



Biological and geochemical controls on CO₂ equilibria in free water wetlands
by Thomas Robert Sharp

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Civil Engineering

Montana State University

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Abstract:

The effect of lime addition and biogeochemical carbon cycling on CO₂ equilibria and pH in free water wetlands (ponds) constructed for aqueous heavy metal remediation was examined. The treatment system consisted of lime addition to the influent and a series of three ponds separated by porous berms. Influent to the system was near surface groundwater collected from a reclaimed historic tailings impoundment, had a neutral pH (~7) and contained elevated concentrations of Zn (~10 mg L⁻¹) and Cu (~1 mg L⁻¹). The solubility of the heavy metals was reduced by increasing the pH either by lime addition to the influent or biological dissolved inorganic carbon (DIC) consumption. Both processes increase the pH by consuming buffering capacity (DIC) and lowering the partial pressure of dissolved CO₂ in the water (pCO₂). Geochemical modeling was used to calculate the pCO₂ and to predict pH of the system if it was in equilibrium with atmospheric CO₂ and/or calcite. The influent was oversaturated with CO₂ relative to equilibrium with atmospheric CO₂ concentrations and undersaturated with respect to equilibrium with calcite. The ponds were generally undersaturated with respect to equilibrium with atmospheric CO₂ and oversaturated with respect to calcite. The only instances when the ponds were close to equilibrium with atmospheric CO₂ occurred when lime addition rates were low, photoautotrophy was N deficient, and during ice cover. These observations suggested that biological carbon cycling influenced the system's pH.

The relative importance of geochemical (calcification) and biological (respiration/photosynthesis) processes controlling the consumption/production of dissolved inorganic carbon was determined by developing an ecosystem level model to account for mass fluxes of nitrogen, carbon and calcium. In the first pond, DIC consumption was 32% biological and 67% geochemical. DIC consumption was about 31% geochemical and 69% biological in the second pond. DIC consumption was 95% biological and only 5% geochemical in the third pond. Because of the spatial variation in the processes responsible for DIC consumption, the initial portion of the system is a chemical treatment system and the latter portion is a natural treatment system.

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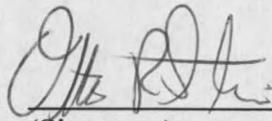
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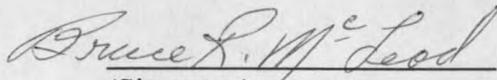


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ABSTRACT

The effect of lime addition and biogeochemical carbon cycling on CO_2 equilibria and pH in free water wetlands (ponds) constructed for aqueous heavy metal remediation was examined. The treatment system consisted of lime addition to the influent and a series of three ponds separated by porous berms. Influent to the system was near surface groundwater collected from a reclaimed historic tailings impoundment, had a neutral pH (~ 7) and contained elevated concentrations of Zn ($\sim 10 \text{ mg L}^{-1}$) and Cu ($\sim 1 \text{ mg L}^{-1}$). The solubility of the heavy metals was reduced by increasing the pH either by lime addition to the influent or biological dissolved inorganic carbon (DIC) consumption. Both processes increase the pH by consuming buffering capacity (DIC) and lowering the partial pressure of dissolved CO_2 in the water ($p\text{CO}_2$). Geochemical modeling was used to calculate the $p\text{CO}_2$ and to predict pH of the system if it was in equilibrium with atmospheric CO_2 and/or calcite. The influent was oversaturated with CO_2 relative to equilibrium with atmospheric CO_2 concentrations and undersaturated with respect to equilibrium with calcite. The ponds were generally undersaturated with respect to equilibrium with atmospheric CO_2 and oversaturated with respect to calcite. The only instances when the ponds were close to equilibrium with atmospheric CO_2 occurred when lime addition rates were low, photoautotrophy was N deficient, and during ice cover. These observations suggested that biological carbon cycling influenced the system's pH.

