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A System Dynamics model of the Bioavailability of Metals in Constructed Wetland Sediment

Timothy S. Wood

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A SYSTEM DYNAMICS MODEL OF THE BIOAVAILABILITY OF METALS IN CONSTRUCTED WETLAND SEDIMENT

THESIS

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AFIT/GEE/ENV/97D-23

DTIC QUALITY INSPECTED 8

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

19980114 137

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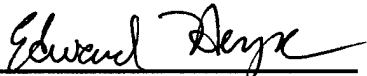
A SYSTEM DYNAMICS MODEL OF THE BIOAVAILABILITY OF

METALS IN CONSTRUCTED WETLAND SEDIMENT

THESIS

Timothy S. Wood, B.S.
Captain, USAF

Presented to the Faculty of the Graduate School of Engineering

of the Air Force Institute of Technology

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering and Environmental Management

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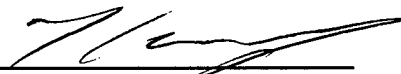
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December 1997

Acknowledgements

The process of creating this thesis has given me a greater respect for those who are immersed in the pursuit of knowledge that continues to be extracted from the earth on which we all live. I am grateful for the effort and patience that Dr. Michael Shelley showed in guiding my research and ensuring I did not stray from the tenants of the system dynamic approach. I appreciate the support from Major Ed Heyse who was able to shed some light into the realm of mystery and confusion that we call chemistry. I am especially grateful for the assistance of Dr. G. Allen Burton whose expertise in sediment toxicology provided foundational support for my research.

I also want to thank my wife, Jennifer, and my two children for their support and encouragement. They constantly help me keep my life in perspective and show me what is truly important in my life.

Finally, I give God the glory for his continual work in and through my life and acknowledge that it is only through Him that my efforts are of any value. His creation continues to provide researchers and scientists with a never-ending wealth of fascinating topics to study.

Timothy S. Wood

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Abstract

Constructed wetlands used for storm water treatment accumulate metals primarily in their sediment. This sediment has the potential to produce toxic effects in benthic or aquatic organisms at some period in time. Bioavailability of metals in sediment is directly linked to pore water metal activity. The mechanisms that influence pore water metal activity are included in physical, chemical, and biological processes. A system dynamics model was developed to represent these processes and the major influences affecting pore water metal activity in a treatment wetland receiving storm water influent. The model structure and behavior was tested and validated using several system dynamics validation techniques. The model was run using the metals Pb, Cu, and Cd. The model indicated that the chemical processes of acid-volatile sulfide (AVS) and organic carbon in binding metal in reduced sediment were the greatest influences in controlling metal bioavailability. The effect of bioturbation, as represented in the model, was negligible. Amount of organic carbon in the sediment seems to play the biggest role in controlling metal bioavailability in the long run. This model provides a platform for guiding future field research in sediment toxicology, specifically in treatment wetlands.

A SYSTEM DYNAMICS MODEL OF BIOAVAILABILITY OF

METALS IN CONSTRUCTED WETLAND SEDIMENT

I. Introduction

General Issue

Heavy metals such as lead, copper, cadmium, and zinc are considered
pollutants and can have toxic effects on animals and plants at varying
concentrations. These metals naturally occur at low concentrations throughout
the world, but have been concentrated by man's activities by what is described
as anthropogenic enrichment (Walker and others, 1996:3).

Metals are removed from industrial and residential areas during storm
events and are carried in suspension or solution in the storm water. Storm water
is responsible for as much as 80 to 95 percent of heavy metals in surface waters
(Livingston and Cox, undated: 289). In 87 storm water samples in Birmingham,
AL, the heavy metals, Pb, Cd, Cu, and Zn were found in almost every sample
(Pitt and others, 1995:262). Urban storm water is typically polluted with both
metals and organic chemicals. The storm water itself is responsible for relatively
few acute toxicity problems, but its associated sediment has frequently caused
chronic toxicity problems, especially in macroinvertebrates (Pitt and others,
1995:268-272). Heavy metals are the likely culprits for many of the chronic

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problems because of their tendency to accumulate without degradation in sediment.

Constructed wetlands, used for treatment of storm water, can become a collection point for these metals. Little scientific evidence is available concerning short- or long- term effects of storm water and metal accumulation in wetlands (Faulkner and Richardson, 1989:61; Livingston, 1989: 253, 261). It is believed that wetlands have a finite capacity to retain metals, but there is no way to predict what that capacity is and what will happen when a wetland reaches the saturation point (Wieder and others, 1989:301,303).

When wetlands receive influent from Superfund sites, ecological risk assessments are required by the EPA. Wetlands receiving contaminants from these sites must be evaluated for actual or potential adverse effects of stress on the ecosystem (Pascoe, 1993:2293). Ecological risk assessments should also be conducted (although not required) for natural or constructed wetlands used to treat storm or waste water. The Clean Water Act which established water quality criteria may not be stringent enough to prevent ecological damage in a wetland. Many feel constructed wetlands used for water treatment may become sinks or sources of contaminants which can produce toxic effects (Knight, 1992:109; Burton and Scott, 1992:2074). One of the major keys in assessing ecological risk in a wetland is determining the degree of contaminant bioavailability (Pascoe, 1993:2294). It is generally agreed that the pore-water concentration of metal in sediment is the fraction that is bioavailable (Di Toro and others, 1990:1500).

The mechanisms that surround sediment toxicity have been a popular subject of research over the last several years as researchers try to find ways to determine what is "safe" sediment and what is not (Burton, 1991:1587). There are numerous complexities that surround metal accumulation and transport in wetland sediment. These include varying pH and redox potential over time and space, the effect of plants and benthic organisms, organic carbon bonding sites, and other potential ligands present in the sediment.

The complexity surrounding the physical, chemical, and biological processes has led many to promote a holistic or systems approach, which includes all the physical, chemical, and biological processes, as the preferred method for studying aquatic sediment systems (Dixon and Florian, 1993:2290; Faulkner and Richardson, 1989:61; Mitsch and others, 1988:221). Most wetland and metal transport models, however, have concentrated on specific parts of the wetland system. A system dynamics model will be developed for this project to study the physical, biological, and chemical influences on the transport of common heavy metals (Pb, Cd, Cu), their accumulation in constructed wetland sediment, and their bioavailability within the sediment.

Problem Statement

Ecological risk is determined by measuring acute and chronic toxicity effects on organisms within an affected ecosystem. Metals only produce toxic effects when they exist in a bioavailable form that can be taken up by organisms. In wetlands, the metals reside predominantly in sediment where bioavailability is

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directly linked to sediment pore-water concentration. The mechanisms that influence metal bioavailability in sediment are poorly understood.

Purpose Statement

The purpose of this research project is to develop quantitative concepts that represent the dynamics of metal bioavailability in wetland sediment and to describe the primary mechanisms that cause pore-water concentrations of metal to reach toxic levels. This will be achieved through the development of a system dynamics model which will attempt to simulate the processes within a wetland sediment exposed to metal-contaminated storm water over a long period of time.

Research Questions

1. What are the physical processes that influence metal transport from storm water to constructed wetland sediment?

2. What role do the biological processes of benthic invertebrates play in changing bioavailability of metals?

3. How do the chemical processes in the sediment's oxidizing and reducing environments affect the chemical forms of metals present?

4. How do the biological, physical, and chemical processes interact to influence metal bioavailability?

II. Literature Review

Introduction

This chapter presents an overview of wetlands, their characteristics, and their importance. Constructed wetlands are addressed as an example of ecological engineering, where a wetland is created to meet human needs. The importance of constructed wetlands for contaminant removal is stressed. Storm water characteristics and contaminants are also reviewed, since many constructed wetlands now are used to treat storm water. The contaminants of interest in this research are the divalent metals, cadmium, lead, and copper. Review of storm water contaminants will focus on concentrations of these metals in storm water, the sources of these metals, and how they are transported. General characteristics, including toxicity and background levels of these metals, are also presented. Constructed wetland sediments used for treating storm water act as a sink for divalent metals. The physical, chemical, and biological processes affecting movement of the metals are addressed. The role of acid volatilized sulfide (AVS), organic carbon, and bioturbation of sediment by benthic organisms are specifically addressed as major processes. Finally, past models are evaluated to assess how they can be incorporated into a single system dynamics model. These models include mathematical models of metal fate and transport, chemical processes in sediment, and sediment bioturbation.

Wetlands

Wetlands are defined, in general, as having the following attributes: (1) At least periodically the land supports hydrophytic vegetation which is macrophytic plant life growing in water, in soil, or on a substrate that is periodically deficient in oxygen as a result of excessive water content. (2) The substrate is predominantly undrained hydric soil or a non-soil substrate. (3) The substrate is saturated to the surface at least seasonally (Carter and others, 1978:344; Hammer and Bastian, 1989:6; Pascoe, 1993:2293). Wetlands have received much attention in recent years because of the unique characteristics of wetland ecosystems and their dwindling numbers throughout the world. Wetlands protect shore areas from waves, provide water storage capacity for flood control, remove contaminants from water, provide breeding ground for fish, provide habitat for diverse species of birds and other wildlife, and some even serve as global sinks for carbon dioxide (Baker, 1993:38; Kusler and others, 1994:64B). In 1993, U.S. wetlands totaled 95 million acres which is down from 99 million acres in the 1970's and about 108 million acres in the 1950's. Most wetland losses have been from crop drainage and timber production. Continued wetland losses are due largely to modern commercial or residential development (Baker, 1993:38; Kusler and others, 1994:64B). Fresh water wetlands comprise 75 to 90 percent of total wetland area in the U.S. (Baker, 1993:38; Richardson, 1978:131). Freshwater wetlands can be divided into three primary categories: wetlands dominated by water-tolerant woody plants and trees are considered *swamps*,

those dominated by soft-stemmed plants are considered *marshes*, and those with mosses are considered *bogs* (Hammer and Bastian, 1989:6).

The wetland characteristic that is probably attracting the most attention recently is the ability to remove contaminants and improve water quality. Wetlands effectively remove or treat water-borne organic matter, suspended solids, metals, and excess nutrients (Baker, 1993:40; Hammer and Bastian, 1989:12). Wetlands' unique characteristics cause them to provide one of the best methods for naturally purifying water. This attribute has led wetlands to be labeled "nature's kidneys" (Kusler and others, 1994:64B). Contaminants are removed by several processes. Sedimentation and filtration, as a result of slow-moving water and abundance of plant life, effectively remove suspended solids and pollutants including metals sorbed to those solids. Once in the sediment, some pollutants are physically or chemically immobilized, while others are decomposed into simpler substances. Wetland plants remove nutrients through absorption and assimilation. Plants also translocate oxygen to their roots which increases dissolved oxygen in the surface water (Baker, 1993:40; Hammer and Bastian, 1989:12). Because of wetlands' natural abilities to remove and treat contaminants, many have proposed that constructed wetlands could be used effectively as an application of ecological engineering to treat water and provide habitat for wildlife (Baker, 1993:41; Hammer and Bastian, 1989:12; Mitsch, 1993:442).

Constructed Wetlands

Constructed wetlands have been defined as "designed and man-made complex of saturated substrates, emergent and submergent vegetation, animal life, and water that simulates natural wetlands for human use and benefits" (Hammer and Bastian, 1989:12-13). A more specific definition which best defines constructed wetlands in the context of this research is:

> a compromise between preservation of existing natural systems and exploitation of the unique biological and physico-chemical processes of wetlands to remove low levels of contamination from large volumes of water (Debusk and others, 1996:2707).

The U.S. EPA considers natural wetlands to be "waters of the United States" and, as such, are protected from point source as well as nonpoint source pollution (Fields, 1991:195). This restricts the use of natural wetlands for water treatment, but the EPA does not apply the same criteria to constructed wetlands.

> If wetlands are designed, constructed, and maintained for the sole purpose of water treatment, they are generally not considered "waters of the United States;" therefore, there are no applicable Federal regulations that govern their use (40 CFR, part 122.2). However, in these cases, water leaving the created wetland cannot significantly degrade or alter the water quality or other designated or existing uses of adjacent waterbody (Fields, 1991:195).

The EPA's regulatory stance on constructed wetlands has prompted their use for a variety of treatment applications, which include waste water treatment, storm water treatment, and acid mine drainage treatment. In 1994, at least 300 constructed wetlands in North America and over 500 in Great Britain and Europe were used to treat municipal, industrial, and agricultural waste water. Seventy

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percent of the systems treated municipal waste water and the remainder treated industrial or agricultural waste water (Knight, 1994:31).

Constructed Wetland Types. There are several types of constructed wetland systems. The most common classification divides constructed wetlands into *free water surface (FWS)* wetlands and *subsurface flow (SF)* wetlands. Of the 176 wetland treatment sites in the North America Wetland Treatment Database, 120 are FWS wetlands, 48 are SF wetlands, and 8 use components of both systems (Kadlec and Knight, 1996:718).

A FWS wetland is similar to a natural marsh with a soil bottom, a natural or constructed subsurface barrier to minimize seepage, emergent vegetation, and a water surface exposed to the atmosphere. These wetlands are generally constructed in long smooth channels to control water depth and minimize short circuiting (Crites, 1994:1; Reed and Brown, 1992:776).

A SF wetland usually contains a gravel or sand media which will support emergent vegetation. This system is designed to allow water flow below the surface of the media. The SF wetland may consist of channels or basins (Crites, 1994:1; Reed and Brown, 1992:776).

Other types of wetland systems are all essentially variations of the FWS or SF wetlands. One of these, the *aquatic plant system* (APS), is a FWS system but with water in deeper ponds and the vegetation consisting of floating or submerged plants (Witthar, 1993:147). The Urban Drainage and Flood Control District in Denver, CO recommends using two variations of the FWS system: *very shallow retention ponds* and *wetland-bottomed channels* (CUDFCD,

1992:7.1). Brix classifies constructed wetlands by the dominating macrophyte into: *free-floating macrophyte-based systems, rooted emergent macrophyte-based systems, submerged macrophyte-based systems,* and *multi-stage systems* consisting of combinations of the above systems (Brix, 1993:12). Table 1, below, delineates the common types of constructed wetlands used for water treatment into shallow or deep FWS systems and SF systems.

Table 1. Constructed Wetland Types

Deep Free Water Surface Wetlands (FWS)
Aquatic Plant System (Witthar, 1993:147)
Very Shallow Retention Ponds (CUDFCD, 1992)
Free-Floating Macrophyte-Based System (Brix, 1993:12)
Submerged Macrophyte-Based System (Brix, 1993:14)
Shallow Free Water Surface Wetlands (FWS)
Wetland-Bottomed Channels (CUDFCD, 1992)
Rooted Emergent Macrophyte-Based System (with surface flow) (Brix, 1993:14)
Submerged Flow Wetlands (SF)
Rooted Emergent Macrophyte-Based System (with subsurface flow) (Brix, 1993:14)

Both systems act as attached growth biological reactors and operate much like trickling filters in a waste water treatment plant. The vegetation serves as a substrate for microbial growth and for transmission of oxygen to the roots in the SF systems (Reed and Brown, 1992:776). The FWS systems have had the

greatest success and require less maintenance than the SF systems (Witthar, 1993:148). This research will concentrate on FWS wetland treatment systems.

Constructed Wetland Design. Design of constructed wetland treatment systems must concentrate on three major areas: physical layout, plant types, and maintenance.

Physical layout encompasses the size of the wetland, water depth, shape, flow velocity, detention time, and substrate. The area required for a constructed wetland is generally expressed in square feet per gallon per minute (sf/gpm). Preliminary results using constructed wetlands to treat mine drainage have found that at least 200 sf/gpm is necessary and, in general, the largest ratio of treatment area to base flow provides the best treatment (Witthar, 1993:148). Water depths of 4 to 18 inches have been used effectively dependent upon the primary plant type. Varying the water depth throughout the wetland is recommended to provide more diverse plant and animal habitats with the primary depth at about six inches. (CUDFCD, 1992; Reed and others,1988:166; Witthar, 1993:148). Constructed wetlands are typically laid out in long rectangular cells which can be arranged to flow in series or in parallel. Some variations include small ponds between the cells and weirs to aerate the water as it falls into the adjoining cell (Steiner and Freeman, 1989:369). Large length-to-width (L/W) ratios are important to ensure the water has maximum contact time with the treatment process. L/W ratios of 4:1 to 96:1 have been used with a minimum L/W ration of 10:1 recommended (Steiner and Freeman, 1989:370; Witthar, 1993:148). A low flow velocity is needed to provide adequate time for water

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treatment. Flow velocities of 0.1 to 1.0 ft/s have been recommended (Witthar, 1993:149). The slope of the wetland channel must be very shallow and should be less than 0.5% for a FWS wetland (Steiner and Freeman, 1989:371). The detention time varies with the type of waste water being treated but generally averages 5 to 7 days (US EPA, 1988:25; Witthar, 1993:149). Almost any available soil will make a suitable wetland substrate with sandy clays and silty clay loam soils providing the best permeability and easy root penetration (Allen and others, 1989:406; US EPA, 1988:15; Witthar, 1993:149). A liner should be installed below the substrate to contain the waste water and prevent contamination of groundwater. The liner can be constructed of clay or a manufactured membrane (Reed and others, 1988:196; Steiner and Freeman, 1989:376).

Wetland plants provide a surface for microorganisms to grow which can cause pollutants to precipitate, filter solids, and transfer oxygen to surface sediment for organic decomposition (Steiner and Freeman, 1989:373). Common plants used in constructed wetlands include cattails (*Typha* spp.), bulrushes (*Scirpus* spp.), reeds (*Phragmites communis*), rushes (*Juncas* spp.), and sedges (*Carex* spp.) (Reed and others, 1988:166; Steiner and Freeman, 1989:375; US EPA,1988:25; Witthar, 1993:150).

FWS wetland systems are typically self-maintaining, so require little maintenance. Lawn mowing along wetland edges limits unwanted vegetation. Debris and litter may need to be removed periodically to improve aesthetics and prevent clogging of the outlet. Sediment removal from the wetland forebay is

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occasionally needed to remove the accumulated solids. Harvesting is usually not necessary for nutrient removal, but burning the vegetation annually is helpful in preventing grassy hillocks that can cause channelization (CUDFCD, 1992; US EPA, 1988:26; Witthar, 1993:150).

Constructed Wetlands for Storm Water Treatment. Constructed wetlands were initially used primarily for municipal waste water treatment, but there has been an increased interest in using their pollution filtering and water storage capacity to treat storm water (Baker, 1993:41). Storm water differs in several ways from municipal waste water. First, flows of storm water are variable with large flows during and after precipitation events. Secondly, the quality of the water changes rapidly and is not always a function of the flow (Silverman, 1989:669). Finally, particulate material in storm water is mostly mineral and the majority of the storm water pollutants are adsorbed to these mineral particulates (Breen and others, 1994:105).

The unique characteristics of storm water require changes to the standard constructed wetland design. Because of the large amount of particulates, or total suspended solids (TSS), a silt trap or detention pond is required for pretreatment of the storm water before entering the wetland (Breen and others, 1994:106; Brix, 1993:1; Jones and others, 1996:54; Livingston, 1989:255). The detention pond not only helps to remove suspended solids, but it also dissipates kinetic energy from the run-off and maintains even distribution of flows over the wetland surfaces (Daukas and others, 1989:691). Many storm water constructed wetland systems will also use detention ponds in combination with wetland areas

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to maximize treatment time and provide flood control (Daukas and others, 1989:691; Livingston, 1989:259; Mesuere and Fish, 1989:126).

Storm water also differs from municipal waster water in the variety of contaminants it carries. Municipal waste water has a high organic content making biochemical oxygen demand (BOD) and nutrient loads important contaminants to treat. Storm water can contain oils and greases, pesticides, and heavy metals. Sometimes these can enter all at once as slugs to the system (Mesuere and Fish, 1989:125; Silverman, 1989:670). Although wetlands provide a good sink for removing these contaminants, there is some concern that wetlands may become toxic to organisms that live there (Burton and Scott, 1992:2074; Katznelson and others, 1995:471). One of the primary storm water contaminants that builds up in wetland sediment is heavy metal. Some researchers are also concerned that a constructed wetland only has a finite capacity for retaining metals and at a point in time, will be no longer useful for treatment (Wieder and others, 1989:301-303; US EPA, 1988:23).

Constructed Wetland Performance. Constructed wetlands perform well in removing BOD, nitrogen, phosphorous, suspended solids, coliforms, and metals from the untreated influent. In wetlands using surface flow with various plants and cell structures, BOD removal efficiencies range from 51 to 96-percent and suspended solids removal efficiencies range from 60 to 95-percent. Highest removal efficiencies are obtained from systems which used marshes, ponds, and meadows in combination (Watson and others, 1989:322). Suspended solids removal generally occurs in the initial 12-20% of the cell and removal efficiency

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appears to be related to detention time more than hydraulic or solids loading (Gearheart and others, 1989:122). Nitrogen removal efficiencies range from 26 to 65 percent and phosphorous efficiencies are 12 to 81 percent (Watson and others, 1989:324-326). Little nitrogen is taken up by plants. The majority of the nitrogen is removed though a process of nitrification/denitrification by bacteria (Watson, 1989:329). Coliform removal efficiency is very high and ranges from 82 to 100 percent (Watson, 1989: 326). Coliform removal is basically a first order decay which is a function of detention time (Gearheart and others, 1989:133; Watson, 1989:332).

Heavy metals, specifically lead, cadmium, copper, and zinc, are typically found in storm water and frequently exceed water quality criteria (Mesuere and Fish, 1989:125). The metals enter the wetland in both dissolved and particulate form. Removal efficiencies for these metals have been cited as 50-90% for cadmium, copper, and zinc; and 80-95% for lead (Daukas and others, 1989:692). Studies of lead and cadmium in wetland microcosms found that nearly all the removed metals were immobilized in the sediment in metal sulfides. Less than 1% of the total lead and cadmium mass in the wetland was present in wetland plants, with the majority of the metal in the plant remaining in the plant roots (Debusk and others, 1996:2715; Watson and others, 1989:331). Systems which used combinations of wetlands and ponds were most efficient at removing metals (Gain and Miller, 1989:7A-18).

Storm Water Characteristics

Storm water runoff has had a large part in the degradation of water quality over the past decade. Urbanization, with its clearing and paving of previously pervious land, continues to accelerate the problem. While the amount of rainfall is constant, the amount of runoff and accompanying pollutant loads increase as the amount of paved or other impervious surfaces increase (Livingston and Cox, 289:undated). Storm water flowing over roofs, streets, lawns, fields, and other permeable and impermeable surfaces transport pollutants into surface water. Rains wash metals from roofs; sediments from bare soil; metals, road salts, oils, and greases from streets and paved areas; nutrients and pesticides from treated lawns and fields; and coliform bacteria from animal wastes into receiving waters (Livingston and Cox, 289:undated; Maltby and others, 1995:1079; Pitt and others, 1995:262). The highest concentration of pollutants in storm water runoff occurs during the "first flush" which describes the earliest part of the storm prior to peak flow (Livingston and Cox, 289:undated). These high pollutant loads produce waters that can be toxic to some aquatic life. In 87 storm water samples from Birmingham, AL, 9% of the samples were considered highly toxic and 32% were considered moderately toxic using the Microtox® toxicity-screening procedure (Pitt and others, 1995:262). Although the water quality varies rapidly with storm events, sediment in receiving waters accumulates pollutants with each storm event. Non-degradable toxins, such as metals and PCBs, accumulate in the sediment. These polluted sediments have been shown to reduce diversity of

benthic macroinvertabrates (Maltby and others, 1995:1088; Pitt and others, 1995:268).

Storm Water Metals. Heavy metals are almost always present in storm water and storm water is blamed for 80 to 95 percent of the heavy metals loading to Florida surface waters (Livingston and Cox, 289:undated). The most common heavy metals found in storm water are copper, lead, cadmium, zinc, and chromium (Maltby and others, 1995:1088; Mesuere and Fish, 1989:125; Pitt and others, 1995:265). From 1978 through 1983 the U.S. EPA conducted a Nationwide Urban Runoff Program (NURP) in 28 cities to study the nature of runoff from commercial and residential areas (US EPA, 1993:61153). In 1992 a similar study was done analyzing 87 storm water samples from Birmingham, Alabama (Pitt and others, 1995:260). Table 2 summarizes the results of these studies.

Table 2. Detection Frequency of Common Heavy Metals

Metal	NURP	Pitt Study
Lead	94%	100%
Zinc	94%	99%
Copper	91%	98%
Chromium	58%	91%
Cadmium	48%	95%
Nickel	43%	90%

Both studies also found that the frequency of detection of the metals in Table 2 was higher than frequency of detection of any other toxic pollutant (Pitt and others, 1995:264; US EPA, 1993:61153).

Lead. Lead in storm water is most often in the divalent form Pb(II), which forms salts with sulfides, carbonates, sulfates, and chlorophosphates. Lead combines with organic ligands to form soluble and colloidal complexes (Kadlec and Knight, 1996:508). The main source of lead in storm water has been emissions from gasoline-powered vehicles and gasoline additives. Lead is also used as a filler in tires (Makepeace and others, 1995:102). The NURP study reported that the mean concentration of lead in storm water was 238 µg/L and recommended using 182 - 443 µg/L for load estimates (US EPA, 1993:61153). It has been found that 80 to 90% of the lead is carried in suspension (Mesuere and Fish, 1989:131; Vaithiyanathan and others, 1993:18).

Zinc. Zinc is present in storm water primarily as the divalent Zn(II) where it forms ionic hydrates, carbonates, and complexes with organics (Kadlec and Knight, 1996:516). Zinc can enter storm water from tire and brake pad wear, corrosion of metal objects, and corrosion of building materials (e.g. galvanized roofs) (Makepeace and others, 1995:106; Pitt and others, 1995, 262). The NURP study reported that the mean storm water concentration of zinc was 353 µg/L and recommended using 202 - 633 µg/L for load estimates (US EPA, 1993:61153). Zinc is usually associated with the dissolved portion as opposed to suspended particles (Gain and Miller, 1989:7A-17; Makepeace and others, 1995:106; Pitt and others, 1995, 262). However, others have found suspended zinc makes up as much as 80% of water-borne zinc (Vaithiyanathan and others, 1993:18).

Copper. Storm water copper is typically present as chelated compounds of Cu(II). Its dissolved portion decreases with increasing organic loads as it has a high affinity for humic substances (Kadlec and Knight, 1996:503). Copper enters storm water from the wear of tires and brake linings, corrosion of building materials, wear of engines, pesticides and fungicides, and industrial emissions. Copper shows a correlation with the intensity of vehicular traffic (Makepeace and others, 1995:100). The NURP study reported that the mean storm water concentration of copper was 53 µg/L and recommended using 43 - 118 µg/L for load estimates (US EPA, 1993:61153). The majority of copper is carried in solution and the amount carried in suspension has been found to only range from 10 to 50% (Mesuere and Fish, 1989:131). However, others have found suspended copper may make up as much as 80% of water-borne copper (Vaithiyanathan and others, 1993:18). The difference may be due to differences in the type and concentration of suspended solids in each study.

Chromium. Chromium is typically present in storm water in the trivalent [Cr(III)] or hexavalent [Cr(VI)] forms. Cr(VI) is unstable and converts to the less-toxic trivalent form in surface waters, especially when organic matter is present (Kadlec and Knight, 1996:501). Chromium can enter storm water from corrosion of welded metal plating, wear of engines, paints and dyes, fertilizers, and pesticides (Makepeace and others,1995:100). The study by Pitt et al. found concentrations of chromium in storm water as high as 710 µg/L and mean values have been reported as 10 to 230 µg/L (Makepeace and others,1995:99; Pitt and others, 1995:265).

Cadmium. Cadmium is typically present in storm water in its divalent Cd(II) form. It forms complexes with carbonate, sulfate, chloride, hydroxides, and humates which are highly adsorbable onto organic particulates (Kadlec and Knight, 1996:499). Sources of cadmium include wear of tires and break pads, corrosion of galvanized metals, and application of fertilizers and pesticides (Makepeace and others,1995:99). The study by Pitt et al. found concentrations of cadmium in storm water as high as 220 µg/L with reported mean values from 3 to 11µg/L (Makepeace and others,1995:98; Pitt and others, 1995:265). Approximately 50% of cadmium may be carried in particulate form (Mesuere and Fish, 1989:131).

Other Factors. The form in which metals are carried in storm water is dependent upon pH and total suspended solids (TSS). Research by Pitt et al. found storm water pH to range from 4.4 to 9.0 and averaged from 7.0 to 8.5 (Pitt and others,1995:262, 265). Storm water carries a high suspended solids load which is typically pretreated prior to entering a wetland. The NURP study reported an average TSS value of 239 mg/L and recommended using 180 to 548 mg/L for load estimates (US EPA, 1993:61153). Pitt's group found mean TSS values typically at or below 100 mg/L (Pitt and others,1995:262, 265).

