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Predicting metal retention in a constructed mine drainage wetland

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Abstract

A computer simulation model was developed to predict metal retention in constructed mine drainage wetlands. The model emphasized the processes of advection, diffusion, and precipitation/sedimentation in both surface and subsurface state variables. The model was calibrated and verified using data from five constructed wetlands in Pennsylvania and Ohio, USA. Simulation of metal retention in a proposed mine drainage wetland in southeastern Ohio was performed using baseline data, collected for 18 months prior to wetland construction as model inputs. Predicted retention ranges from 0 to 93% for aluminum and from 50 to 99% for iron for the proposed wetland, depending on season and whether surface or subsurface flow is used. Diffusion of metals from water to sediments limits metal retention in low pH wetlands while metal precipitation rates from the water column limit metal retention in circumneutral wetlands.

Key words: Acid mine drainage; Constructed wetland; Metal; Mine drainage; Model

1. Introduction

The natural oxidation of pyritic materials in coal-bearing strata exposed during mining has resulted in one of the most serious water pollution problems now confronting coal-producing regions. Mine drainage produced by this process can cause damage to agricultural, municipal and industrial water supplies; navigational structures and equipment; and fisheries. Mine drainage also adversely affects lake and stream ecosystems into which it drains (Yeasted and Shane, 1976). As mine

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drainage enters natural waters, chemical and biological processes act to oxidize ferrous iron, yielding a ferric hydroxide precipitate commonly referred to as "yellowboy". This precipitate covers stream bottoms and smothers most biological activity (Letterman and Mitsch, 1978).

Studies have suggested that natural and artificial wetland systems represent alternatives to more conventional chemically based methods of mine drainage treatment (Wieder and Lang, 1982; Tarleton et al., 1984; Fennessy and Mitsch, 1989a,b). Wetlands were claimed to have the advantage of being self-repairing, low-maintenance, cost-efficient systems. They serve as interface systems to lessen the impact of mine drainage on adjacent downstream areas (Mitsch et al., 1985). Wieder (1989) surveyed 147 operational mine drainage wetlands and was unable to find a variable with a strong correlation with the percent reduction in metal concentrations between inflows and outflows. He concluded that the performance of mine drainage wetlands is highly variable and difficult to predict.

Several processes are key when predicting wetland performance and dynamic models may be well suited to the simulation of such systems. Few models exist which have simulated the impact of mine drainage on wetlands or the impact of constructed wetlands on mine drainage. Mitsch et al. (1981, 1983) and Fennessy and Mitsch (1989a,b) developed conceptual models to describe the impacts of coal mining on wetlands and to predict iron retention and cycling in wetland ecosystems. Baker et al. (1991) developed a model that simulates the retention of iron in mine drainage wetlands as affected by influent pH, iron loading rates, and *Typha* spp. biomass. This model requires modest data inputs, and it predicted iron retention in mine drainage wetlands for a limited set of conditions. That model simulated only iron retention in wetlands and did so with a very simple linear sedimentation pathway for iron sedimentation. The Baker et al. (1991) model also included an economic submodel for estimating the cost of a wetland treatment system and comparing it with conventional treatment approaches.

The objectives of this study were to develop and validate a dynamic computer model that simulates specific pathways for metal retention in mine drainage wetlands. The model was calibrated and validated using water chemistry data, hydrologic data, and wetland design specifications from existing constructed wetlands in the Eastern United States. The validated model and a baseline data set were then used for an a priori prediction of metal fate in a wetland proposed for a stream impacted by acid mine drainage in southeastern Ohio, USA. Simulations included a proposed subsurface mine drainage flow through the wetland substrate.

2. Methods

2.1. Modelling techniques

The goal of the wetland model development was to enable the prediction of wetland performance before construction. The model utilizes STELLA^{TM} II (version 1.02), a higher-order object-oriented modelling language designed for use on

Apple Macintosh^{TM} computers. The model is zero dimensional and uses an Eulerian reference system that describes dynamic processes from a fixed reference point. The model includes several simultaneous first-order differential equations, each having one or more associated algebraic equations. The integration technique used in this model is the fourth-order Runge–Kutta, an appropriate method in continuous systems that have inherent oscillatory tendencies (Richmond and Peterson, 1992). The simulation times are variable and the time step is 0.5 day. Data from several previously constructed wetlands in Ohio and Pennsylvania were used to calibrate the model.

Model assumptions

Assumptions frequently allow reduced model articulation which may, in turn, increase the model's descriptive accuracy — how well the model explains what is being attempted (Costanza and Sklar, 1985; Jørgensen, 1988). The assumptions made in developing the wetland model were that:

- influent water chemistry is a valid predictor of metal retention rates in mine drainage wetlands;
- the standing stock of aquatic macrophytes has a positive influence on the rate of metal retention in wetlands (Fennessy, 1988; Fennesy and Mitsch, 1989b; Baker et al., 1991);
- a solid phase (mineral) can be identified that primarily controls the solubility of a given metal;
- the rate of metal precipitation is a function of the extent that the ion activity product exceeds the solubility product of the controlling mineral (Sposito, 1989); and
- the majority of influent iron will be as ferric (Fe^{3+}) iron.

This final assumption is supported by data from several sites. At Friendship Hill, Pennsylvania (Hedin et al., 1991) data show approximately 90% of the iron to be as ferric iron. The Simco (Ohio) and Cedar (Pennsylvania) mine drainage wetlands have circumneutral influent pH values that lead to rapid ferrous iron oxidation (Fennessy and Mitsch, 1989a,b; Hedin and Nairn, 1993). Mine drainage upstream of the Lick Run wetland site described has a pattern of declining pH and development of red coloration, the latter an indicator of ferric iron. The fact that several wetlands have effluents that have a high proportion of ferrous iron does not invalidate this assumption. Influents are almost always high in ferric iron or the water is quickly oxidized in the wetland.

Model limitations

The wetland model has the following limitations to its utility:

- the model predicts iron and aluminum retention in wetlands; it does not address all constituents present in mine drainage that may have negative impacts on aquatic ecosystems;
- the model may not be applicable to a mine drainage wetland where influent iron is predominantly in the ferrous state and water column dissolved oxygen limits ferrous iron oxidation;

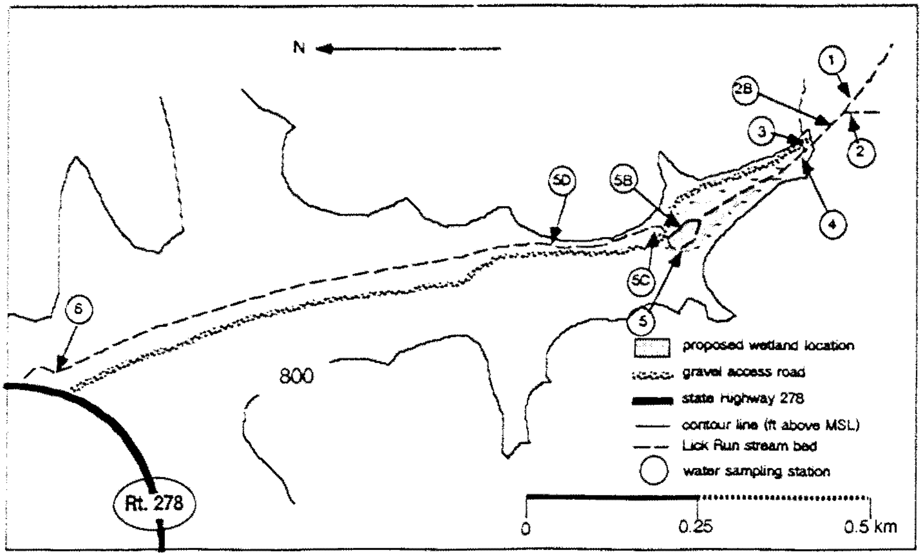

Fig. 1. Lick Run watershed, Athens County, OH, USA, showing sampling stations and proposed site of constructed wetland for mine drainage control.

- the model may not be applicable when kinetic constraints prevent the realization of equilibrium chemical conditions within the time periods defined by wetland retention times;
- the model simulates net rates of metal removal and does not address the dissolution of minerals within the wetland.