The relative importance of geochemical (calcification) and biological (respiration/photosynthesis) processes controlling the consumption/production of dissolved inorganic carbon was determined by developing an ecosystem level model to account for mass fluxes of nitrogen, carbon and calcium. In the first pond, DIC consumption was 32% biological and 67% geochemical. DIC consumption was about 31% geochemical and 69% biological in the second pond. DIC consumption was 95% biological and only 5% geochemical in the third pond. Because of the spatial variation in the processes responsible for DIC consumption, the initial portion of the system is a chemical treatment system and the latter portion is a natural treatment system.

INTRODUCTION

Metal contamination can threaten the biological diversity, productivity and stability of unperturbed environments. Historic and operating mines and mineral processing facilities are potential sources of heavy metal contamination. Mineral extraction exposes mineral deposits to the biosphere and subsequently enhances the rate at which they are weathered. Metals derived from weathered ore deposits or mineral wastes can be spread through the environment as airborne particulates or solutes in surface or ground water (Salomons 1995). For the reclamation of sites previously impacted by mineral extraction or the compliance of active mines or mineral processing facilities, metal contamination in surface and groundwater often must be treated prior to discharge.

Treatment of Metal Contaminated Wastewater

Treatment options for wastewater containing significant concentrations of dissolved metals include; removing the metals by reverse osmosis, adsorption, ion exchange, or altering the aqueous chemistry such that the formation of metal precipitates is favored (Faust and Aly 1983). Alterations in aqueous chemistry to reduce the solubility of dissolved metals (i.e. form precipitates) either decrease the electron potential (E_h) or increase the pH of the solution by the addition of a strong base.

Chemical treatment of a waste stream containing dissolved metals is accomplished by the addition of a chemical to alter the aqueous chemistry to reduce

metal solubility. Chemical additives such as NaOH, CaO, Ca(OH)₂ and sulfidic salts are all means of lowering metal solubility. The increase in pH that occurs when one of the aforementioned bases is added to metalliferous solutions promotes the formation of metal hydroxides, oxy-hydroxides, carbonates or mixtures of these compounds (Stumm and Morgan 1981). The addition of a sulfidic salt removes dissolved metals by forming metal sulfide precipitates. The resulting metal precipitates are then separated from the free water.

The use of natural treatment systems has been proposed as an alternative to chemical treatment of metalliferous wastewater. Constructed wetlands are a type of natural treatment system. The anticipated cost of a wetland treatment system operating as designed is much less than a conventional chemical treatment system (Cohen and Gorman 1991). Wetland treatment systems utilize natural processes such as sorption and beneficial changes in water chemistry mediated by microorganisms to sequester the metals within the system. While the cost of operating a wetland treatment system may be less than conventional treatment, constructed wetlands are affected to a greater extent by ambient environmental conditions. Nutrient availability, temperature, and metal toxicity all can influence the efficiency of metal removal (Wildman et al. 1993). If constructed wetlands are used to lower the solubility of dissolved metals and attenuate the precipitates, designers need to understand how environmental conditions affect treatment efficiency.

Study Purpose

This study examined biological, physical and geochemical processes which governed pH in a combined chemical and biological natural treatment system for the remediation of metal contamination in surface and groundwaters. The system used lime addition to initially modify the influent pH. The pH in free water systems is controlled by equilibrium with atmospheric CO₂ and biogeochemical carbon cycling. To predict the fate and transport of dissolved metals, the factors that regulate system pH, and hence metal solubility need to be quantified (e.g. Choi et al. 1998).

Alternative modes of operation may optimize the performance of chemical/biological treatment systems by capitalizing on the photoautotrophic consumption of CO₂ and the resulting increase in pH. This may include recirculating planktonic photoautotrophic biomass that has accumulated at the tail of the system to the head. Increasing photoautotrophic biomass in the first pond in a series of ponds will increase the consumption of DIC and increase the pH as long as there are sufficient nutrients and light available to support photoautotrophic growth. If biomass can be recirculated to head of the treatment system and the environmental conditions are favorable for growth, the amount of lime (CaO, Ca(OH)₂) that is added to the water to maintain the optimal pH for treatment can be reduced. Without recirculation, the benefit of photosynthetic CO₂ consumption would be realized only at the tail of the treatment system where the planktonic biomass has accumulated. The environmental factors that control whether the trophic state of system is net autotrophic (CO₂ sink; pH increase) or net heterotrophic (CO₂ source; pH decrease) are important design and operational

considerations for engineering a treatment system for metals reduction that relies, in part, on these natural processes for heavy metal remediation.