Metal Characteristics and Toxicity

Background. Wetlands have proven to be effective at removing and immobilizing heavy metals in their sediment through adsorption and burial (Gambrell, 1994:889-890; Ton and others, 1993:436). This ability to store up

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metals cause many to wonder if and when the sediment may become toxic to some organisms (Burton and Scott, 1992:2074). Knight indicates that there may be a trade-off between wetland benefits, like water treatment and habitat for large numbers of animal species, versus drawbacks, such as toxicity to invertebrates and larval fish (Knight, 1992:109). Sediment toxicity, in general, is a fairly young field but research in this area has dramatically increased in recent years as the U.S. EPA tries to develop sediment toxicity standards called Sediment Quality Criteria (SQC) (Adams and others, 1992:1865; Burton and Scott, 1992:2068; US EPA, 1994). Adams et al. defines sediments and their important role:

> Aquatic sediments can be loosely defined as a collection of fine-, medium-, and coarse-grain minerals and organic particles that are found at the bottom of lakes, rivers, bays, estuaries, and oceans. Sediments are an important component of aquatic ecosystems because of the niche they provide for benthic aquatic organisms. Sediments provide a substrate for a wide variety of organisms to live in or on, including shrimp, crayfish, lobster, crab, mussels, clams, flounder, many other important species as well as species important in the food chain—including many species of worms, amphipods, oligochaetes, chironomids, bivalves, and insects. In recent years, protecting sediment quality has been viewed as a logical and needed extension of water quality protection. The basic premise that has been used to protect water quality has been used to restrict chemicals from occurring in water at concentrations above the known "safe" philosophy is now being considered for sediments (Adams and others, 1992:1865).

Sediment toxicity studies have focussed primarily on benthic invertebrates because they are exposed to a much different concentration of toxins than are organisms that remain entirely in the water column (DeWitt and others, 1996:2097; US EPA, 1994:11-19). In fact, no official method existed for sediment toxicity testing until 1990 when the American Society for Testing and

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Materials (ASTM) approved three standard guides for toxicity testing using

marine and freshwater benthic invertebrates (Burton and Scott, 1992:2070).

Since 1990, much research has been conducted and a plethora of articles have

been published on metal toxicity to various sediment-dwelling invertebrates

under varying conditions.

Metal Characteristics and Toxicity. Bioavailability of metals and many

nonionic chemicals in sediment generally correlates with their interstitial (pore)

water concentration (Ankley and others, 1991:1299; Hall, 1996:357; Pesch and

others, 1995:136; Wenholz and Crunkilton, 1995:676). Recently, a better

correlation has been found linking bioavailability to the actual free metal activity

in the pore water (Ankley, 1996:2060; Di Toro and others, 1990:1490).

> Metal activity is the molar divalent concentration $[M^{2+}]$ corrected for the
> shielding effect of anions that are electrostatically attracted to the atoms in
> high ionic strength (e.g., concentrated) solutions (Ankley, 1996:2060).

However, some argue that simply equating metal activity or pore water

concentration to bioavailability and, therefore, toxicity is an oversimplification.

This method ignores species-specific mechanisms such as routes of exposure,

method of ingestion, and the process of adsorption across the gut walls (Kaag

and others, 1997:842; Mayer and others, 1996:2645; Rainbow, 1996:415).

Importance of AVS. Di Toro et al. first proposed that sediment toxicity

from metals correlates to the divalent metal activity $\{Me^{2+}\}$ in sediment pore

water. They also concluded that this toxicity can be predicted from the

concentration of acid-volatile sulfide (AVS) in the sediment which is "the solid

phase sulfide that is soluble in cold acid (HCl)" (Di Toro and others, 1990:1488-

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1491). Their studies with cadmium showed that by simply dividing the total cold acid extractable metal concentration in the sediment, $[Me_T]$, by the AVS concentration one could predict when the sediment would become toxic. If the molar sum of the divalent metals is less than the AVS, then no metal toxicity would be expected.

$$\frac{[Me_T]}{[AVS]} < 1 \tag{1}$$

On the other hand, if this ratio is greater than one then the sediment could be toxic and the metals with the lowest sulfide solubility parameters would exist as free (bioavailable) metal (Di Toro and others, 1990:1498).

$$\frac{[Me_T]}{[AVS]} > 1 \tag{2}$$

Work by Di Toro's group was followed by several studies examining the role of AVS on cadmium and nickel toxicity. They all concluded that in both freshwater and marine sediments that concentrations of divalent metal below the AVS concentration are not bioavailable and therefore will produce no toxic effect (Ankley and others, 1991:1299; Carlson and others,1991:1309; Di Toro and others, 1992:96; Pesch and others, 1995:129). These conclusions are only applicable to organisms who predominantly dwell in anaerobic sediments, but it is hypothesized that the metal activity in the anaerobic layer may be sufficient enough to control the metal activity in a thin surficial aerobic layer, thus influencing all benthic organisms (Di Toro and others, 1992:99).

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Benthic Organisms and Bioturbation

Benthic organisms or benthos are not only the most affected animal community from sediment contaminants, but they in turn affect the sediment through their burrowing and feeding mechanisms.

Background. Freshwater macrobenthos (adult length > 1 mm) are made up primarily of chironomids, amphipods, oligochaetes, and bivalves. The Chironomidae (commonly called "midges") are a family of insects whose closest familiar relatives are the mosquitoes (McCall and Tevesz, 1982:113). Most of their life cycle is spent in the larval stage which can last form several weeks to 2 years, depending on the latitude. The adult flying stage only lasts a few days to a few weeks (McCall and Tevesz, 1982:113). Larvae live in the upper 8-10 cm of sediment, but have been found at 40 to 50 cm depths. Most chironomids live in U-shaped or straight tubes lined with transparent salivary secretions. They feed by either drawing water through the sides of their tube or by scraping the top 1-2 mm of sediment around their burrows for detritus and bacteria (McCall and Tevesz, 1982:115).

Amphipods consist of several hundred species, but only a few (*Hyalella azteca*, species of *Gammarus*, and *Pontoporeia hoyi*) are widespread and abundant. Adult amphipods are typically 5-10 mm long and range from a few hundred to over 14,000 per square meter of lake sediment. Most profundal amphipods derive their nutrition from bacteria and algae obtained by surface

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deposit feeding. Amphipods live in simple mud burrows in the top 1 to 2 cm of sediment (McCall and Tevesz, 1982:116-118).

"Oligochaetes are typically bilaterally symmetrical, segmented, hermaphroditic annelids" (McCall and Tevesz, 1982:118). The three most common of these worms are the Tubificadae, Naididae, and Lumbriculidae. Tubificid oligochaete worms and chironomids are typically the most dominant microfauna in lake sediment. Their populations can range from a few hundred to several million per square meter. Higher populations are associated with fine-grained sediment, higher inputs of organic matter, and higher temperatures (McCall and Tevesz, 1982:118). Tubificids can be 2 to 15 cm long and are found mostly in the upper 20 cm of sediment. They feed primarily in the top 2-8 cm of sediment. Tubificids typically live and feed head down in the sediment. They ingest small sediment particles as they feed on microflora attached to these particles. Fecal pellets are deposited at the sediment-water interface (McCall and Tevesz, 1982:120).

Bivalves (clam-like, hinged shell organisms) consist of Unionacea and Pisiidae. Unionaceans are the largest members of the permanent freshwater infauna, averaging 7 cm in length. Unionaceans are filter feeders that spend most of their lives in one position feeding on plankton and organic detritus at the sediment-water interface. Pisiidae are much smaller than unionaceans (2-20 mm) and are typically more abundant and are found at greater depths. Pisiidae can be filter feeders like the unionaceans or deposit feeders, burying themselves

in the sediment and filtering pore water for food (McCall and Tevesz, 1982:120-124).

The invertebrates described above, which have been studied predominantly in freshwater lakes, are the same types or organisms that reside in wetland sediment. They play a crucial role in the wetland by providing a link in the food chain, processing living and dead organic matter, and physically modifying the wetland habitat. The abundance of wetland invertebrates is a function of "wetland size, location relative to other wetlands, wetland setting, substrate, vegetation structure, water regime, water quality, competition, and predation" (Feierabend, 1989:110).

Bioturbation. Bioturbation can be defined as the mixing of aquatic sediment by the feeding, burrowing, locomotory, respiratory, and excremental activities of sediment dwelling macrobenthos. Through these activities, macrobenthos alter the physical and chemical properties of the environment in which they live (Fisher and others, 1980:3997; Matisoff and others, 1985:19). Tubificid oligochaetes are one of the primary agents of bioturbation. Tubificids feed head down at some depth in the sediment and deposit fecal pellets at the sediment-water interface. This kind of vertical mixing has given these worms the label "conveyor belt species" (Fisher and others, 1980:3997; McCall and Tevesz, 1982:125). While the tubificids typically burrow to depths of 25 cm, maximum feeding usually occurs at 7-8 cm. This feeding depth is what controls the zone of mixing (McCall and Tevesz, 1982:130-131). Mixing rates are highly variable and are dependent on worm species, water temperature, worm density, sediment

type, dissolved oxygen, and import of organic matter (Fisher and others, 1980:4003; McCall and Tevesz, 1982:131-135). Studies of bioturbation using cesium 137 as a radiotracer have computed a per individual particle reworking rate of $59.7 \pm 10.1 \times 10^5$ cm^3/hr. With a density of 100,000 individuals/m^2, the downward velocity from tubificid feeding came to 0.12 ± 0.02 cm/day. Calculated subduction velocities in Lake Erie based on worm populations ranged from 0.02 to 6.26 cm/day (Fisher and others, 1980:3999). Fisher et al. concluded that the bioturbation process will cause significant sediment mixing where the downward velocity from tubificid feeding is greater than the upward velocity from sedimentation (Fisher and other, 1980:4004).

Effects of Bioturbation. Matisoff et al. studied how chemical diagenesis is affected by bioturbation. They found that macrobenthos aid in the transport of electron acceptors (O_2, NO_3, SO^2_4, etc.) into sediments which increases the depth over which organic decomposition reactions occur (Matisoff and others, 1985:32). The increased oxidation layer in the sediment from benthos mixing may hinder metal binding and retention in the sediment since they are dependent on reduced conditions. Reduced conditions are especially important for AVS binding. Studies have found that metal bioavailability in surficial sediments may be substantially greater than slightly deeper sediments, especially when burrowing organisms are present. The bioturbation causes a significant reduction in AVS in surficial sediments as sulfide complexes are oxidized (DeWitt and others, 1996:2100; Peterson and others, 1996:2154).

Sediment Metal Interactions

Wetlands have been found to effectively remove and immobilize metals, much more than upland or unsaturated soils (Gambrell, 1994:890; Ton and others, 1993:436). This process of removal and immobilization of metals occurs within the wetlands' aerobic and anaerobic zones.

Aerobic and Anaerobic Processes. When there is a free water surface, aerobic conditions generally occur throughout the water column, but become anaerobic just below the soil surface (Eger, 1994:20; Faulkner and Richardson, 1989:51). Also, an aerobic zone exists around plant roots which extend into the anaerobic zone. Metal removal occurs in the thin aerobic zone through adsorption, chelation, and ion exchange (Eger, 1994:250). The primary metal binding mechanism in the aerobic zone is adsorption to iron and manganese oxyhydroxides (Burton, 1991:1588). Transport to the anaerobic zone occurs through diffusion, sedimentation, and bioturbation where the metal is effectively immobilized (Eger, 1994:252; Fisher and others, 1980:4004). Immobilization of metal generally occurs through metal sulfide formation because of its insolubility (Faulkner and Richardson, 1989:61).

AVS Binding. It has long been established that acid-volatile sulfide (AVS) binding is one of the most effective and important metal immobilization processes in reduced environments (Eger, 1989:61; Debusk and others, 1996:2713-2715; Di Toro and others, 1990:1493; Holmes and others, 1974:258). Many wetlands are effective sulfur sinks. Sulfur enters the system as SO_4^{2-} from the atmosphere through runoff and precipitation. It is reduced as it enters the

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anaerobic sediment to S^{2-}, where it quickly forms metal sulfides, usually with iron

(FeS or FeS_2) or Manganese (MnS) (Di Toro and others, 1990:1494; Di Toro and

others, 1992:97; Faulkner and Richardson, 1989:58-60). Sulfur is lost from the

system by being oxidized and flushed from the system or through volatilization as

H_2S, methyl sulfide (MS) or dimethyl sulfide (DMS) (Faulkner and Richardson,

1989:60).

When a divalent metal is introduced to the system (e.g., Ni, Zn, Cd, Pb,

Cu), the metal that is least soluble will replace the more soluble metal to form a

solid metal sulfide (Di Toro and others, 1990:1494). Table 3 presents the

solubility products of different metals and their ratio with iron sulfide's K_{sp}. The

table shows which metals will form the most insoluble sulfide bonds, in

descending order, it also shows that the magnitude of the solubility product is so

small that virtually all the metal will exist in the solid phase.

Table 3. Metal Sulfide Solubility Products[a]

metal sulfide	log $K_{sp,2}$	log K_{sp}	log (K_{MS}/K_{FeS})
FeS	-3.64	-22.39	
NiS	-9.23	-27.98	-5.59
ZnS	-9.64	-28.39	-6.00
CdS	-14.10	-32.85	-10.46
PbS	-14.67	-33.42	-11.03
CuS	-22.19	-40.94	-18.55
HgS	-38.50	-57.25	-34.86

[a]Solubility products, $K_{sp,2}$, for the reaction $M^{2+} + HS^- \leftrightarrow MS(s) + H^+$ for CdS (greenockite), FeS (mackinawite), NiS (millerite), CuS (covellite), HgS (metacinnabar), PbS (galena), and ZnS (wurzite). K_{sp}, for the reaction $M^{2+} + S^{2-} \leftrightarrow MS(s)$ is computed from log $K_{sp,2}$ and pK_2 (Di Toro and others, 1992:97).

Based on the above conclusions and that bioavailability is linked to pore water metal activity, it is theorized that the metal activity will approximate the metal in excess of the AVS. This metal activity in the sediment pore water will likely be toxic to sensitive organisms, so long as there are no other strong complexing ligands present. Therefore, the concentration of AVS determines the boundary between low metal activity and potentially high metal activity (Di Toro and others, 1992:97).

The AVS concentrations have been measured in various sediments. AVS in samples from Lake Michigan ranged from non-detectable (ND) to 4.49 µmol/g and from ND to 175 µmol/g in marine sediment from the Virginia coast (Leonard and others, 1996:2224, 2227). Marine sediment typically contains higher AVS concentrations because seawater has a higher sulfate concentration than freshwater (Di Toro and others, 1990:1497). Other freshwater AVS samples in the lake sediments ranged from 7.5 to 112.0 µmol/g (Di Toro and others, 1990:1498). In sediment samples from western Montana, the Clark Fork River sediment AVS ranged from 0.3 to 19.1 µmol/g and Milltown Reservoir sediment AVS from 0.6 to 23.3 µmol/g (Brumbaugh and others, 1994:1974). Concentrations of AVS are known to vary seasonally with fluctuations in water temperature. They tend to be highest in late summer and lowest in late winter, ranging seasonally from 1 µmol/g to 7 µmol/g in the studied lake (Howard and Evans, 1993:1056).

Organic Carbon Binding. It is evident that AVS is not the only significant binding phase for metals in sediment. Even when AVS binding sites are exceeded, pore water concentrations are not immediately toxic. One possible binding phase is organic carbon (Ankley and others, 1991:1306; Brumbaugh and others, 1994:1980; DeWitt and others, 1996:2099). Metal ion binding to organics typically follows the Langmuir adsorption isotherm (Drake and Rayson, 1996:25A). The Langmuir equation has the general form:

$$S = \frac{K_L A_m C}{1 + K_L C} \tag{3}$$

where
  S = mass sorbed at equilibrium per mass of sorbent
  C = sorbate concentration in solution at equilibrium
  K_L = Langmuir sorption constant
  A_m = maximum sorption capacity of sorbent

This relationship describes a non-linear sorption process with a maximum sorption capacity (Rand: 1995:475). The Langmuir model was used by Mahony et al. to fit relationships of non-AVS sorbed metal to metal activity for Cd, Cu, and Pb in sediment (Mahony and others, 1996:2191). Their work also included calculating the sorption constant at three pHs (Mahony and others, 1996:2193). They found this additional binding phase (non-AVS) to be significant for lead and copper, but not for cadmium (Mahony and others, 1996:2196). Some studies, however, have not found a direct correlation between metal pore water concentrations and organic carbon (Pascoe and others, 1994:2045).

Carbon plays a significant role in wetlands as it cycles between the atmosphere, plant, surface water, detritus, and sediment compartments. The net effect is a fixing of carbon from the atmosphere and deposition in the wetland

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sediment (Kadlec and Knight, 1996:345-346). Some northern peat lands may actually help moderate climatic change by serving as such a large sink for carbon dioxide (Kusler and others, 1994:64B).

Sediment Quality Criteria. The U.S. EPA is in the process of developing sediment quality criteria (SQC). Criteria based on equilibrium partitioning has already been developed for four hydrophobic organic compounds (Hassan and others, 1996:2198). The EPA has recently proposed similar SQC for five divalent metal cations: cadmium, copper, nickel, lead, and zinc (USEPA, 1994:11-1). The EPA has proposed four procedures to derive the SQC: (1) comparing the sum of their molar concentrations [Simultaneously Extracted Metals (SEM)] to the molar concentration of AVS in sediment (AVS criteria); (2) comparing measured pore water concentrations of metals to water quality criteria (WQC) final chronic values (FCVs) (interstitial water criteria); (3) using organic carbon based partition coefficients, in addition to the AVS and SEM relationships, to compute pore water concentrations and compare to WQC FCVs (AVS and organic carbon criteria); and (4) using minimum partition coefficients (e.g., generated from chromotographic sand) and AVS to compute the lower bound sediment concentrations that are unlikely to cause toxicity (minimum partitioning criteria) (Ankley and others, 1996:2060; USEPA, 1994:11-1, 11-2). Failing all of the above procedures is indicative of a potential problem that will require further investigation. Exceeding an SQC using only one procedure should not produce toxicity (Ankley and others, 1996:2060). The technical basis is currently available for implementing procedures (1) and (2), but further

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research is required to implement procedures (3) and (4) (Ankley and others, 1996:2060; USEPA, 1994:11-2). All of these procedures are intended to give "no effect" versus "effect" values and are intended only to protect benthic organisms from direct toxicity associated with exposure to metal-contaminated sediments (Ankley and others, 1996:2063-2064; USEPA, 1994:11-19). Some feel the equilibrium-partitioning approach for assessing sediment toxicity is too simplistic and does not take into account behaviors of individual organisms, such as food source and ingestion route, nor does it allow for non-steady state conditions (Landrum and others, 1994:1769-1779).

Existing Models

Many various mathematical and deterministic models have been constructed to simulate various wetland functions, show effects of bioturbation, and represent contaminant fate and transport in wetlands and other aquatic systems. The complexities surrounding the numerous processes affecting metal fate and transport in wetlands, require the integration of many specialized disciplines to understand and develop models that accurately reflect these processes (Dixon and Florian, 1993:2290). Some propose that modeling wetlands as systems may, therefore, be the most appropriate way to understand overall wetland processes. "Holistic approaches, not seeking details but general rules, are much more important than for simpler systems where adequate details can be incorporated into models more easily" (Mitsch and others, 1988:221).

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Wetland Models. Costanza and Sklar reviewed 87 models of wetlands and shallow lakes in 1985. The majority of the models dealt with shallow lakes (30), forested swamps (18), and emergent marshes (14). The models primarily examined cycling of water, biomass, energy, or various nutrients through the wetland (Costanza and Sklar, 1985:51). None of the models in this study dealt with constructed wetlands or contaminant removal. Wetlands present a unique modeling challenge. First, wetlands are made up of several types, each with its unique characteristics. Second, their hydrology is very important and complex, affecting the chemical and biological processes of the wetland. Third, wetlands are constantly changing over time; they are a transitional ecosystem. Fourth, interfaces play an important role in wetland dynamics; these include the sediment-water exchange of chemical species, interactions of water and soil, and soil water and plants. Finally, wetlands are dependent on outputs from other ecosystems and their interrelationships; simply drawing the wetland boundary is a difficult task (Mitsch and others, 1988:218). Because of the overall complexity of wetlands, they need to be viewed as a system. A holistic approach is recommended where general rules are sought, not details (Mitsch and others, 1988:221). However, modelers who prefer models with a very high degree of accuracy disagree with the systems approach (Costanza and Sklar, 1985:61).

Bioturbation Models. Post-depositional models of sediment attempt to represent how contaminants or sediment particles are transported and mixed within the sediment. These are typically mathematical models which model

sediment or contaminant movement over space and time. There are two general types: particle transport models and fluid transport models.

Particle transport models, typically, represent mixing by macrobenthos as a diffusive process (Matisoff, 1982:293). Burial, sedimentation, and compaction are represented as an advective process. A decay process is used to represent biodegradation and consumption of organic or degradable substances (Fisher and others, 1980:4000-4002; Matisoff and Robbins, 1987:145). In addition to diffusion models, some have used box models to represent the mixing layer of sediment, immediately beneath the sediment-water interface as a completely homogenized compartment. Beneath this bioturbation layer, the sediment is buried. This can be thought of as a very rapid diffusion model (Matisoff, 1982:305-306). A third type of bioturbation model is the Markov chain model. This model is made up of three compartments: surficial fecal pellets, "free" sediments within the bioturbation zone, and buried sediments below the bioturbation zone. The Markov model is able to represent the selection of "free" sediment particles, for ingestion and ultimate excretion, by organisms using probabilities (Matisoff, 1982:311-312).

Fluid transport models attempt to represent the exchange of water and solutes across the sediment-water interface. These models are very similar to the particle transport models, except that they deal with movement of fluids versus particles. Diffusion models are used to represent the fluid movement between the soil and water and, in some cases, between benthos burrow walls and the actual burrow (Matisoff, 1982:314-322). Advection models are used to

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Gerald, undated:1). This model assumes reactions within the wetland are at equilibrium. It divides the wetland into three compartments: surface water, surficial sediment (≈ 1 cm), and active sediment (5-15 cm). Metals are removed from the system using solid-water partitioning coefficients and settling of particles with sorbed metals (Dortch and Gerald, undated:10, 37).

The EPA uses a geochemical equilibrium model, MINTEQ, that has been linked with EXAMS, a steady-state aquatic exposure assessment model to produce MEXAMS, the Metals Exposure Analysis System (Felmy and others, 1984b). MINTEQ can predict the form of 11 different metals in storm water in order to determine their bioavailability. This equilibrium model is based on data from the EPA's National Urban Runoff Program (NURP) and is helpful in predicting toxicity of runoff (Paulson and Amy, 1993:45; Schnoor and others, 1987:4). Statistical analysis and modeling of the NURP data suggest that the four most controlling factors in metal bioavailability in storm water are: suspended solid types and concentrations, pH, total metal concentrations, and dissolved organic carbon concentrations and character (Paulson and Amy, 1993:48). MEXAMS strength is its ability to perform as a screening-level model to predict speciation of several metals simultaneously in aquatic systems which can then be related to toxicity (Felmy and others, 1984a:6). Limitations to this model, however, include: its assumption that chemical reactions are at thermodynamic equilibrium (Felmy and others, 1984b:4 ;Schnoor and others, 1987:177), its ability to predict speciation only in the aquatic aerobic environment

describe the pumping of water between the surface and pore water through worm burrows (Matisoff, 1982:322-325).

One model which incorporates both particle and fluid transport, "DYNMX" (Dynamic Mixing Model), describes movement of a radioactive tracer in sediment. The model includes:

> sediment accumulation, depth-dependent porosities, biogenic diffusivities and biological feeding rates (advection), linear adsorption of the tracer between solid and solution phases, molecular diffusion of solute, particle selectivity, radioactive decay, and time-dependent depositional fluxes (Matisoff and Robbins, 1987:144).

In general, bioturbation models have been used to represent sedimentation and mixing processes that may affect geological dating. They have not played much of a role in modeling contaminant transport.

Metal Fate and Transport Models. Various mathematical models have been developed to represent movement of specific metals in storm water, detention ponds, wetlands, and sediment. Most of the models have concentrated on the aquatic environment and only the aerobic portion of the sediment. More recently some system dynamics models have been developed to try to represent constructed wetlands and the optimum design parameters for BOD and metal removal.

The U.S. Army Corps of Engineers developed a "screening-level" model for estimating pollutant removal by wetlands. With input of basic wetland characteristics, this model will produce removal efficiencies for total suspended solids, total coliform bacteria, biochemical oxygen demand, total nitrogen, total phosphorous, and contaminants (organic chemicals and metals) (Dortch and

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and not in the anaerobic sediment, and its inability to compute chemical speciation over time.

Several other metal-specific models focus entirely on the removal process of metals by sediment. One model represents the cycling of manganese in coastal sediment between the sediment and water column using five compartments. It showed that the redox boundary between the oxidizing and reducing environments was very important in manganese removal (Sundby and Silverberg, 1985:379). NONEQUI is a non-equilibrium model developed to simulate metals in acidic lake and stream environments and predict metal speciation in water and sediment. It is unique in that it incorporates substrate binding capacities and can demonstrate chemical kinetics over short periods of time (Fontaine, 1984:287-288). Finally, copper removal in wetlands was modeled using a non-equilibrium model, WASP, divided into three main compartments: water column, top sediment, and bottom sediment. This model included plant uptake and nutrient and biomass cycling. Key processes included sedimentation, bioturbation, and diffusion. The model produces time-series data and simulations of up to one year have been run. A linear isotherm is used to represent partitioning of copper between dissolved and particulate phases in both the surface water and the sediment. Copper favors the particulate phase in the surface water and the dissolved phase in the sediment. Chemical speciation is calculated using MINTEQA2 which shows similar copper species in the top and bottom sediment. This model showed that biomass harvesting in the modeled wetland was not an effective way to remove copper from wetlands

(Lung and Light, 1996:91, 98). The major limitation to this model is that is does not take into account the chemical processes in the reduced sediment and the recent studies on AVS and OC-binding in reduced sediment. Using the old MINTEQ model, both the top and bottom sediments are treated as oxidized sediments.

Two other models focused on post-depositional activity in sediment. One showed vertical redox gradients in sediment, represented by six different reactions or "reaction zones." The model showed flux of primary electron acceptors such as oxygen and nitrate from the surface water to the benthic sediment governed redox conditions near the sediment-water interface. Bioturbation and rate of pore-water infiltration are controlling parameters of this flux (Park and Jaffe, 1996:172, 180). The first model to represent the importance of sediment AVS, models cadmium and AVS concentrations over time and space in order to study the effects of seasonal AVS variations. The model focuses on the chemical reactions occurring within the aerobic and anaerobic zones which change the chemical form of the metal. The model was able to reproduce temperature-dependent ratios of SEM to AVS in experimental data, but not pore water cadmium concentrations (Di Toro and others, 1996:2168-2186). Both of these models focused on specific processes in the system, but did not seek to determine what the other processes were and which had the greatest influence on the system.

Recent system dynamic models have addressed the processes and interactions in constructed wetlands. A preliminary model was developed in

1994 to study metal fate and transport, concentrating on hydrologic and microbiological mechanisms (Smekrud, 1994). Mudgett created a model to simulate BOD degradation in constructed wetlands (Mudgett, 1995). More recently, a model was proposed to show metal fate and transport in constructed wetlands with an emphasis on plant uptake and the potential for bio-remediation (Peake, 1996). Although these models represented behavior of a treatment wetland over time, none of them focused on the metal interactions in the sediment except to represent it as simple equilibrium partitioning.

Currently, no model exists to represent the long-term state of a treatment wetland and general trends in the condition of the reduced wetland sediment receiving metal-contaminated influent. Specifically, the wetland's capacity to absorb metal, as well as its ability to support sensitive benthic or aquatic organisms need to be addressed.

III. Methodology

Introduction

The wetland ecosystem is made up of a web of physical, biological, and chemical processes that change over time. The complexity of these changes stem from the internal interactions of the system as well as forces external to the system. To understand the magnitude of the various influences and the implications of different management alternatives on such a dynamic system, systems thinking and system dynamics modeling prove ideal. By modeling the variables and relationships which drive the system's behavior, the system dynamics approach enables one to understand both the short-term and long-term consequences of management alternatives. It should be noted that the system dynamics process is an iterative one, requiring the relationships in the model to be reworked as necessary to ensure the model becomes a reasonable mechanistic representation of the actual system. The final output should yield insights in overall system behavior and general trends, as opposed to precise numbers (e.g., the exact pore water concentration of cadmium at year ten).

The modeling process is divided into four stages: conceptualization, formulation, testing, and implementation (Randers, 1996:284).

Conceptualization

To properly identify the problem to be solved and to represent it in a model, one must become familiar with the general problem scenario.

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Conceptualization requires extensive literature review and input from experts in the various fields involved in the system. From this information, an initial problem and purpose statement can be formulated, research questions developed, the model's expected behavior described (reference mode), and an initial influence diagram constructed.

Preliminary Conceptualization. Initially, an extensive literature was conducted in order to fully comprehend the entities and relationships driving system behavior. It was important to continue the literature review throughout the model building phase as questions dealing with plausible parameter values, system mechanisms, and system relationships arose. Once a general literature review was completed, a formal problem and purpose statement were derived. Finally, research questions were developed which established questions to be answered in the modeling effort. The finalized problem, purpose statement, and research questions were used to focus the overall modeling effort (see Chapter I).