2.2. *Mine drainage wetland pre-construction data collection and design*

Data collection

The model, after validation, was used to predict the metal retention of a wetland being constructed in southeastern Ohio, USA, approximately 3 km west of Nelsonville, for the control of mine drainage. Water sampling stations on Lick Run (Fig. 1) were located upstream (stations 1, 2, 2B, 3, and 4), and downstream (stations 5, 5B, 5C, 5D, and 6) of the proposed wetland. Base line data collection began at the Lick Run project site 18 months prior to the construction of the wetland system from December, 1990 through March, 1992. Samples were collected monthly during the spring, fall and winter quarters, and twice per month during the summer quarter. Two separate unfiltered water samples were collected from each station. One sample was preserved with 2 ml of 30% nitric acid for the determination of total iron, total manganese, and total aluminum. The other sample was taken for the determination of alkalinity, acidity, turbidity and sulfate concentration. A summary of methods used in field and laboratory tests is presented in Table 1. Streamflow was measured on the site from April, 1991 to

Table 1
Analytical methods and instrumentation for each water quality parameter measured at the Lick Run, Ohio, site

Parameter	Analytical instrument	Analytical method	EPA procedure [a]
Acidity	titration glassware	titrimetric	305.1
Alkalinity	titration glassware	titrimetric	310.1
Lab conductivity	YSI 32 conductance meter	electrometric	120.1
Field conductivity	Hach DREL 1/C conductivity meter	electrometric	120.1
Iron Perkin	Elmer 2380 atomic absorption meter	Atomic absorption–direct aspiration	236.1
Manganese	" "	" "	243.1
Aluminum	" "	" "	273.1
Field pH	Fisher Acumet pH meter	electrometric	150.1
Lab pH	Orion 710 Ion Analyzer	electrometric	150.1
Sulfate	turbidimeter	turbidimetric	375.3, 375.4
Turbidity	Hach ratio turbidimeter model 18900	turbidimetric	

[a] Source: U.S. EPA (1983).

March, 1992 during water sample collection at Stations 2B, 3, 5B, and 5D using a bucket and stop watch. Flow data were collected monthly during the spring, fall and winter quarters, and bimonthly during the summer quarter. Flow data were not collected at the downstream stations during August and September of 1991 due to the beginning of construction at the project site.

Wetland design — Lick Run wetland

When completed, the proposed wetland at Lick Run will consist of six basins (9 cells) with a total area of 0.38 ha (Fig. 2). Wooden weirs divide basins 1 and 2 into a total of 5 cells labeled A–E. Cells A–G were designed to encourage aerobic processes of iron removal. Common cattail (*Typha latifolia*) will be planted in these basins and should be the dominant vegetation type. To encourage aerobic conditions throughout the water column, these basins are designed to be extremely shallow ($\approx$ 8 cm). Hay bale dikes will be constructed to encourage a serpentine flow pattern. The substrate in these cells will have an upper layer of organic material consisting of 30 cm of spent mushroom compost or manure, underlain by 23 cm of limestone. Cells H and I use subsurface flow systems to maximize contact between mine drainage and the wetland substrate. Coincident with this process will be the generation of alkalinity and the removal of iron and sulfate through the formation of iron sulfides. To increase retention time, 46 cm of mine drainage will cover these final cells. The substrate has an upper layer of organic matter that consists of 46 cm of compost, underlain by 30 cm of gravel. Buried within this gravel layer will be a network of perforated tubing (infusion pipes in Fig. 2) designed to force the flow of mine drainage through the substrate and upward into the wetland's water column. Underlying the gravel layer is 15 cm of limestone

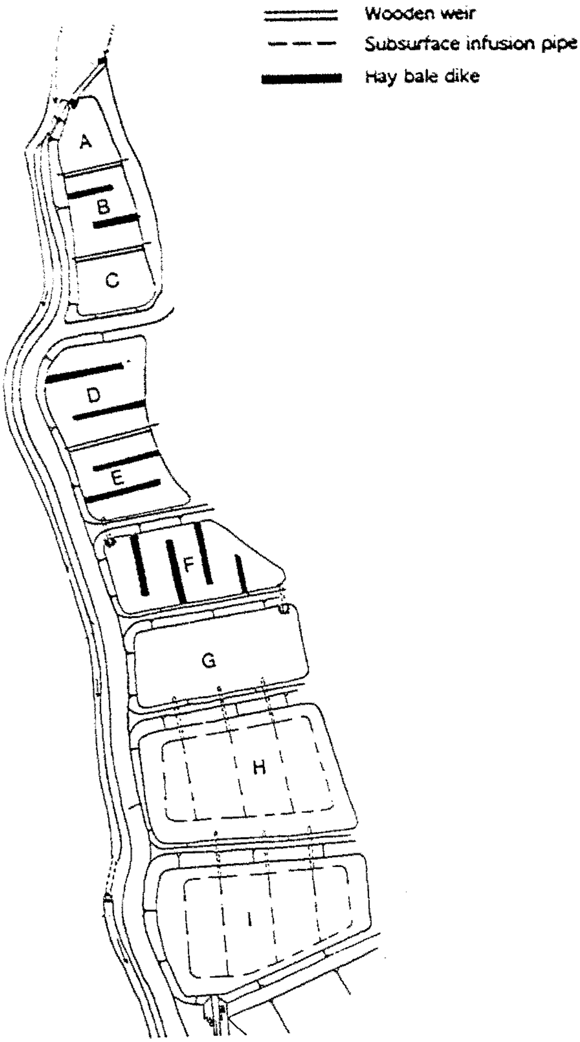

Fig. 2. Plan view of the Lick Run mine drainage wetland.

screenings. Construction on the site began in the summer 1991 and was completed in the fall of 1992, after the completion of this model.

3. Mine drainage wetland model

Fig. 3 presents a conceptual diagram of the mine drainage wetland model. Table 2 presents the names, symbols, and values for all pathways, state variables,

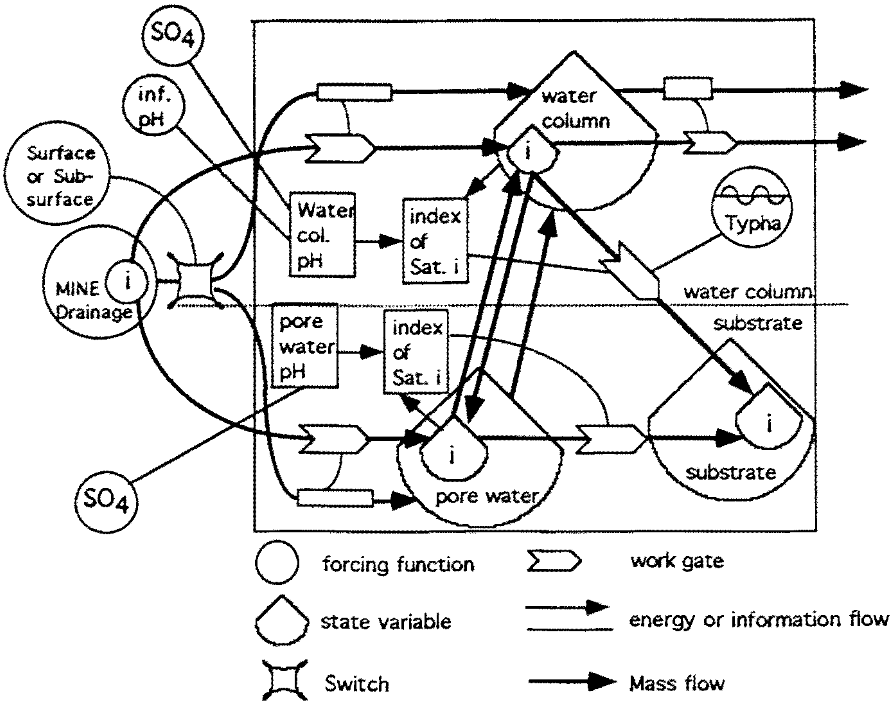

Fig. 3. Conceptual diagram of the mine drainage wetland model.

auxiliary variables, forcing functions and coefficients. The model uses functions describing simple transport processes to simulate metal retention in mine drainage wetlands. In wetlands where the influent pH values favor the formation of precipitates, metal retention occurs primarily through precipitation and sedimentation from the water column. In wetlands where this is not the case, metal retention occurs through the transport of soluble species into the wetland substrate. Within the substrate, conditions occur which are more favorable to the formation of metal precipitates. This transport process occurs through diffusion or by advection through subsurface infusion pipes. The model can describe wetland systems in which mine drainage flows both over the substrate surface and through the substrate by the use of infusion pipes.

