Pergamon

Wat. Sci. Tech. Vol. 29, No. 4, pp. 219–226, 1994.

0273–1223/94 $7·00 + 0·00

USING DECOMPOSITION KINETICS TO MODEL THE REMOVAL OF MINE WATER POLLUTANTS IN CONSTRUCTED WETLANDS

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ABSTRACT

Although numerous mathematical models have been used to describe decomposition, few, if any, have been used to model the removal of pollutants in constructed wetlands. A steady-state model based on decomposition kinetics and reaction stoichiometry has been developed which simulates the removal of ferrous iron entering wetlands constructed for mine drainage treatment. Input variables for the model include organic matter concentration, reaction rate coefficient, porosity and dry density, and hydraulic detention time. Application of the model assumes complete anaerobic conditions within the entire substrate profile, constant temperature, no additional organic matter input, and subsurface flow only. For these ideal conditions, model simulations indicate that wetlands constructed with readily decomposable substrates rich in organic carbon are initially capable of removing far greater amounts of iron than wetlands built with less biodegradable substrates. However, after three to five years of operation this difference becomes negligible. For acceptable long-term treatment performance, therefore, periodic additions of decomposable organic matter will be required.

KEYWORDS

Mine waste; modelling; organics removal; subsurface systems; decomposition; kinetics.

INTRODUCTION

The decomposition of organic matter often directly or indirectly affects the chemistry of the sediment interstitial solution and is a major process by which nutrients are regenerated and immobilized (Waples and Sloan, 1980). Although decomposition is important for nutrient cycling and energy transfer in natural wetlands, it has largely been ignored in the design and construction of wetlands built for mine drainage treatment. Understanding the factors which control the rate of organic matter decomposition and how these factors affect the fate of pollutants will allow engineers to design more effective wetland treatment systems.

The organic materials used in constructed wetlands decompose rather slowly, especially under waterlogged conditions. Nevertheless, decomposition drives the chemical diagenetic changes that occur in sediments (Berner, 1980). The majority of the sediment depth profile in wetlands is anoxic with only a thin oxic layer at the surface (Mitsch and Gosselink, 1986; Tarutis *et al.*, 1992). If long-term retention of mine water pollutants is to be accomplished, wetlands must be constructed such that natural decomposition processes enhance anoxic metal removal mechanisms.

Current research indicates that the dominant metal removal mechanism in surface-flow wetlands is the formation of oxides near the sediment surface. Plant metal absorption, cation exchange, and adsorption to organic matter contribute little to the overall retention, although the relative contribution of each depends on the sediment redox profile and the particular metal of concern (Tarutis and Unz, 1990; Tarutis *et al.*, 1992). A potentially important anoxic removal mechanism in subsurface-flow wetlands is the formation of iron sulfides produced in conjunction with bacterial sulfate reduction (Hedin, 1989; Stark *et al.*, 1991). Although numerous models have been used to describe organic matter decomposition (e.g., Wieder and Lang, 1982), few, if any, have been used to model the removal of pollutants in constructed wetlands. The purpose of this paper is to develop a conceptual model based on anaerobic decomposition kinetics and reaction stoichiometry to simulate the removal of ferrous iron entering wetlands constructed for mine drainage treatment.

MODEL DEVELOPMENT

Numerous variations of a first-order model have been employed to describe the kinetics of organic matter decomposition, almost all of which assume that the rate of decomposition is limited solely by the amount of decomposable organic carbon. Boudreau and Westrich (1984) have concluded that for sulfate concentrations typical of mine drainage (≥ 3 mM), sulfate exerts only a limited influence on the rate of sulfate reduction; therefore, application of a first-order model to mine drainage environments is valid.

The most simplistic first-order model is a single negative exponential model, in which organic matter is assumed to be homogeneous and degrades at a constant specific rate (Berner, 1964). More complex models relax this homogeneity assumption. The composite exponential model treats organic matter as consisting of two or more components of different reactivity, each of which degrades at a specific rate (Westrich and Berner, 1984). The decaying coefficient model treats organic matter in total but assumes its reactivity decreases with time (Godshalk and Wetzel, 1978; Middelburg, 1989). The model that follows is an extension of the decaying coefficient models of Janssen (1984) and Middelburg (1989) in which the degradation coefficient decreases as a power function.