Reference Mode. The reference mode focuses research and model structure on the causal mechanisms driving a specified output. It is generally portrayed graphically as the expected system behavior over the time period of interest (Randers and others, 1996:287). A reference mode was derived by analyzing the purpose statement, available historical data of the system, and theories of expected behavior by experts in literature. The reference mode for this model represents the behavior of pore-water metal concentration over time. The reference mode for this model is hypothetical versus historical in nature

because of a lack of existing long-term data on contaminant build-up in constructed wetlands. Available literature indicates that AVS will initially immobilize metals in sediment until the sulfide binding capacity is exceeded. At this point the pore water concentration will rise dramatically until reaches a point where the same amount of metal is leaving the system through burial as is entering through settling. This implies that reference mode behavior will graphically appear as an S-shaped curve. The initial portion of the curve represents the influence of AVS. The rest of the curve then displays the progression to a new steady-state pore water concentration. A graphical depiction of this reference mode is shown as Figure 1.
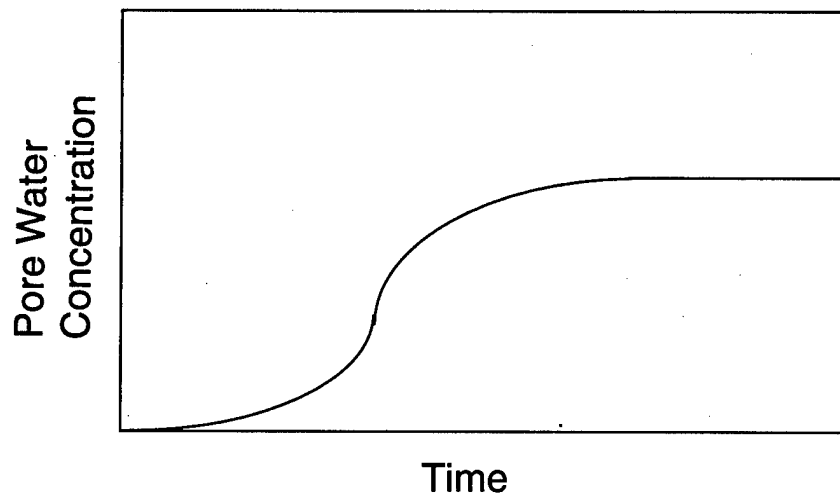

Figure 1. Hypothetical Reference Mode

Influence Diagram. Once the reference mode is derived, a system structure is sought that consists of the influences which will produce the reference mode behavior. An influence diagram demonstrating the causal relationships between these important entities was constructed. Using data

gathered from the literature review, entities essential to the system were initially

identified. Based upon this data, the influences between these entities were

defined and feedback loops generated describing the basic mechanisms

responsible for behavior of the system. A top-level influence diagram is shown

below as Figure 2. This diagram includes the key entities and influences which

drive the reference mode behavior in the model. The S-shaped behavior is

produced by the negative and positive feedback loops shown below. Metal

initially binds to AVS, once AVS binding capacity is exceeded, metal partitions

between organic carbon and pore water until the concentration of metal entering

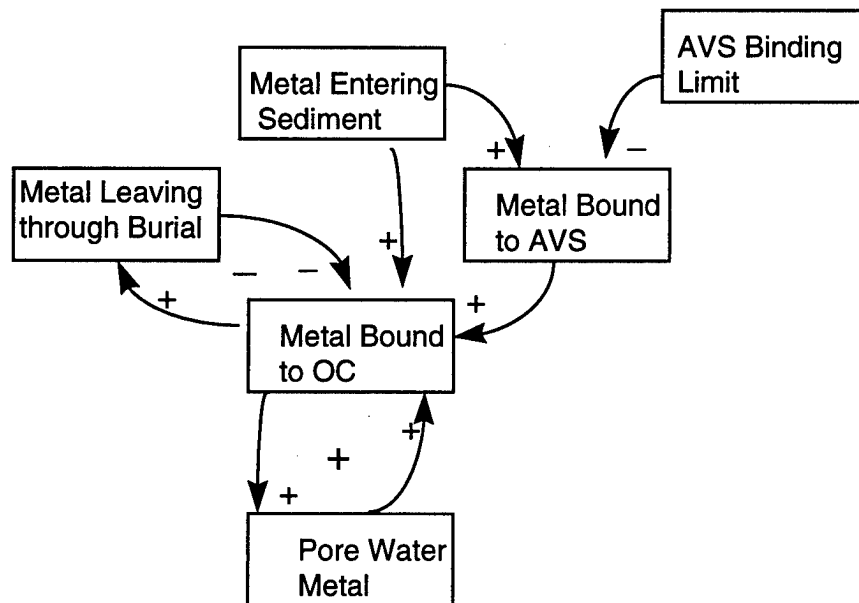the system is the same as that leaving the system.

Figure 2. Model Influence Diagram

Formulation

Model Construction. Once the system's mechanisms were defined in an

influence diagram, a flow diagram was created to represent the mechanisms.

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The system dynamics model was constructed by coding the flow diagram into STELLA II software. This software, made by High Performance Systems, Inc., allows one to graphically create a complex numerical integration problem. Stella II, then solves the problem using traditional numerical integration techniques over time (Peterson and Richmond, 1994:12-3).

The model's physical characteristics are based on an existing constructed wetland in Sacramento, CA. This wetland was designed for tertiary treatment of municipal waste water. It consists of ten 384-meter long parallel cells. Each cell is divided into a series of six small ponds and wetlands, which is typical of modern constructed wetlands (Figure 3). Each cell has an average flow rate of 378.5 cubic meters per day (Crites and others, 1997:132).
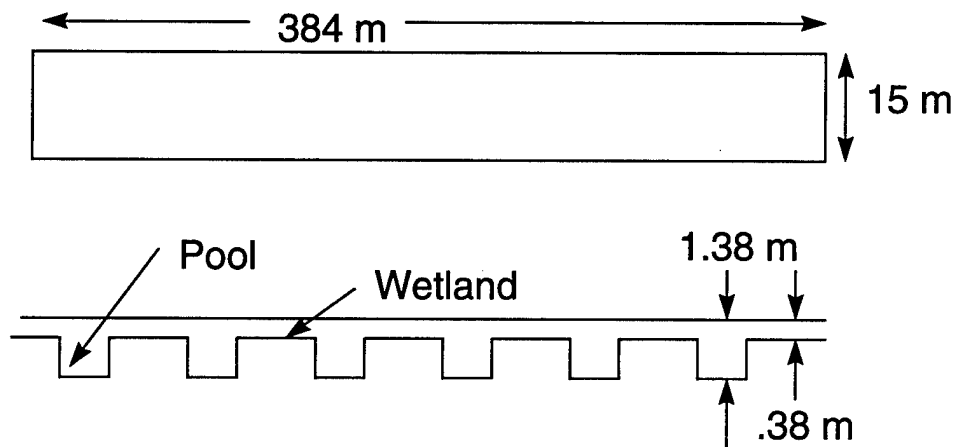

Figure 3. Wetland Cell: Plan and Section Views

An actual wetland was chosen, so physical parameter values in the model would be based on an actual constructed wetland system designed for treatment and not a hypothetical system developed only for the model. To avoid the oversimplification of assuming an entire wetland cell is a well-mixed system, only

the first two sectors (pool and wetland) of one wetland cell are modeled. These

first two sectors receive the bulk of sediment and contaminant loading, so should

display a higher toxicity at a faster rate. The model contains two main sectors:
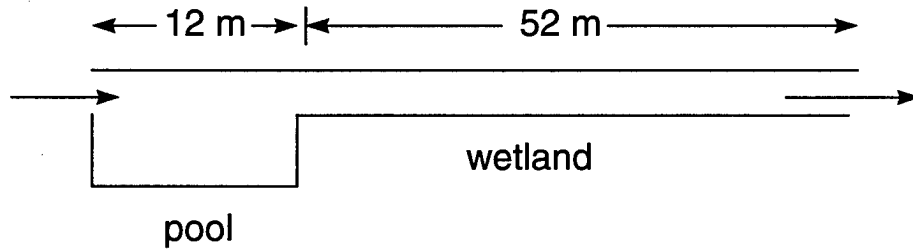
pool and wetland (Figure 4).

Figure 4. First Two Sectors of Wetland Cell

Each sector is divided into four layers: surface water, surficial sediment, deep

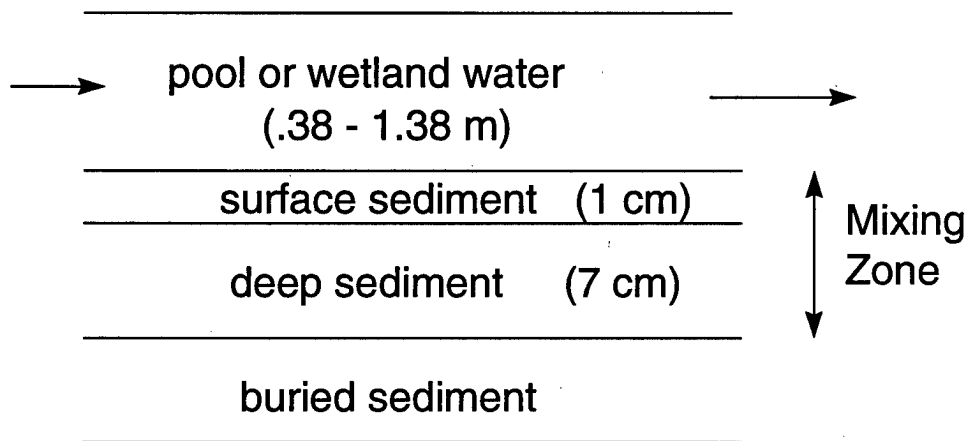sediment, and buried sediment (Figure 5).

Figure 5. Four Layers Modeled Within Each Sector

The surface sediment is considered aerobic and the deep sediment anaerobic.

The top 8 centimeters are mixed through bioturbation and sediment below the

mixing zone is considered permanently buried. Each layer is modeled in a

detailed flow diagram with the major internal and external influences and

feedback loops affecting the metal movement. Equations defining the

relationships within each layer, as well as parameter values, are formulated from

the most reliable literature data. Figure 6 shows the basic model structure. The

detailed flow diagram and governing equations can be found in Appendix 1. The

key mechanisms controlling metal movement are: settling, solid-water

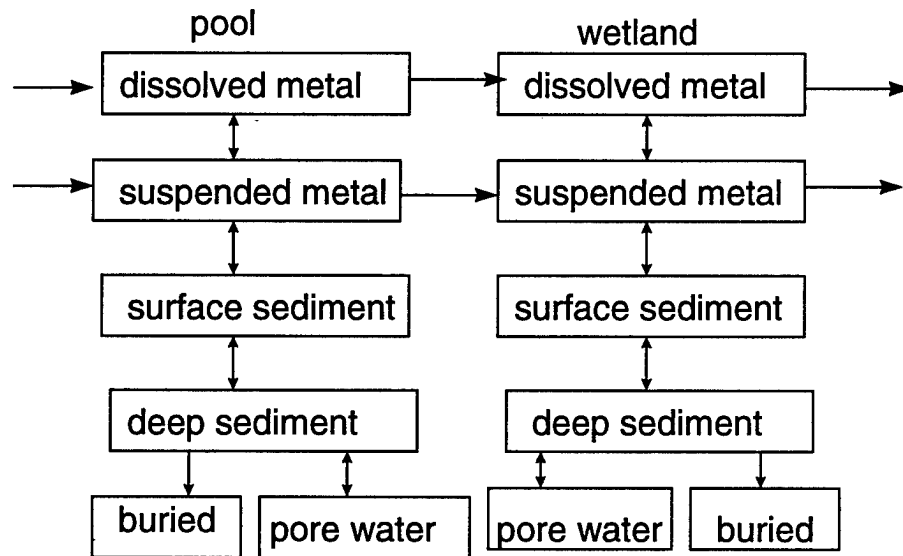partitioning, burial, bioturbation, AVS binding, and organic carbon binding.

Figure 6. Basic Model Structure

<u>Model Assumptions</u>. In creating the model, the following overall

assumptions were made (other, lower level assumptions are described in

Chapter IV):

- The precipitation falling on the wetland cell and the evapotranspiration across
  the cell are constant over time and space.
- The flow rate, metal concentration, and total suspended solids of the influent
  are not constant over time, but pulse with storm events. This represents "first
  flush" behavior.
- Each metal is modeled separately, so only one metal enters the system for
  any model run. The initial model is built using lead (Pb).
- Each sector (pool or wetland) is well mixed.
- Each layer of sediment within each sector is well mixed.

- The surface sediment layer is 1 cm deep and aerobic. Partitioning of metal between sorbed and dissolved phases is essentially the same as in the surface water.
- The primary mechanism for movement of metals to the deep sediment is bioturbation and sedimentation. Diffusion of dissolved metal between surface water and pore water is insignificant.
- The deep sediment layer is 7 cm deep and is anaerobic. The key binding sites for metal are AVS and organic carbon (OC).
- The concentration of AVS and OC are constant over time and space within the pool sector. This means that sediment entering the system has the same concentration of AVS and OC as what is there initially.
- The concentration of AVS is constant over time and space in the wetland sector, but the OC concentration increases over time from 5% to 40% in the deep sediment over 20 years. This is to simulate the increase in organics from wetland plants.
- The water depth in both sectors is controlled, so the wetland cell cannot drain below a controlled water depth.

Testing and Validation

Testing is "the comparison of a model to empirical reality for the purpose of corroborating or refuting the model" and validation is "the process of establishing confidence in the soundness and usefulness of a model" (Forrester and Senge, 1980:210). Validation comes through confidence gained as tests are run and assumptions, relationships, and parameter values are verified.

Testing the Dynamic Hypothesis. The model was run and tested throughout the model-building process to ensure the basic mechanisms of the model were represented correctly. Once the model was completed, its output was compared to the expected output or reference mode to verify that the relationships described in the model produced the expected behavior.

Testing the Model Structure and Behavior. Testing of model structure and behavior includes determining: if all important variables are included, if the

assumed relationships are reasonable, and if parameter values are plausible (Randers and others, 1996:285). Model structure tests that were employed were: the parameter verification test, the extreme conditions test, and the boundary adequacy (structure) test.

The parameter verification test consists of verifying that parameter values match those of the real system and ensuring that derived parameters are reasonable and do not adversely affect model output. Actual parameter values from the real system are ideal, but some values must be derived. The model behavior must be examined when using derived parameter values to validate that the model structure represents the real system.

The extreme conditions test verifies that model output is reasonable when plausible maximum and minimum parameter values are inserted in the model. A model should exhibit reasonable behavior when tested at extremes outside the normal operating region. This test is useful in identifying flaws in the model and in analyzing system behavior outside its historic operating region. Parameters tested were: total suspended solids, storm water flow rate, AVS concentration, and OC concentration.

The boundary adequacy test examines the degree of model aggregation by testing mechanisms within the model structure. If mechanisms in the model are found to have no effect on model output, then they can be aggregated with existing mechanisms. This test aids in understanding the key mechanisms that drive model behavior.

The model behavior tests employed were the behavior-reproduction test and the behavior anomaly test.

The behavior-reproduction test evaluates how well model-generated behavior matches observed behavior of the real system. This can be done by observing output of various entities within the model and comparing them with historical data. Predicting exact future values or fitting points on a curve is not the goal in a system dynamics model. Generating general trends or patterns of behavior over time that match the real system is what is desired with this test.

The behavior anomaly test identifies and traces anomalous behavior back to a structural cause. This test must be employed throughout the model building process to detect flaws in model structure or model assumptions (Forrester and Senge, 1980:211-222).

Implementation

Once the testing and validation of the model was complete, sensitivity analysis was conducted. Sensitivity Analysis is the process of studying model output when key parameters are varied to plausible extremes. Through the testing and validation process, what appeared to be the most influential parameters were identified for sensitivity analysis. The sensitivity analysis, then identified which of these entities have the greatest influence on the reference mode behavior.

Other scenarios were run to evaluate the system under different conditions. One scenario compared the effects of three different divalent metals

(cadmium, copper, and lead) on metal bioavailability in sediment. Another scenario, evaluated pool versus wetland behavior to compare how each removed and immobilized metal.

IV. Results and Analysis

Introduction

In system dynamics modeling, as much insight is gained into the system in creating the model as there is in analyzing the model output. Therefore, this chapter will discuss the creation of the model as well as sensitivity analysis and other model output. After discussing the initial creation of the model, testing and validation will be presented including testing of the dynamic hypothesis and testing of model structure and behavior. Sensitivity analysis was conducted on the final refined model. The results of the sensitivity analysis, as well as other scenario results will be displayed and discussed.

Model Presentation

Model Creation. The model was created iteratively, so each layer was tested before creating the next layer. The following discussion describes how the model was constructed. This discussion will focus on the pool sector and only discuss the wetland sector when it differs from the pool. The initial model was built using the parameter values for lead (Pb). Values of cadmium and copper can be found in Appendix A in the model equations.

The first layer of the model is surface water and deals mainly with physical (hydrological) processes (Figure 7). The key stocks are pool volume and wetland volume. The initial volume values are based on the dimensions of the actual wetland cell being modeled (Crites and others, 1997:132). The flows into

the surface water are precipitation, based on 38 cm/year of rainfall (Peake, 1996:80), and storm water flow, based on an average flow of 378.5 cubic meters per day (Crites and others, 1997:132) plus a storm event every 30 days. The flows out of the surface water are evapotranspiration and outflow to the next sector. Evapotranspiration is estimated at a constant 6.4 mm/day (Kadlec, 1989:26; Mudgett, 1995:122). The outflow rate is designed to maintain a constant water level and is the sum of the inflows less the other defined losses plus the water lost due to sedimentation (volume of water must decrease as volume of sediment builds).
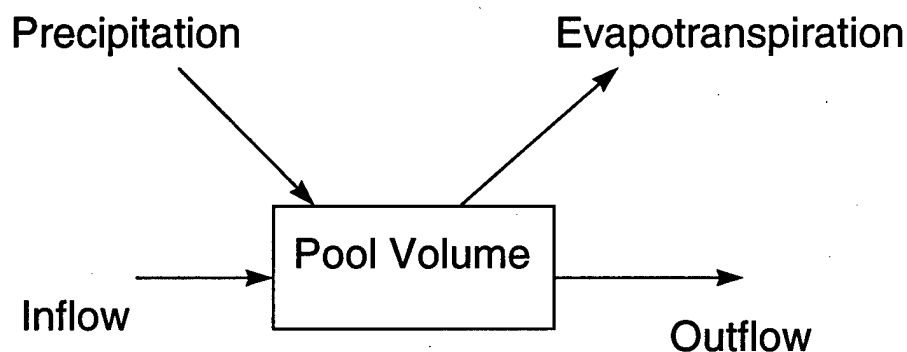

Figure 7. Surface Water Hydrological Processes

Within the surface water layer is a stock of suspended soil which settles into a stock of settled surface soil with a portion continually being resuspended (Figure 8). The stock of suspended soil has two inputs. First, it is a function of the total suspended solids concentration entering the pool multiplied by the flow rate. Total suspended solids enters the system at a concentration of 85 mg/L and pulses every 30 days with storm events (Pitt and others, 1995:265; Taylor and others, 1993:141). Second, the settled soil is resuspended into the

suspended soil stock at a constant rate due to bioturbation plus an additional

amount dependent on flow velocity in the pool (Kadlec and Knight, 1996:321-

322). In the wetland sector, there is a third input of organic litter fall from the

vegetation of 0.16 g/sq m/day into the suspended soil stock (Kadlec and Knight,

1996:324,329). The outputs from the suspended soil stock are settling to the

settled surface soil stock and outflow into the next sector. The settling rate is a

function of the suspended soil, the settling velocity, the pool area and pool

volume. The settling velocity is computed assuming that soil entering the pool is,

on average, silt-size particles and the soil entering the wetland sector is a very

fine silt (Kadlec and Knight, 1996:319). The outflow of soil into the next sector is

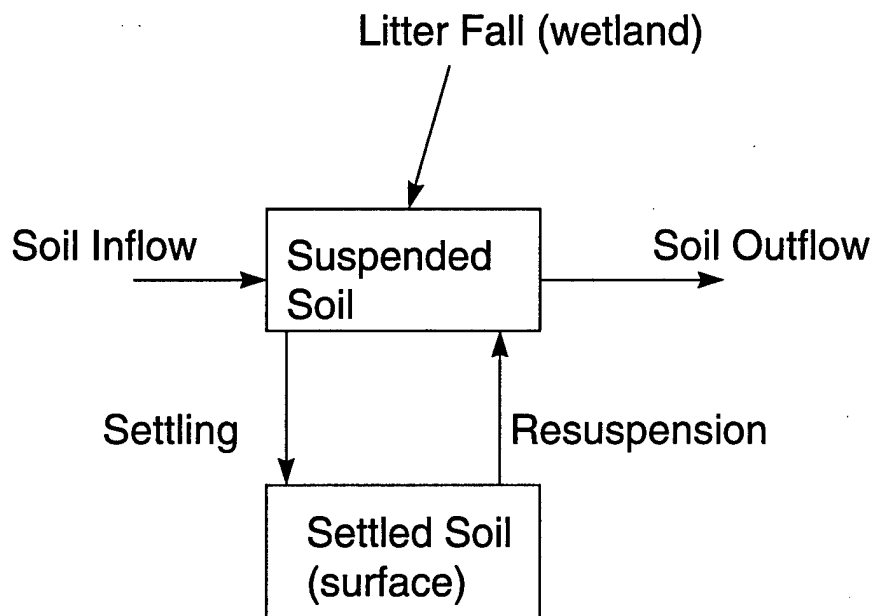a product of the suspended soil in the pool and the outflow rate.

Figure 8. Soil Flows within the Surface Water

Also, within the surface water layer are two stocks of metal: suspended

metal and dissolved metal (Figure 9). The percent of metals carried in

suspension versus in solution in the storm water influent is based on empirical studies (for lead, 95% is in suspension) (Pitt and others, 1995:265). The total storm water influent metal concentration is 0.35 mg/L (Pitt and others, 1995:265) and pulses with storm events. While in the pool, the metal partitions between the suspended and dissolved phases according to a partitioning coefficient, K_d. The value of this coefficient was calculated based on empirical data from metals in filtered and non-filtered samples in detention ponds and compared to other values in literature (for lead, $K_d = 1059$ m^3/kg) (Pitt and others, 1995:265; Young and others, 1992:653). Using a single K_d value assumes that partitioning follows a linear isotherm. This assumption is valid as long as metal and sediment concentrations in the model do not reach extremes. The calculation of K_d, as well as percent metal carried in suspension, for Pb, Cu, and Cd are shown in Appendix B. Metal partitioning is not instantaneous; the reaction occurs very quickly, but cannot be assumed to be instantly at equilibrium. To represent this process mechanistically, a transfer rate applied to the concentration gradient must be used. A rate was derived by testing various transfer rates in the model to find one that would produce reasonable rapid partitioning behavior. A value of 0.01 days^{-1} was derived for this transfer rate. Its magnitude has little effect on the model output (see Sensitivity Analysis). The suspended metal settles out of the surface water and is resuspended into the surface water with the soil it is sorbed to. Dissolved metal flows to the next sector as a function of the water outflow rate and suspended metal leaves its stock as a function of the soil outflow rate.
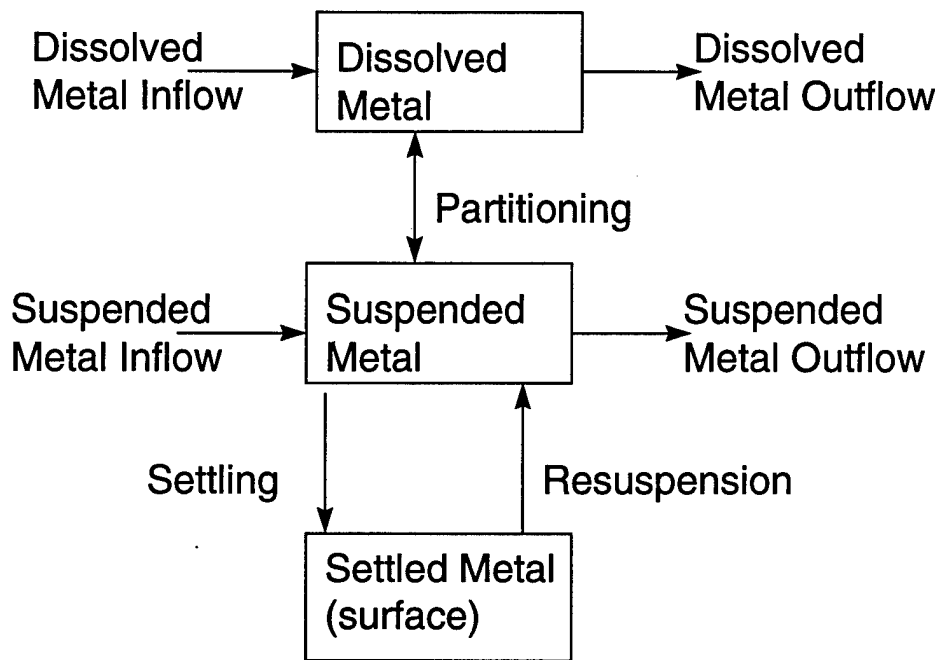
Figure 9. Metal Flows within the Surface Water

Once suspended metal has reached the surface sediment, it is

transported to deep anaerobic sediment and then permanently buried (Figure

10). The sedimentation rate is equal to the soil settling rate plus the bioturbation

rate less the resuspension rate. Bioturbation essentially mixes the surface

sediment and the deep sediment through biological movement of sediment

particles from the deep sediment to the surface sediment. The bioturbation rate

was estimated at .04 cm/day of soil flux, based on studies from Lake Erie (Fisher

and others, 1980:4004). The rate that metal is moved by bioturbation or

sedimentation is based on the metal's concentration within the sediment layer.

Deep sediment is moved to the buried sediment (soil deeper than 8 cm,

therefore below the mixing zone) compartment at a rate equal to the settling rate

less the resuspension rate. Metal in the deep sediment is partitioned to pore water in a manner similar to its partitioning in the surface water, but with a more complex mechanism. Initially, any available AVS is assumed to bind with the metal which prevents any detectable concentration of metal in the pore water. After the AVS binding sites are taken, the metal is assumed to bind with organic carbon following a Langmuir sorption model derived by Mahony et al. (Mahony and others, 1996:2191). The sorption could not be represented in a linear model as it was in the surface water because of the metal's potential to accumulate and approach a sorption capacity in the sediment. This sorption model is a function of pH and a metal-specific partitioning coefficient, $K_{d,OC}$. The general form of the equation is shown below:

$$C_{s,OC} = \frac{C^0_{s,OC} K_{d,OC} C_f}{C^0_{s,OC} + K_{d,OC} C_f} \qquad (4)$$

where

$C_{s,OC}$ = non-AVS-sorbed metal (M) per weight of OC (mg M/kg OC)
C_f = aqueous metal activity (mg M/L)
$K_{d,OC}$ = partition coefficient (L/ kg OC)
$C^0_{s,OC}$ = sorption capacity (mg M/kg OC)

Equation (4) varies slightly from the standard Langmuir model in that the sorption capacity is used in the denominator and a partitioning coefficient is used versus a Langmuir constant. This configuration will cause the equation to reduce to linear partitioning ($C_{s,OC} = K_{d,OC} C_{s,OC}$) at low aqueous metal concentrations. At large aqueous metal concentrations, the sorbed metal will approach the sorption capacity ($C_{s,OC} = C^0_{s,OC}$).

Solving for C_f yields: $\qquad C_f = \dfrac{C^0_{s,OC} C_{s,OC}}{K_{d,OC}(C^0_{s,OC} - C_{s,OC})} \qquad (5)$

By applying equation (5) to the non-AVS-sorbed metal in the deep sediment, one

can predict the pore water concentration of metal. As in the surface water

partitioning, the metal does not partition to its equilibrium concentration

instantaneously. A transfer rate was derived to describe the time it takes the

pore water to reach the concentration calculated by equation (5). The rate

describing this transfer from instantaneous concentration to actual concentration

was found by testing various rates in the model to find one that would produce

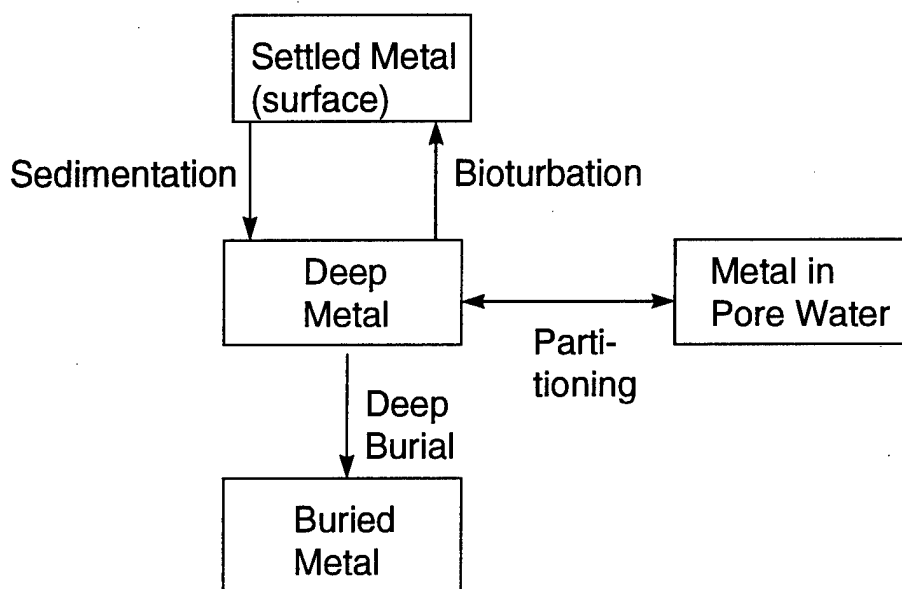reasonable rapid partitioning behavior. A transfer rate of 0.1 days^{-1} was used.