The wetland model consists of two control volumes: the wetland water column and the substrate pore water. A state variable exists for each constituent under consideration in the wetland water column and pore water with inflows and outflows that describe the following processes: loading, outflow, sedimentation rates, rates of diffusion between the water column and pore water, and advection rates from the pore water to the water column. There are submodels describing the fate of iron and, where applicable, aluminum. The submodel for each metal is essentially identical with the exception of functions that calculate the degree of metal saturation.

Table 2
State variables, forcing functions, pathways and coefficients for mine drainage wetland model. Volume refers to the water volume of the wetland unless otherwise noted

State variable	Description	Initial value	Source
WC_i	water column conc. metal *i*	$0.1\ \mathrm{g\ m^{-3}}$	Assumption
PW_i	pore water conc. metal *i*	$0.1\ \mathrm{g\ m^{-3}}$	Assumption
SED_i	sediment accumulation of metal *i* precipitates	$0\ \mathrm{g\ m^{-3}}$	Assumption
Pathway	**Description**	**Unit**	**Source**
LWC_i	loading of metal *i* into water column	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
LPW_i	loading of metal *i* into pore water by infusion pipes	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
$PWPt_i$	metal precipitation from pore water	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
$WCPt_i$	metal precipitation from water column	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
$DIFF_i$	diffusion of metal *i* into porewater	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
ADV_i	advection of metal *i* from pore into water column	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
OUT_i	metal *i* load leaving wetland	$\mathrm{g\ m^{-3}\ day^{-1}}$	Calculation
G_{adv}	flow of water through diffusion pipes	$\mathrm{l\ min^{-1}}$	
Parameter	**Description**	**Unit**	**Source**
G_o	substrate flow	$\mathrm{m^3}$	Field data
S_o	wetland surface flow	$\mathrm{m^3}$	Field data
PS	proportion of mine drainage flowing through substrate	%/100	Field data
pH_{inf}	pH value of wetland influent	S.U.	Field data
pH_{sub}	pH value of wetland substrate	S.U.	Assumption
A	wetland area	$\mathrm{m^2}$	Field data
EC	conductivity of wetland influent	μmhos/cm	Field data
C_i	influent conc. of metal *i*	mg Fe/l	Field data
Ω_{iwc}	water column relative saturation metal *i*	unitless	Calculation
Ω_{ipw}	pore water relative saturation metal *i*	unitless	Calculation
γ_i	activity coefficent, metal *i*	unitless	Calculation
V_{wc}	volume of wetland water column	$\mathrm{m^3}$	Calculation
V_{pw}	volume of substrate porewater	$\mathrm{m^3}$	Calculation
h_{wc}	depth of water column	m	Field data
SS	*Typha* spp. standing stock	$\mathrm{kcal/m^2}$	Calculation
$\emptyset$	substrate porosity	80%	Estimation
V_s	substrate volume	$\mathrm{m^3}$	
$WCEQ_i$	equilibrium concentration of metal *i*	$\mathrm{g\ m^{-3}}$	Calculation
Coefficient	**Description**	**Value**	**Unit**
K_{diff}	mass transfer coefficient	0.01	$\mathrm{m \cdot day^{-1}}$
K_{pwpt}	pore water precipitation coefficient	0.1	$\mathrm{day^{-1}}$
K_{wcpt}	water column precipitation coefficient	0.00025	$\mathrm{m^2\ kcal^{-1}\ day^{-1}}$

3.1. Water column state variable

The model water column has a state variable for each constituent simulated. The following equation governs the state variable (definitions of terms in Table 2):

$$\frac{d[WC_i]}{dt} = LWC_1 - DIFF_i - WCPt_1 + \frac{V_{pw}}{V_{WC}} * ADV_i - OUT_i. \qquad (1)$$

Inflow of metal

The first term in Eq. 1 represents the load of metal i entering the wetland system through surface flow. This term is calculated using the following equation:

$$\mathrm{LWC}_i = \frac{(C_i * S_o * 1.44)}{V_{\mathrm{WC}}}, \tag{2}$$

where 1.44 = unit conversion factor ($\mathrm{mg \cdot min^{-1}}$ to $\mathrm{g \cdot day^{-1}}$).

Diffusion

Once the transportation of species i into the wetland water column occurs, two main processes result in metal retention. The first process is the transport of soluble species into the wetland substrate through diffusion. This process is described by the pathway DIFF_i which has the following equation:

$$\mathrm{DIFF}_i = \frac{K_{\mathrm{diff}}}{h_{\mathrm{WC}}} * [\mathrm{WCEQ}_i - \mathrm{PW}_i]. \tag{3}$$

The equilibrium concentrations (WCEQ) of Fe and Al are calculated using equations described by Karathanasis et al. (1988). The activity of Fe^{3+} was described in surface waters and soil solutions contaminated by mine drainage and was calculated from total Fe distribution into the species $\mathrm{Fe(OH)}^{2+}$, $\mathrm{Fe(OH)}_2^-$, $\mathrm{Fe(SO_4)}^+$ plus Fe^{2+}. Fe^{3+} solubility in mine drainage was controlled by a mineral with a stoichiometry similar to jarosite but having a much higher solubility. Nordstrum (1982) found that aluminum concentrations in mine drainage where $\mathrm{pH} < 4.5$ is related to the solubility of the aluminum sulfate minerals alunite, jurbanite, and basalumite. Chapman et al. (1983) found that Al^{3+} solubility in mine drainage was controlled by the basic aluminum sulfate, basaluminite. The model calculates the activities of iron and aluminum using the equations proposed by Karathanasis et al. (1988):

$$\mathrm{pFe} = 0.96\left(2\mathrm{pH} - (2/3) * \mathrm{pSO_4^{2-}}\right) - 1.6, \ (4)$$

and Chapman et al. (1983):

$$\mathrm{pAl} = (5/2)\mathrm{pH} + (1/4)\mathrm{pSO_4^{2-}} - 6.0, \tag{5}$$

where p(metal i) = the negative log of metal i activities, and $\mathrm{pSO_4^{2-}}$ = the negative log of $\mathrm{SO_4^{2-}}$ activity.

The activity of a dissolved species was calculated by multiplying species concentration by an activity coefficient (γ_i). This activity coefficient was obtained using the Davies equation and is unitless (Sposito, 1989):

$$\log \gamma_i = -0.512 * Z^2 \left[\frac{\sqrt{\mathrm{IS}}}{1 + \sqrt{\mathrm{IS}}} - 0.3 * \mathrm{IS} \right], \tag{6}$$

where IS = the ionic strength of the mine drainage solution (unitless) and Z = valence of metal i.

Ionic strength is calculated from field conductivity using the relationship (Stumm and Morgan, 1990):

$$\mathrm{IS} = 1.5 * 10^{-5} * \mathrm{EC}, \tag{7}$$

where EC = electrical conductivity (μmhos · cm^{-1}).

Precititation of metal

Precipitation of metal i within the water column is described by the pathway WCPt_i. This pathway has the equation:

$$\mathrm{WCPt}_i = K_{\mathrm{wcpt}} * \log \Omega_i * \mathrm{SS} * \mathrm{WC}_i, \tag{8}$$

where Ω_i = relative saturation of metal i (unitless).

If the influent mine drainage is saturated with respect to metal i, colloids and metastable solids will be present and will settle from the water column. The degree to which the influent is saturated with respect to metal i is indicated by the magnitude of the relative saturation (Ω_i), which is calculated using a function specific to the mineral controlling the solubility of metal i. The relative saturation (Ω_i) is calculated as the ratio of the ion activity product (IAP) to the solubility constant (K_{sp}) (Sposito, 1989):

$$\Omega_i = \mathrm{IAP}/K_{\mathrm{sp}}. \tag{9}$$

For iron, this ratio takes the form:

$$\text{relative saturation } (\Omega_{\mathrm{Fe}}) = \frac{(\mathrm{Fe})(\mathrm{SO_4})^{0.64}}{(\mathrm{H})^{1.92} 10^{1.6}}. \tag{10}$$

For aluminum the equation is rearranged in the form:

$$\text{relative saturation } (\Omega_{\mathrm{Al}}) = \frac{(\mathrm{Al})^{4}(\mathrm{SO_4})}{(\mathrm{H})^{10} 10^{24}}. \tag{11}$$

According to Sposito (1989), the rate of precipitation of metal i is a function of Ω_i. If the relative saturation is less than 1, then the influent mine drainage is undersaturated with respect to metal i, and no precipitation should occur. If $\Omega_i > 1$, the rate of precipitation is proportional to the $\log \Omega_i$ (see Eq. 8).