Organic matter decomposition is assumed to follow first-order kinetics:

$$dG/dt = -k(t)G, \qquad (1)$$

where G is the concentration of total organic carbon (TOC) and $k(t)$ is a time-dependent first-order rate parameter. Assuming that k is constant over the interval Δt, k can be estimated by:

$$k = 1/\Delta t \ \ln\,[G(t)/G(t+\Delta t)], \qquad (2)$$

where $G(t)$ is the TOC concentration at a certain time. A plot of k and t yields an equation of the form:

$$k = bt^m, \qquad (3)$$

where t is the time since decomposition began and m and b are model parameters. However, Eq. (3) cannot be solved for t = 0; so, a fixed "starting time" or "apparent initial age" is introduced (Janssen, 1984):

$$k = b(a + t)^m, \qquad (4)$$

where a is the apparent initial age, the value of which is directly related to the degree of humification. Substituting Eq. (4) into Eq. (1) and integrating yields:

$$G(t) = \begin{cases} G(0)[a/(a+t)]^{b}, & m = -1 \qquad (5a) \\ G(0)\exp\{b\,[a^{m+1} - (a+t)^{m+1}]/(m+1)\}, & m \neq -1 \qquad (5b) \end{cases}$$

where $G(0)$ is the initial TOC concentration. The value of a can be calculated using Eq. (5). Solving Eq. (5) for t when $G(t) = 0.5G(0)$ yields an expression for the organic matter half-life ($t_{1/2}$):

$$t_{1/2} = \begin{cases} a\,(2^{1/b} - 1), & m = -1 \qquad (6a) \\ [a^{m+1} + 0.693\,(m+1)/b]^{1/(m+1)} - a, & m \neq -1 \qquad (6b) \end{cases}$$

Using reaction stoichiometry, the model can be modified to describe sulfate reduction in mine drainage wetlands assuming sulfate is the only organic matter oxidant, no additional input of organic matter, and subsurface flow only.

Sulfate reduction may be described by the following overall reaction:

$$2\,CH_2O + SO_4^{2-} \longrightarrow HS^- + 2\,HCO_3^- + H^+, \qquad (A)$$

where CH_2O represents the amount of decomposable sedimentary organic matter. For modeling purposes the sulfide ions generated are assumed to react instantaneously with ferrous iron present in the interstitial solution:

$$Fe^{2+} + HS^{-} \dashrightarrow FeS + H^{+}. \qquad \text{(B)}$$

For modeling purposes, define a unit wetland as having a sufficient size (i.e., area) so as to have a detention time (t^*) of one day and let C represent the concentration of sulfate or ferrous iron and t the time since decomposition began (i.e., the age of the wetland). Assuming $t^* << t$, $k(t)$ is constant over the interval t^*. The time rate of change of C in the unit wetland is then:

$$dC/dt^* = -f\beta k(t)G(t), \qquad (7)$$

where f is the molar ratio of sulfate reduced to carbon oxidized ($f = 0.5$) and $G(t)$ is calculated using Eq. (5). The factor β converts solid concentration (mmol/kg dry soil) to aqueous concentration (mmol/L) and is given by:

$$\beta = \rho(1 - \phi)/\phi, \qquad (8)$$

where ϕ is porosity and ρ is the dry density of the organic substrate. Solving Eq. (7) assuming steady state gives R, the amount of ferrous iron removed (R) (stoichiometrically equivalent to sulfate) due to decomposition in a unit wetland of age t:

$$R = f\beta G(t)\{1 - \exp[-k(t)t^*]\}. \qquad (9)$$

RESULTS AND DISCUSSION

During simulation runs, spent mushroom compost, an inexpensive by-product of the mushroom industry commonly used in wetland construction in Pennsylvania, was used as the organic substrate in the hypothetical unit wetland described above. Simulation of decomposition alone requires that the values of three parameters (a, b, and m) be specified, while four additional parameters ($G(0)$, ϕ, ρ, and t^*) are needed for simulating sulfate reduction within the wetland. Parameter estimates used in simulations are given in Table 1 and are typical of organic substrates used in constructed wetlands. Sensitivity analyses were performed to determine which parameters had the greatest effect on model output.