The goal of this study was to determine the effect of varying modes of operation on regulating pH in the system. These operational changes included drawing influent from two sources with different nutrient (nitrate) concentrations and using recirculation to redistribute planktonic biomass. The longitudinal extent that a given trophic state persists along the flow path through the system will be impacted by these operational changes. However, the effect of these operational changes can only be superimposed on the prevailing seasonal pattern of organic carbon production and consumption.

An ecosystem level approach was used to examine how these operational changes affected pH regulation in the treatment system. To demonstrate the effect that system trophic state has on the pH of the system, mass balances of calcium, phosphorus, nitrogen, dissolved inorganic carbon, dissolved organic carbon and particulate organic carbon (algal biomass) for the water of the ponds were developed. Changes in mass that were not due to the varying influent fluxes to each pond were assigned to a net reaction term (ΣR). This term represents the net effect of the various processes that consume or produce that constituent. Sediment from the ponds was analyzed to verify the results of the mass balances. By prescribing DIC production and consumption to specific physical, geochemical and biological processes, their relative importance in regulating pH was evaluated.

Study Objectives

Data analysis addressed the following objectives:

- 1) Model DIC production and consumption by the biological and geochemical processes within the system and their spatial and temporal variation,
- 2) Use a geochemical equilibrium model to determine the effect of equilibria with atmospheric CO₂ and calcite on DIC concentrations and pH, and
- 3) Verify the results of the mass balances by comparing material lost from the water to the composition and amount of sediments produced.

Meeting these objectives will permit an evaluation of an appropriate mode of operation for the treatment system, the relative importance of the geochemical, physical and biological processes regulating pH and the composition and accumulation rates of sediment. The results will be applicable to other systems that use pH adjustment to treat heavy metal contaminated groundwaters that may impact surface water quality.

Constructed Wetlands

There are two general types of treatment wetlands: free surface flow and subsurface flow wetlands (Kadlec and Knight 1996). Free surface wetlands are ponds with emergent vegetation. Subsurface flow wetlands are constructed of a porous medium and water flows within the medium along a hydraulic gradient set up by piezometric potential difference between the influent distribution pipe and effluent collection pipe.

Subsurface flow wetlands

Subsurface flow wetlands sequester metals by precipitation and adsorption (Machemer and Wildeman 1992). Adsorption of metals is viewed as a short-term metal removal mechanism because the availability of adsorption sites decreases over time. The precipitation of metals results from the effect anaerobic microbial respiratory products (HCO_3^- and H_2S) have on aqueous chemistry. Bicarbonate produced from anaerobic respiration will consume acidity (Eger 1992) and H_2S will react with dissolved metals to form relatively insoluble metal sulfides (McIntire et al. 1990). Subsurface wetlands are constructed using materials to create an environment, which supports the growth of consortia of microorganisms that are responsible for these changes in water chemistry.

Subsurface flow wetland cells are composed of a porous media such as gravel mixed with a variety of differing organic carbon sources including manure, composted sewage sludge, brewery waste, or straw (Wildeman 1993). Organic carbon is added to these systems as a source of electron donors for heterotrophic bacteria. As an alternate to loading the sediments of a constructed wetland with organic matter from an allochthonous source, *in situ* primary production can supply a seasonal pulse of organic carbon to the sediments. Aquatic macrophytes, and benthic microalgae contribute to the flux of organic carbon to the sediments. Sedimentary organic carbon sets up a thermodynamic disequilibrium between the organic carbon and potential electron acceptors for microbial metabolism (Van Cappellin and Wang 1996).