Role of vegetation

Based on previous field studies (e.g., Fennessy and Mitsch, 1989a,b) *Typha* spp. standing stock (SS) is assumed to have a positive influence on the rate of sedimentation precipitates. Standing stock is defined as the sum of living and dead biomass which is held above the surface of the wetland substrate and influences water movement. An approximation of seasonal variation in *Typha* spp. standing stock was made by the sine function:

$$\mathrm{SS} = 1800 + 400 * \sin(0.17 * \mathrm{time} + 60). \tag{12}$$

The output of this equation agrees well with predictions of *Typha* spp. standing stock generated by Baker's model of an Ohio mine drainage wetland (Baker, 1989).

The equation fails to predict the long-term rise or decline in *Typha* spp. biomass in the wetland, i.e., it assumes the same biomass pattern every year.

Advection with subsurface pipes

The term ADV_i describes the advection of metal from the substrate of wetlands using subsurface infusion pipes. The pathway has the following equation:

$$\mathrm{ADV}_i = \frac{\mathrm{PW}_i * G_{\mathrm{adv}} * 1.44}{V_{\mathrm{pw}}}. \qquad (13)$$

This term is multiplied by the ratio of pore water volume to water column volume ($V_{\mathrm{pw}}/V_{\mathrm{wc}}$) in order to account for dilution. G_{adv} describes the volume of water flowing through subsurface infusion pipes. In simulations, the percentage of influent flow which is forced through these infusion pipes is specified in proportion-subsurface (PS). Surface flow (S_{o}) and subsurface flow (G_{o}) are then calculated using the following equations:

$$G_{\mathrm{o}} = \mathrm{Flow} * \mathrm{PS}, \qquad (14)$$

$$S_{\mathrm{o}} = \mathrm{Flow} * (1 - \mathrm{PS}). \qquad (15)$$

Outflow of metal

The final term in Eq. 1 describes the transport of species i from the wetland. This process is dependent upon the flow of water out of the wetland and the metal i concentration with the water column. This pathway has the equation,

$$\mathrm{OUT}_i = \frac{[\mathrm{WC}_i * S_{\mathrm{o}} * 1.44]}{V_{\mathrm{WC}}}. \qquad (16)$$

3.2. Pore water state variable

The pore water state variable in each submodel is governed by the following equation:

$$\frac{\mathrm{d}(\mathrm{PW}_i)}{\mathrm{d}t} = \mathrm{LPW}_i + \frac{V_{\mathrm{WC}}}{V_{\mathrm{pw}}} * \mathrm{DIFF}_i - \mathrm{PWPt}_i - \mathrm{ADV}_i. \qquad (17)$$

Inflow to subsurface

The first term in Eq. 17 (LPW_i) describes the loading of species i into the wetland pore water through subsurface infusion pipes). The pathway has the following equation,

$$\mathrm{LPW}_i = \frac{(G_{\mathrm{adv}} * C_i * 1.44)}{V_{\mathrm{pw}}}, \qquad (18)$$

where C_i = influent concentration of species i (mg/l).

The volume of pore water within the wetland substrate (V_{pw}) is calculated using this equation:

$$V_{pw} = V_s * \emptyset. \tag{19}$$

Diffusion and precipitation

$DIFF_i$ is multiplied by the ratio of water column volume to pore water volume (V_{wc}/V_{pw}) in Eq. 17 to account for dilution. The third term in Eq. 17, $PWPt_i$, represents the precipitation of metal i from pore water solution. The pathway has the equation:

$$PWPt_i = K_{pwpt} * \log \Omega_{ipw} * PW_i. \tag{20}$$

Calculation of the relative saturation within the pore water uses Eqs. 10 and 11. In this pathway the substrate pH (pH_{sub}) replaces influent pH. In simulations where the substrate is assumed to be circumneutral a pH value of 6.5 is used; otherwise substrate pH one unit greater than influent pH was assumed. The bases of these assumptions are the observations of McIntire and Edenborn (1990), who found that substrate pH generally remained between 6.0 and 7.0 but fell within the range 3.2–4.5 when the substrate neutralization potential was exhausted. The surface water in this wetland had pH values in the range of 2.5 to 3.5, approximately one pH unit lower than observed substrate pH values. Simulations that assume the exhaustion of acid neutralization capacity yield conservative estimates of metal retention.

Table 3
Simulations performed with a brief description of purpose, assumptions (if any) and data sources

Simulation number	Description
1	calibration K_{pwpt}, Friendship Hill wetland [a]
2	calibration K_{wcpt} Simco no. 4 wetland [c]
3	sensitivity analysis, diffusion coefficient (K_{diff})
4	sensitivity analysis, water column ppt. coefficient (K_{wcpt})
5	sensitivity analysis, pore water ppt. coefficient (K_{pwpt})
6	validation, surface flow, Latrobe wetland [b]
7	validation, surface flow, Somerset wetland [b]
8	validation, surface flow, Emelenton wetland [b]
9	validation, surface flow, Cedar wetland [b]
10	validation, subsurface flow, circumneutral substrate pH, Friendship Hill [a]
11	validation, subsurface flow, low substrate pH, Friendship Hill wetland [a]
12	prediction, subsurface flow, circumneutral substrate pH, Lick Run
13	prediction, subsurface flow, low substrate pH, Lick Run

[a] Input data from Hedin et al. (1991).
[b] Input data from Hedin and Nairn (1993).
[c] Input data from Fennessy (1988).

4. Results and discussion

The model was used to simulate metal retention in several wetland systems. Simulations had three purposes: model calibration, model validation, and metal retention prediction for a proposed wetland. Table 3 summarizes each simulation with a brief description of purpose, data source, and assumptions.

4.1. Simulation results — calibration and validation

The process of calibration consists of adjusting key model parameters so that simulated values for a modeled variable are in agreement with in situ data. The calibration process used data from two wetland systems. Different processes limited metal retention in each simulation.

Calibration of the pore water precipitation coefficient (simulation 1)
The purpose of this simulation was to calibrate the pore water precipitation coefficient (K_{pwpt}). This simulation examined iron and aluminum retention in a low pH, surface flow wetland. Input data for this simulation came from the Friendship Hill experimental wetland in Pennsylvania (Hedin et al., 1991). The simulation period was from June 6, 1990, to June 5, 1991. The wetland had a mean influent pH of 2.7, an area of 667 m^2, and a mean depth of 15 cm (see McIntire and Edenborn, 1990 and Hedin et al., 1991 for a complete description of the Friendship Hill site).

Because of low influent pH, the model predicts no precipitation of iron or aluminum within the water column. This situation allowed the calibration of the pore water precipitation pathway by adjusting the pore water precipitation coefficient (K_{pwpt}) such that simulated effluent values were in agreement with observed effluent values. The diffusion pathway used a coefficient obtained from De Pinto et al. (1989) and thus was not used for calibration. Figs. 4a and 4b show good agreement between observed and simulated effluent concentrations of total iron and total aluminum. Rates of iron diffusion remained constant throughout the simulation, though iron loading rates varied considerably. This implies that rates of diffusion are limited by physical constraints such as substrate hydraulic conductivity, not by loading rates. Retention efficiencies are highest when loading rates approach diffusion rates. In this simulation the differences between loading and diffusion rates were generally large, resulting in low removal efficiencies. Fig. 4 suggests that iron retention efficiency in low pH wetlands ($pH < 3.5$) can improve through decreased iron loading rates or increased rates of metal transport into the wetland substrate.