Figure 10. Metal Flows within the Sediment

Model Parameters. Initial parameter values were entered into the model

based on literature data and derived, as described above, within the model

structure. The sensitivity of the model to these parameters was tested during

and after the model construction. Table 4 shows the initial parameter values for

the pool and wetland sectors.

Table 4. Initial Parameter Values

Parameter Value	Pool	Wetland	Reference
Volume	248.4 m^3	300.35 m^3	Crites and others, 1997:132
Area	180 m^2	790.4 m^2	Crites and others, 1997:132
Depth	1.38 m	0.38 m	Crites and others, 1997:132
Surf. Sed. Depth	1 cm	1 cm	Eger, 1994:20[a]
Deep Sed. Depth	7 cm	7 cm	McCall and Tevesz, 1992:130[a]
Avg. Flow Rate	378.5 m^3/day	378.5 m^3/day	Crites and others, 1997:132
Precipitation	.00401 m/day	.00401 m/day	Peake, 1996:80
Evapotranspiratio	6.4 mm/day	6.4 mm/day	Kadlec, 1989:26
Average TSS	85 mg/L	NA	Pitt and others, 1995:265[a]
Litter Fall	NA	28800	Kadlec and Knight, 1996:324
Soil Settling Vel.	0.001 cm/s	0.00015 cm/s	Kadlec and Knight, 1996:319[a]
Sed. Bulk	500 kg/ m^3	500 kg/ m^3	Kadlec and Knight, 1996:329[a]
Metal Conc. In	0.35mg/L	NA	Pitt and others, 1995:265
% Metal Susp.	95.4%	NA	Pitt and others, 1995:265
K$_d$ for Pb	1059 m^3/kg	1059 m^3/kg	Pitt and others, 1995:265
K$_d$ for Cu	68 m^3/kg	68 m^3/kg	Pitt and others, 1995:265
K$_d$ for Cd	176 m^3/kg	176 m^3/kg	Pitt and others, 1995:265
K$_d$ Transfer Rate	0.01 day^{-1}	0.01 day^{-1}	(derived)[b]
Bioturbation Rate	0.04 cm/day	0.04 cm/day	Fisher and others, 1980:4004[a]
AVS Conc.	200 µg/g	200 µg/g	Kemble & others, 1994:1989[a]
Fraction OC	5 %	5 to 40 %	Faulkner,Richardson,1989:49[a]
pH	7.0	7.0	Pitt and others, 1995:262[a]
Porosity	65%	65%	Mitsch & Gosselink, 1993:117[a]
K$_{d,OC}$ for Pb	2510000 L/kg	2510000 L/kg	Mahony & others, 1996:2191
K$_{d,OC}$ for Cu	2570000 L/kg	2570000 L/kg	Mahony & others, 1996:2191
K$_{d,OC}$ for Cd	251000 L/kg	251000 L/kg	Mahony & others, 1996:2191
K$_{d,OC}$ Transfer	0.1 day^{-1}	0.1 day^{-1}	(derived)[b]

[a]The literature presented a range of parameter values and a reasonable
or average value was chosen for the model.
[b]Values were derived through testing within the model structure to
produce reasonable behavior as discussed previously in this section.

Testing and Validation

Before conclusions can be drawn from the model, it must be tested and validated. This includes testing the dynamic hypothesis and testing model structure and behavior.

Testing the Dynamic Hypothesis. Testing of the dynamic hypothesis involves comparing model output to expected behavior, otherwise known as the reference mode. Figure 11 shows the reference mode represented by deep sediment pore water metal concentrations in the pool and wetland sectors in mg/L. This output was produced over a 6000-day run which is approximately 16 years.
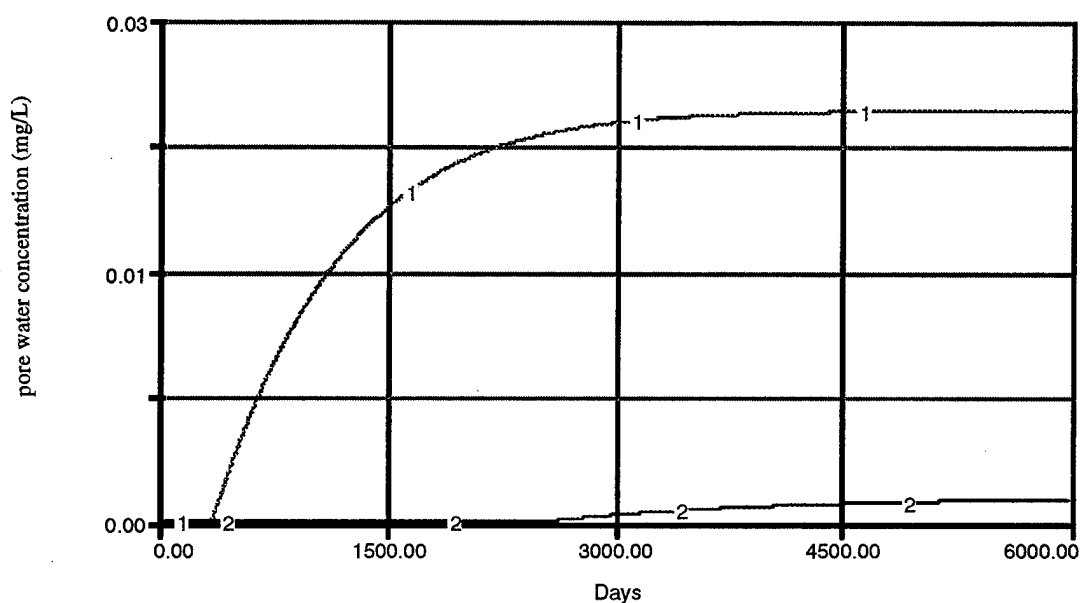
Figure 11. Pore Water Pb Concentrations in Pool and Wetland

Trace 2 represents the pore water concentration in the pool sector and trace 1 represents the pore water concentration in the wetland sector. In both the

pool and wetland sectors, the concentration displays a behavior similar to the S-shaped behavior that was hypothesized. Although instead of a true S-shape, it can better be described as goal-seeking behavior with an initial delay. In the pool, it reaches a steady-state of nearly 0.03 mg/L. The pore water concentration in the wetland sector does not reach steady-state after the 16-year simulation, but continues to rise, approaching a steady-state that is still future. The behavior can be described in three phases. The first, low pore water concentration phase, is a result of the immobilization of metal by AVS. Once the AVS binding capacity is exceeded, the pore water metal concentration begins to rise as the metal partitions between the OC-sorbed and dissolved phases. This rising pore water concentration is considered phase 2. The third phase is the steady-state concentration which is achieved when the rate of metal entering the deep sediment is the same as the rate of metal leaving the deep sediment through burial.

Testing the Model Structure and Behavior. Testing the model includes both tests of model structure and tests of model behavior. Tests of model structure employed are: the parameter verification test, the extreme conditions test, and the boundary adequacy test. The model behavior tests employed were the behavior-reproduction test and the behavior anomaly test.

Parameter Verification Test. The first test of model structure is the parameter verification test. Most of the parameters used in this model were obtained through a careful review of existing literature and are listed in Table 4. Other parameter values, however, were difficult to obtain as values in the

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literature were inconsistent. This was the case for values of dissolved and suspended metal in the storm water, equilibrium partitioning values (K_d) in the surface water, and partitioning transfer rates. The first two values were obtained using empirical data from a 1995 article by Pitt et al (Pitt and others, 1995:265). Percentages of suspended versus dissolved metals were calculated from the results of parking and street runoff concentrations from filtered and non-filtered samples. The equilibrium partitioning coefficients were derived from detention pond samples (where there is adequate time to partition) of filtered and non-filtered metals. These calculations are shown in Appendix B.

Calculations from the study by Pitt et al. show that 95% of lead is carried in suspension. Figure 12 shows the sensitivity of pore water metal concentration to changes in the percent of metal suspended.
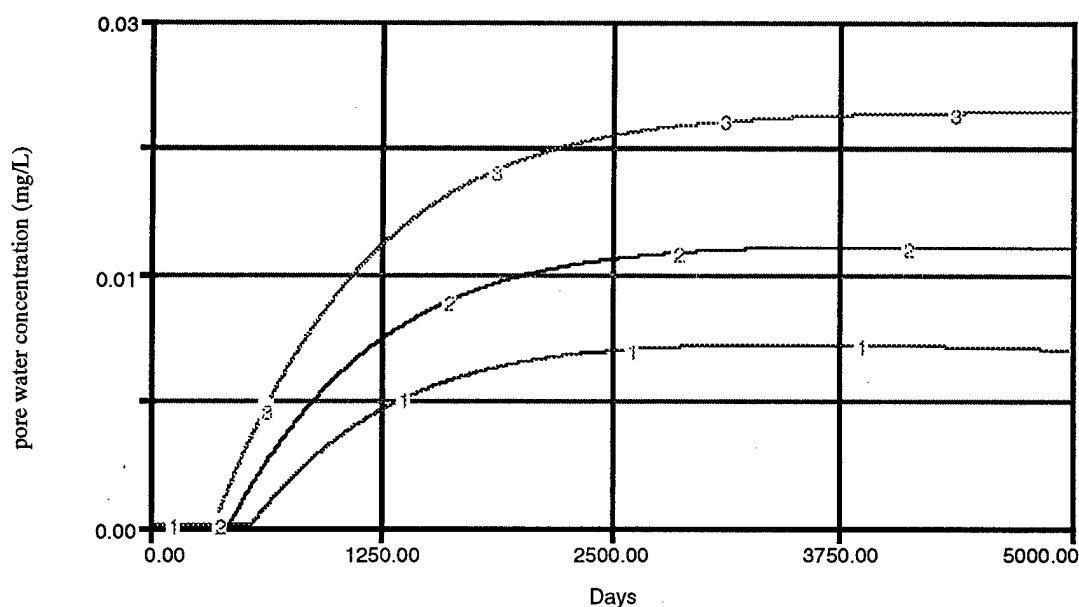

Figure 12. Pore Water Pb Concentration at Percent Pb Suspended = 0.5, 0.7, and 0.95

The percent metal suspended in the storm water entering the wetland is set at 50%, 70%, and 95%. The pore water metal concentration is fairly sensitive to the parameter value chosen, so it is important to use good empirical results for this parameter and not an assumed value.

The pore water metal concentration is not as sensitive to changes in the solid-water partitioning coefficient (Figure 13). The K_d value is set at 50, 1059, and 2000 m^3/kg with little change to the pore water. This value varies widely in literature and is dependent on pH (Young and others, 1992:653) and other influences. The K_d value calculated from the study by Pitt et al. (1059 m^3/kg) and the linear isotherm assumption should be adequate for reasonable model output (Pitt and others, 1995:265).
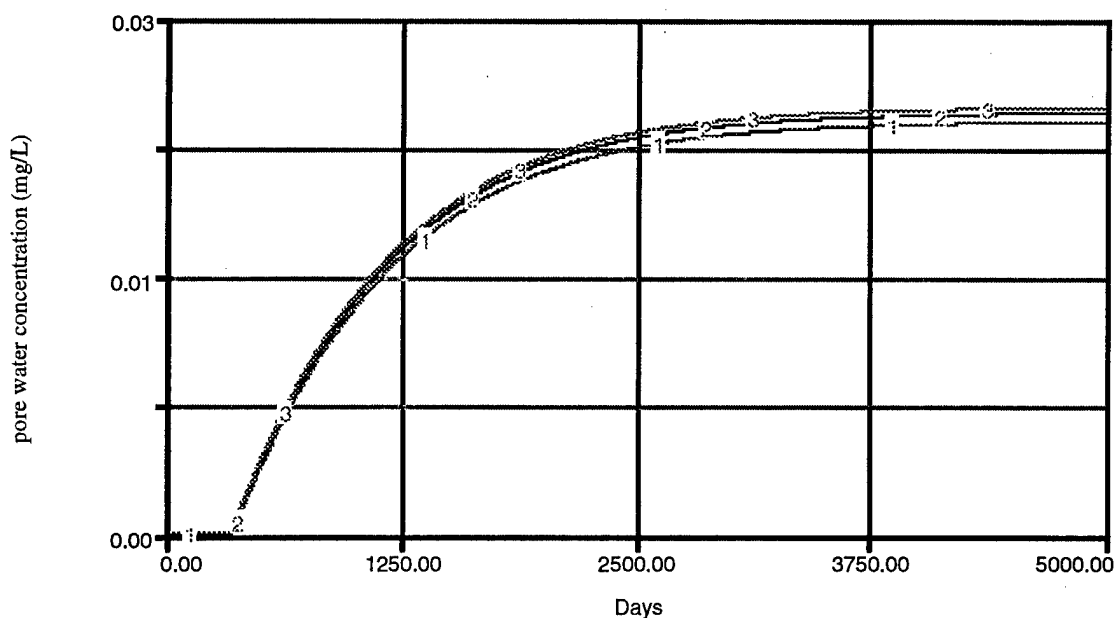

Figure 13. Pore Water Pb Concentration at K_d = 50, 1059, and 2000 m^3/kg

When metal partitions between solid and liquid phases, it does not occur instantaneously, so a transfer rate must be applied to this movement. This parameter value was obtained through experimenting with the model to find a rate that was fairly quick and gave reasonable behavior. Figure 14 shows the pore water metal concentration when the surface water transfer rate is set at an order of magnitude higher and lower than the derived rate of 0.01 days^{-1}. The model shows little sensitivity to the magnitude of this parameter. Similar results were obtained when testing the sensitivity to changes in the pore water transfer rate used in the deep sediment layer. These derived transfer rate values appear to be adequate for reasonable model behavior.
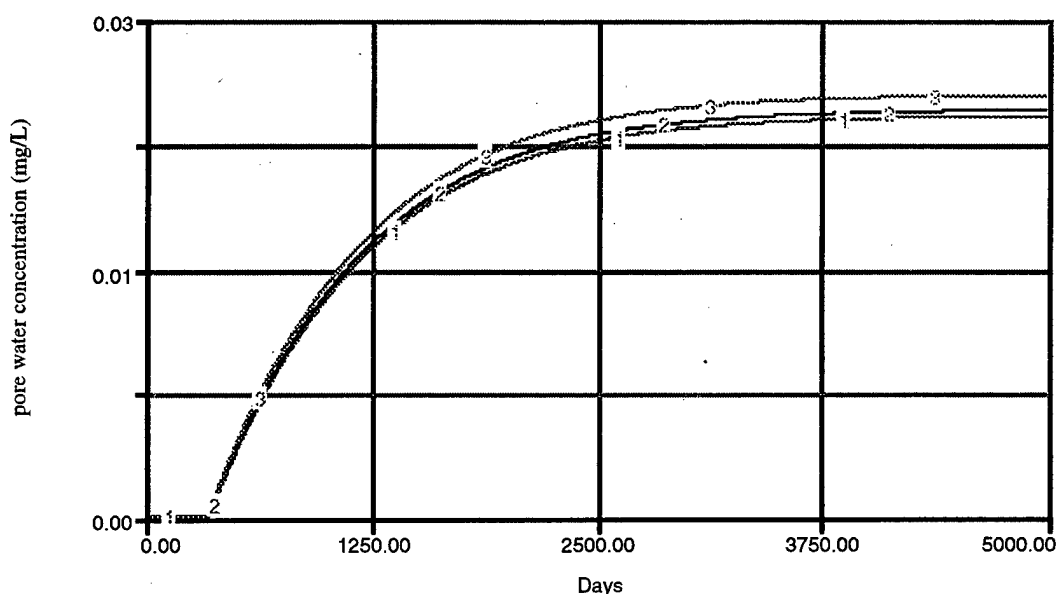

Figure 14. Pore Water Pb Concentration at Transfer Rate = .001, .01, and .1 days^{-1}

Extreme Conditions Test. The second model structure test employed is the extreme conditions test. This test is used to ensure reasonable

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model behavior when parameter values outside the normal operating region are used. The parameters tested were: total suspended solids, storm water flow rate, AVS concentration, and OC concentration.

Figure 15 shows the behavior of the pore water metal concentration under extreme suspended solids conditions. Trace 1 represents the pore water when the suspended solids entering the system are 5 mg/L and trace 2 represents the pore water when the suspended solids are 300 mg/L. In both cases all other parameters are kept the same.
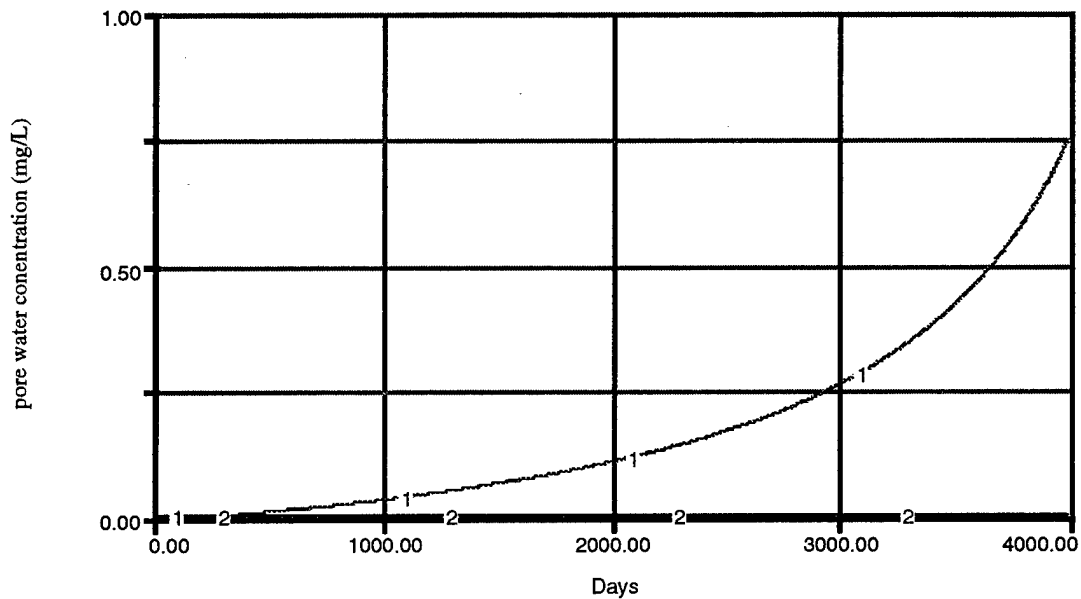
Figure 15. Pore Water Pb Concentration when TSS = 5 and 300 mg/L

In the first case, the lack of solids entering the sediment gives the metal a reduced carrying capacity resulting in high sediment metal concentrations and, therefore, high pore water metal concentrations. For trace 2, the opposite is true. With the large influx of sediment, there is a tremendous capacity to carry

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the metal. Sediment metal concentrations remain low enough to prevent any metal from entering the pore water. These extreme conditions produce reasonable results from the model.

The surface water flow rate was also tested at extremes. Figure 16 shows the pore water metal concentration when the flow is 1000, 379, 100, and 10 m^3/day. (This test is done over a shorter time with a smaller time increment (dt) to avoid system anomalies which arise at shallow pool depths). At very low flows (trace 3 = 10 m^3/day) it takes over 3000 days to produce a pore water metal concentration. At very high flows (trace 3 = 1000 m^3/day), the pore water concentration reaches steady-state much faster. Trace 2 represents the standard value of 379 m^3/day.
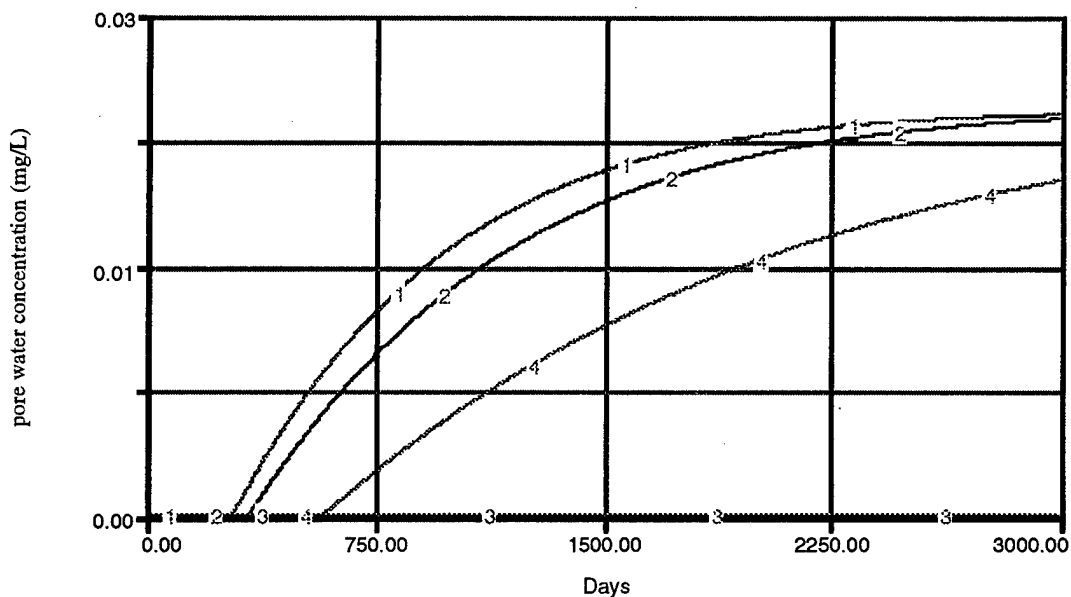

Figure 16. Pore Water Pb Concentration at Flow Rate = 1000, 379, 100, and 10 m^3/day

Essentially, changing the flow rate, simply alters the time it takes for the pore water to reach steady-state, but not the value of that steady-state condition. This extreme behavior is reasonable and verifies the model structure.

Figure 17 shows the effects of extremely low AVS and organic carbon concentrations in the deep sediment on the pore water metal concentration. Trace 1 represents the sediment with no AVS and the OC held at 5%. The pore water immediately begins to increase, but is limited by organic carbon and reaches a steady state concentration slightly higher than the reference mode. The effect is much more dramatic when the organic carbon fraction of sediment is dropped from 5% to 1% (trace 2) and the AVS held at 6.25 μmol/g.
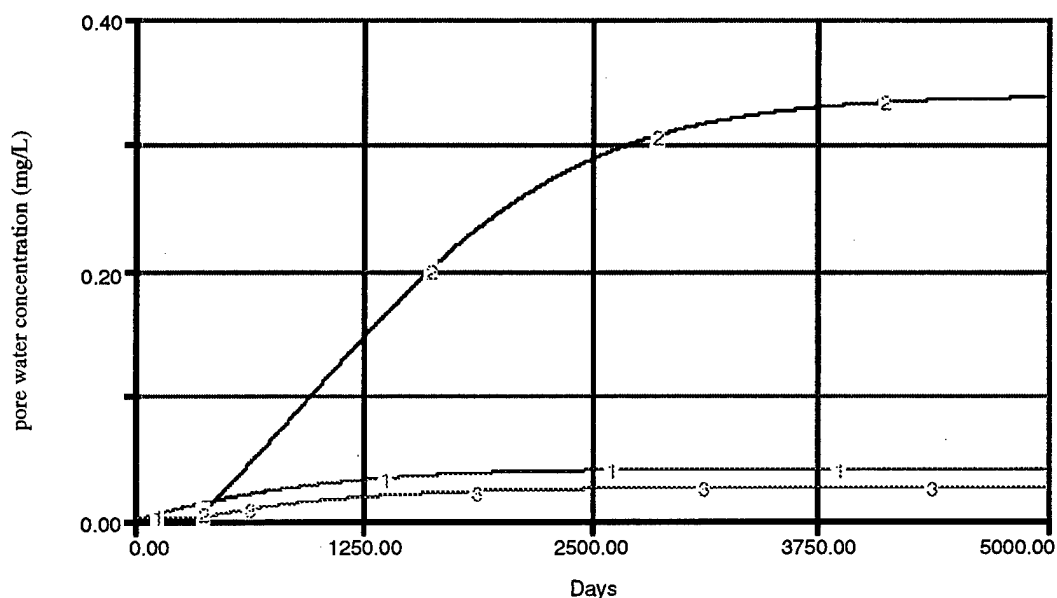

Figure 17. Pore Water Pb Concentration with no AVS, 1% OC, and Reference Mode

The AVS initially limits the metal in the pore water, but once the AVS is saturated, metals are only limited by organic carbon and reach a steady

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state ten times greater than the reference mode. Trace 3 represents the reference mode. The sensitivity of the system to organic carbon is further discussed in Sensitivity Analysis. The behavior to note here is that the system performs reasonably at the extremes.

Boundary Adequacy Test. The final model structure test is the boundary adequacy test. This test is used to ensure the correct amount of model aggregation is in place. This test justified aggregation of non-constant water flows, TSS concentrations, metal concentrations, and AVS concentrations into constant flows and concentrations. The test also showed that system inputs from precipitation and evapotranspiration can be ignored.