Heterotrophic bacteria derive energy for growth by capitalizing on this thermodynamic disequilibrium; the bacteria catalyze the reaction between organic carbon

and terminal electron acceptors. Electron acceptors used by bacteria for the oxidation of organic carbon are molecular oxygen, nitrate, manganese oxides, iron oxides, and sulfate. These electron acceptors are consumed within the sediments in order of decreasing thermodynamic energy yield. As the sequential consumption of electron acceptors progresses, the pore water in the sediments becomes more reduced, from the transformation of relatively oxidized electron acceptors to more reduced respiratory products. The degree to which this thermodynamic sequence progresses is dependent on the availability of organic carbon and the abundance of each electron acceptor (Berner 1980). If this thermodynamic sequence proceeds to sulfate reduction, the hydrogen sulfide produced can react with dissolved metals to form metal sulfides. The production of metal sulfides and adsorption or occlusion of other metals to metal sulfides may improve the water quality (Morse and Arakaki 1993).

Potential drawbacks of subsurface flow wetlands are short-circuiting of flow and organic carbon depletion. The development of preferential flow paths within the subsurface causes decreased contact area and hydraulic residence time, resulting in decreased treatment efficiency (Fisher 1990). The life expectancy of subsurface flow wetland treatment cells may be shortened by the depletion of readily degradable organic carbon (Taurtis and Unz 1994). As the production rate of fermentation products decreases within the sediments, owing to the depletion of larger hydrolyzable dissolved organic carbon, the consumption rate of terminal electron acceptors for organic carbon will concomitantly decrease (Alperin et al. 1994). Because of these shortcomings, an alternative method of treatment is desirable.

Free Water Wetlands

Free water wetlands remove dissolved metals by sorption and precipitation similar to subsurface flow wetlands. A difference between the two natural treatment systems with regard to the precipitation of metals is that, in free water wetlands, metal solubility is decreased because of an increase in pH as opposed to a decrease in redox potential. As mentioned previously, a chemical additive can be used to increase pH of the influent and/or biological processes in the ponds can increase the pH. To engineer a combined chemical/biological treatment system for pH adjustment, the principals governing pH buffering in water must be examined.

An optimal pH, at which the solubility of the metals of concern is reduced to meet the applicable discharge standard, must be established and maintained for a duration longer than the time it takes for the settling of the metal precipitates to prevent their resolubilization. When adjusting the pH to the optimal level, enough base must be added to overcome any buffering capacity present in the solution, as well as to change the pH. The buffering capacity of water is often measured as alkalinity. Alkalinity (eq L^{-1}) is the difference in charge between dissolved cations and anions that is neutralized by dissolved inorganic carbon species and is defined as

$$\text{alkalinity} = \sum (n_i \times C_i^{n+}) - \sum (m_i \times A_i^{m-}) = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{OH}^-] \quad (1)$$

where $[C_i^{n+}]$ is the concentration (M) of the i-th cation, $[A_i^{m-}]$ is the concentration (M) of the i-th anion, and n and m are the charge on the cation and anion (Drever 1988). The buffering capacity of water results from the presence of significant concentrations of an acid/base pair (e.g. $\text{H}_2\text{CO}_3/\text{HCO}_3^-$) in solution. The effect of adding an acid or a base to

water on pH is mitigated by the redistribution of DIC species according to a new equilibrium. In most waters, carbonate alkalinity ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) is the primary buffering mechanism of the solution; however other weak acids such as organic, boric and orthosilicic acids can buffer solution pH. Boric and orthosilicic acids buffer the pH of a solution near 8.9 and 9.5, respectively (Stumm and Morgan 1981). The addition of CaO or $\text{Ca}(\text{OH})_2$ can produce significant amounts of calcium carbonate (calcite), thereby removing carbonate alkalinity (Butler 1982).