Calibration of the water column precipitation coefficient (simulation 2)
The water column precipitation pathway ($WCPt_i$) was calibrated in this simulation. Input chemistry data and wetland design specifications used in this simulation are from the Simco wetland near Coshocton, Ohio (Fennessy, 1988; Fennessy and Mitsch, 1989a,b; Baker et al., 1991). The wetland receives circumneutral mine

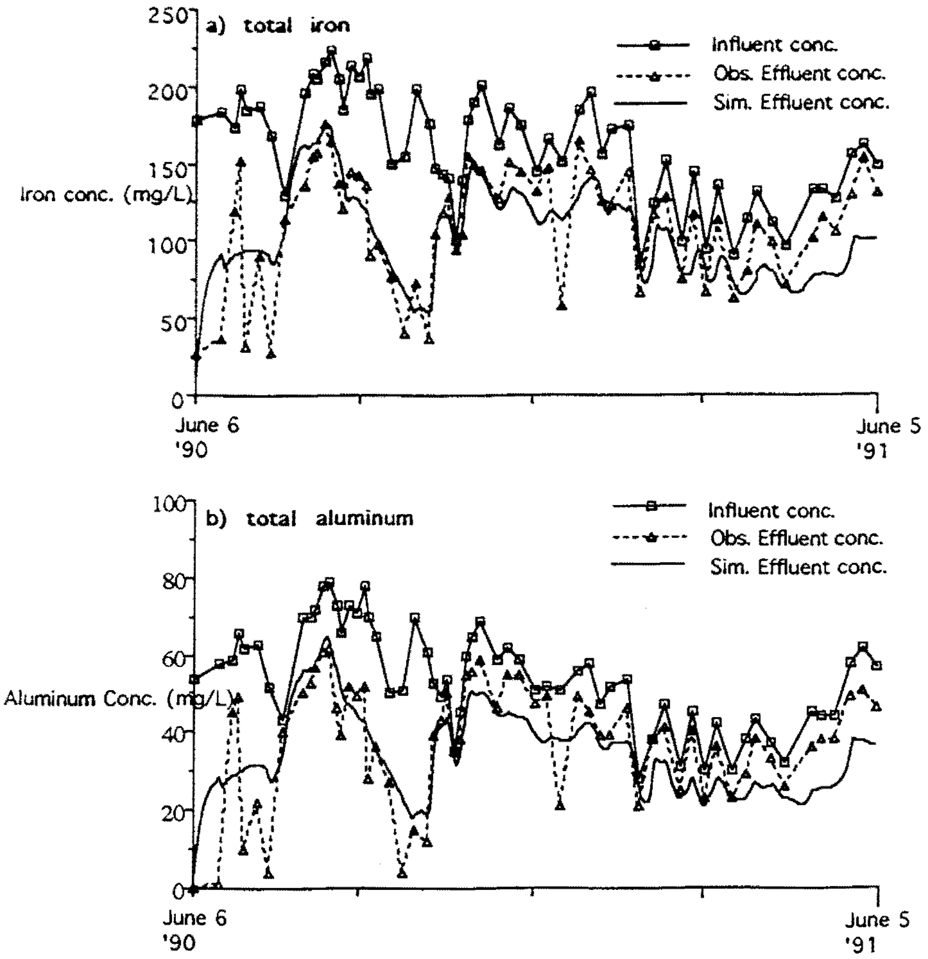

Fig. 4. Simulated and observed effluent concentrations of (a) total iron and (b) total aluminum at the Friendship Hill, Pennsylvania, USA, wetland site, surface flow only.

drainage. Because of these pH values, the model predicts rapid iron precipitation from the water column, allowing calibration of the water column precipitation pathway. The lack of reported data on aluminum concentrations from this site precluded simulation of aluminum retention. Fig. 5a shows good agreement between simulated and observed effluent iron concentrations. Fig. 5b shows removal efficiencies increasing as loading rates approach precipitation rates. Precipitation rates are lowest in the winter and fall periods and increase during the spring and summer growing season. Iron loading rates are highest in the spring, diminish through the summer, and remain low through the fall.

The wetland model suggests that seasonal variations in retention rates are not entirely due to variability in loading rates. If this were the case, removal rates

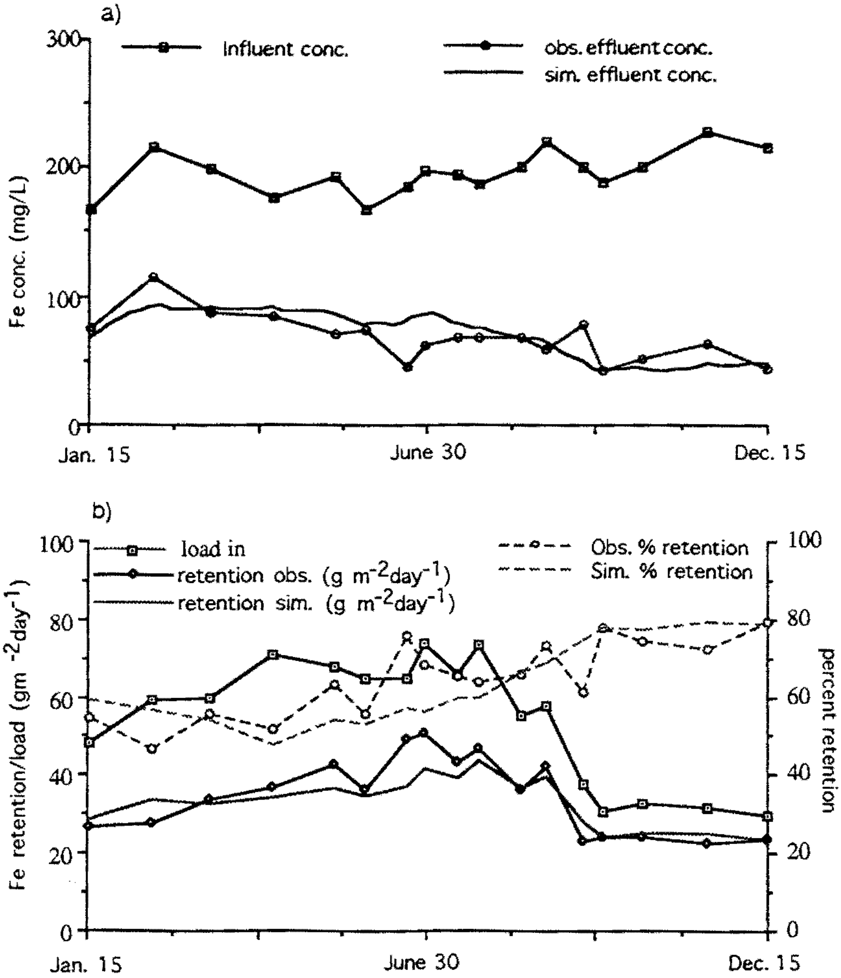

Fig. 5. Simulated and observed (a) effluent iron concentrations and (b) iron loading, iron retention (g m^{-2} day^{-1}), and percent retention for the Simco no. 4 wetland, Coshocton County, Ohio, USA, surface flow only (January 15–December 15, 1987).

would have decreased in proportion to loading during the late summer and fall. Instead, spring loading rates are nearly double fall rates, while retention rates during the spring and fall periods are approximately equal. This suggests a seasonal phenomenon is partially responsible for increases in retention rates during the summer. Although the model assumes that *Typha* spp. standing stock positively influences sedimentation rates, several other seasonally variable processes could be responsible for the observed seasonality in iron retention.

Sensitivity analysis

Using data from the Friendship Hill site, a sensitivity analysis assessed changes in water column iron concentrations resulting from changes in the diffusion coefficient. Fig. 6a shows the regression between the change in iron concentration