Figures 18, 19, and 20 show the various flow configurations used to represent storm events in the model. Figure 18 represents a 30 day storm event where the water flow cycles sinusoidally around its average value and the TSS and metal concentrations pulse from their average near the beginning of each storm event ("first flush" effect). Figure 19 also represents a 30 day storm event where all three parameters are pulsed simultaneously. Figure 20 represents constant flows and concentrations. These three ways to represent storm events in the system were tested to examine their effect on the pore water metal concentration (Figure 21). The effect to the pore water was negligible. All three reach the same steady-state level with approximately the same behavior over time. Because the system is not sensitive to the way storm events are represented, I will represent storm events with constant flows and concentrations.
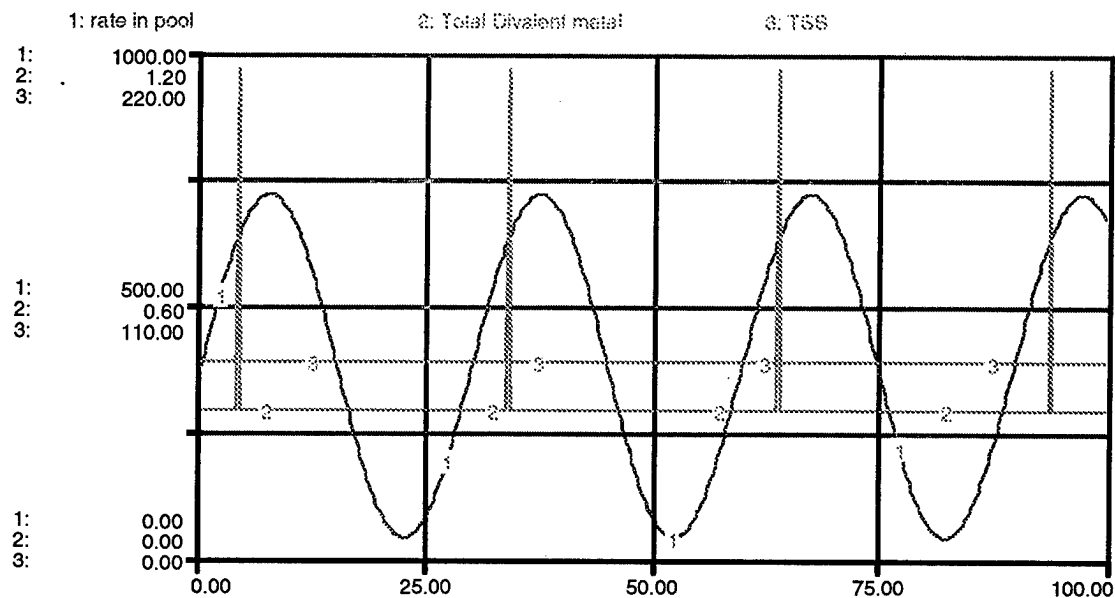
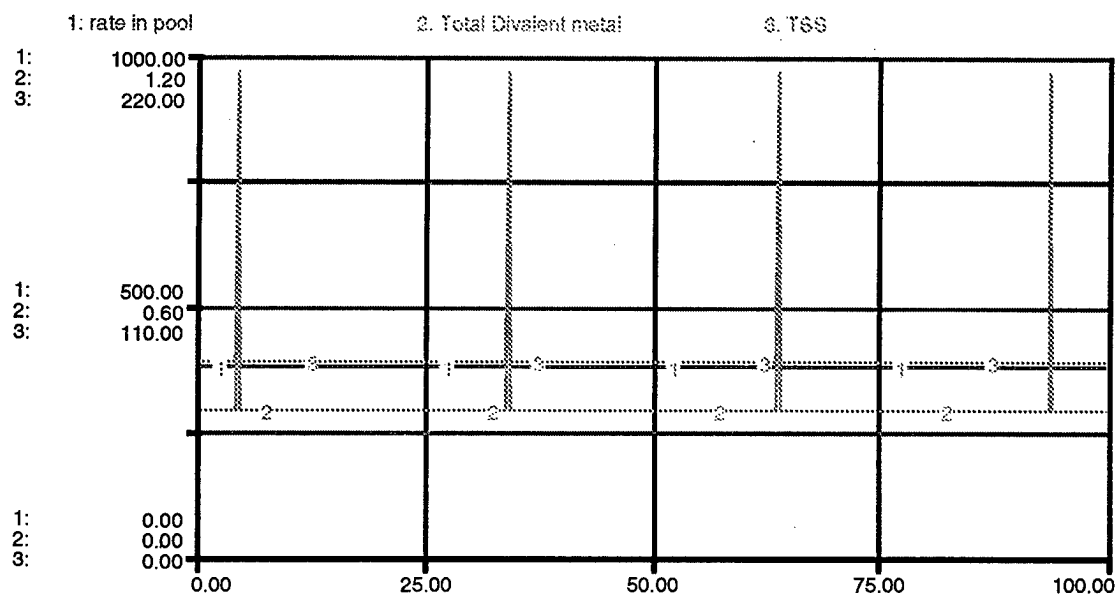**Figure 18. Sinusoidal Water Flows with Pulsing TSS and Metal Concentrations**

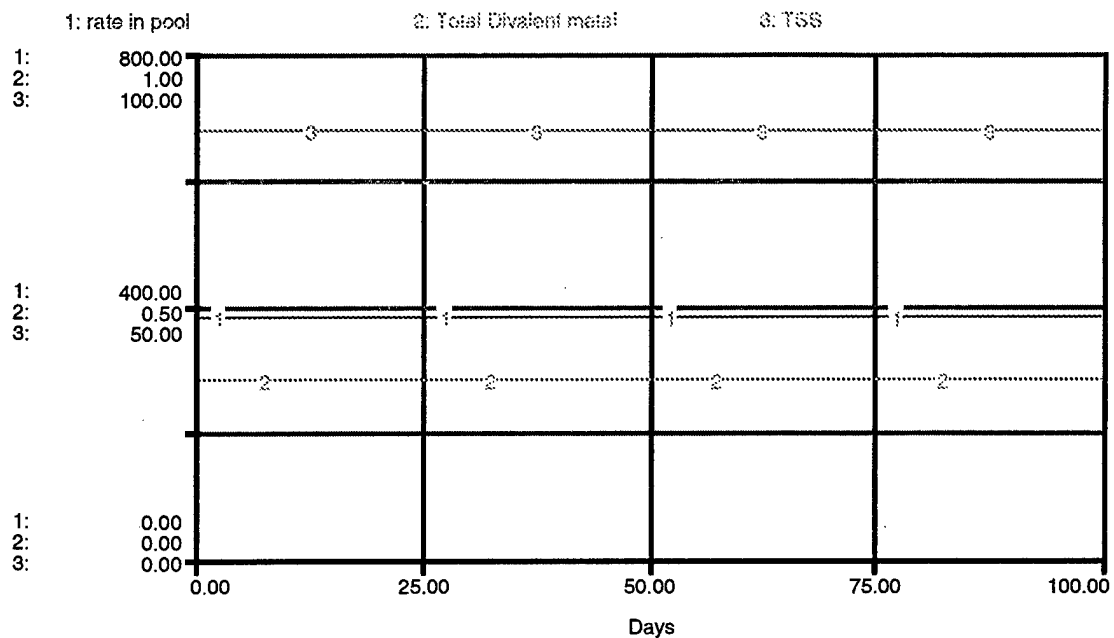

Figure 19. Pulsing Water Flows, TSS, and Metal Concentrations

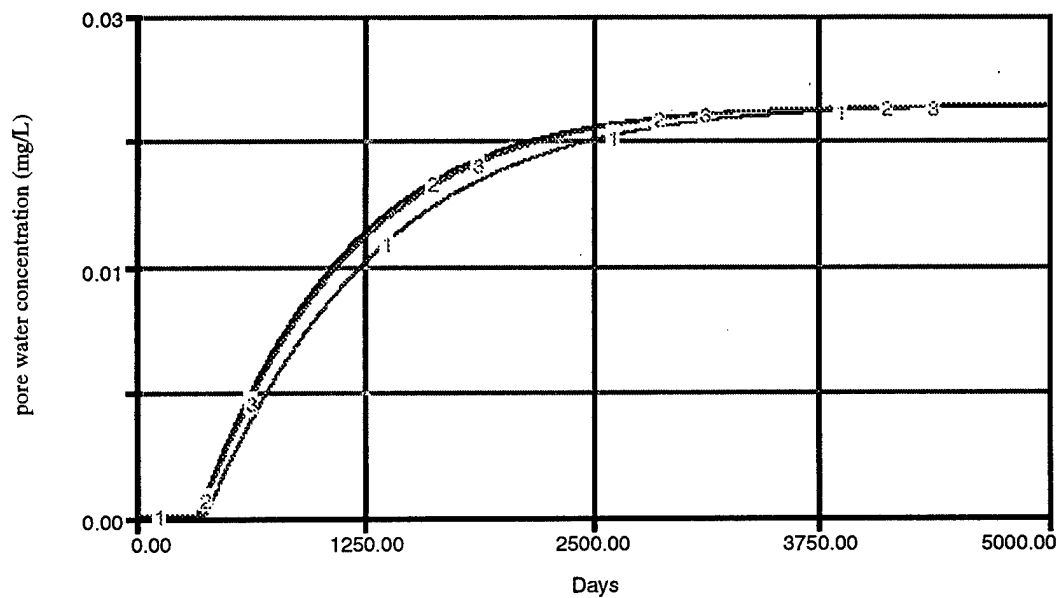**Figure 20. Constant Water Flow, TSS, and Metal Concentrations**

Figure 21. Pore Water Pb Concentration Using 3 Storm Scenarios

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A similar aggregation must be evaluated for representing AVS over time. It has been established that AVS varies seasonally (Howard and Evans, 1993:1056). Figure 22 shows the pore water metal concentration when AVS is a constant 5 μmol/g (trace 1) and when it fluctuates seasonally between 2 and 8 μmol/g (trace 2). The long term behavior of the pore water does not change when the seasonal variation is introduced. Representing the AVS as a constant concentration is, therefore, adequate for this model in evaluating long term metal bioavailability in sediment.
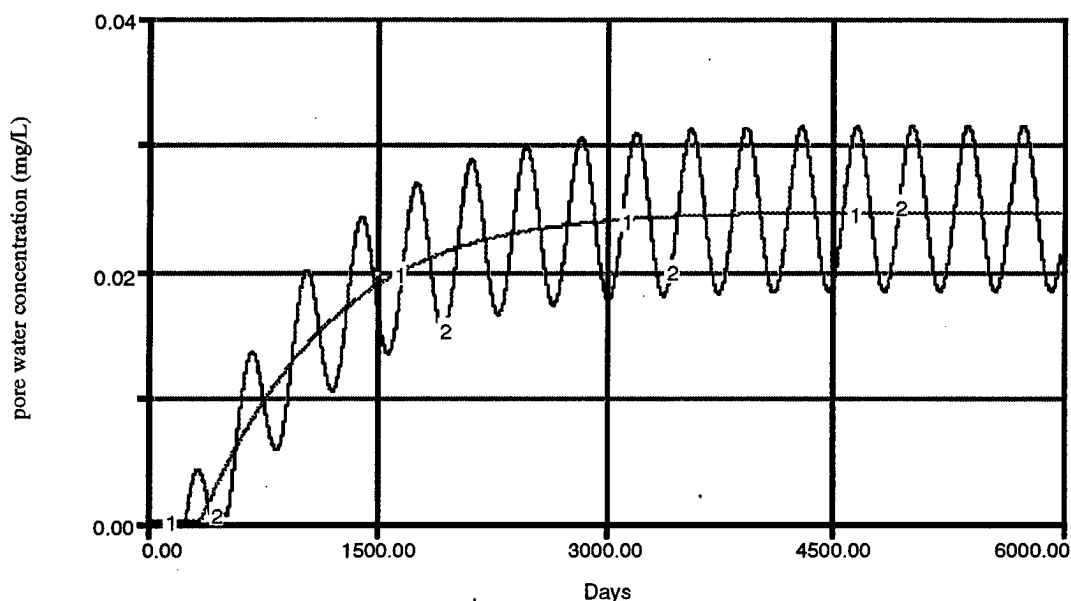

Figure 22. Pore Water Pb Concentration with Constant and Seasonal AVS

The inflow directly into the system from precipitation and the outflow of evapotranspiration were also tested. Figure 23 shows the pore water metal concentration with and without the influence of precipitation and evapotranspiration. The effect of these two flows is negligible compared to the

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large surface water flows in and out of the system. Therefore, these influences are not required for this model. However, models using smaller surface water flows will need to take these influences into consideration.
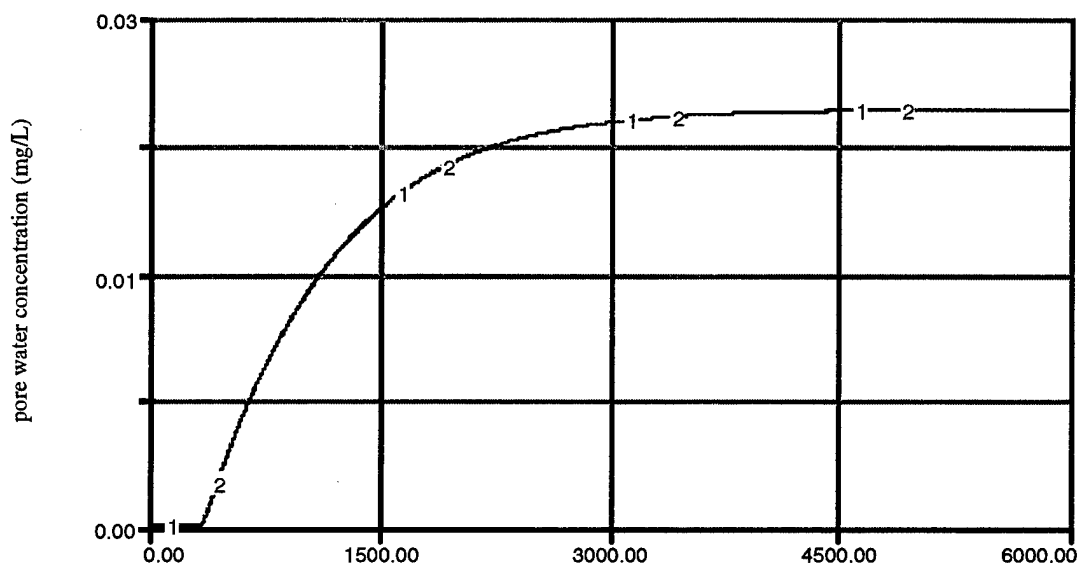

Figure 23. Pore Water Pb Concentration with and without Precipitation and Evapotranspiration

Behavior-Reproduction Test. The first model behavior test is the behavior-reproduction test which ensures the model behavior matches the real system behavior. Discussed below are five different outputs from the model to help verify the assumptions driving the model behavior.

First, in Figure 24, the suspended solids flow is shown at three points in the system: before entering the pool sector, leaving the pool sector, and leaving the wetland sector. The plots are in mass flow rates of mg/day. The system predicts about a 45% loss in suspended solids in the first two sectors of the constructed wetland, with the bulk of it being lost in the first sector. This appears

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to be reasonable. Constructed wetland cells with alternating pool and wetland

sectors can remove 72-84% of suspended solids over their entire length (Gain

and Miller, 1989:7A-18; Gearheart and others, 1989:128), so removing 45% in

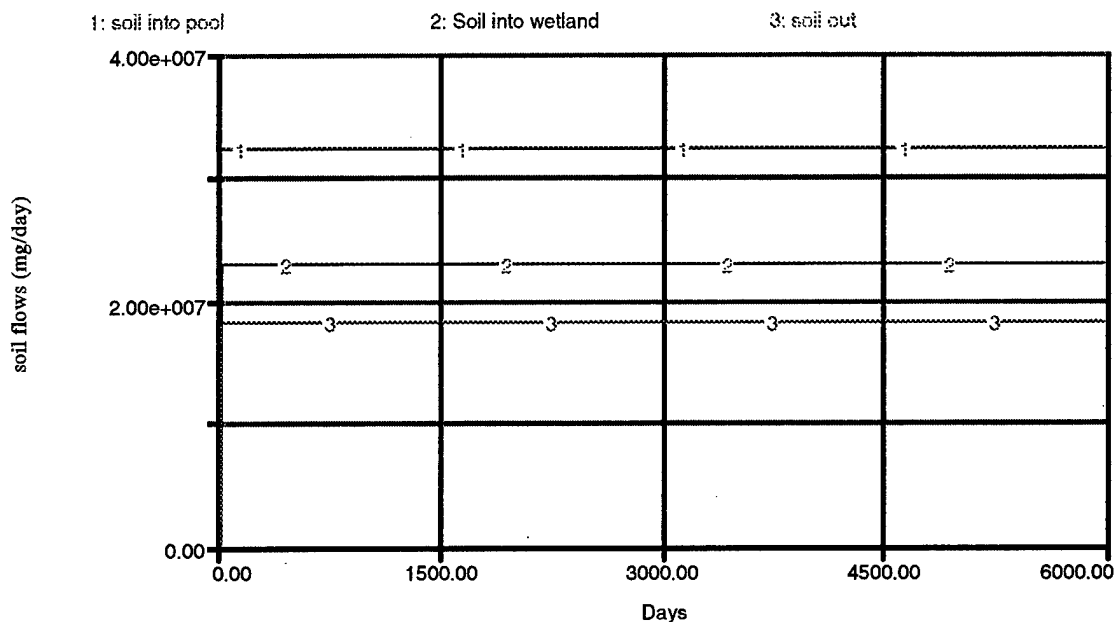the initial portion of the wetland cell is not unreasonable.

Figure 24. Soil Flow Rates at Three Locations in the System

Figure 25 shows metal concentrations at three locations in the system:

before entering the pool sector, leaving the pool sector, and leaving the wetland

sector. The plots are in mg/L and include both dissolved and suspended metal

(Pb in this case). Metal is removed from the system at a similar rate to the

suspended solids because lead is carried primarily in suspension. The

concentration drops from 0.35 mg/L to about 0.20 mg/L. This also appears

reasonable for the initial portion of a constructed wetland that is expected to

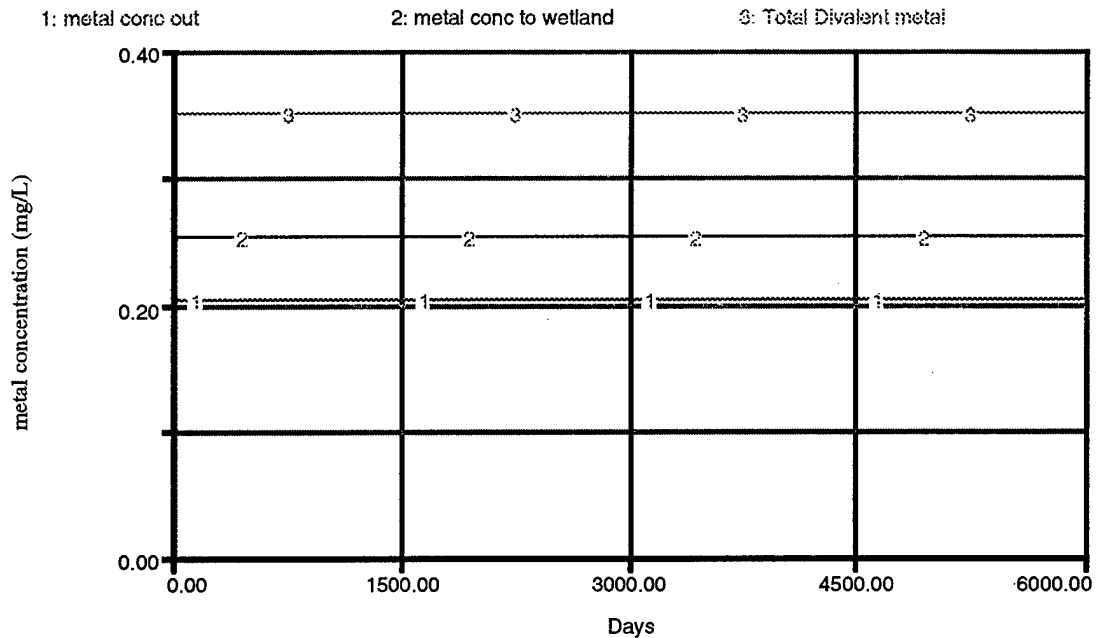remove 80 to 90% of lead (Gain and Miller, 1989:7A-18).

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Figure 25. Metal Concentrations in Surface Water at Three Locations

Figure 26 shows the behavior of the pool and wetland surface water

volumes and depths over the 6000 day simulation. Volumes are shown in cubic

meters and depths in meters. The pool volume and depth, as well as the

wetland volume and depth decrease over time. The wetland sector fills up with

sediment at a slower rate than the pool sector because it receives less

suspended sediment and has a larger area to receive the sediment. The pool

sector loses about half its depth and volume over 16 years with a conservative

input of 85 mg/L of suspended solids. This phenomenon causes many wetland

designers to recommend a silt trap or detention pond to pre-treat the storm water

prior to entering the wetland (Breen and others, 1994:106; Brix, 1993:11; Jones

and others, 1996:54; Livingston, 1989:255). The build-up of sediment in the pool

sector is, therefore, reasonable and helps verify the model assumptions.
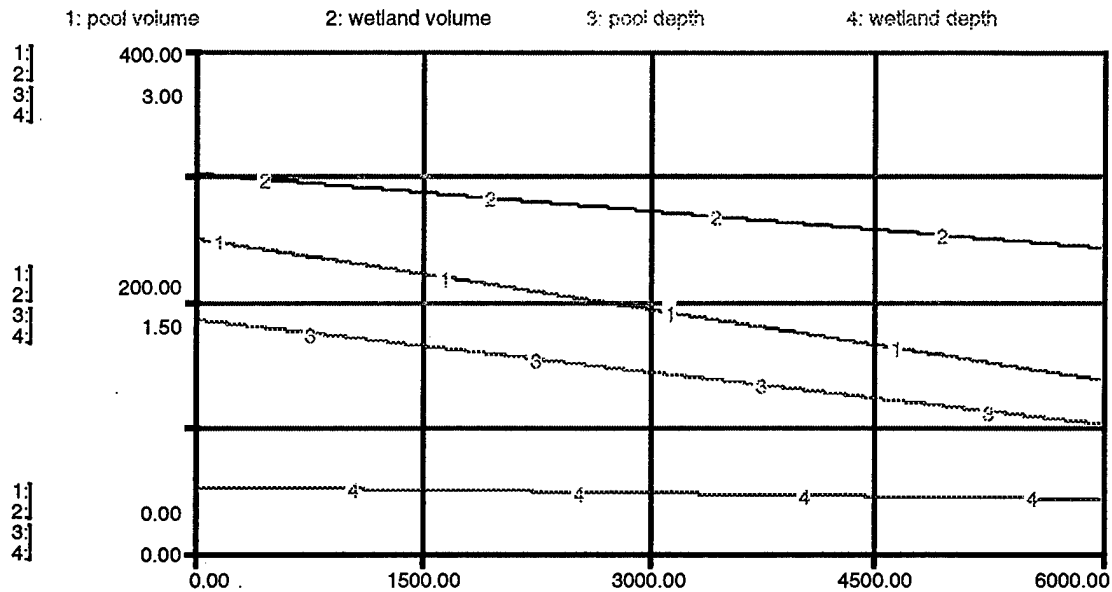
74

Figure 26. Pool and Wetland Water Volumes and Depths

Figure 27 shows the settling, burial, and re-mixing rates that move metals from the surface water to the surface sediment, from the surface sediment to the deep sediment, and from the deep sediment to the buried sediment in mg metal/day. Trace 4 represents the settling rate of metal from suspension into the pool surface sediment. Trace 1 represents the rate of metal movement from surface to deep sediment and trace 3 represents the movement of metal, through bioturbation, from the deep sediment back to the surface sediment. Trace 2 represents the deep burial rate of metal from the deep sediment to the buried sediment. The settling rate and deep burial rate (trace 4 and trace 2) reach a steady state of about 40,000 mg/day. The net rate of movement from the surface sediment to the deep sediment (trace 1 - trace 3) is also about 40,000 mg/day. This test verifies that the rates of metal movement through the model are consistent.
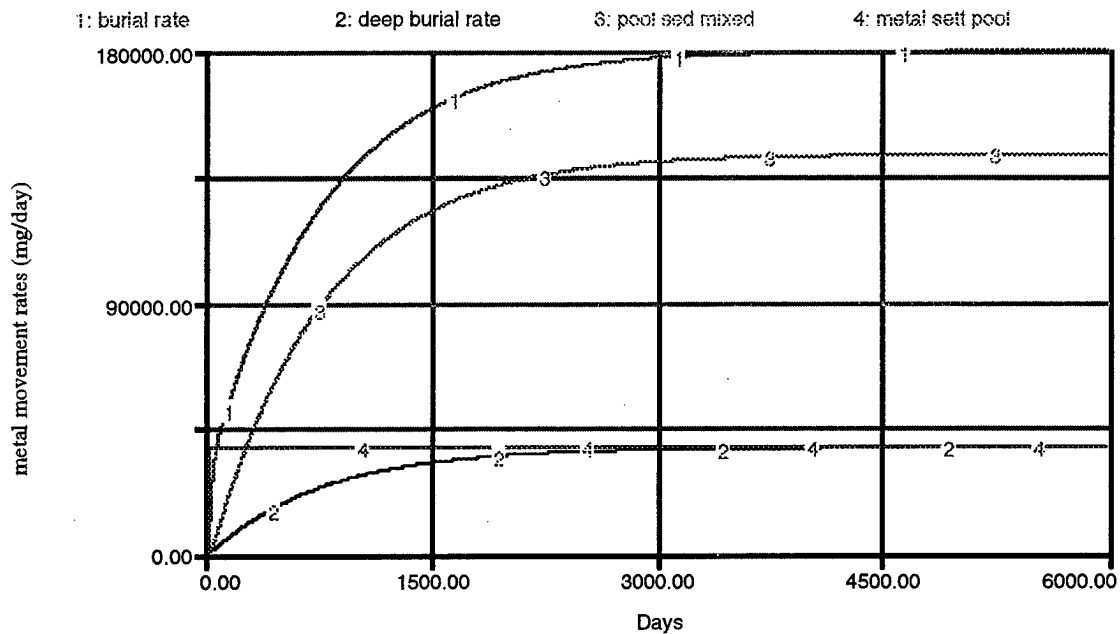
75

Figure 27. Metal Settling, Burial, and Re-mixing Rates

Figure 28 shows the deep sediment concentrations of metal in the pool.

Trace 1 represents the metal sulfide concentration (mg/kg) which is shown to

increase with the total metal concentration until all AVS binding sites are

exceeded. Trace 2 represents the metal bound to organic carbon concentration

(mg/kg) which increases after all the AVS has been exhausted to a steady-state

level. Trace 3 represents the total metal concentration (mg/kg) in deep sediment

which is the sum of the AVS-bound metal and OC-bound metal. All sediment-

bound metal is accounted for either in metal sulfides or sorbed to OC, which

verifies that the structure and assumptions of the this portion of the model are
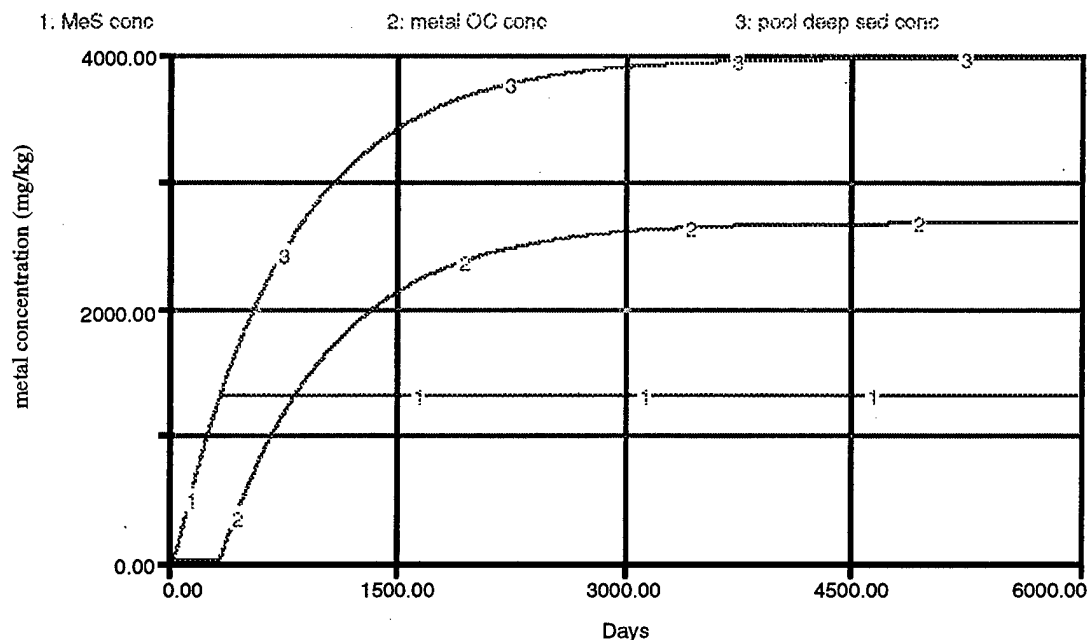
correctly represented.

Figure 28. Metal Concentrations in Pool Deep Sediment

Behavior Anomaly Test. The behavior anomaly test was applied

throughout the model building process to eliminate modeling errors as each part

of the system was built and tested.

One example of an anomaly that was discovered and corrected was that

when the model was initially run, the volumes of water in the pool and wetland

sectors did not change through time. This behavior was anomalous because the

depths of both these water compartments decreased. An influence was added

to the outflows of each sector which accounted for the water that was displaced

as the sediment built up within each sector.

Another anomaly was encountered when running the model with the

parameters for cadmium. The cadmium has a high affinity for solids in the

surface water which cause it to settle in high quantities. But, its affinity for

organic carbon particles in the deep sediment is much lower; so much lower that

cadmium can be brought into the deep sediment at a concentration higher than its sorption capacity. The result, based on equation (5) in this chapter, is a negative pore water concentration. This anomalous behavior indicates a limitation to the model in representing metals with high solubility in pore water. This limitation could probably be overcome if the effects of diffusion between the surface water and pore water were represented in the model.

Other anomalies that came up in the model were usually related to unit conversions. These were all carefully checked and verified.

Sensitivity Analysis

Once the model was tested and validated to an acceptable confidence level. Various entities were evaluated in the system to see which had the greatest influence on the pore water metal concentration. Key entities tested were: pH, AVS concentration, organic carbon concentration, and bioturbation. These entities were chosen because they were internal influences that had the greatest potential to affect metal bioavailability.

Figure 29 shows the pore water metal concentration when the sediment pH is 6.5, 7.0, and 7.5. The pH in the sediment influences the partitioning coefficient between OC-sorbed metal and soluble metal. Figure 29 shows that the pore water concentration is sensitive to small changes in the pH. Storm water pH is known to vary widely from 4.4 to 9.0 (Pitt and others, 1995:262). Wetland sediment pH is typically 6.0 to 7.0 for mineral soils and less than 6.0 for organics soils (Faulkner and Richardson, 1989:42). Low pH conditions in

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surface water or sediments can significantly increase metal bioavailability. It appears that there is a trade-off in using organic sediments for metal retention. On one hand the organics provide a large capacity for binding metals, but on the other hand, they drive down pH which reduces the amount of metal that can partition to the organic carbon. This may be one reason that constructed wetlands made up of both mineral and organic sediment sectors (pool and wetland sectors) perform better than ones that have more homogeneous sediment characteristics.
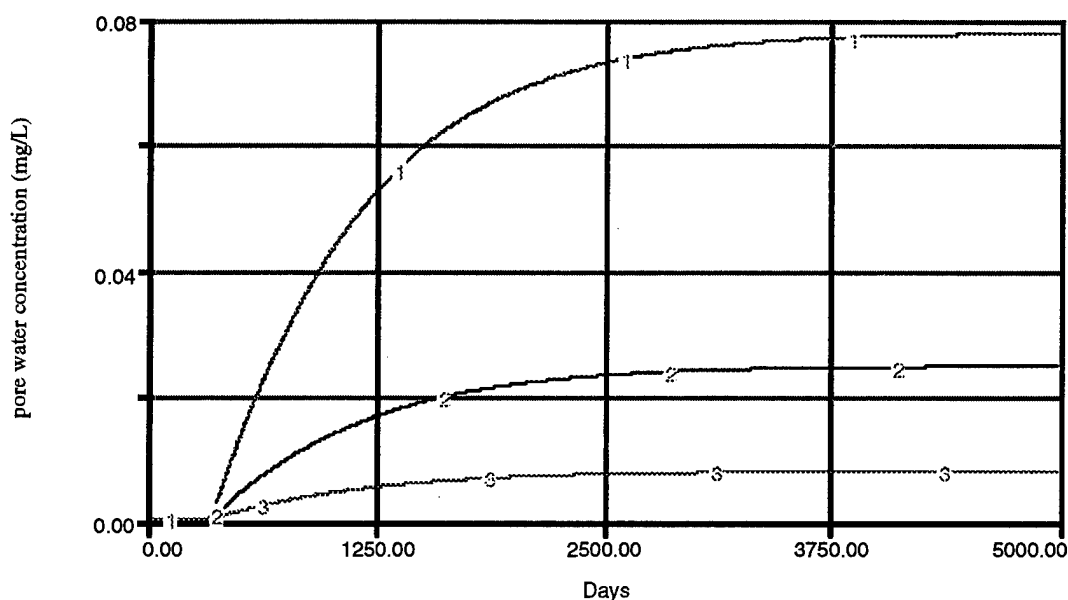

Figure 29. Pore Water Pb Concentration at pH = 6.5, 7.0, and 7.5.