Carbonate equilibria and equilibrium with atmospheric CO_2 regulate the pH in most natural waters (Wetzel 1983). Hydrogen ion activity and carbonate equilibrium determine the proportion of each species (H_2CO_3^* , HCO_3^- , or CO_3^{2-}) of dissolved inorganic carbon (DIC) to the total amount of DIC. By convention, the sum of the concentrations of dissolved CO_2 and H_2CO_3 will be denoted as H_2CO_3^* , because concentrations of H_2CO_3 are three orders of magnitude lower than dissolved CO_2 ; the slow hydration of CO_2 (aq) is the cause for the greater abundance of CO_2 (aq) relative to H_2CO_3 . The kinetics of acid-base reactions ($\text{H}_2\text{CO}_3^* \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ and $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$) are fast enough to be essentially instantaneous (Stumm and Morgan 1981). Processes that affect carbonate equilibrium are diffusion of CO_2 to/from the water from/to the atmosphere and sediments, the precipitation of CaCO_3 , and the consumption or production of CO_2 by biological processes (Fig. 1).

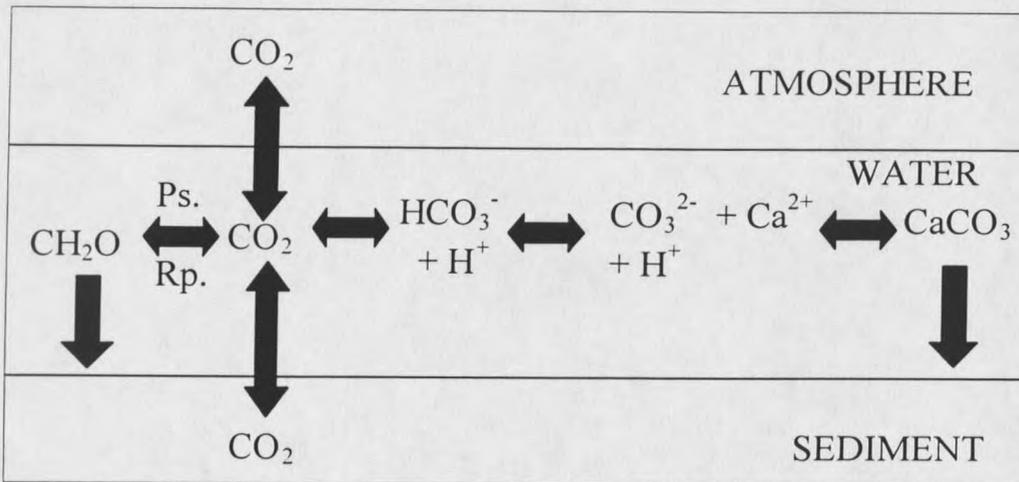


Figure 1. A sketch of the processes and fluxes associated with carbon cycling. Photosynthesis (Ps.) and respiration (Rp.) consume and produce CO₂, respectively. Advection into and out of the system is not shown.

Algae (oxygenic photoautotrophs) suspended within the water and attached to the surficial sediments can alter the chemistry of the pond water by photosynthetic consumption of dissolved CO₂ in water. Alternatively, heterotrophic consumption of organic carbon can increase the DIC concentration in the water. As DIC is produced/consumed by respiration/photosynthesis, the species (H₂CO₃^{*}, HCO₃⁻, and CO₃²⁻) comprising the DIC will be redistributed as defined by the pH and total DIC concentration of the water.

If the alkalinity remains constant, changes in the partial pressure of CO₂ (*p*CO₂) within the water due to photosynthetic consumption or respiratory production will change the abundance of other DIC species (e.g. [HCO₃⁻] + 2[CO₃²⁻]). In order to maintain the charge balance (alkalinity) hydroxyl ions are produced, causing the pH to increase. If DIC produced by respiration is greater than that consumed by photosynthesis, the pH will decrease as hydroxyl ions are consumed to maintain the charge balance (Stumm and Morgan 1981). The environmental conditions regulating the balance between

photosynthetic DIC consumption and respiratory DIC production need to be examined to capitalize on biologically mediated pH changes.