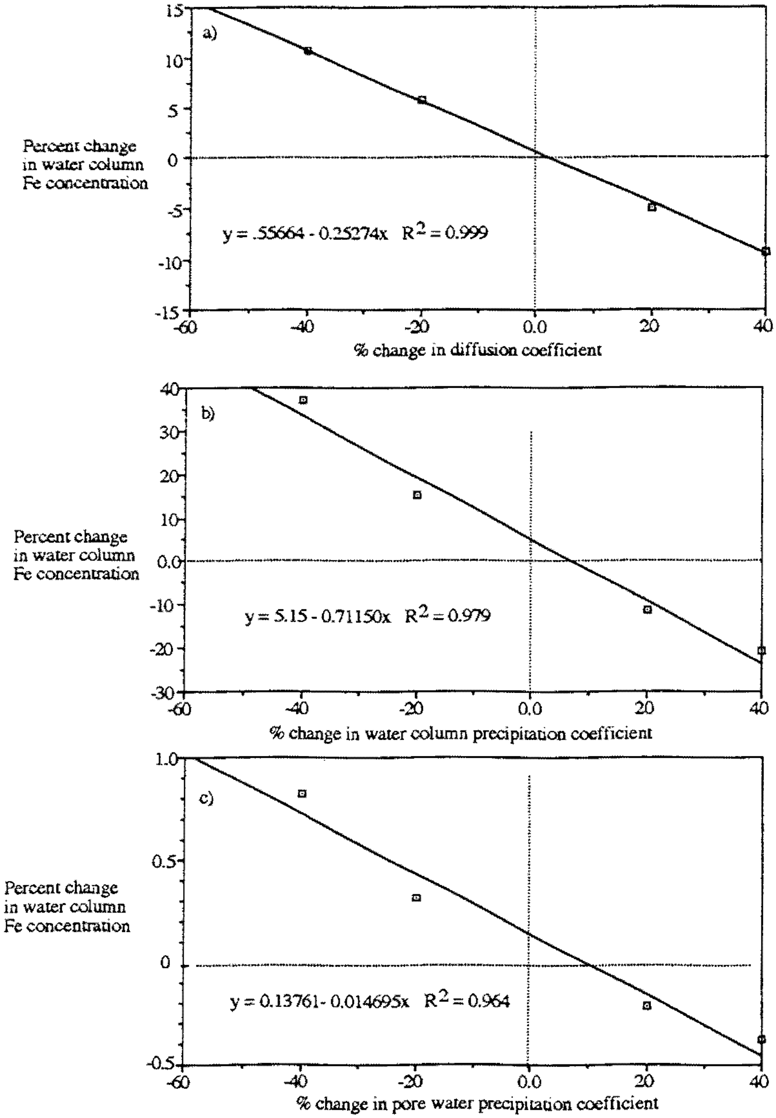

Fig. 6. Sensitivity analysis of parameters in wetland model showing percent change in water column iron concentration for the Friendship Hill wetland vs. (a) diffusion coefficient (K_{diff}), (b) water column precipitation coefficient (K_{wcpt}), and (c) pore water precipitation coefficient (K_{pwpt}).

and the change in the mass transfer coefficient (K_{diff}). The low slope of −0.25 is due to the large magnitude of loading rates relative to diffusion rates. This implies that significant increases in metal retention efficiency require large increases in rates of passive diffusion across the water column–substrate interface. Therefore, increased treatment efficiency can be attained only through non-passive iron transport by systems such as subsurface infusion pipes, or by greatly reducing loading rates.

In simulations of the Friendship Hill wetland, precipitation of iron and aluminum did not occur within the water column, due to low pH values. In these simulations the model is insensitive to changes in the water column precipitation coefficient (K_{wcpt}). Therefore, the analysis of the model's sensitivity to changes in the water column precipitation coefficient (K_{wcpt}), used data from the Simco no. 4 wetland (Fennessy, 1988). Fig. 6b shows a regression of the change in water column iron concentration versus the change in the sedimentation coefficient. The slope of this line (−0.71) shows that the model is very sensitive to sedimentation coefficients relative to diffusion coefficients. This suggests that sedimentation will be the dominant process of metal retention in wetlands where pH values allow precipitation from the water column. Small changes in pH values can have a large impact on precipitation rates by increasing the degree of metal saturation.

A sensitivity analysis was performed to measure model response to changes in the substrate sedimentation coefficient (K_{pwpt}). Several simulations of Friendship Hill wetland were performed in which surface flow and low substrate pH were assumed. Fig. 6c shows the model to be very insensitive to changes in this coefficient (slope = −0.015), suggesting this process does not limit metal retention.

Validation — surface flow

Simulations of four other wetland systems were run to validate the model (simulations 6–9). These simulations used input data from existing mine drainage wetlands as described in Hedin and Nairn (1993). This paper describes a total of 11 sites, of which four sites were *Typha* spp. wetlands having reported iron removal rates. The simulated wetlands are all surface flow systems. Table 4 summarizes input data, simulated iron removal rates, and observed removal rates for each simulation. In all cases, the simulated removal rates are within 10% of observed

Table 4
Model inputs, observed iron removal rates, simulated iron removal rates and model errors for surface flow validation simulations [a]

Site	Area (m^2)	Water depth (cm)	flow rate (l/min)	pH	Fe conc. (mg/l)	Fe load ($g\ m^{-2}\ day^{-1}$)	Sim. removal rate ($g\ m^{-2}\ day^{-1}$)	Obs. removal rate ($g\ m^{-2}\ day^{-1}$)	Model error (%)
Cedar	1360	15	568	6.3	95	57.1	22.2	24.2	10
Emlenton	643	50	61	4.5	96	13.1	10.1	10.4	5
Somerset	1005	15	27	3.7	202	7.8	4.8	4.8	−1
Latrobe	2800	15	86	3.5	125	5.5	2.0	2.1	−3

[a] Data from Hedin and Nairn (1993).

rates. Influent pH values for the wetlands ranged from 3.5 to 6.5, influent total iron concentrations ranged from 96 to 202 mg/l, and flow ranged from 27 to 568 l/min. These simulations indicate the model is capable of accurately simulating wetland iron retention across a wide range of conditions.

Validation — subsurface system

The objective of the following two simulations (10 and 11) is to validate the model in subsurface flow wetlands. Subsurface infusion pipes can significantly increase rates of metal transport across the water column–substrate interface,

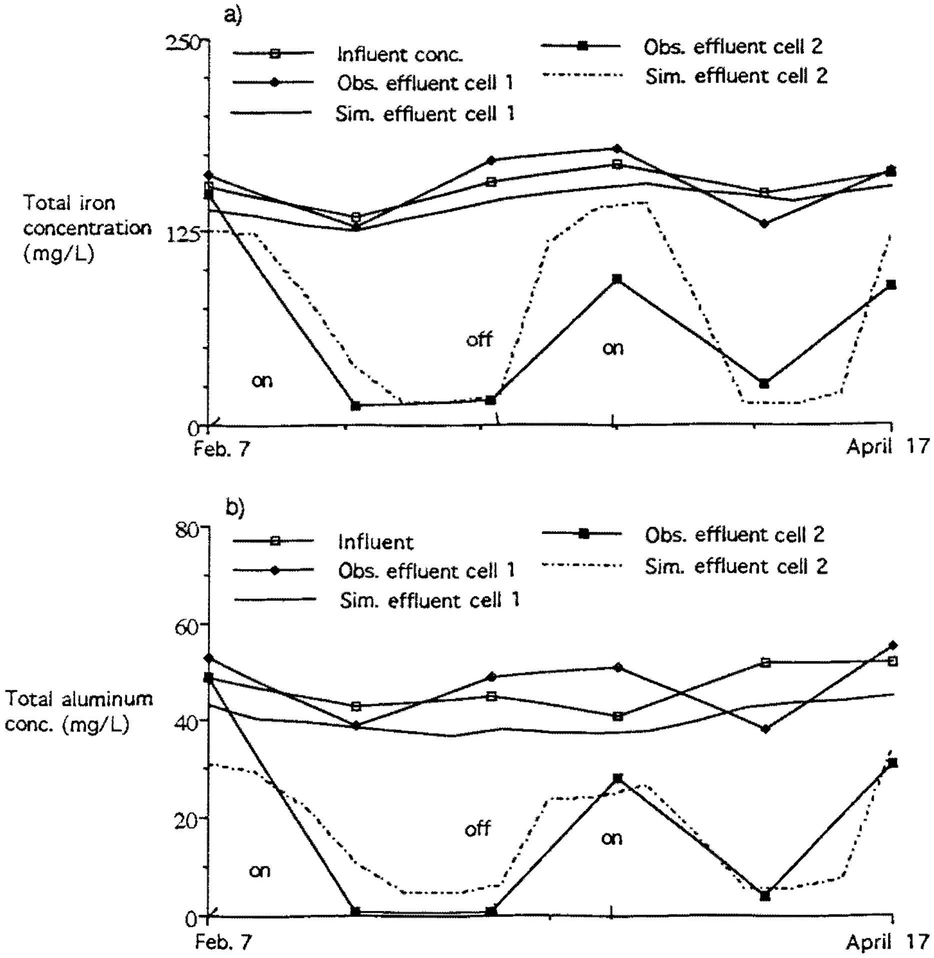

Fig. 7. Simulated and observed effluent concentration of (a) total iron and (b) total aluminum at the Friendship Hill wetland site, surface flow and subsurface flow. Circumneutral substrate pH is assumed (February 7–April 17, 1989).

causing other processes to limit metal retention. With infusion pipes in operation, metal transport occurs through the process of advection. Therefore, the rate of metal transport is a function of the subsurface flow rate.