The influence of organic content on sediment pH is not represented in this model. To evaluate this influence, additional simulations were run and shown in Figure 30. This figure represents pore water metal concentration when the organic carbon in the sediment is set at 20% and the pH is set and 6.0 and 6.5.

The increased OC appears to limit the effect of the lowered pH on metal solubility. This can be noted by comparing the pore water concentration at pH = 6.5 in Figure 29 to the pore water concentration at pH =6.0 in Figure 30. With 5% OC and a pH of 6.5, the pore water metal concentration rises to almost 0.08 mg/L. With 20% OC and a lower pH of 6.0, the pore water metal concentration does not even reach 0.06 mg/L.
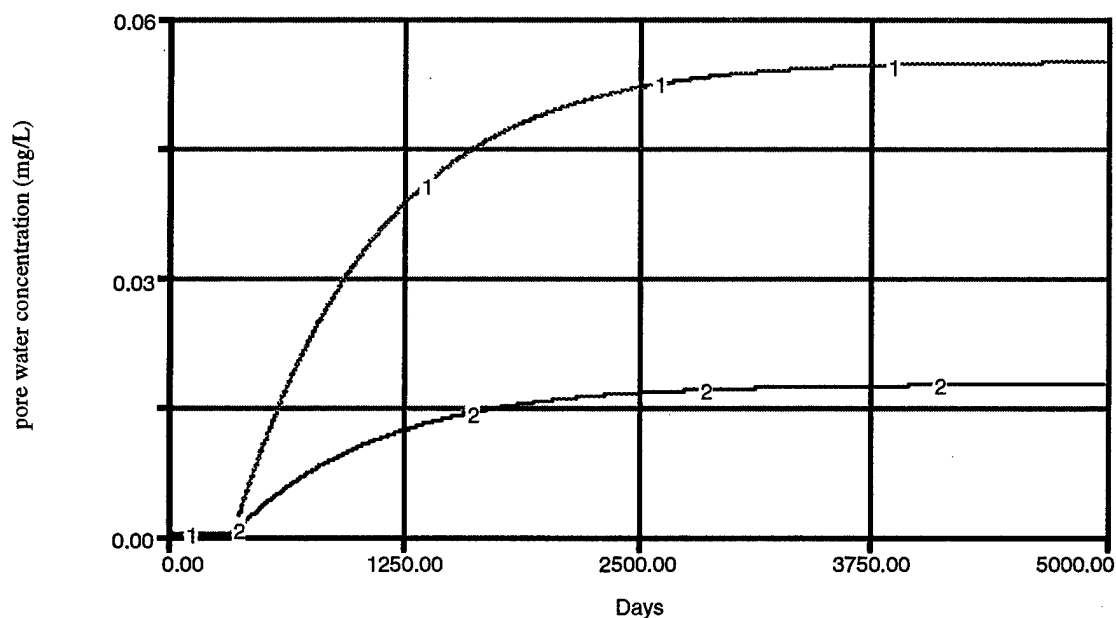

Figure 30. Pore Water Pb Concentration at OC = 20% and pH = 6.0 & 6.5

The importance of AVS for binding metals and preventing toxicity has been documented extensively in recent years and is used for three of the four procedures to determine bioavailability of metals in EPA's SQC standards. Figure 31 shows the pore water metal concentration when AVS is 0, 6.25 μmol/g, and 15 μmol/g. These AVS concentrations represent reasonable minimums and maximums in freshwater sediment. AVS does prevent metals from entering the pore water, but once the AVS binding capacity is exceeded, organic carbon

becomes the controlling factor in limiting metal pore water concentrations. The

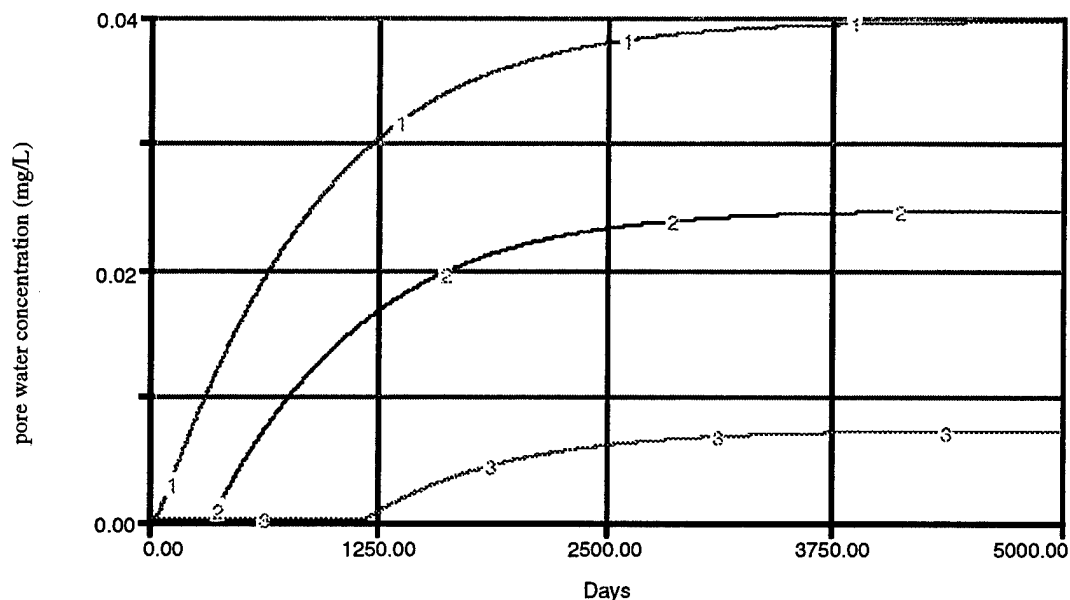pore water is only slightly sensitive to changes in AVS concentration.

Figure 31. Pore Water Pb Concentration at AVS = 0, 6.25, and 15 μmol/g

The fraction of organic carbon in the sediment is a much stronger

influence on pore water concentration and bioavailability than AVS. Figure 32

shows the pore water metal concentration when the organic carbon is 1%, 5%,

and 20%. A wetland's highly organic soil can prevent high pore water

concentrations. When organic carbon is low the pore water can reach a level

near that of the total (suspended and dissolved) metal concentration in the

surface water. Conversely, in very humic soils, the pore water metal

concentration can be kept near 0.01 mg/L. This demonstrates the importance of

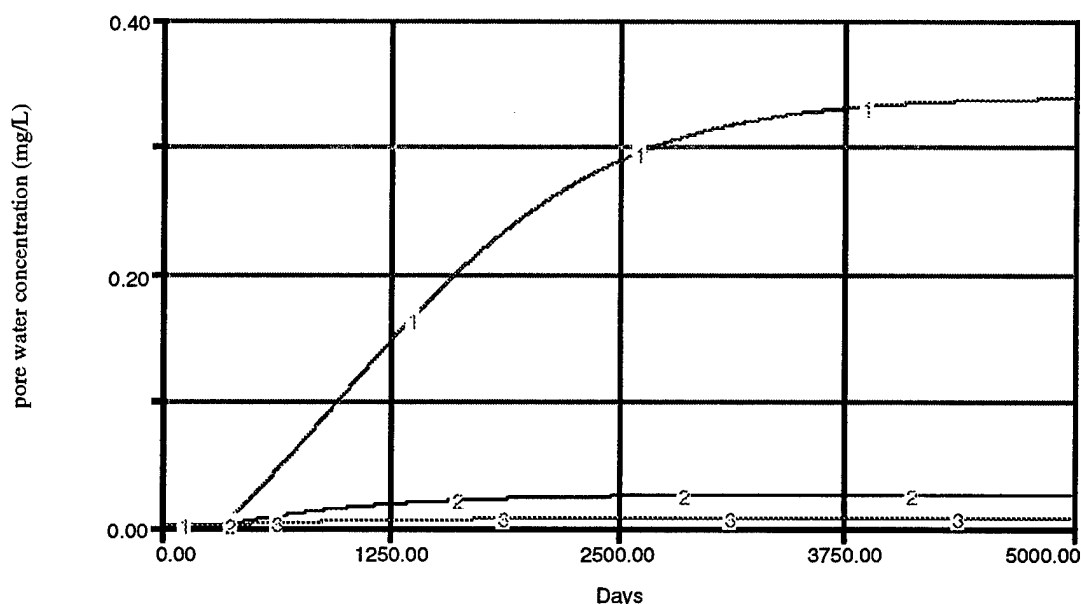wetlands for treatment versus detention ponds.

Figure 32. Pore Water Pb Concentration at OC = 1%, 5%, and 20%

Bioturbation is thought to play a key role in mixing aquatic sediment. This model represents the effects of the "conveyor belt" species of benthic organisms which bring up sediment from 6 to 8 centimeters deep and deposit them on the surface. Figure 33 shows the effect of bioturbation on pore water metal concentration. The flux of sediment due to bioturbation is set at plausible extremes of 0, 0.04, and 0.1 cm/day. This mixing has no effect on the pore water concentration, contrary to my initial hypothesis and common belief. The effect it has on the model is to essentially move the two-compartment sediment representation towards one well-mixed compartment. Although the movement of sediments from deep sediment to surface sediment seems to be the major effect of bioturbation, other aspects of bioturbation (not modeled here) may have a stronger influence on metal bioavailability. One possible influence is

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bioturbation's oxidizing effect on surficial sediment. There is some evidence that bioturbation increases the depth of the aerobic surficial sediment layer where AVS is oxidized and, therefore, pore water metal concentration can increase above what it is in the anaerobic sediment (Peterson and others, 1996:2154).
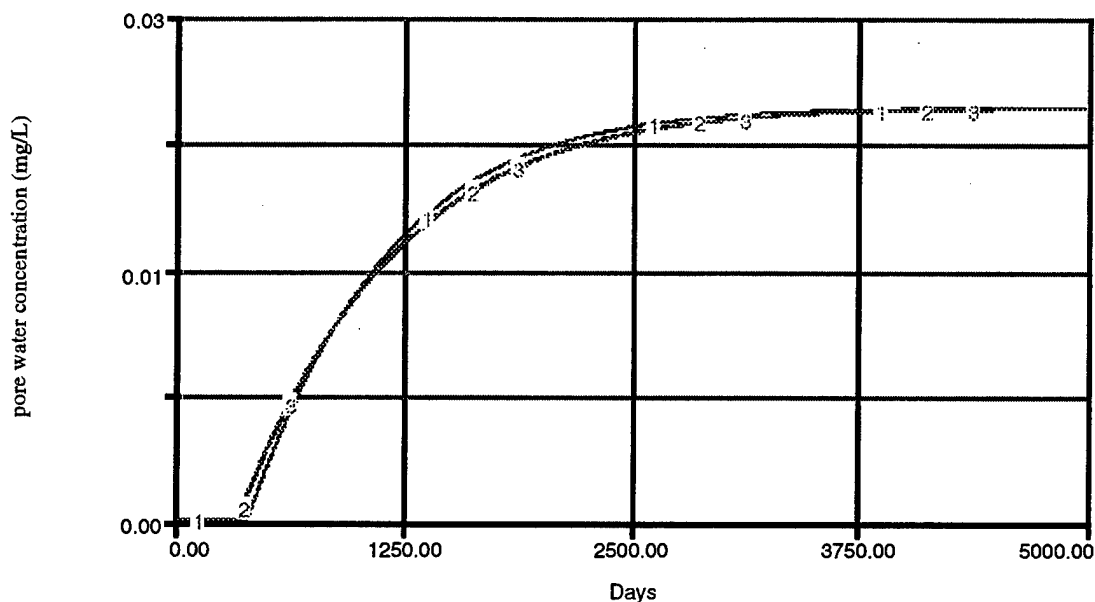
Figure 33. Pore Water Pb Concentration at Bioturbation Rate = 0, 0.04, and 0.1 cm/day

Other Scenarios

Other scenarios that were evaluated included a comparison of three divalent metals (Pb, Cu, and Cd) and a study of differences in metal removal between the pool and wetland sectors.

Behavior of Pb, Cu, and Cd in Sediment. Different metals are transported and behave differently in sediment due largely to differences in solid-water partitioning, both in the surface water and in the pore water. Also, differences in

molecular weights of metals result in differences in chemistry, specifically in binding with AVS. Figure 34 shows the behavior of pore water copper compared to lead in deep sediment. Differences to note in copper versus lead behavior (trace 2 versus trace 1) is that copper exceeds the AVS capacity faster and reaches a higher concentration of metal in the pore water.
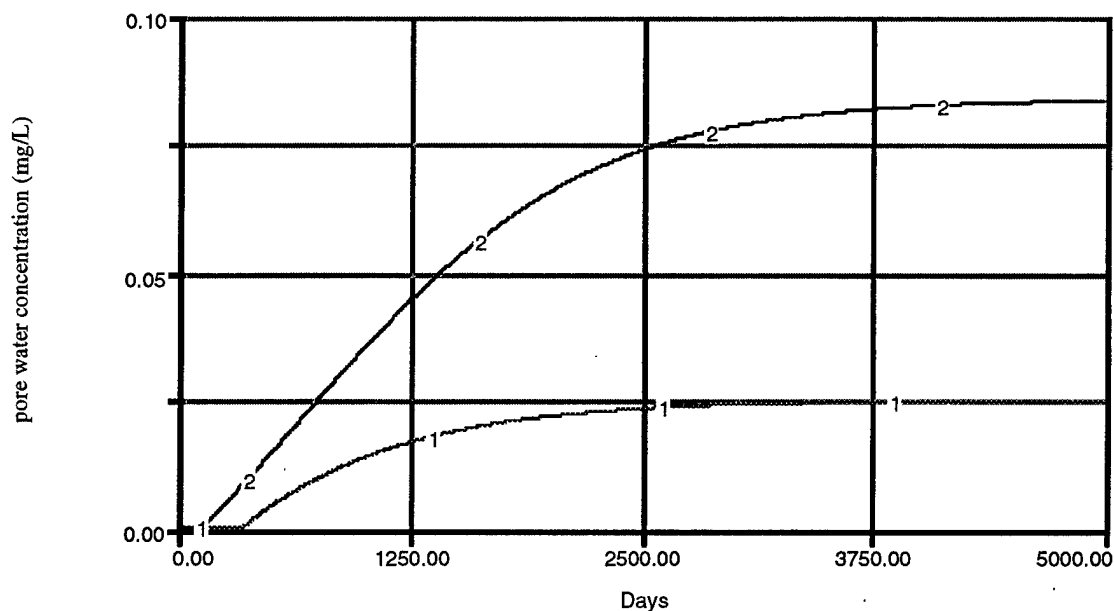
Figure 34. Pore Water Cu Concentration

Cadmium has a much lower affinity for solids than copper or lead in the pore water. A comparison could not be run with 0.35 mg/L of Cd entering the treatment wetland because it exceeds the OC sorption capacity for cadmium as described previously in the section on anomalous behavior. However, Figure 35 shows cadmium behavior in the deep sediment at an input concentration of 0.30 mg/L. Even with the lower input concentration, the pore water metal concentration reaches nearly 20 mg/L after 6000 days. This behavior demonstrates the difference cadmium's solubility as compared to the other two

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metals. This behavior could never occur, however. Cadmium is normally found in lower concentrations (.01 mg/L) and diffusion would begin to play a dominant role in regulating the pore water concentration. (Effects of diffusion are not modeled as movement of sediment-bound metal by burial and bioturbation are assumed to be the major influences).
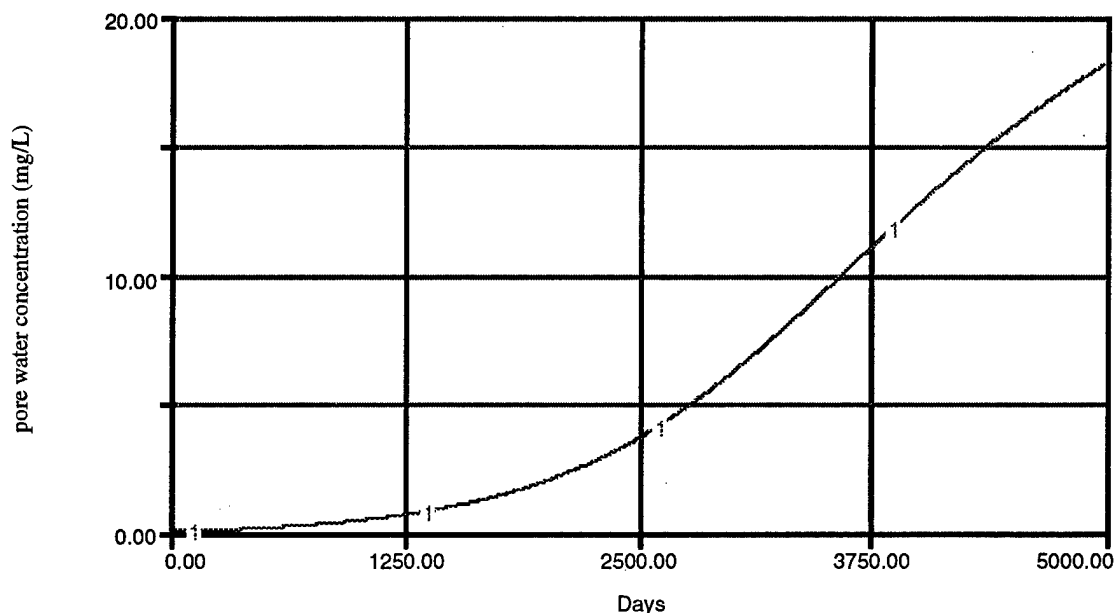
Figure 35. Pore Water Cd Concentration

To demonstrate the differences in the three metals, Table 5 was constructed. Table 5 shows the pore water concentration every 1000 days for three different input concentrations of metal (0.1, 0.2, and 0.3 mg/L). It is clear from Table 5 that organics play a strong role in limiting Pb and Cu pore water concentrations, but have little effect on Cd. This was also noted by Mahony et al. (Mahony and others, 1996:2196).

Table 5. Pore Water Concentration Comparison of Pb, Cu, and Cd (mg/L)

Days	Lead			Copper			Cadmium		
	0.1	0.2	0.3	0.1	0.2	0.3	0.1	0.2	0.3
1000	0.00	0.003	0.010	0.003	0.012	0.026	0.009	0.111	0.391
2000	0.00	0.007	0.016	0.006	0.019	0.044	0.031	0.225	1.92
3000	0.00	0.008	0.018	0.006	0.021	0.050	0.037	0.270	6.10
4000	0.00	0.008	0.019	0.006	0.022	0.052	0.039	0.283	12.6
5000	0.00	0.008	0.019	0.007	0.022	0.053	0.039	0.287	18.1

A variety of metals may exist in the sediment, creating competition for binding sites. Table 2 in Chapter 2 shows metal sulfide solubility products. The first metals released from the sulfide bond are, in the following order: $Fe>Ni>Zn>Cd>Pb>Cu>Hg$. Once released from the AVS, these pore water metal concentrations are only limited by organic carbon bonding. Since cadmium is both more soluble than Cu or Pb in sulfides and with organic complexes, it along with Ni or Zn will probably produce the highest pore water concentrations in sediments with competing metals. A wetland receiving storm water with a mix of heavy metals, will likely exhibit toxicity in sediment from nickel, zinc, or cadmium first, before lead or copper become a problem.

Pond versus Wetland Removal Capabilities. In order to compare the capability of the pond sector versus the wetland sector in treating lead-laden storm water, the wetland sector of the model was run with the initial input

parameters of the pool sector. Figure 36 shows the pore water concentrations of the pool and wetland sector when both are receiving the same influent (trace 1 = pool and trace 2 = wetland) over 3000 days. The wetland sector, because of its large area and high organic content, is able to maintain a very low pore water concentration (less than 0.005 mg/L). However, because of its shallow depth, it can quickly become saturated with soil and lose its metal removing capability. These factors make it necessary to use a pre-treatment detention pond or similar device to remove the bulk of the solids before they enter the wetland. The wetland, with its high organic content, can then efficiently remove contaminants.
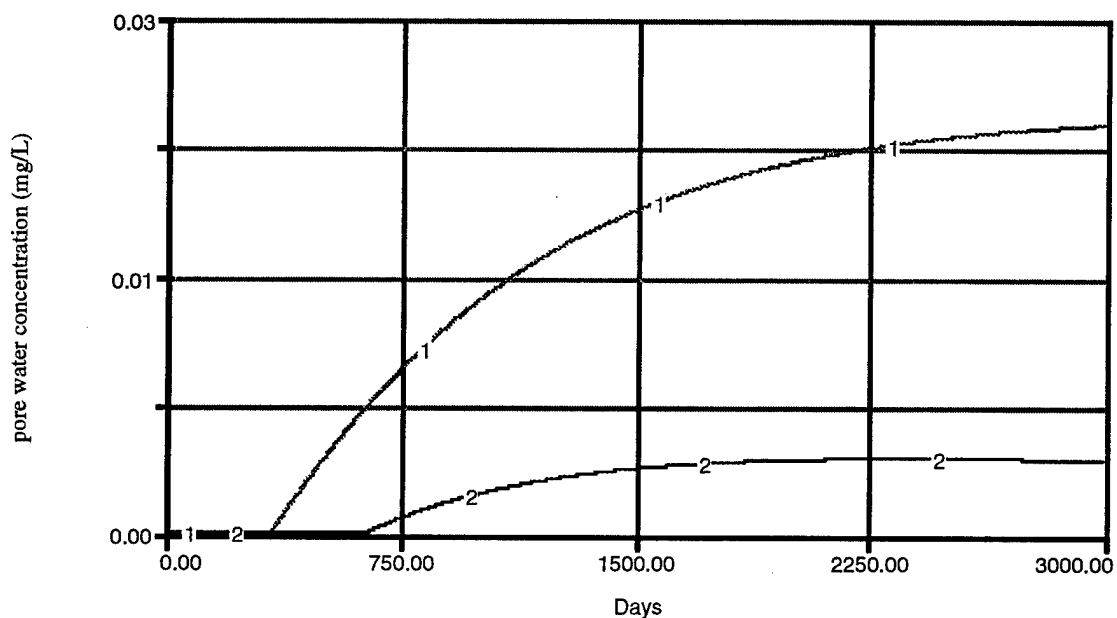

Figure 36. Pore Water Concentrations in the Pool and Wetland Sectors

V. Conclusions and Recommendations

Introduction

The purpose of this research was to develop quantitative concepts that represent the dynamics of metal bioavailability in constructed wetland sediment and to describe the primary mechanisms that cause pore-water concentrations of metal to reach toxic levels. This was achieved by developing a system dynamics model to simulate the processes within the sediment exposed to metal-contaminated storm water over a period of time of up to 16 years. This model was then tested and validated to ensure entities and influences were represented correctly. Influences that proved to have little effect on metal bioavailability were aggregated with other influences that did affect bioavailability. The model was then used to examine the sensitivity of pore water metal concentrations to changes in influential parameters. Additional simulations were run to examine other metals and the differences in behavior in pool versus wetland sediment.

Conclusions

The final model, after testing and validation, seems to represent a holistic or systems view of the major processes controlling metal bioavailability in sediment. The model shows that sediment pH, AVS concentration, and OC concentration all influence metal bioavailability. The movement of particles through bioturbation has little influence on metal bioavailability. The OC in the

deep anaerobic sediment appears to be the biggest influence on metal bioavailability. An additional process of diffusion between pore water and surface water may also be a significant influence on bioavailability for some metals, but was not represented in this model.

Answers to Research Questions. The following discussion describes the answers the model and the model-building process provided for the research questions that were posed.

Research Question One. *What are the physical processes that influence metal transport from storm water to constructed wetland sediment?* The major physical processes that influence metal transport are the storm water flow rate and settling rate. The resuspension rate is typically insignificant and only reaches significant levels when the water depth is very low. The three divalent metals that were studied tend to favor suspension versus dissolution. Therefore, sediment movement largely controls metal movement. Other, more soluble metals, like zinc, would not be influenced to the same degree by settling, but would depend on other chemical processes to remove them from the surface water.

Research Question Two. *What role do biological processes of benthic invertebrates play in changing bioavailability of metals?* The major bioturbation process of moving sediment particles from the 6-8 cm depth to the sediment-water interface has little to no effect on the bioavailability of metals in deep sediment. Other bioturbation mechanisms, however, may increase the depth of the aerobic sediment layer where metals are typically more bioavailable.

However, there is little data on this influence and it was not represented in the model.

Research Question Three. *How do the chemical processes in the sediment's oxidizing and reducing environments affect the chemical forms of metals present?* The majority of sediment is in a reduced state, so bioavailability is predominantly controlled by anaerobic reactions. The most influential chemical processes are the creation of metal sulfides from available AVS and the complexation of metals by organic carbon. The organic carbon binding is reduced by lowered pH. However, even at pH's of 6.0, the organic carbon is the biggest controller of metal bioavailability over the long run (after AVS is expended).

Research Question Four. *How do the biological, physical, and chemical processes interact to influence metal bioavailability?* The model represents all three processes, their interactions, and feedback loops. Physical and biological processes control the movement of soil in the surface water and in the sediment through flow rates and settling rates. Metal is partitioning (a chemical process) with this soil simultaneously in the surface water and within the sediment. The overall metal bioavailability within the sediment is a function of all three dynamic processes occurring at the same time. The chemical processes are the most influential in long term metal bioavailability, while the biological processes have little effect on metal bioavailability.

Model Strengths and Limitations. The model does a good job of representing a macro-view of the interacting process which influence sediment

bioavailability of metal. It provides a way to view the results of these processes as general trends over time. The model also provides a platform to guide future research by predicting what the most influential mechanisms are expected to be over the long term.

The model is limited in that it will not adequately represent highly soluble metals, metal bioavailability in aerobic sediment, and processes at shallow surface water depths.

The model works well for metals with low solubilities like lead and copper. More soluble metals require the influence of diffusion to represent movement of dissolved metal between the sediment and surface water. The model also only concentrates on anaerobic sediment which is typically the dominant portion of the wetland sediment. Sediments that have a large oxidized sediment layer will experience a different degree of metal bioavailability which is not represented in this model. Finally, the well-mixed assumption for the surface water stocks does not hold when pool or wetland sectors become very shallow. Therefore, this model does not adequately represent conditions when these sectors approach a shallow depth from build-up of sediment.

Recommendations

The model's time-dependent output provided insights into how best to prevent metal toxicity in constructed wetland sediment. The most important ways to control metal bioavailability are to reduce suspended solids content and increase organic carbon concentration in sediment.

Reducing suspended solids in the influent removes the solid-borne metal from the surface water. This is typically done through a pre-treatment detention pond and/or pools within the treatment wetland structure.

Organic carbon is critical in limiting the aqueous concentration of non-AVS bound metals. Although some metals show a stronger affinity for OC than others, its binding capacity can greatly exceed that of the AVS. Treatment wetlands should use organic soil in their construction and should allow for the increase of organics through decomposition into the wetland sediment. Detention pond systems, with low organic soils, cannot approach the metal-binding capacity of organic wetland soils.

Recommendations for Future Research. This is a preliminary model which incorporates the results of current research in the field of sediment toxicity. Many assumptions were made where data was not yet available. The model does give guidance into what key influences or entities need further research. The areas which require further research are:

1. The sulfur cycle and its influence on AVS in wetland sediment needs further study to understand the processes that may increase or decrease AVS in the sediment.

2. Actual treatment wetlands should be studied to see if the long term behavior of metal in sediments follows those predicted by the model. Specifically, the areas of AVS and organic carbon influences on metal should be studied.

3. Studies of processes within the aerobic layer are needed to understand differences in toxicity between the aerobic and anaerobic layers, including the effects of a wetland "drying out" on metal bioavailability.

4. The remaining divalent metals used in EPA's SQC (Ni and Zn) need further research to determine their binding relationship with organic carbon.

5. Improvements to the model should be made to include the effects of diffusion between the surface water and pore water, as well as representing the competing effects of the various metals.

Equations

Hydrology

Pool

pool_volume(t) = pool_volume(t - dt) + (Precip + rate_in_pool - rate_in_wetland - Evapo) * dt
INIT pool_volume = 248.4
DOCUMENT: The wetland cell pool designed for SRCSD is 15 m x 12m x 1.38m = 248.4 cubic meters (Crites, 1997:132).

INFLOWS:

Precip = pool_area*.001041
DOCUMENT: Precipitation rate is 38 cm/yr which equates to .00401 meters per day (Peake, 1996:80).

rate_in_pool = average_flow+pulse_switch*pulse(.3*average_flow,4,30)
DOCUMENT: Flow rate averages 378.5 cubic meters/day (Crites and others, 1997:132). Storm event occurs every 30 days.

OUTFLOWS:

rate_in_wetland = rate_in_pool+sediment_rate+Precip-Evapo

Evapo = pool_area*.8*.008
DOCUMENT: The evapotranspiration rate can be represented by 0.8 of the pan evaporation rate (Kadlec, 1989:26). The pan evaporation rate is estimated at 8 mm/day (Mudgett, 1995:122).

Wetland

wetland_volume(t) = wetland_volume(t - dt) + (rate_in_wetland + precip_2 - effluent_rate - evapo_2) * dt
INIT wetland_volume = 300.35
DOCUMENT: Wetland segments of treatment cell are 52m x 15.2m x .38m = 300.35 cubic meters (Crites, 1997:132).