To illustrate the kinetic behavior of the decomposition model (Eq. 5), normalized total organic matter concentration $[G(t)/G(0)]$ is shown as a function of time for various values of organic matter apparent initial age (Fig. 1). The smaller the ratio $G(t)/G(0)$, the further decomposition has progressed. This asymptotic pattern is typical of both field and laboratory studies in which heterogeneous organic matter undergoes exponential decay. Relatively reactive organic matter is depicted by small a values (<1 yr), while more refractory organic matter is indicated by large *a* values (>4 yr). The value of *a* can range from hours for plankton to tens of thousands of years for deep-sea sediments (Middelburg, 1989); thus, the apparent initial age (i.e., degree of humification) exerts a dominant control on organic matter decomposition rates.

TABLE 1 Parameter Estimates Used In Model Simulations

Parameter	Value	Reference
a (yr)	0.5 - 8	Janssen (1984)
b	0.16	Middelburg (1989)
m	-1.0	Middelburg (1989)
$G(0)$ (% dry wt.)	20	Lohr *et al.* (1984)
ϕ	0.85	Lohr *et al.* (1984)
ρ (g/cm^3)	2.0	Lohr *et al.* (1984)
t^* (day)	1.0	----

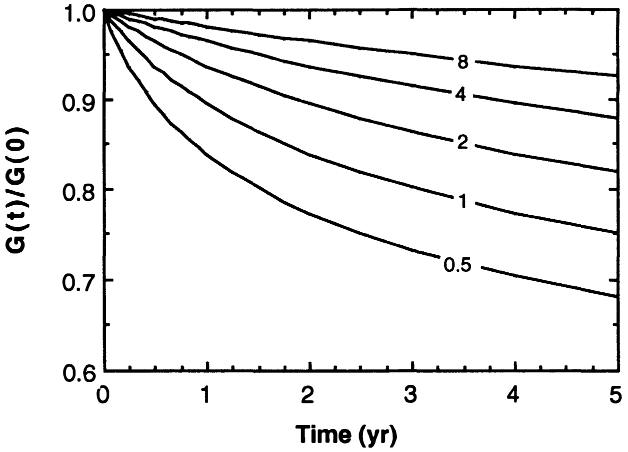

Fig. 1. Normalized total organic matter concentration over time for various values of apparent initial age (a). Model predictions were obtained using Eq. (5).

An important secondary control on decomposition estimates is the value of the model parameters m and b (Table 1). It should be noted that the use of these values leads to conservative estimates of the decomposition rate. Tarutis (1992) suggested that these parameters were sensitive to temperature and should not always be treated as constants. The sensitivity of the model to deviations (±25%) in m and b as a function of organic matter apparent initial age is shown in Figs. 2A and 2B, respectively. Deviations in both parameters lead to significant differences in organic matter half-life, but the magnitude of these differences depends on organic matter age. In general, the model is more sensitive to *b* than it is to *m*.

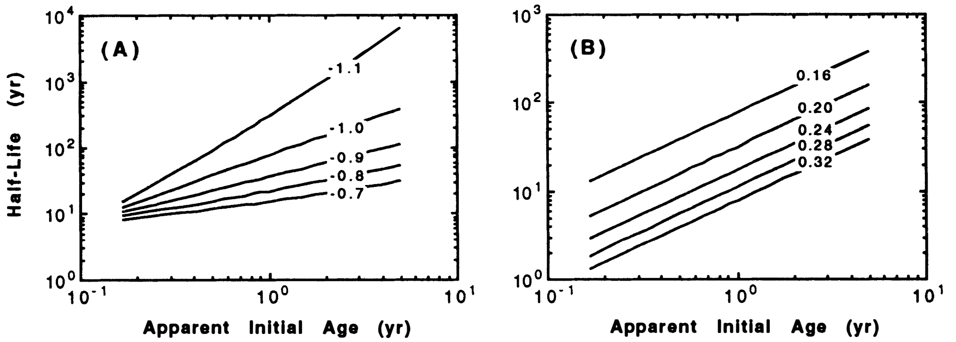

Fig. 2. Sensitivity of model parameters *m* and *b* showing organic matter half-life as a function of apparent initial age. (A) $-1.1 \leq m \leq -0.7$, $b = 0.16$; (B) $m = -1.0$, $0.16 \leq b \leq 0.32$. Model predictions were obtained using Eq. (6).