In the first simulation a circumneutral substrate pH (6.5) was assumed. There are separate submodels for a surface flow cell (cell 1) and a subsurface flow cell (cell 2). The submodels are in series and have different areas (A), water column depths (h_{wc}), and flow paths. They are otherwise identical. The period of simulation is from February 7 to April 17, 1989. Simulated and observed effluent metal concentrations show good agreement in both cell 1 and cell 2 (Figs. 7). When the

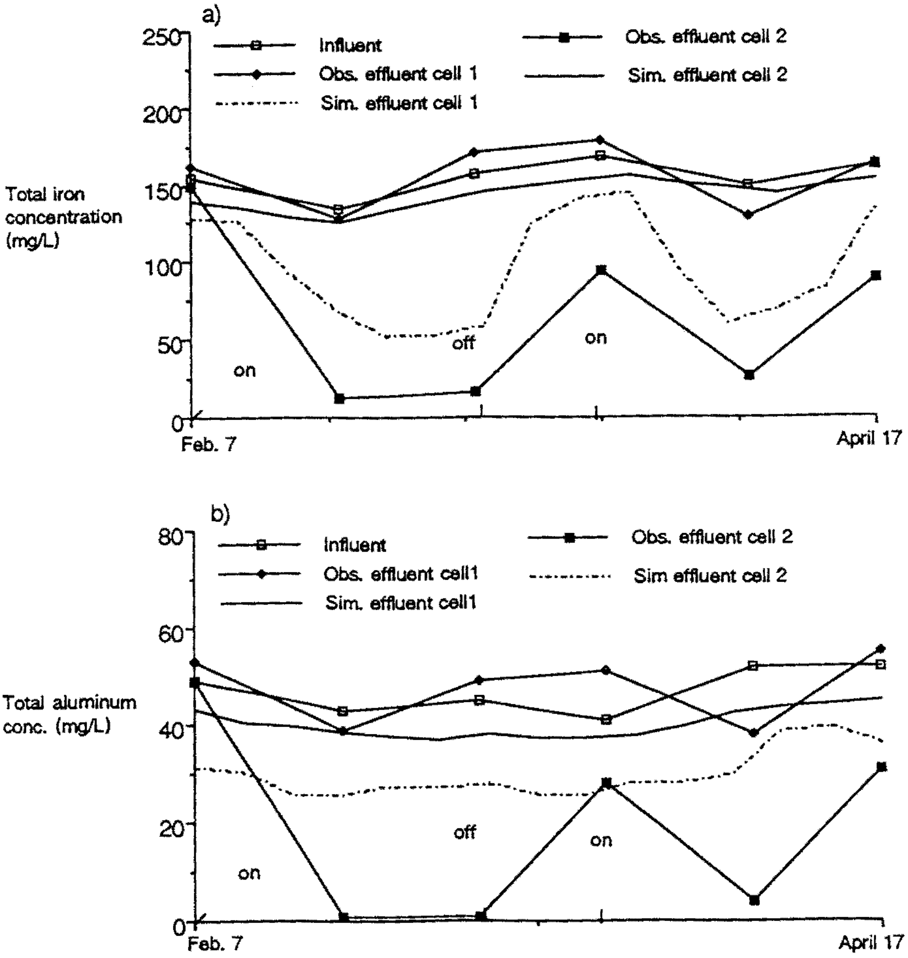

Fig. 8. Simulated and observed effluent concentration of (a) total iron and (b) total aluminum at the Friendship Hill wetland site, surface flow and subsurface flow. Low substrate pH is assumed (February 7–April 17, 1989).

infusion pipes are operating, iron and aluminum concentrations drop rapidly below 5 mg/l. With the infusion pipes turned off, iron and aluminum concentrations rebound to values greater than 90 mg/l and 25 mg/l, respectively. The infusion pipes are switched on a second time, and iron and aluminum concentrations again drop rapidly. This improvement in metal retention supports the hypothesis that transport across the water column–substrate interface limits metal retention in acidic mine drainage wetlands. High treatment efficiencies should continue while the infusion pipes continue to operate. Metal retention may be limited by the ability of the wetland to generate alkalinity and maintain circumneutral pore water pH values. Literature from the Friendship Hill wetland suggests the substrate's ability to generate alkalinity may rapidly diminish as limestone "armouring" occurs, and constant flow through the substrate disrupts anaerobic microbial populations (McIntire and Edenborn, 1990).

In the second simulation (no. 11) it was assumed the wetland substrate was not able to maintain a circumneutral pH. The model's structure and input data are identical to the previous simulation (no. 10), with the exception of the substrate pH, which is assumed to be one pH unit higher than the influent pH. Fig. 8 shows simulated and observed effluent concentrations from cell 1, and the simulated effluent concentration from cell 2. Effluent aluminum and iron concentrations drop rapidly when the infusion pipes are in operation, and then rebound to previously observed values when the infusion pipes are turned off. In this simulation, the mean effluent concentrations of iron and aluminum are 50 mg/l and 30 mg/l, respectively. These concentrations are higher than in the previous simulation, but substantially lower than effluent concentrations observed in simulation 1. In low pH systems small changes in pH can have a large influence on the solubility of iron and aluminum. Therefore, the use of a system to encourage subsurface flow may be beneficial even if the wetland substrate is not able to maintain circumneutral pH.

4.2. Simulated predictions of new mine drainage wetland performance

The validated wetland model was used to simulate metal retention prior to wetland construction at the Lick Run site from southwestern Ohio. Model inputs included baseline water chemistry data and proposed design specifications. The collection of water quality data occurred during an extended period of drought. Therefore, the simulations may represent wetland performance under unusually severe operating conditions.

Two simulations were run for the proposed wetland system (12 and 13). The first simulation (12) assumes the subsurface infusion pipes are in operation and the substrate will maintain circumneutral pH values. The second simulation (13) again assumes subsurface flow, but in this simulation substrate pH values are only one unit higher than influent pH values. In actuality, substrate pH values between those assumed in simulations 12 and 13 are likely. Therefore, simulation 13 is a conservative prediction of wetland performance while simulation 12 predicts optimal performance.

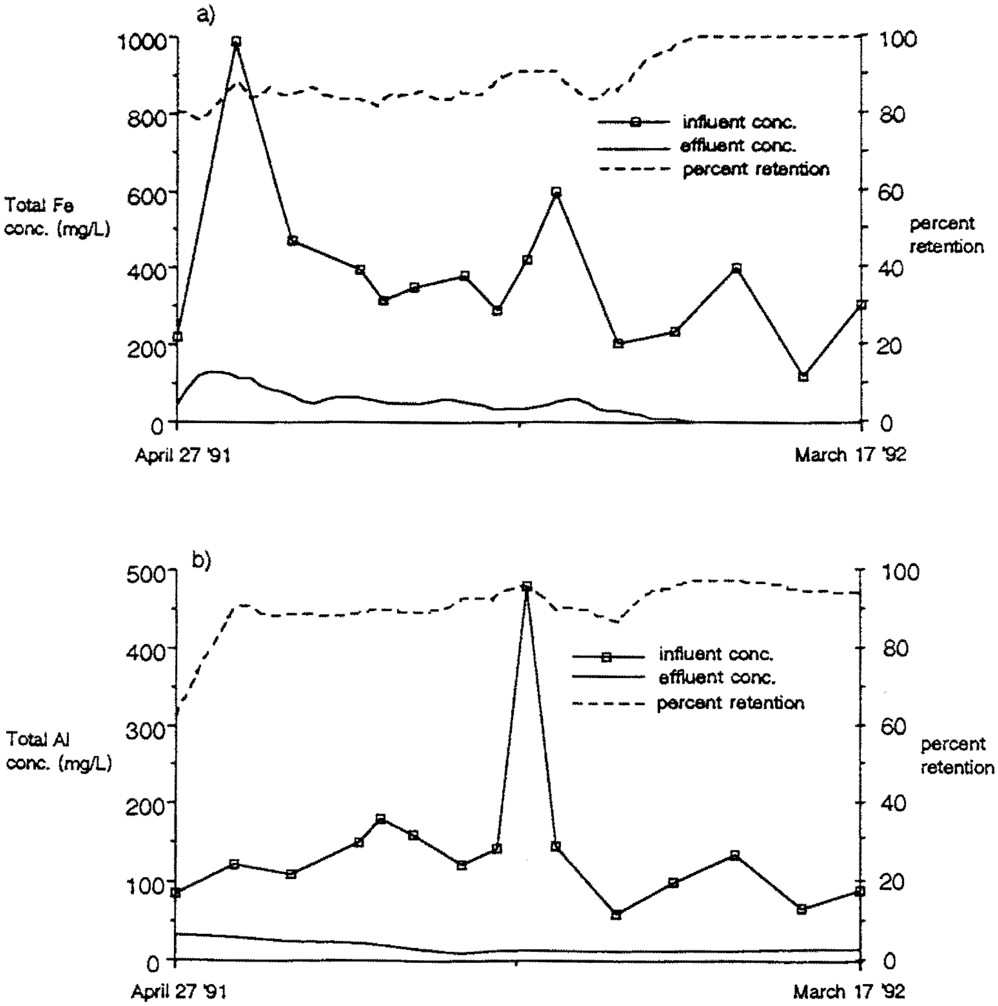

Fig. 9. Predicted effluent concentrations of (a) total iron and (b) total aluminum for the Lick Run wetland site. Surface and subsurface flow and circumneutral substrate pH are assumed.

Prediction — Lick Run wetland, circumneutral substrate pH (simulation 12)

In this simulation the model has two submodels connected in series. The first submodel represents a surface flow cell with an area of 1700 m^2 and a mean depth of 7.6 cm. The second submodel represents a wetland cell with infusion pipes in operation, an area of 2100 m^2, and a mean depth of 45 cm. This simulation assumes both cells maintain circumneutral substrate pH values. Fig. 9 shows simulated iron retention to range from 78 to 99% and aluminum retention to range from 63 to 93%. These results are expected, as the two potentially limiting

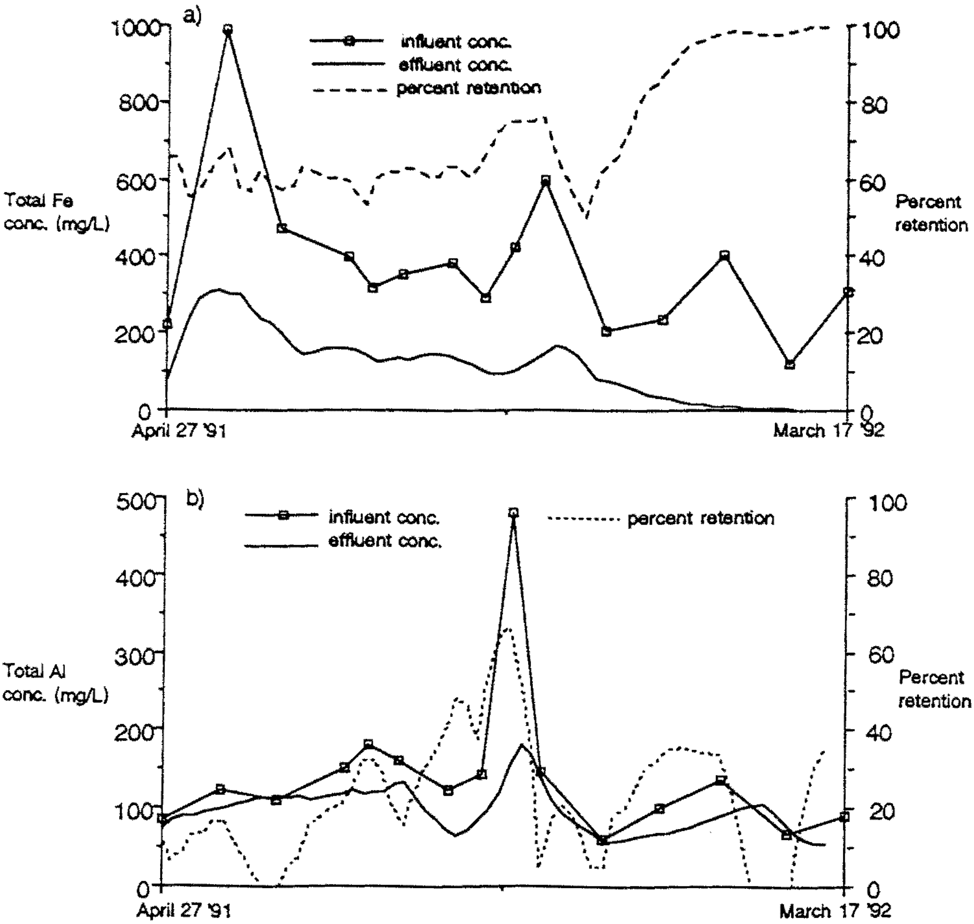

Fig. 10. Predicted effluent concentrations of (a) total iron and (b) total aluminum for the Lick Run wetland site. Subsurface flow and low substrate pH are assumed.

processes, transport and precipitation, occur at optimal rates. This implies that very high removal efficiencies will occur in wetlands that maintain subsurface flow and circumneutral pH values.

Prediction — Lick Run wetland, low substrate pH (simulation 13)

This simulation assumes the acid-neutralizing capacity of the wetland substrate is insufficient to maintain circumneutral pH values. The substrate pH value in this simulation is assumed to be one pH unit higher than influent pH values (2.7–3.0). Fig. 10 shows the removal of iron and aluminum to be less efficient under these conditions than in the previous simulation. However, iron removal efficiencies are still quite high. Iron removal efficiencies range from 50 to 98%. Due to the higher solubility of aluminum, removal efficiencies ranged from 0 to 60%.

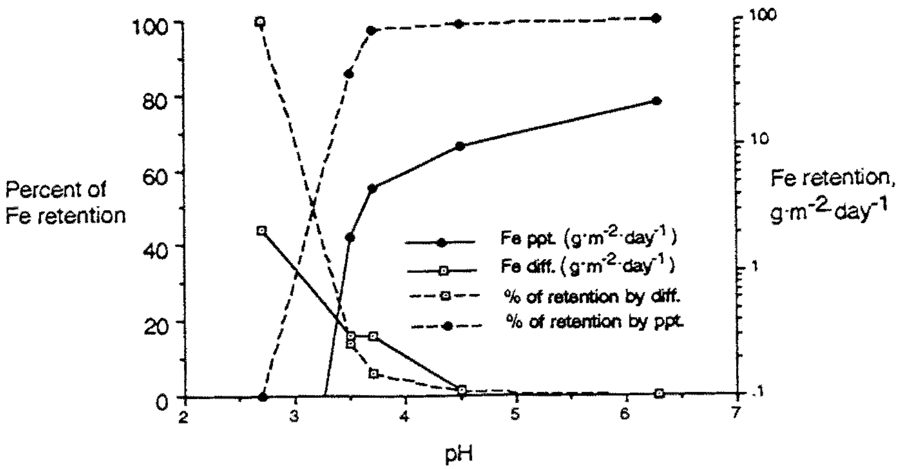

Fig. 11. The relative importance of the processes of diffusion (diff.) and precipitation (ppt.) in simulations of total iron retention in several mine drainage wetlands.

Simulation of the Lick Run site predicts high levels of treatment efficiency for iron. The model predicts low to moderate treatment efficiencies for aluminum. These predictions should be viewed with caution as the dissolution of ferrous minerals in the wetland substrate may result in lower net rates of iron retention. In addition, subsurface flow systems tend to become plugged with precipitates making them inoperative (McIntire and Edenborn, 1990; Hedin et al., 1991). Design modifications incorporated into the Lick Run wetland will hopefully prevent the clogging of these infusion pipes.

4.3. High vs. low pH wetlands

Fig. 11 shows the simulated proportion of iron retention occurring through diffusion and water column precipitation in wetlands over influent pH values from 2.5 to 6.5. In wetlands with influent pH values below 3.1, iron retention is limited by the process of diffusion. Water column precipitation dominates metal retention in simulations where influent pH is greater than 3.1. Maximal rates of iron retention occurring by diffusion were approximately 2.3 g m^{-2} day^{-1} in simulations performed for this study. Retention rates of greater than 20 g m^{-2} day^{-1} occurred when conditions favored water column precipitation. Sensitivity analysis of the diffusion coefficient indicates that large increases in rates of diffusion will yield only small increases in treatment efficiency.

5. Conclusions

These findings imply that in low pH wetlands increases in metal retention rates (g m^{-2} day^{-1}) can occur either by increasing influent pH sufficiently to allow metal precipitation from the water column or by encouraging the advection of metals into the substrate. Increases in influent pH can be accomplished through chemical treatment or by installing pretreatment systems that encourage passive contact with limestone under anoxic conditions (Hedin et al., 1991). Mechanical systems, such as infusion pipes, encourage advective transport of metal species into the wetland substrate. High pH wetlands continue to be the most effective for removal of metals both in field experience and in our modelling results. We recognize the importance of including a dynamic pH in future models of this type. For some mine drainage wetlands, the pH can change by several units as it passes through the wetland. Nevertheless we believe this model to be a good first start for providing a priori estimates of these wetlands prior to their construction across a wide range of influent pH values.

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