INFLOWS:

rate_in_wetland = rate_in_pool+sediment_rate+Precip-Evapo
precip_2 = wetland_area*.001041
DOCUMENT: Precipitation rate is 38 cm/yr which equates to .001041 m/day
(Peake, 1996:80).

OUTFLOWS:

effluent_rate = rate_in_wetland+sediment_rate_2+precip_2-evapo_2

evapo_2 = wetland_area*.8*.008
DOCUMENT: The evapotranspiration rate can be represented by 0.8 of the pan
evaporation rate (Kadlec, 1989:26). The pan evaporation rate is estimated at 8
mm/day (Mudgett, 1995:122).

Parameters

average_flow = 378.5
DOCUMENT: Flow rate averages 378.5 cubic meters/day (Crites and others,
1997:132).

pool_area = 15*12
DOCUMENT: Sacramento wetland cell pool is 15m x 12m (Crites, 1997:132).
Each wetland cell has six mosquitofish refuge pools separated by shallow
wetland areas.

pulse_switch = 0
DOCUMENT: Multiplier of 1 or 0 which controls whether storm water flow, TSS,
and metal concentrations entering the system are pulsed or are constant.

sediment_rate = ((Settling_Rate-resusp_rate)/1000000)/density_of_sediment
DOCUMENT: This rate in cubic meters/day is how much water is displaced from
pool from sedimentation. (mg soil/day / 1000000 mg/kg / kg/cubic meter) = cubic
meters/day

sediment_rate_2 = ((Settling_Rate_2-
resusp_rate_2)/1000000)/density_of_sediment
DOCUMENT: This rate in cubic meters/day is how much water is displaced from
wetland from sedimentation. (mg soil/day / 1000000 mg/kg / kg/cubic meter) =
cubic meters/day

wetland_area = 52*15.2
DOCUMENT: Wetland cell is a series of 6 pools and wetlands. Each wetland
segment is 15.2m x 52m (Crites and others, 1997:132).

Soil in Pool

Surface Soil

soil_in_pool(t) = soil_in_pool(t - dt) + (Settling_Rate - resusp_rate) * dt
INIT soil_in_pool = 0

INFLOWS:

Settling_Rate = Suspended_Soil_in_pool*settling_velocity/pool_depth
DOCUMENT: mg * m/day / m = mg/day

OUTFLOWS:

resusp_rate = GRAPH(pool_velocity)
(0.00, 60000), (140, 60000), (280, 60000), (420, 150000), (560, 285000), (700, 735000), (840, 1.5e+006), (980, 2.5e+006), (1120, 2.8e+006), (1260, 2.9e+006), (1400, 3e+006)
DOCUMENT: Resuspension is represented by a constant amount from bioturbation plus a velocity dependent amount (Kadlec and Knight,1996:322).

Suspended Soil

Suspended_Soil_in_pool(t) = Suspended_Soil_in_pool(t - dt) + (soil_into_pool + resusp_rate - Soil_into_wetland - Settling_Rate) * dt
INIT Suspended_Soil_in_pool = 0

INFLOWS:

soil_into_pool = TSS*rate_in_pool*1000
DOCUMENT: mg/L * cubic meter/day * 1000 L/cubic meter = mg/day

resusp_rate = GRAPH(pool_velocity)
(0.00, 60000), (140, 60000), (280, 60000), (420, 150000), (560, 285000), (700, 735000), (840, 1.5e+006), (980, 2.5e+006), (1120, 2.8e+006), (1260, 2.9e+006), (1400, 3e+006)
DOCUMENT: Resuspension is represented by a constant amount from bioturbation plus a velocity dependent amount (Kadlec and Knight,1996:322).

OUTFLOWS:

Soil_into_wetland =
Suspended_Soil_in_pool*rate_in_wetland/(pool_area*pool_depth)
DOCUMENT: mg*cubic meters/day/(cubic meters) = mg/day

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Settling_Rate = Suspended_Soil_in_pool*settling_velocity/pool_depth
DOCUMENT: mg * m/day / m = mg/day

Parameters

average_TSS = 85
DOCUMENT: TSS of 50 to 110 mg/L are typical of parking area and street
runoff (Pitt and others, 1995:265).

density_of_sediment = 500
DOCUMENT: Density of sediment is 500 kg/cubic meter converted from 0.5
g/cm cubed (Kadlec and Knight, 1996:329).

pool_depth = 1.38-((soil_in_pool/1000000)/density_of_sediment)/pool_area
DOCUMENT: Water depth begins at 1.38 meters and sediment reduces depth
thereafter. (1.38m - mg/1000000 mg/kg / kg/cubic meter / cubic meters =
meters)

pool_velocity = rate_in_pool/(pool_depth*15)
DOCUMENT: Rate in (cubic meters/day)/depth (m) * width (m) = velocity
(m/day)

settling_velocity = (.001/100)*3600*24
DOCUMENT: Silt particle has settling velocity of .001 cm/s (Kadlec and Knight,
1996:319). This is converted to m/day.

TSS = average_TSS+PULSE(.3*average_TSS,4,30)*pulse_switch
DOCUMENT: TSS of 50 to 110 mg/L are typical of parking area and street
runoff (Pitt and others, 1995:265). Metals and TSS peaks during storm events
prior to storm peak (first flush) (Taylor and others, 1993:141).

Soil in Wetland

Surface Soil

soil_in_wetland(t) = soil_in_wetland(t - dt) + (Settling_Rate_2 - resusp_rate_2) *
dt
INIT soil_in_wetland = 0

INFLOWS:

Settling_Rate_2 = suspended_soil_in_wetland*setling_velocity_2/wetland_depth
DOCUMENT: mg * m/day / m = mg/day

OUTFLOWS:

resusp_rate_2 = GRAPH(wetland_velocity)
(0.00, 60000), (140, 60000), (280, 60000), (420, 150000), (560, 315000), (700, 585000), (840, 945000), (980, 2.2e+006), (1120, 2.6e+006), (1260, 2.8e+006), (1400, 3e+006)
DOCUMENT: Resuspension is dependent on bioturbation and wetland velocity (see Resusp Rate 1).

Suspended Soil

suspended_soil_in_wetland(t) = suspended_soil_in_wetland(t - dt) + (Soil_into_wetland + Litterfall + resusp_rate_2 - soil_out - Settling_Rate_2) * dt
INIT suspended_soil_in_wetland = 0

INFLOWS:

Soil_into_wetland   (IN SECTOR: Pool Soil)

Litterfall = .16*wetland_area*1000
DOCUMENT: Wetlands produce about 0.16 g/sq m/day of litter (Kadlec and Knight, 1996:324, 329). This rate is multiplied by the wetland area in square meters and and converted from grams to mg. (g/ sq m/day * sq m * 1000 mg/g = mg/day)

resusp_rate_2 = GRAPH(wetland_velocity)
(0.00, 60000), (140, 60000), (280, 60000), (420, 150000), (560, 315000), (700, 585000), (840, 945000), (980, 2.2e+006), (1120, 2.6e+006), (1260, 2.8e+006), (1400, 3e+006)
DOCUMENT: Resuspension is dependent on bioturbation and wetland velocity (see Resusp Rate 1).

OUTFLOWS:

soil_out =
suspended_soil_in_wetland*effluent_rate/(wetland_area*wetland_depth)
DOCUMENT: mg * cubic meters/day / cubic meters = mg/day

Settling_Rate_2 = suspended_soil_in_wetland*setling_velocity_2/wetland_depth
DOCUMENT: mg * m/day / m = mg/day

<u>Parameters</u>

setling_velocity_2 = (.00015/100)*3600*24
DOCUMENT: Settling velocity of fine silt is .00015 cm/s this is converted to meters/day (Kadlec and Knight,1996:319). The average size of particle is assumed to be smaller than what was in the influent.

wetland_depth = .38-
(((soil_in_wetland/1000000)/density_of_sediment)/wetland_area)

wetland_velocity = rate_in_wetland/(wetland_depth*15.2)
DOCUMENT: cubic meters/day / square meter cross section = m/day

Metal in Pool Surface Sediment

    <u>Dissolved Metal</u>

Dis_metal_in_pool(t) = Dis_metal_in_pool(t - dt) + (Dis_to_pool - Dis_Susp_Flow - Dis_to_wetland) * dt
INIT Dis_metal_in_pool = 0

INFLOWS:

Dis_to_pool = rate_in_pool*Total_Divalent_metal*1000*(1-perc_susp)
DOCUMENT: flow rate in cubic meters/day * metal in mg/L * 1000 L/cubic meter = metal in mg/day

OUTFLOWS:

Dis_Susp_Flow = transfer_rate*gradient*Suspended_Soil_in_pool/1000000
DOCUMENT: 1/day * mg metal/kg soil * mg soil/1000000 mg/kg = mg metal/day

Dis_to_wetland = rate_in_wetland*Dis_metal_in_pool/(pool_area*pool_depth)
DOCUMENT: Flow rate in cubic meters/day * mg / volume in cubic meters = mg/day of dissolved metal

    <u>Suspended Metal</u>

Susp_metal_in_pool(t) = Susp_metal_in_pool(t - dt) + (Dis_Susp_Flow + Sus_to_pool + metal_resusp_pool - Susp_to_wetland - metal_sett_pool) * dt
INIT Susp_metal_in_pool = 0

INFLOWS:

Dis_Susp_Flow = transfer_rate*gradient*Suspended_Soil_in_pool/1000000
DOCUMENT: 1/day * mg metal/kg soil * mg soil/1000000 mg/kg = mg metal/day

Sus_to_pool = rate_in_pool*Total_Divalent_metal*1000*perc_susp
DOCUMENT: flow rate in cubic meters/day * metal in mg/L * 1000 L/cubic meter
= mg/d of metal

metal_resusp_pool = resusp_rate*(metal_in_pool_surf_sed/soil_in_pool)
DOCUMENT: Soil resuspension rate in mg/day * ratio of metal to soil in mg/mg
= metal resuspension rate in mg/day

OUTFLOWS:

Susp_to_wetland =
rate_in_wetland*Susp_metal_in_pool/(pool_area*pool_depth)
DOCUMENT: Flow rate in cubic meters/day * mg metal / volume in cubic meters
= mg/day of suspended metal

metal_sett_pool = Settling_Rate*(Susp_metal_in_pool/Suspended_Soil_in_pool)
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

Metal in Surface Sediment

metal_in_pool_surf_sed(t) = metal_in_pool_surf_sed(t - dt) + (metal_sett_pool +
pool_sed_mixed - metal_resusp_pool - burial_rate) * dt
INIT metal_in_pool_surf_sed = 0

INFLOWS:

metal_sett_pool = Settling_Rate*(Susp_metal_in_pool/Suspended_Soil_in_pool)
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

pool_sed_mixed =
pool_deep_sed_conc*bioturbation_rate*pool_area*density_of_sediment
DOCUMENT: mg metal/kg soil * m/day * square meters * kg/cubic meter = mg
metal/day

OUTFLOWS:

metal_resusp_pool = resusp_rate*(metal_in_pool_surf_sed/soil_in_pool)
DOCUMENT: Soil resuspension rate in mg/day * ratio of metal to soil in mg/mg
= metal resuspension rate in mg/day

burial_rate   (IN SECTOR: Pool Deep Sediment Metal)

<u>Parameters</u>

average_metal = .35
DOCUMENT: .35 mg/L of Pb, Cd, Cu, Ni and Zn in parking area and street
runoff (Pitt and others, 1995:265).

Dis_Conc = Dis_metal_in_pool/(pool_area*pool_depth)
DOCUMENT: Dissolved metal concentration in mg/cubic meter.

gradient = (Kd*Dis_Conc)-Sus_conc
DOCUMENT: (cubic meters/kg * mg/cubic meter) - mg/kg = mg/kg

Kd = 1059
DOCUMENT: Ratio of suspended metal in mg/kg to dissolved metal in mg/cubic
meter. Value of 1059 cubic meters/kg for Pb, 68 for Cu, and 176 for Cd is based
on data from (Pitt and others, 1995:265).

perc_susp = .95
DOCUMENT: 95.4% of Pb, 94.7% of Cu, and 94.8% of Cd is suspended versus
dissolved (Pitt and others, 1995:265).

Sus_conc = (Susp_metal_in_pool/Suspended_Soil_in_pool)*1000000
DOCUMENT: Suspended metal concentration in mg/kg. (mg metal/mg soil) *
1000000 mg soil/kg

Total_Divalent_metal =
average_metal+PULSE(.3*average_metal,4,30)*pulse_switch
DOCUMENT: .35 mg/L of Pb, Cd, Cu, Ni and Zn in parking area and street
runoff (Pitt and others, 1995:265). Metal and TSS concentrations peak just prior
to strom event peak which is known as first flush (Taylor and others, 1993:141).

transfer_rate = .01
DOCUMENT: 1/days

Metal in Wetland Surface Sediment

<u>Dissolved Metal</u>

Dis_metal_in_wetland(t) = Dis_metal_in_wetland(t - dt) + (Dis_to_wetland -
Dis_Susp_Flow_2 - Dis_metal_out) * dt
INIT Dis_metal_in_wetland = 0

INFLOWS:

Dis_to_wetland   (IN SECTOR: Pool Surface Sediment Metal)

OUTFLOWS:

Dis_Susp_Flow_2 =
transfer_rate*gradient_2*suspended_soil_in_wetland/1000000
DOCUMENT: 1/day * mg metal/kg soil * mg soil/1000000 mg/kg = mg metal/day

Dis_metal_out =
effluent_rate*Dis_metal_in_wetland/(wetland_area*wetland_depth)

Suspended Metal

Susp_metal_in_wetland(t) = Susp_metal_in_wetland(t - dt) + (Susp_to_wetland
+ Dis_Susp_Flow_2 + metal_resusp_wetl - Susp_metal_out - metal_sett_wetl) *
dt
INIT Susp_metal_in_wetland = 0

INFLOWS:

Susp_to_wetland   (IN SECTOR: Pool Surface Sediment Metal)

Dis_Susp_Flow_2 =
transfer_rate*gradient_2*suspended_soil_in_wetland/1000000
DOCUMENT: 1/day * mg metal/kg soil * mg soil/1000000 mg/kg = mg metal/day

metal_resusp_wetl =
resusp_rate_2*(metal_in_wetland_surf_sed/soil_in_wetland)
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

OUTFLOWS:

Susp_metal_out =
effluent_rate*Susp_metal_in_wetland/(wetland_area*wetland_depth)
DOCUMENT: cubic meters/day * mg/cubic meters = mg/day

metal_sett_wetl =
Settling_Rate_2*Susp_metal_in_wetland/suspended_soil_in_wetland
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

Metal in Surface Sediment

metal_in_wetland_surf_sed(t) = metal_in_wetland_surf_sed(t - dt) +
(metal_sett_wetl + wetl_sed_mixed - metal_resusp_wetl - burial_rate_2) * dt
INIT metal_in_wetland_surf_sed = 0

INFLOWS:

metal_sett_wetl =
Settling_Rate_2*Susp_metal_in_wetland/suspended_soil_in_wetland
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

wetl_sed_mixed =
wetl_deep_sed_conc*bioturbation_rate*wetland_area*density_of_sediment
DOCUMENT: mg metal/kg soil * m/day * square meters * kg soil/cubic meter =
mg metal/day

OUTFLOWS:

metal_resusp_wetl =
resusp_rate_2*(metal_in_wetland_surf_sed/soil_in_wetland)
DOCUMENT: mg soil/day * mg metal/mg soil = mg metal/day

burial_rate_2   (IN SECTOR: Wetland Deep Sediment Metal)

Parameters

Dis_Conc_2 = Dis_metal_in_wetland/(wetland_area*wetland_depth)
DOCUMENT: Dissolved metal concentration in mg/cubic meter.

gradient_2 = (Kd*Dis_Conc_2)-Sus_conc_2
DOCUMENT: cubic meters/kg * mg/cubic meters - mg/kg = mg metal/kg soil

Sus_conc_2 = (Susp_metal_in_wetland/suspended_soil_in_wetland)*1000000
DOCUMENT: Suspended metal concentration in mg/kg.

Metal in Pool Deep Sediment

Deep Sediment Metal

metal_in_pool_deep_sed(t) = metal_in_pool_deep_sed(t - dt) + (burial_rate +
partitioning - deep_burial_rate - pool_sed_mixed) * dt
INIT metal_in_pool_deep_sed = 0

INFLOWS:

burial_rate = ((Settling_Rate-resusp_rate)*pool_surf_sed_conc/1000000)+(pool_surf_sed_conc*bioturbation_rate*pool_area*density_of_sediment)
DOCUMENT: The surface sediment is buried to the deep sediment as soil builds up from settling and from benthic organisms bringing up deep sediment. The rate of sediment burial is converted to metal burial using metal concentration in the surface sediment. (mg soil/day * mg metal/kg soil / 1000000 mg/kg) + (mg/kg * m/day * m^2 * kg/cubic meter) = mg metal/day

partitioning = IF(metal_activity>0)OR(metal_activity<0)THEN(-trans_rate*pore_volume*(metal_activity-pore_conc))ELSE(0)
DOCUMENT: If metal activity is not zero, then rate transferred to pore water = transfer rate * gradient * volume. (1/days * mg/L * Liters = mg metal/day)

OUTFLOWS:

deep_burial_rate = (Settling_Rate-resusp_rate)*pool_deep_sed_conc/1000000
DOCUMENT: The sediment in the deep sediment layer is permanently buried at the same rate that sediment builds up on the surface. The soil burial rate is converted to a metal burial rate using the metal concentration. (mg soil/day * mg metal/kg soil / 1000000 mg soil/kg = mg metal/day)

pool_sed_mixed   (IN SECTOR: Pool Surface Sediment Metal)

Buried Metal

metal_buried(t) = metal_buried(t - dt) + (deep_burial_rate) * dt
INIT metal_buried = 0

INFLOWS:

deep_burial_rate = (Settling_Rate-resusp_rate)*pool_deep_sed_conc/1000000
DOCUMENT: The sediment in the deep sediment layer is permanently buried at the same rate that sediment builds up on the surface. The soil burial rate is converted to a metal burial rate using the metal concentration. (mg soil/day * mg metal/kg soil / 1000000 mg soil/kg = mg metal/day)

Metal in Pore Water

metal_in_pore_water(t) = metal_in_pore_water(t - dt) + (- partitioning) * dt
INIT metal_in_pore_water = 0

OUTFLOWS:

partitioning = IF(metal_activity>0)OR(metal_activity<0)THEN(-trans_rate*pore_volume*(metal_activity-pore_conc))ELSE(0)
DOCUMENT: If metal activity is not zero, then rate transferred to pore water = transfer rate * gradient * volume. (1/days * mg/L * Liters = mg metal/day)

<u>Parameters</u>

average_AVS = 200/32
DOCUMENT: Average AVS concentrations observed have been about 200 micro grams/gram (Kemble and others, 1994:1989). Molecular weight of sulfur is 32 g/mol. AVS is in micro moles/g.

AVS = average_AVS+SINWAVE(3,365)*AVS_switch
DOCUMENT: Average AVS concentrations observed have been about 200 micro grams/gram (Kemble and others, 1994:1989). Molecular weight of sulfur is 32 g/mol. AVS is in micro moles/g.

AVS_switch = 0
DOCUMENT: Multiplier of 1 or 0 which controls whether AVS is constant or varies seasonally.

bioturbation_rate = .0004
DOCUMENT: Benthic macroinvertabrates were observed to mix sediment in Lake Erie at a subduction velocity of .0024 to .0626 cm/day. Shallower areas were mixed at a faster rate. A value of .04 cm/day is used (Fisher and others, 1980:4004). (m/day)

fraction_OC = .05
DOCUMENT: Total organic carbon is 5% of sediment.

Kd_OC = 10^log_Kd_OC
DOCUMENT: L/kg OC   (Mahony and others, 1996:2191).

mass_pdeep_sed = .07*pool_area*density_of_sediment
DOCUMENT: Deep sediment (lower 7 centimeters) mass is sediment volume * density = mass in kg

mass_psurf_sediment = .01*pool_area*density_of_sediment
DOCUMENT: Mass of surface sediment (top one centimeter) is sediment volume * density = soil mass in kg

metal_activity = (OC_sorption_cap*metal_per_OC)/(Kd_OC*(OC_sorption_cap-metal_per_OC))
DOCUMENT: Langmuir sorption model of metal to OC from (Mahony and others, 2191:1996). Results are in mg metal per liter. Langmuir model is of the form q = bKC/(b+KC). (mg metal/ kg OC * mg metal/ kg OC) / (L/kg OC * mg metal/kg OC) = mg metal/L

metal_per_OC = IF(AVS>SEM)THEN(0)ELSE((SEM-AVS)*MW/fraction_OC)
DOCUMENT: (non-AVS bound metal in umol/g * g/mol * mol/1000000 umol * 1000 mg/g * 1000 g/kg) / kg OC per kg sediment = mg metal per kg of OC

Metal_Sulfide = IF(AVS>SEM)THEN(SEM)ELSE(AVS)
DOCUMENT: Metal sulfide concentration in micro moles/g of sediment. All metal in sediment is bound with sulfide until all AVS is used.

MW = 207.2
DOCUMENT: Pb molecular weight is 207.2 g/mol, 63.5 for Cu, and 112.4 for Cd.

OC_sorption_cap = 389045
DOCUMENT: Metal-specific sorption capacity in mg metal/kg OC (Mahony, 1996:2191). (380945 mg M/kg OC for Pb, 104713 for Cu, and 53703 for Cd.)

pH = 7.0

pool_deep_sed_conc = metal_in_pool_deep_sed/mass_pdeep_sed
DOCUMENT: Deep sediment concentration in mg/kg.

pool_surf_sed_conc = metal_in_pool_surf_sed/mass_psurf_sediment
DOCUMENT: Concentration of metal in surface sediment in mg/kg.

pore_conc = metal_in_pore_water/pore_volume
DOCUMENT: Pore water concentration in mg/L.

pore_volume = .07*pool_area*porosity*1000
DOCUMENT: Volume of pore water in liters. (m * square meters * 1000 L/cubic meter) = liters

porosity = .65
DOCUMENT: Porosity ranges from 45% to 55% for mineral soils while it hovers around 80% for organic soils (Mitsch and Gosselink, 117:1993).

SEM = pool_deep_sed_conc/MW
DOCUMENT: Metal concentration in mg/kg / 1000 mg/g / MW in g/mol * 1000000 mico mol/mol / 1000 g/kg = metal conc in micro mol/g

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trans_rate = .1
DOCUMENT: 1/days

log_Kd_OC = GRAPH(pH)
(0.00, 0.00), (1.00, 0.00), (2.00, 1.40), (3.00, 2.40), (4.00, 3.40), (5.00, 4.40),
(6.00, 5.40), (7.00, 6.40), (8.00, 7.40), (9.00, 8.40), (10.0, 9.40)
DOCUMENT: Relationship based on (Mahony, 1996:2193).

Metal in Wetland Deep Sediment

<u>Deep Sediment Metal</u>

metal_in_deep_wetl_sed(t) = metal_in_deep_wetl_sed(t - dt) + (burial_rate_2 -
deep_burial_rate_2 - partitioning_2 - wetl_sed_mixed) * dt
INIT metal_in_deep_wetl_sed = 0

INFLOWS:

burial_rate_2 = ((Settling_Rate_2-
resusp_rate_2)*wetland_sed_conc/1000000)+(wetland_sed_conc*bioturbation_r
ate*wetland_area*density_of_sediment)
DOCUMENT: The surface sediment is buried to the deep sediment as soil
builds up from settling and from benthic organisms bringing up deep sediment.
The rate of sediment burial is converted to metal burial using metal concentration
in the surface sediment. (mg soil/day * mg metal/kg soil/1000000mg soil/kg +
mg metal/kg soil * m/day * cubic meters * kg soil/cubic meter = mg/day)

OUTFLOWS:

deep_burial_rate_2 = (Settling_Rate_2-
resusp_rate_2)*wetl_deep_sed_conc/1000000
DOCUMENT: The sediment in the deep sediment layer is permanently buried at
the same rate that sediment builds up on the surface. The soil burial rate is
converted to a metal burial rate using the metal concentration. (mg soil/day * mg
metal/kg soil / 1000000 mg soil/kg = mg/day)

partitioning_2 =
IF(metal_activity_2>0)OR(metal_activity_2<0)THEN(trans_rate*pore_volume_2*(
metal_activity_2-pore_conc_2))ELSE(0)
DOCUMENT: If metal activity is not zero then rate transferred to pore water =
transfer rate * gradient. (L/days * mg/L = mg/day)

wetl_sed_mixed   (IN SECTOR: Wetland Surface Sediment Metal)

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Buried Metal

metal_buried_2(t) = metal_buried_2(t - dt) + (deep_burial_rate_2) * dt
INIT metal_buried_2 = 0

INFLOWS:

deep_burial_rate_2 = (Settling_Rate_2-
resusp_rate_2)*wetl_deep_sed_conc/1000000
DOCUMENT: The sediment in the deep sediment layer is permanently buried at
the same rate that sediment builds up on the surface. The soil burial rate is
converted to a metal burial rate using the metal concentration. (mg soil/day * mg
metal/kg soil / 1000000 mg soil/kg = mg/day)

Metal in Pore Water

metal_in_pore_water_2(t) = metal_in_pore_water_2(t - dt) + (partitioning_2) * dt
INIT metal_in_pore_water_2 = 0

INFLOWS:

partitioning_2 =
IF(metal_activity_2>0)OR(metal_activity_2<0)THEN(trans_rate*pore_volume_2*(
metal_activity_2-pore_conc_2))ELSE(0)
DOCUMENT: If metal activity is not zero then rate transferred to pore water =
transfer rate * gradient. (L/days * mg/L = mg/day)

Parameters

mass_wdeep_sed = .07*wetland_area*density_of_sediment
DOCUMENT: Deep sediment is 7 centimeters deep. Mass is kg of sediment.

mass_wsurf_sed = wetland_area*.01*density_of_sediment
DOCUMENT: Surface sediment is 1 centimeter deep. Mass is sediment volume
* density = mass in kg.

MetalSulfide_2 = IF(AVS>SEM_2)THEN(SEM_2)ELSE(AVS)
DOCUMENT: Metal sulfide concentration in micro moles/g of sediment. Metal
susfide is onlsy form of metal in sediment until all AVS is used.

metal_activity_2 =
(OC_sorption_cap*metal_per_OC_2)/(Kd_OC*(OC_sorption_cap-
metal_per_OC_2))
DOCUMENT: Langmuir sorption model of metal to OC from (Mahony and
others, 2191:1996). Results are in mg metal per liter. (mg metal /kg OC * mg
metal/Kg OC) / (L/kg OC * mg metal/kg OC) = mg metal/L

metal_per_OC_2 = IF(AVS>SEM_2)THEN(0)ELSE((SEM_2-
AVS)*MW/wetland_OC)
DOCUMENT: (non-AVS bound metal in umol/g * g/mol * mol/1000000 umol *
1000 mg/g * 1000 g/kg) / kg OC per kg sediment = mg metal per kg of OC

pore_conc_2 = metal_in_pore_water_2/pore_volume_2
DOCUMENT: Pore water concentration in mg/L.

pore_volume_2 = .07*wetland_area*porosity*1000
DOCUMENT: Volume of pore water in liters. (m * square meters * 1000 L/cubic
meter) = liters

SEM_2 = wetl_deep_sed_conc/MW
DOCUMENT: Metal concentration in mg/kg / 1000 mg/g / average MW in g/mol
* 1000000 mico mol/mol / 1000 g/kg = metal conc in micro mol/g

wetland_OC = .05+RAMP(.00005,1)
DOCUMENT: Organic carbon content of wetland increases from 5% to 40%
over 20 years.

wetland_sed_conc = metal_in_wetland_surf_sed/mass_wsurf_sed
DOCUMENT: Concentration of metal in mg/kg.

wetl_deep_sed_conc = metal_in_deep_wetl_sed/mass_wdeep_sed
DOCUMENT: Concentration of metal in mg/kg.

