest the presence of plants has little influence on metal retention in constructed wetlands (Sencindiver and Bumbla 1988, Hedin and Nairn 1993). It should be noted, however, that the positive effects of plants may go undetected in mesocosm experiments conducted for one, or a few, growing seasons. In the long term, a wetland without plants is likely to suffer from inadequate carbon sources to fuel sulfate reduction and iron oxidation. Furthermore, total vegetative cover was cited as the principal factor in preventing metal release from constructed wetlands during storms (Taylor et al. 1993).

Phases of iron that are undesirable for increasing longevity include water-soluble, exchangeable, carbonates, and amorphous iron oxides. Of these, only amorphous oxides constituted a significant portion of the retained iron in simulated wetlands (as reducible iron). These findings suggest that ferrous iron in mine water is treatable over the long term using constructed compost wetland technology, as long as the wetland is designed to maintain a reducing environment (at least at depth within the solid matrix). The retention of iron in such a system can be augmented by the addition of dairy whey.

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