A community of organisms will maintain a positive carbon balance (photosynthesis > respiration) given sufficient light, nutrients and a tolerable temperature (Cole et al. 1992). If nutrients become depleted or light decreases below the compensation irradiance for net photoautotrophic production, the photosynthetic consumption of DIC will decrease. Resource depletion or limitation for photoautotrophs may result in the respiratory production of DIC exceeding photosynthetic consumption of DIC, causing the system to switch from net autotrophy to net heterotrophy, as is often observed in unproductive aquatic ecosystems (del Giorgio et al. 1998). High nutrient loading, DIC consumption and high pH characterize autotrophic systems, while low nutrient loading, DIC production and low pH characterize heterotrophic systems.

CO₂ Equilibria and pH in Lakes

Most lakes are oversaturated with respect to atmospheric CO₂ levels independent of geographical location and season, although the degree of CO₂ oversaturation is often decreased during the photoautotrophic growing season (Cole et al. 1994). This work implied that most lakes are sources of CO₂ to the atmosphere rather than sinks for atmospheric CO₂. The authors contend that CO₂ oversaturation in most lake ecosystems results from respiration exceeding photosynthesis and inflows of groundwater that are supersaturated with CO₂ relative to equilibrium with the atmosphere. Lakes receive allochthonous organic carbon from the surrounding watershed, which is subsequently remineralized within the water column and sediment. CO₂ supersaturation of the lake

water will depress the pH below what it would be if the system were in equilibrium with the atmosphere. The effect *in situ* organic carbon production and the simultaneous respiration of allochthonous and autonomous organic carbon has on the pH of a free water system should be evaluated if free water systems (ponds) are used for engineering applications.

The work of Schindler, Emerson and others in the 1970's on C, N and P limitation of primary production in the Experimental Lakes Area (Canada) is one the most thorough studies to date on the effect of nutrient additions on CO₂ equilibria in freshwater systems. The study was initiated by controversy over whether the eutrophication of lakes was the result of increased carbon or nutrient (N and/or P) availability. In these Laurentian Shield lakes DIC concentrations are extremely low (~0.2 – 1.2 mg L⁻¹) owing to the absence of calcareous material in the bedrock or glacial overburden and low weathering rates in the watershed (Schindler and Fee 1974; Emerson 1975a). Because of the extremely soft water in these lakes, they were an ideal experimental system for examining the potential role of inorganic carbon limitation of algal biomass accumulation. The results of their study showed that the flux of atmospheric CO₂ to lakes is sufficient to produce an algal bloom in proportion to the amendment of N or P (Schindler et al. 1972). The atmospheric flux of CO₂ to the experimental lake was in excess of the flux predicted by physical diffusion across the air-water interface (Verduin 1975). Enhanced flux over that predicted by diffusive boundary layer models is due to the consumption of CO₂ (aq) within the boundary layer by reaction with OH⁻ to produce HCO₃⁻, which increased the CO₂ (aq) gradient, thus increased the flux of atmospheric CO₂ to the lakes (Emerson 1975b). Photoautotrophic consumption of CO₂ in the soft

water Canadian Shield lakes reduced the aqueous partial pressure of CO_2 ($p\text{CO}_2$) up to four orders of magnitude below equilibrium with the atmosphere (Schindler et al. 1975). Owing to this reduction of $p\text{CO}_2$ in the lake water, the pH increased, thereby increasing the rate of CO_2 hydroxylation and the flux of CO_2 to the lake was enhanced. The ratio of enhanced CO_2 flux to that predicted by physical diffusion alone ranged from 5-10 with a theoretical maximum of 21 (Emerson 1975b). Chemical enhancement of atmospheric CO_2 diffusion is an important process in soft water lakes but its effect is mitigated in lakes with harder waters (higher DIC concentrations).

Depletion of CO_2 (aq) from photosynthetic uptake and the concomitant increase in pH is only of concern in waters where the amount of DIC present in water can not meet this demand (Verduin 1975). In lakes with higher DIC concentrations, the impact of the photosynthetic consumption of CO_2 on pH is not as great, owing to the increased buffering capacity. For photoautotrophic production to increase the pH of the solution, this initial buffering capacity must be overcome. Chemical addition (water softening) may be required to remove carbonate alkalinity (as CaCO_3) to poise the water (i.e. reduce the buffering capacity) such that photosynthetic DIC consumption/production can increase/decrease the pH. Determining the maximum potential photoautotrophic production a treatment system can produce, or the portion of the treatment system that will consume more DIC than it will produce, will aid in selecting an optimum management strategy for these combination chemical and biological treatment systems.

Despite the differences between the two types of constructed wetlands, both are impacted by meteorologic and climatic variation. Additionally, each type of wetland relies upon the production of organic carbon, either to provide a source of electrons for

microbial respiration and depletion of electron acceptors or to consume DIC and subsequently increase pH. In temperate and polar climates, photoautotrophic growth is restricted to the portion of the year when temperature, light intensity and photoperiod are favorable. Due to decreased biological rates during the winter, additional measures must be taken to obtain the same degree of treatment observed in the summer. These can include increasing the hydraulic residence time for subsurface flow wetlands or chemically treating the water for free water wetlands.

Constructed wetland treatment systems remove metal contamination from the aqueous phase to produce a solid waste in which the metal contamination is more concentrated than it was in the wastewater initially. The resulting solid phase waste will reside in the sediments of the system. Determining the composition and accumulation rate of sediments within these systems is integral component for evaluating the performance, cost and longevity of the treatment system.

Sediment Characteristics

Unlike hydrocarbon remediation, where it is theoretically possible for the pollutant to be completely mineralized to CO₂ and water, aqueous heavy metal remediation can only reduce metal solubility. Water treatment to reduce soluble metal concentrations produces brine or sediment that will have a higher concentration of metals than the original solution. The volume of the pollution may be reduced, but the total mass of the contaminant will be the same. Treatment of metal contaminated water can be viewed as a means to concentrate the contamination prior to resource recovery or ultimate disposal in a wet or dry closure/repository. With any treatment remedy reducing

metal solubility, the type of waste concentrate (sediment, brine), its stability, and rate at which it is produced must be considered when selecting the treatment option. In the case of free water wetlands, sediments may need to be periodically dredged from the initial pond over the lifetime of the system. The rate of sediment accumulation and its composition must be estimated to project maintenance and to select the appropriate means of disposal. In addition to heavy metal precipitates, the sediment will also contain other solid phases such as calcite (CaCO_3) or amorphous silica (SiO_2) that also form in response to the increased pH. These environmentally benign precipitates may comprise a majority of the sediment mass.

Calcite sediment deposition has beneficial implications for retaining the metal precipitates within the sediments. Because the metals are removed as hydroxides, oxyhydroxides, carbonates, or mixed hydroxide carbonates, their long-term sequestration within the sediments is dependent on maintaining the proper pH in the sediment porewater to prevent their dissolution. Calcite aids in buffering the pore water of the sediments and maintaining low metal solubility. The presence of calcite in the sediment will buffer the pH by its dissolution near 8 in waters in equilibrium with atmospheric CO_2 (Butler 1982). Additionally, there is a potential that the sediment produced, if it contains an overabundance of calcite, can be used as a soil amendment for acidic soils (Mikkelsen and Camberato 1995). Ultimate disposal is dependent on the metals concentration and stability of the sediment. Increased calcite and amorphous silica deposition will increase the volume of sediment produced and subsequently decrease the metal content of the sediment.

MODEL DEVELOPMENT

Material Balances

A mass balance model was developed for a series of free water wetlands with recirculation of a portion of the effluent back to the head of the system and the addition of quick or hydrated lime at a variable rate to the influent. Each free water wetland cell (pond) in the series was treated as a continuously stirred tank reactor (CSTR). The general form of the mass balance is written such that

$$V \frac{dC}{dt} = Q_{in}C_{in} + Q_r C_r - Q_{out}C - Q_s C + \Sigma R \quad (2)$$

where V is the pond volume, dC/dt is the change in concentration between sampling dates, Q_{in} is the influent rate, C_{in} is the influent concentration, Q_r is the recirculated flow rate, C_r is the concentration of the recirculated water, C is the concentration in the pond, Q_s is the infiltration rate out of the cell, Q_{out} is the effluent flow rate, and ΣR is the net effect of biogeochemical reactions that either produce or consume the constituent. Chemical additions are included in the reaction term. Implicit in this approach is that the water level in the ponds remains constant; the ponds do not gain or lose water. Therefore, at any given time the influent rate is equal to the effluent rate plus the seepage and evaporation rates. Changes in concentration of dissolved constituents from evaporation were assumed to be negligible.

Mass balances were developed for calcium, zinc, silicon, manganese, copper, total phosphorus (TP), total nitrogen (TN), dissolved nitrogen (DN), particulate organic carbon

(PC), dissolved organic carbon (DOC) and DIC. This approach quantified the variation in the flux through each pond and determined changes in concentrations due to processes other than transport. Similar material balances have been used to construct carbon and material balances for lakes (Otsuki and Wetzel 1974; McConnaughey et al. 1994), lagoons (Lvov et al. 1996) and wetlands (Kadlec and Hammer 1988; Dombek et al. 1998).

Developing the mass balances permitted material retained within the system to be quantified, which permitted the rate of sediment accumulation to be projected. Also, the mass balance approach enabled the quantification of the various processes consuming or producing DIC in the water. Processes consuming DIC in water are both geochemical (calcification and other mineral formation) and biological (photosynthetic DIC consumption). The remineralization of organic carbon within the system is a biological process that produced DIC. Atmospheric CO₂ diffusion to or from the water can be a source or sink of DIC within the system. The net reaction term for the DIC mass balance (ΣR_{DIC}) is composed of the consumption of DIC by Ca and Zn precipitation (Ca_{ppt} and Zn_{ppt}), production of organic carbon by planktonic and benthic photoautotrophs ($P_{Plankton}$ and $P_{Benthic}$, respectively), remineralization of previously reduced organic carbon in the system with the exception of DOC remineralization (R_{system}), the transfer of carbon between the DOC and DIC pools (ΣR_{DOC}) and gains from the atmosphere ($Atmflux$). The processes composing ΣR_{DIC} are written as

$$\Sigma R_{DIC} = Atmflux - Ca_{ppt} - Zn_{ppt} - P_{Plankton} - P_{Benthic} - \Sigma R_{DOC} + R_{system} \quad (3)$$

Each of the processes listed in equation 3 are determined from other mass balances as outlined below.

Consumption of DIC by planktonic photoautotrophic production is set equal to the net reaction term for the suspended particulate organic carbon (ΣR_{PC}) mass balance (Eqn. 4).

$$P_{Plankton} = \Sigma R_{PC} \quad (4)$$

$P_{Plankton}$ is the net primary production of the phytoplankton and represents a portion of total system primary production. Phytoplankton are microalgae that are suspended in the water column of the ponds.

To estimate the contribution of the attached benthic algal community to the total productivity of the system, a mass balance for the dissolved nitrogen (DN, nitrate) was developed. Rates of DN consumption by phytoplankton were estimated by dividing $P_{Plankton}$ by the C:N ratio for phytoplankton (Eqn. 5).

$$\left(\frac{dDN}{dt} \right)_{Plankton} = \frac{P_{Plankton}}{(C:N)_{Plankton}} \quad (5)$$

This planktonic DN consumption rate was subtracted from ΣR_{DN} determined from the DN mass balance to yield DN consumption/production by processes other than planktonic uptake (Eqn. 6). DN consumption is assumed to be due only to photoautotrophic assimilation; denitrification is assumed to be insignificant relative to photoautotrophic consumption.

$$\left(\frac{dDN}{dt} \right)_{Benthic} = \Sigma R_{DN} - \left(\frac{dDN}{dt} \right)_{Plankton} \quad (6)$$

To convert this rate of DN consumption by benthic attached algal biomass to organic C production, a C:N (g:g) ratio of 10 was used (Lohman and Priscu 1992; Wetzel 1983).

This ratio was similar to that calculated from sediment data collected from the study site;