The preceeding decomposition model can be used to simulate the removal of ferrous iron entering wetlands constructed for mine drainage treatment assuming the stoichiometric removal of iron and sulfate via bacterial sulfate reduction (Reactions A and B). Application of the model (Eq. 9) to the unit wetland described above assumes complete anaerobic conditions within the entire substrate profile, constant temperature, no additional organic matter input, and subsurface flow only. For these ideal conditions, model simulations indicate that wetlands constructed with readily decomposable substrates (a<1 yr) rich in organic carbon are initially capable of removing far greater amounts of iron than wetlands built with less biodegradable substrates (a>4 yr) (Fig. 3). After three to five years of operation, this difference becomes negligible; however, the actual amounts of iron removed depend on the detention time of the wetland and the physical characteristics of the organic material used in construction (Table 1). During the first three years of operation, the readily decomposable components of the initial organic matter have been oxidized, leaving relatively refractory components behind. As a wetland ages a continual decrease in both organic matter quantity [$G(t)$] and quality [$k(t)$] reduces the rate of sulfate reduction, and therefore its metal removal capacity. Tarutis *et al.* (1992) suggested that insufficient decomposable organic matter existed in the anoxic sediments of a natural wetland to support sulfate reduction. Stark *et al.* (1991) have observed significantly higher iron and sulfate retention in simulated wetlands to which a carbon supplement (cheese whey) was added, which they attributed to stimulated rates of sulfate reduction. Simulation results indicate that without a regular carbon input, periodic additions of decomposable organic matter will be required for acceptable long-term treatment performance.

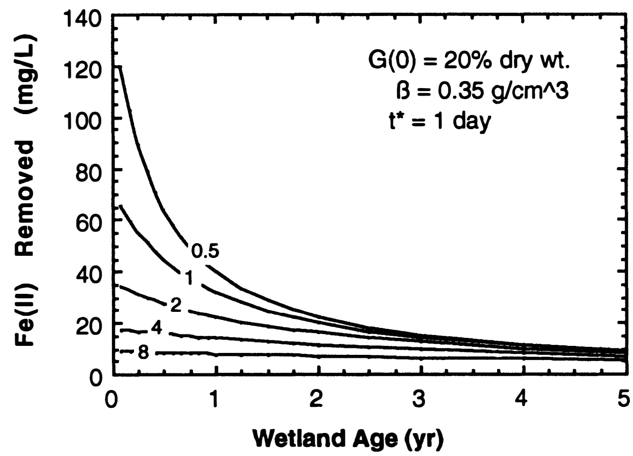

Fig. 3. Simulation of ferrous iron removal as a function of wetland age for various values of organic matter apparent initial age. Model predictions were obtained using Eq. (9) with parameter estimates in Table 1.

The simulation model presented here provides an insight into how factors affecting the rate of organic matter decomposition may influence the fate of at least some mine water pollutants in subsurface-flow constructed wetlands. It may also be applicable to surface-flow wetlands if it is used as a submodel describing removal in the anoxic zone. The model should not, however, be applied to variable-temperature environments without modification because of statistical considerations (Tarutis, 1992). It will be necessary to address these issues in order to apply this model successfully to wetlands in the natural setting.

ACKNOWLEDGEMENTS

The activities on which this paper is based were financed by the U.S. Department of the Interior, Bureau of Mines, under Cooperative Agreement No. CO388026 through the National Mine Land Reclamation Center and the Environmental Resources Research Institute at The Pennsylvania State University.

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