Concentrations of Interest

MeS_conc = Metal_Sulfide*MW
DOCUMENT: Metal sulfide in umol/g * g/mol * 1 mol/1000000 umol * 1000 mg/g
*1000 g/kg = metal sulfide concentration in mg/kg

MeS_conc_2 = MetalSulfide_2*MW
DOCUMENT: Metal sulfide in umol/g * g/mol * 1 mol/1000000 umol * 1000 mg/g
*1000 g/kg = metal sulfide concentration in mg/kg

metal_conc_out =
((Dis_metal_out/effluent_rate)+(Susp_metal_out/effluent_rate))/1000
DOCUMENT: Concentration of metal leaving the wetland in mg/L.

metal_conc_to_wetland =
((Dis_to_wetland/rate_in_wetland)+(Susp_to_wetland/rate_in_wetland))/1000
DOCUMENT: Concentration of metals leaving the pool and entering the wetland
in mg/L.

metal_in_OC = metal_per_OC*fraction_OC*mass_pdeep_sed
DOCUMENT: mg metal / kg OC * kg OC/kg sediment * kg sediment = mg metal
in OC bond

metal_in_OC_2 = metal_per_OC_2*wetland_OC*mass_wdeep_sed
DOCUMENT: mg metal / kg OC * kg OC/kg sediment * kg sediment = mg metal
in OC bond

metal_in_sulfide = Metal_Sulfide*MW*mass_pdeep_sed
DOCUMENT: Metal sulfide in umol/g * (g/mol / 1000000 umol/mol) * kg
sediment * 1000 g/kg * 1000mg/g = mg metal in AVS bond

metal_in_sulfide_2 = MetalSulfide_2*MW*mass_wdeep_sed
DOCUMENT: Metal sulfide in umol/g * (g/mol / 1000000 umol/mol) * kg
sediment * 1000 g/kg * 1000mg/g = mg metal in AVS bond

metal_OC_conc = metal_per_OC*fraction_OC
DOCUMENT: mg metal/kg OC * kg OC/kg sediment = OC metal in mg/kg

metal_OC_conc_2 = metal_per_OC_2*wetland_OC
DOCUMENT: mg metal/kg OC * kg OC/kg sediment = OC metal in mg/kg

Pool Soil

pool depth

pool area

Soil into wetland

rate in wetland

rate in pool

pool velocity

resusp rate

soil in pool

density of sediment

pool depth

Suspended Soil in pool

pool area

rate in pool

Settling Rate

TSS

settling velocity

soil into pool

average TSS

pulse switch

TSS

density of sediment

112

Pool Surface Sediment Metal

113

Pool Deep Sediment Metal

Wetland Surface Sediment Metal

117
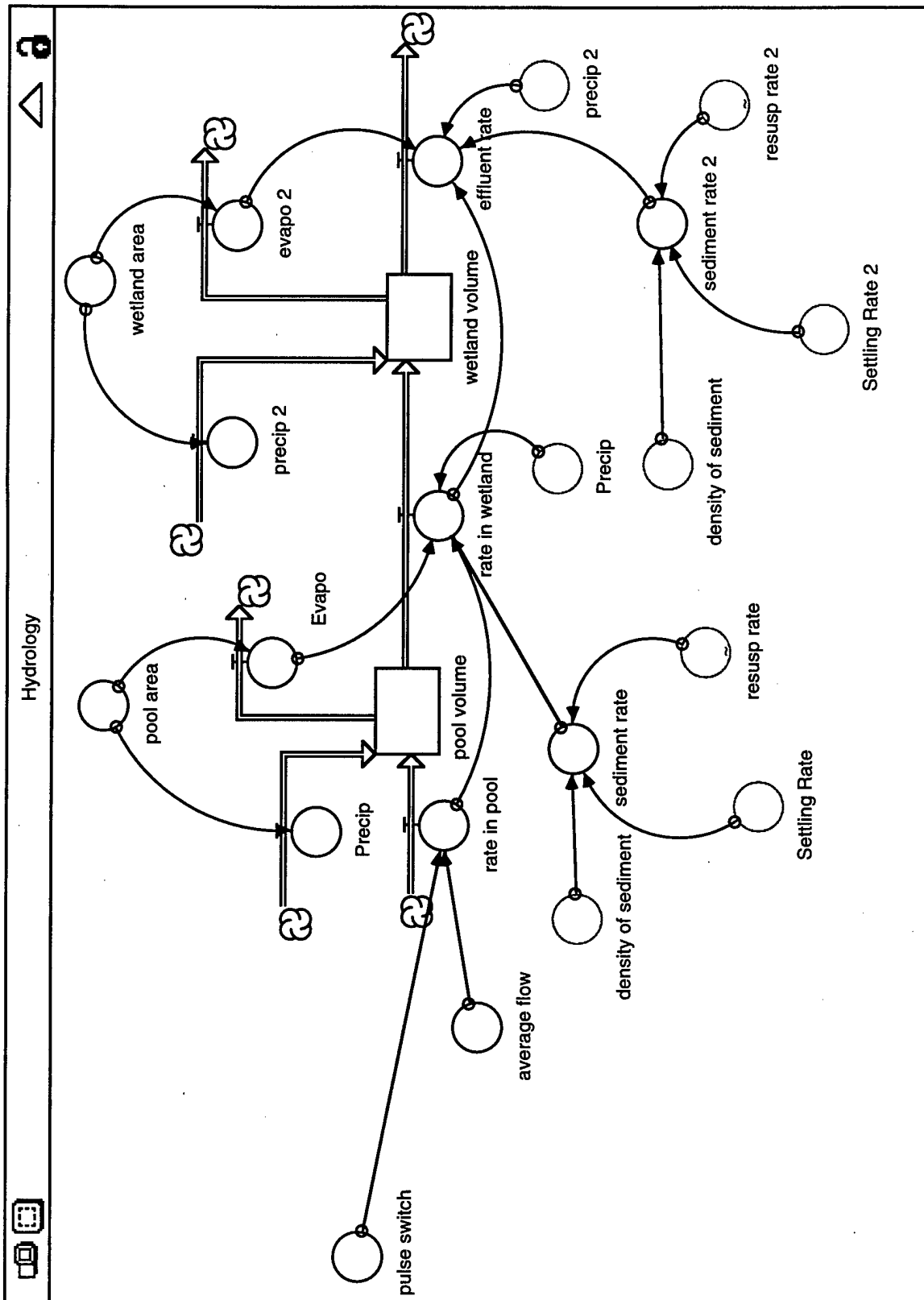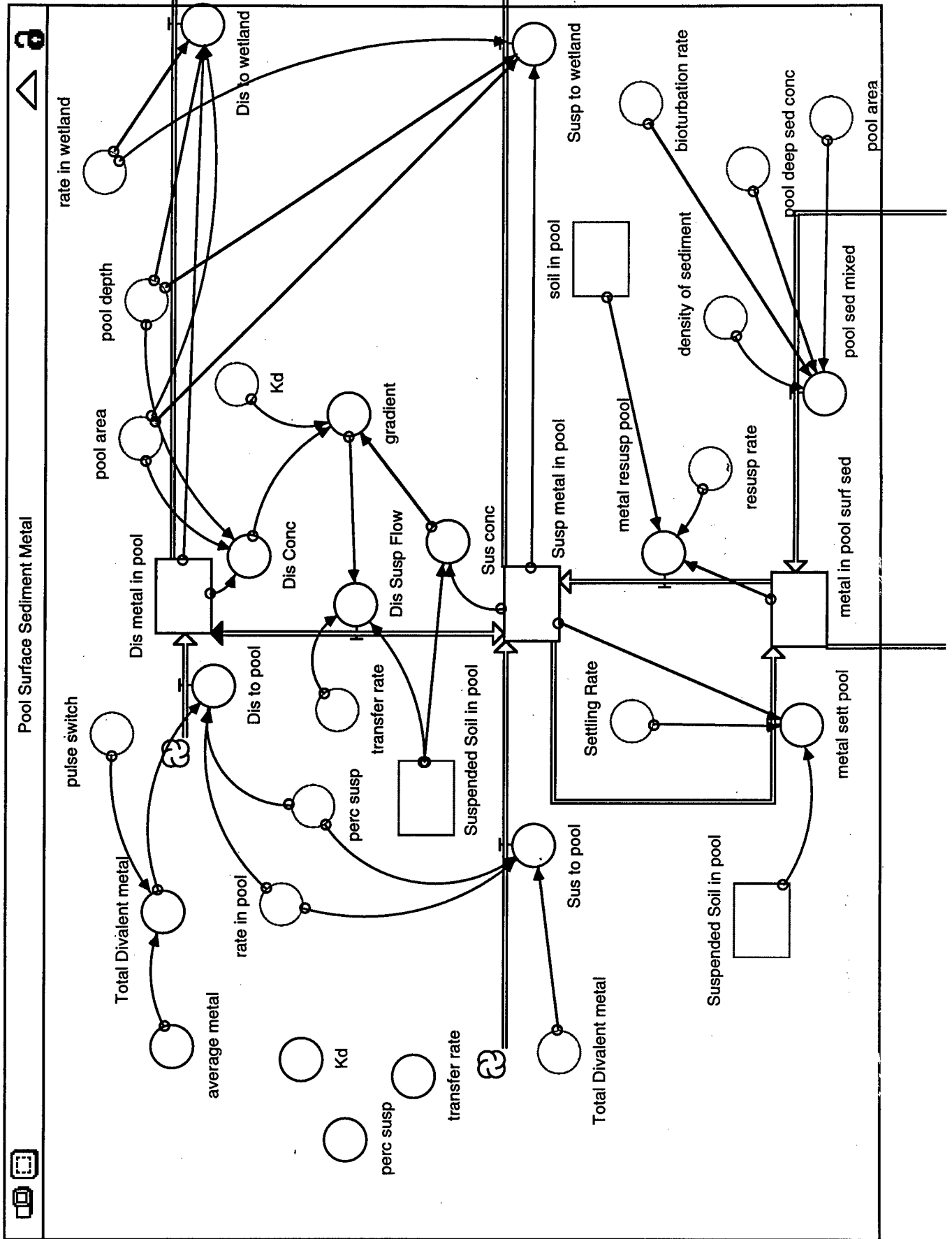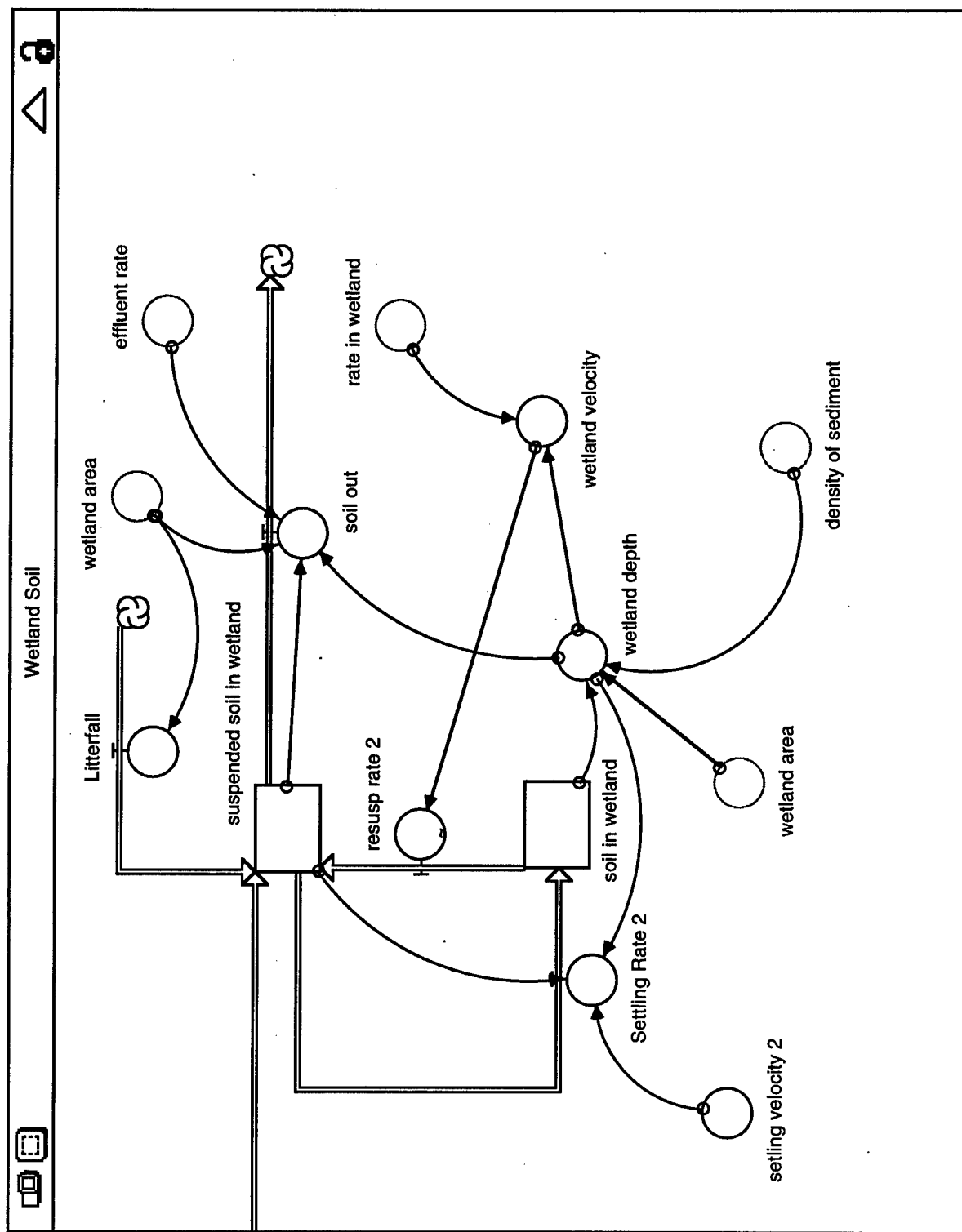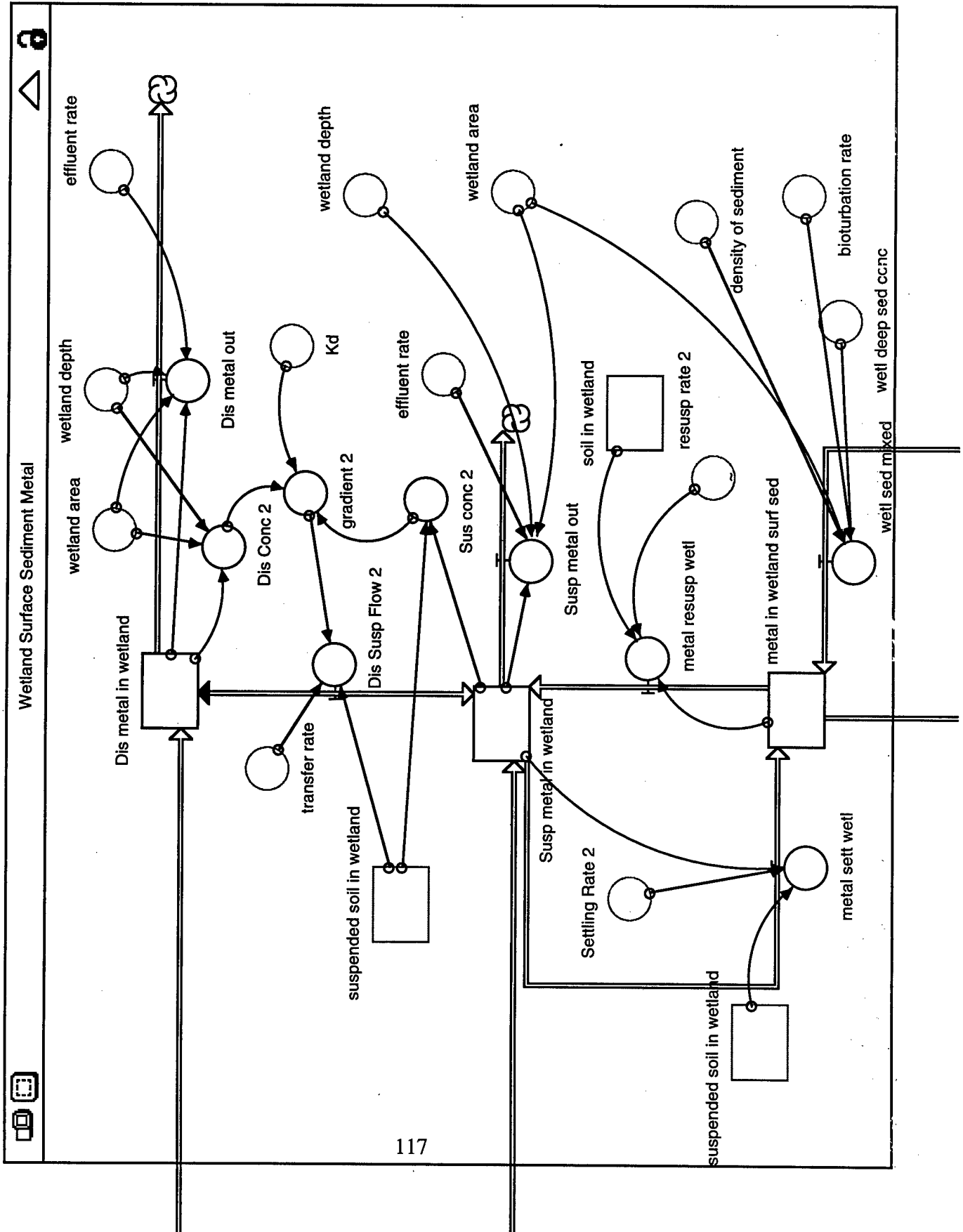
Wetland Deep Sediment Metal

Appendix B. Calculations for Kd and Percent of Metal Suspended

Lead Calculations

The template below uses storm water data from parking and street runoff to calculate the percent of lead carried in suspension (Pitt and others, 1995:265).

Calculate the percent of metal in suspension by averaging the percent of metal in filtered samples from parking and street runoff and subtract from 1.

$$perc := 1 - \left(\frac{\frac{2.1}{46} + \frac{2}{43}}{2} \right)$$

Average total lead in samples is .045 mg/L

$$metal := .045 \quad (mg/L)$$

Suspended concentration:

$$S := perc \cdot metal \quad (mg/L)$$

Dissolved concentration:

$$D := (1 - perc) \cdot metal \quad (mg/L)$$

Total suspended solids = 80 mg/L

$$TS := 80 \quad (mg/L)$$

Suspended concentration per mass of solids:

$$Sconc := \frac{S}{TS} \cdot 1000000 \quad (mg/kg)$$
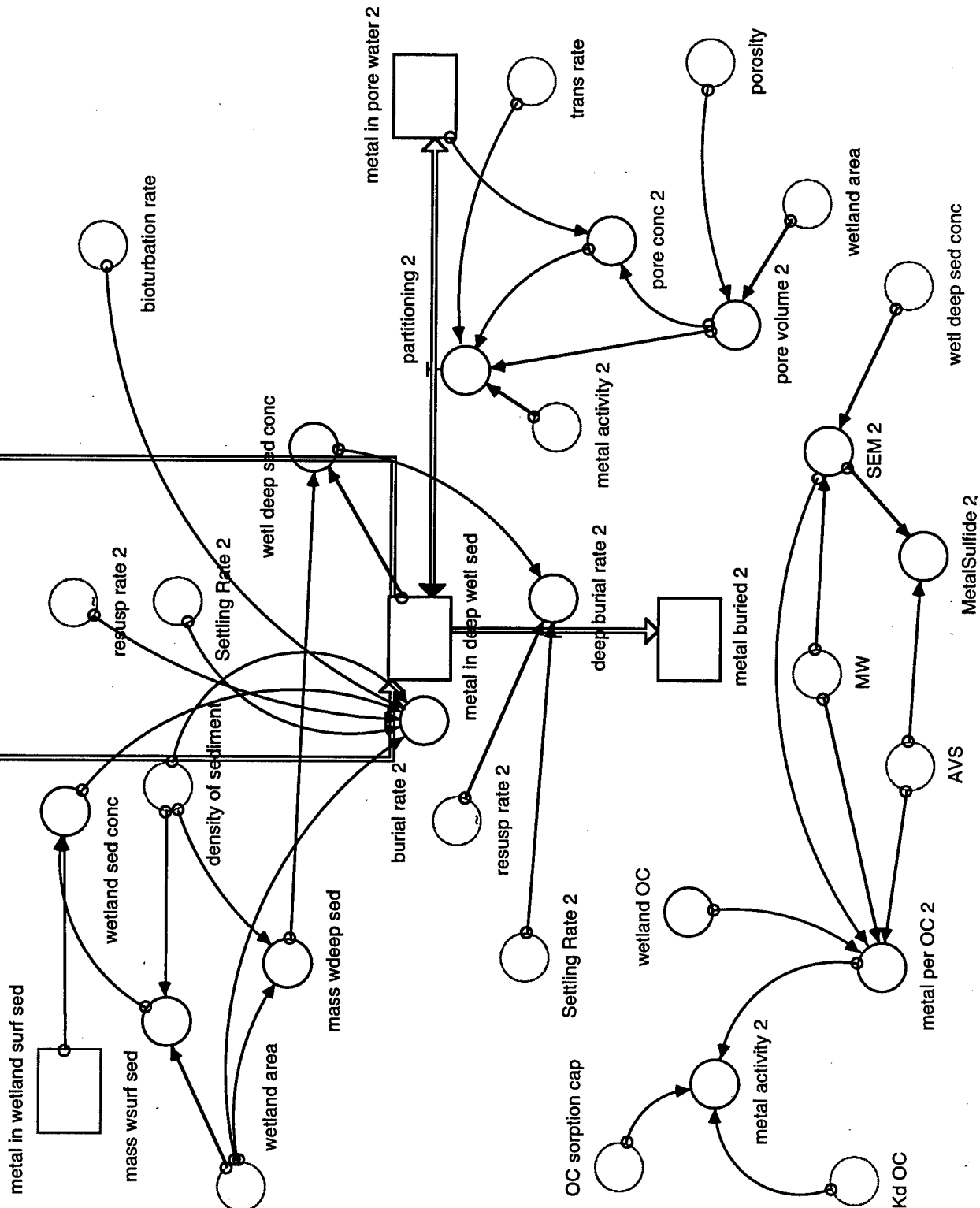
Dissolved concentration per cubic meter:

$$Dconc := D \cdot 1000 \quad (mg/m^3)$$

Partitioning coefficient in cubic meters per kg:

$$Kd := \frac{Sconc}{Dconc} \quad (m^3/kg)$$

Partitioning coefficient and percent metal suspended in the storm water influent:

$$Kd = 258.756 \quad (m^3/kg)$$

$$perc = 0.954$$

The percent of lead carried in suspension is 95.4%.

Lead Calculations

The template below calculates the partitioning coefficient in the surface water based on data from detention ponds (Pitt and others, 1995:265).

Calculate the percent of metal in suspension by calculating the percent of metal in filtered samples from detention ponds and subtract from 1.

$$perc1 := 1 - \frac{1}{19}$$

Average total lead in samples is .019 mg/L

$$metal1 := .019 \quad (mg/L)$$

Suspended concentration: $\quad S1 := perc1 \cdot metal1 \quad (mg/L)$

Dissolved concentration: $\quad D1 := (1 - perc1) \cdot metal1 \quad (mg/L)$

Total suspended solids = 17 mg/L $\quad TS1 := 17 \quad (mg/L)$

Suspended concentration per mass of solids: $\quad S1conc := \frac{S1}{TS1} \cdot 1000000 \quad (mg/kg)$

Dissolved concentration per cubic meter: $\quad D1conc := D1 \cdot 1000 \quad (mg/m^3)$

Partitioning coefficient in cubic meters per kg: $\quad Kd1 := \frac{S1conc}{D1conc} \quad (m^3/kg)$

Partitioning coefficient and percent metal suspended in the storm water influent:

$$Kd1 = 1.059 \cdot 10^3 \quad (m^3/kg)$$

$$perc1 = 0.947$$

The partitioning coefficient for lead is 1059 cubic meters per kg.

Copper Calculations

The template below uses storm water data from parking and street runoff to calculate the percent of copper carried in suspension (Pitt and others, 1995:265).

Calculate the percent of metal in suspension
by averaging the percent of metal in filtered samples
from parking and street runoff and subtract from 1.

$$perc := 1 - \left(\frac{\frac{11}{116} + \frac{3.8}{280}}{2} \right)$$

Average total copper in samples is .198 mg/L $\qquad$ $metal := .198 \qquad$ (mg/L)

Suspended concentration: $\qquad$ $S := perc \cdot metal \qquad$ (mg/L)

Dissolved concentration: $\qquad$ $D := (1 - perc) \cdot metal \qquad$ (mg/L)

Total suspended solids = 80 mg/L $\qquad$ $TS := 80 \qquad$ (mg/L)

Suspended concentration per mass of solids: $\qquad$ $Sconc := \frac{S}{TS} \cdot 1000000 \qquad$ (mg/kg)

Dissolved concentration per cubic meter: $\qquad$ $Dconc := D \cdot 1000 \qquad$ (mg/m^3)

Partitioning coefficient in cubic meters per kg: $\qquad$ $Kd := \frac{Sconc}{Dconc} \qquad$ (m^3/kg)

Partitioning coefficient and percent metal
suspended in the storm water influent: $\qquad$ $Kd = 218.129 \qquad$ (m^3/kg)

$perc = 0.946$

The percent of copper carried in suspension is 94.6%.

Copper Calculations

The template below calculates the partitioning coefficient in the surface water based on data from detention ponds (Pitt and others, 1995:265).

Calculate the percent of metal in suspension by calculating the percent of metal in filtered samples from detention ponds and subtract from 1.

$$perc1 := 1 - \frac{20}{43}$$

Average total copper in samples is .043 mg/L

$$metal1 := .043 \quad (mg/L)$$

Suspended concentration:

$$S1 := perc1 \cdot metal1 \quad (mg/L)$$

Dissolved concentration:

$$D1 := (1 - perc1) \cdot metal1 \quad (mg/L)$$

Total suspended solids = 17 mg/L

$$TS1 := 17 \quad (mg/L)$$

Suspended concentration per mass of solids:

$$S1conc := \frac{S1}{TS1} \cdot 1000000 \quad (mg/kg)$$

Dissolved concentration per cubic meter:

$$D1conc := D1 \cdot 1000 \quad (mg/m\wedge 3)$$

Partitioning coefficient in cubic meters per kg:

$$Kd1 := \frac{S1conc}{D1conc} \quad (m\wedge 3/kg)$$

Partitioning coefficient and percent metal suspended in the storm water influent:

$$Kd1 = 67.647 \quad (m\wedge 3/kg)$$

$$perc1 = 0.535$$

The partitioning coefficient for copper is 68 cubic meters per kg.

Cadmium Calculations

The template below uses storm water data from parking and street runoff to calculate the percent of cadmium carried in suspension (Pitt and others, 1995:265).

Calculate the percent of metal in suspension
by averaging the percent of metal in filtered samples
from parking and street runoff and subtract from 1.

$$\text{perc} := 1 - \left(\frac{\frac{.6}{6.3} + \frac{.3}{37}}{2} \right)$$

Average total cadmium in samples is .022 mg/L $\text{metal} := .022$ (mg/L)

Suspended concentration: $S := \text{perc} \cdot \text{metal}$ (mg/L)

Dissolved concentration: $D := (1 - \text{perc}) \cdot \text{metal}$ (mg/L)

Total suspended solids = 80 mg/L $TS := 80$ (mg/L)

Suspended concentration per mass of solids: $\text{Sconc} := \frac{S}{TS} \cdot 1000000$ (mg/kg)

Dissolved concentration per cubic meter: $\text{Dconc} := D \cdot 1000$ (mg/m^3)

Partitioning coefficient in cubic meters per kg: $Kd := \frac{\text{Sconc}}{\text{Dconc}}$ (m^3/kg)

Partitioning coefficient and percent metal
suspended in the storm water influent:

$Kd = 229.405$ (m^3/kg)

$\text{perc} = 0.948$

The percent of cadmium carried in suspension is 94.8%.

Cadmium Calculations

The template below calculates the partitioning coefficient in the surface water based on data from detention ponds (Pitt and others, 1995:265).

Calculate the percent of metal in suspension by calculating the percent of metal in filtered samples from detention ponds and subtract from 1.

$$perc1 := 1 - \frac{.5}{2}$$

Average total cadmium in samples is .002 mg/L

$metal1 := .002$ (mg/L)

Suspended concentration:

$S1 := perc1 \cdot metal1$ (mg/L)

Dissolved concentration:

$D1 := (1 - perc1) \cdot metal1$ (mg/L)

Total suspended solids = 17 mg/L

$TS1 := 17$ (mg/L)

Suspended concentration per mass of solids:

$$S1conc := \frac{S1}{TS1} \cdot 1000000 \ \text{(mg/kg)}$$

Dissolved concentration per cubic meter:

$D1conc := D1 \cdot 1000$ (mg/m^3)

Partitioning coefficient in cubic meters per kg:

$$Kd1 := \frac{S1conc}{D1conc} \ \text{(m^3/kg)}$$

Partitioning coefficient and percent metal suspended in the storm water influent:

$Kd1 = 176.471$ (m^3/kg)

$perc1 = 0.75$

The partitioning coefficient for cadmium is 176 cubic meters per kg.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 1997	Master's Thesis

4. TITLE AND SUBTITLE
A SYSTEM DYNAMICS MODEL OF THE BIOAVAILABILITY OF
METALS IN CONSTRUCTED WETLAND SEDIMENT

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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2750 P Street
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8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/97D-23

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
N/A

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
Constructed wetlands used for storm water treatment accumulate metals primarily in their sediment. This sediment has the potential to produce toxic effects in benthic organisms at some period in time. Bioavailability of metals in sediment is directly linked to pore water metal activity. The mechanisms that influence pore water metal activity are included in physical, chemical, and biological processes. A system dynamics model was developed to represent these processes and the major influences affecting pore water metal activity in a treatment wetland receiving storm water influent. The model structure and behavior was tested and validated using several system dynamics validation techniques. The model was run using the metals Pb, Cu, and Cd. The model indicated that the chemical processes of acid volatile sulfide (AVS) and organic carbon in binding metal in reduced sediment were the greatest influences in controlling metal bioavailability. The effect of bioturbation, as represented in the model, was negligible. Amount of organic carbon in the sediment seems to play the greatest role in controlling metal bioavailability in the long run. This model provides a platform for guiding future research in sediment toxicology, specifically in treatment wetlands.

14. SUBJECT TERMS
Models, Metals, Sediment, Wetlands, Bioavailability

15. NUMBER OF PAGES
147

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL