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Modeling Plant Uptake of Metal in Constructed Wetlands Supported by Experimentally Derived Uptake Rates

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THESIS

Michael B. Peake, 1st Lieutenant, USAF

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THESIS

Michael B. Peake, B.S.
1st Lieutenant, 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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Abstract

Many communities and Air Force installations are using constructed wetlands to filter trace metals from their stormwater runoff. Constructed wetlands are attractive to industry for runoff mitigation because they are relatively cheap to build and operate and require little or no energy for operation.

The purpose of this research project is to develop quantitative concepts for understanding the dynamics of metal uptake in constructed wetland plants by constructing a system dynamics model supported by experimental observation and offer environmental managers a tool to simulate, under a broad range of conditions, long-term wetland exposure to stormwater runoff contaminated with trace metals. There are two phases in this project, a modeling phase and an experimental phase. Greater emphasis was given to model development initially in order to determine aspects of the experimental design.

The results of the study indicate that metal can accumulate in wetland plants and sediment. Changes in different wetland parameters affect the rate at which metal accumulates in wetland plants and other components. A complete understanding of which wetland parameters to manipulate is essential for proper management of constructed wetlands for stormwater treatment.

MODELING PLANT UPTAKE OF METAL IN CONSTRUCTED WETLANDS SUPPORTED BY EXPERIMENTALLY DERIVED UPTAKE RATES

1. Introduction

The paradigm of wetland use is shifting. Wetlands once considered a nuisance are now commonly regarded as practical pollutant filters for urban and industrial runoff. In fact, many corporations and communities have begun to construct artificial wetlands in the absence of natural wetlands in order to filter polluted stormwater runoff. Constructed wetlands are attractive to industry for runoff mitigation because they are relatively cheap to build and operate and require little or no energy for operation (Dunbabin and Bowmer, 1992: 151). It is evident that to manage wetland systems properly with respect to the environment, quantitative understanding of how these systems work and how they react to anthropogenic disturbance is necessary.

Numerous researchers and government agencies offer several different definitions of wetlands. Defining wetlands is a complicated task. According to Kent, they are transitional habitats, neither terrestrial, nor aquatic, but show characteristics of both. Their boundaries may expand and contract over time as precipitation, evapotranspiration, and watershed volume change. Five systems are recognized: marine, estuarine, riverine, lacustrine, and palustrine. These are further divided into ten subsystems which are then divided into fifty-five classes based on substrate and vegetation type (1994:1). Section 404 of the Clean Water Act describes a wetland as an area inundated by water at a frequency and duration to support vegetation typically adapted to life in saturated conditions (Kent, 1994:6).

This broad definition paints a rather ambiguous illustration for a novice to wetland identification. Characteristics made quite clear in wetland literature, though, are the values and functions of wetlands. Wetlands not only act as natural purifiers, they attenuate flooding by absorbing, slowing, or storing flood waters headed for downstream property. Because of their unique location in transition between aquatic and terrestrial habitats, wetlands also support a tremendously diverse ecosystem of plants and animals. Plants and animals accustomed to land and those accustomed to water habitats cohabitate wetland systems, where both water and soil are abundant.

One of the many consequences of such a rich diversity is a wetland's ability attenuate natural and manmade disturbances. With such an attribute, wetlands appear to be robust and able to rebound quite easily. However, continued accumulation of these disturbances can eventually induce irreversible injury and degrade a system's ability to recover. Long-term accumulation of metals in wetland vegetation or sediment reduces widespread distribution in the environment, but concentrated sinks may eventually contribute to bioaccumulation and require intense recovery procedures or restrictions on the use of these lands (Hammer, 1989:16). As such, responsible management of these systems is necessary in order to conserve the natural order of the ecosystem. However, because wetland systems are so diverse and dynamic, it has proven difficult to create policies to preserve them.

From nearly the 1780's, wetland area in the United States drastically decreased from an estimated 392 million acres to 274 million acres for mainly the benefit of land development (Young, 1996:292). Beginning in 1972, Congress enacted laws which led to a wetland management strategy commonly referred to as a "no net loss" and mitigation strategy (Young, 1996:292). This strategy allowed developers to damage or destroy a natural wetland as long as they agreed to repair it to its original state or construct a new one where one had not previously existed. Hence, the United States has been in the wetland management strategy business for some time. Too often, however, the management objective was obscured.

In efforts to effectively manage wetland systems, understanding of the internal mechanisms of behavior of the entire system is crucial. Many constructed wetlands were built without such knowledge and subsequently failed to provide proper conditions for the wetland to survive (Young, 1996:292). Engineers and biologists are now coordinating their efforts and are slowly beginning to realize some of the intricacies hidden within wetland systems. Many of these recently discovered secrets make it possible to construct mathematical expressions to describe wetland processes. A collection of these expressions can be used to describe how wetland processes interrelate. These interrelations offer insight to the dynamics of the entire wetland. The method of collecting and combining expressions to study the interrelations and behavior of a system is called system dynamics modeling.

The field of environmental modeling has developed very rapidly during the last decade due to essentially two factors: (1) the development of computer technology, which has enabled us to handle complex mathematical problems, and (2) a general understanding of the pollution problems currently confronting society (Jorgensen, 1991:22). When models are used as a process integration tool, they do not contain all features of the real system itself -- otherwise a model would be unnecessary. However, when used properly to answer specific questions under certain conditions, a system dynamics model can reveal interesting, perhaps unforeseen behavior.

This research project accomplishes two tasks. It acquaints us with the metal uptake rates of specified plants common to constructed wetlands and it enables us to model these uptake rates based on experimental observations. There are two phases in this project, a modeling phase and an experimental phase. Both phases, for the most part, occur simultaneously. However, greater emphasis is given to model development in order to determine aspects of the experimental design. Several different parameters are addressed in the initial development. These include plant type, metal type, plant physiological parameters, soil characteristics, influent pollution concentrations, and others related to wetland dynamics. The study of these parameters and subsequent development of the model aid in the design of an experiment to support the model. This experiment ultimately produces metal uptake rates in a specified plant which are then used to describe plant metal uptake in the model.

Purpose Statement

The purpose of this research project is to develop quantitative concepts for understanding the dynamics of metal uptake in wetland plants by constructing a system dynamics model supported by experimental observation and offer environmental managers a tool to simulate, under a broad range of conditions, long-term wetland exposure to stormwater runoff contaminated with trace metals.

Research Objectives

(1) Determine model structure, parameters, and mathematical equations to describe the fate, transport and plant uptake of metal in a constructed wetland ecosystem.

(2) Experimentally obtain data for model parameters whose values cannot be taken from the literature.

(3) With the operational system dynamics model, ascertain long-term behavior of a constructed wetland exposed to stormwater runoff laden with trace metals.

Project Limitations

Several different variables and parameters must be addressed in the initial model development. These include plant type, metal type, plant physiological parameters, soil characteristics, influent pollution concentrations, and others. Those variables and parameters that cannot be taken from the literature must be found experimentally. The study of these variables and parameters and subsequent development of the model will aid in the design of the experiment to support the model. This experiment will ultimately produce metal uptake rates in a specified plant which can then be used to calibrate and verify the model once it is complete. It is important to note here that the model will be validated against the data obtained experimentally. Metal uptake in plants may be very sensitive to parameter value changes and any environmental manager wishing to use this model as a tool will need to adjust those variables and parameters and then revalidate the model against respective data. Although a wide range of characteristic plants and metals are presented in this model, stormwater contaminants and wetland vegetation vary by location and further adjustments may need to be made to obtain representative output. Finally, since the main emphasis of this project was given to model development, strict experimental guidelines were relaxed in some circumstances. These circumstances will be further discussed in Chapter 3.

2. Literature Review

A review of recent research in the United States concerning the roles of wetlands as sources, sinks, and transformers of heavy metals and other elements revealed that most wetland ecosystem research has not generated substantial information pertinent to addressing water quality functions of wetlands (Hammer, 1989:355). Many of the concepts presented were born under other areas of specialization and can also be found in other environmental or chemical modeling research. Wetland modeling happens to combine these concepts along with those of its own to describe wetland ecosystems. Specifically, the concepts pertinent to this project are wetland characteristics, hydrologic design, substrate characteristics, plant characteristics, metal behavior in a wetland system, and plant/metal interactions. Ultimately, all these concepts can be incorporated into a system dynamics methodology where all are investigated interdependently and system behavior can be studied.

Wetland Characteristics

Wetland classifications encompass bogs, swamps, and marshes. Those 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, 1989:6). Given the fact that many different types of wetlands exist, managers have often had to choose which type of wetland to imitate with a constructed wetland. Many have chosen to follow a bog or swamp design. However, swamps containing woody plants and trees may take up to twenty years to develop to full operation and moss in bogs is difficult to establish at all and has limited retention capacity. Therefore, most constructed wetlands emulate marshes. Marshes are typically dominated by emergent herbaceous plants including cattails, bulrush, grasses, and sedges which can adapt to fluctuating water levels and offer the most promise for water treatment (Hammer, 1989:13).

The actual presence or absence of water cannot be used as a sole indicator of a wetland ecosystem. Obviously, wetlands are not continuously dry lands, nor must they be continuously wet. Predominant types of wetlands can vary from one region to another based not only on water capacity, but also on soil and vegetation type. Vegetation often dictates local soil conditions. As water saturates wetland soil, oxygen is depleted in the soil pores and conditions appropriate for most plant growth terminate. At this point, only plants with special abilities to scavenge oxygen from other sources can survive. These plants are commonly called hydrophytes. The presence or absence of plants with the ability to grow in saturated or hydric soil conditions is a common indicator many experts use to delineate wetlands.

The ability of a wetland to provide runoff storage and detention enhances its ability to control pollutants. There are many physical and chemical responses by which a wetland can remove pollutants from stormwater (Kent, 1994:253).

Sedimentation. Sedimentation is the most important process by which particulates are removed from stormwater. Slower velocities and flow rates result in more sedimentation and pollutant removal.

Filtration. Particulates in stormwater can be obstructed by vegetation and thus removed by a filtering process. Filtration is promoted by reduced flow velocity and dense vegetation.

Adsorption. Dissolved elements can adsorb onto particulate matter by various chemical and physical reactions. Conditions such as longer retention and shallow water depth increase the opportunity for these dissolved elements to come into contact with particulates. Once adsorbed, the particle is subject to sedimentation or filtration.

Precipitation. Certain dissolved elements (such as metal) can form chemical precipitates and settle. Precipitation depends on a number of factors such as pH, oxygen content, and temperature.

Volatilization. Pollutants may also enter the atmosphere via evapotranspiration or aerosol formation. This process is effective for volatile organic chemicals such as oils and chlorinated hydrocarbons.

Microbial Decomposition. Microorganisms can use soluble organics and to some extent, fix inorganic elements. As they use oxygen, soils tend to become anaerobic which can facilitate precipitation.

Vegetative Uptake. Wetland plants are capable of nutrient, heavy metal, and organic chemical uptake. Uptake can occur from the soil through the roots and from the water column in dissolved form. These elements can also be released back into the water when the plant dies and decays.

All of these processes hold a different pollutant removal effectiveness based on site specific conditions; therefore, removal efficiency generalizations need to be made with caution. There is plenty of evidence to suggest, however, that a wetland can be designed to provide acceptable pollution removal for design specific conditions (Kent, 1994:254).

The ability of wetlands to capture and reduce pollution has earned them the nickname “nature’s kidneys” (Kusler and others, 1994:64). One specific management practice becoming more popular is the use of constructed wetlands as natural filters for anthropogenic pollutants. Many practices are in place which allow constructed wetlands to receive stormwater runoff. Among other pollutants in stormwater are trace metals. Very little consideration has been given to the effects these metals may bring about if these stormwater filtering practices are left unchecked. Heavy metals, in particular copper, lead, cadmium, and zinc, are among the most prevalent pollutants in urban and highway runoff. If left unmanaged, resulting long-term accumulation of these metals and ultimate damage to the wetland system is impending. Just how much damage will result is yet unforeseen and most likely depends on a number of criteria such as metal speciation, duration of storms, hydraulic retention time of the basin, soil and water chemistry, and vegetation type (Mesuere and Fish, 1989:125). Generally, acute effects of metal contamination in a wetland are not seen because concentrations of incoming stormwater are not high enough to be immediately toxic to any particular organism. The problem with stormwater runoff contamination with respect to wetland systems is its continued accumulation within the system. Continued accumulation increases the stress to a system and could eventually induce chronic effects such as decreased species diversity and biomass, altered biogeochemical nutrient cycling, altered trophodynamics, and changes in photosynthesis/respiration budgets (Catallo, 1993:2212). These chronic effects dictate a method of study be used to determine how long-term behavior of a wetland system is influenced by continued metal accumulation.

For the purpose of water treatment, natural or constructed wetlands exhibit five components: a substrate with varying hydraulic conductivity, plants adapted to saturated soil conditions, a water column, invertebrates and vertebrates, and an aerobic and anaerobic microbial population (Hammer, 1989:14). Although all components are important and necessary for the proper function of wetland ecosystems, this research will focus mainly on the substrate, plant, and water components. Uptake of metal by microbial populations and vertebrates and invertebrates is beyond the scope of this project and will not be addressed. However, it is important to realize that microorganisms can potentially play a large role in metal cycling in a wetland. Upon completion of this project, further investigation in this area is recommended.

There are several advantages and disadvantages of using constructed wetlands as filters for stormwater runoff. Advantages consist of the relatively low cost to build, maintain, and operate; relative tolerance to fluctuating hydrologic conditions; and ability to support a diverse wildlife habitat and pleasing aesthetic and landscaping properties. Disadvantages include improper design and operation; biological and hydrological complexity and lack of understanding of process dynamics; possible pest problems; and the requirement for a large land area for treatment (Hammer, 1989:16). Proper design relies, in part, on understanding of how hydrology, substrate, and vegetation interact.

Hydrologic Design

In 1987 and again in 1990, the Clean Water Act was amended to introduce requirements concerning non-point source effluent. These amendments require National Pollutant Discharge Elimination System (NPDES) permits to be obtained for discharges of stormwater. The regulations applied to municipalities with population over 100,000 served by separate storm drainage systems, industrial sites meeting any one of eleven industrial categories, and certain construction sites. Additionally, EPA is developing stormwater runoff regulations for communities with fewer than 100,000 people (Kent, 1994:244). With these new regulations came new stormwater treatment systems -- one of which is the use of constructed wetlands.

As constructed wetland technology is continually emerging, there are no strict rules of thumb for stormwater treatment design (Kent, 1994:256). The general purpose of a constructed wetland for water treatment is to hold the water while natural processes mitigate the contamination. In attempting to design a wetland for a specific purpose, one of the most important factors is the length of the hydroperiod. The hydroperiod is defined as periodic or regular interval of flooding and/or saturation (Marble, 1991:15). For the purpose of stormwater treatment, constructed wetlands are generally designed with a semi-permanently or permanently flooded hydroperiod. This allows the basin to retain surface water for all or most of the year, specifically during growing seasons when runoff volumes tend to be high.

Water retention and water flow retardation are important factors in a wetland designed to treat runoff. As water velocities decrease and retention times increase, the potential to remove pollutants improves. A wetland with a gentle gradient and constricted outflow will slow water flow and allow for maximum sedimentation time. Yet another method to retard water flow through a wetland is the use of dense vegetation which, in effect, forces the water through a longer, more tortuous path as it travels through the wetland (Marble, 1991:47). As a consequence of retarding and retaining water flows, designers must also consider the sediment load of the incoming and outgoing flows. If incoming loads continually exceed outgoing loads, the wetland water storage capacity will eventually decrease and loss in filtering efficiency will result (Marble, 1991:29). If the opposite is true, erosion of shoreline could potentially be a problem.

In general, constructed wetlands are combined with a group of other treatment processes to achieve specified management goals. Federal guidance regarding treatment types and designs is lacking partly because varying stormwater characteristics, poor understanding of wetland processes, and a general lack of knowledge and design guidance make treatment efficiency predictions of constructed wetland systems unachievable (Hammer, 1989:255). Therefore, many systems currently in place have been adapted to site specific conditions and take into account differing watershed areas and inlet and outlet sizes to improve removal efficiencies.

As a consequence of minimal federal guidance, many states have created their own wetland design criteria for stormwater treatment. Maryland, Florida, and Washington all assembled such legislation beginning in 1982. The following table illustrates and summarizes the concepts discussed above.

Design Criteria	Florida	Maryland	Washington
Runoff Volume Storage	1" above pool	1 year-24 hr storm or surface area	6 month-24 hr storm below pool; 100 yr storm
Hydraulic Residence Time	>14 days; all volume released >120 hr; half volume released > 60 hr	--	--
Depth	Shallow marsh 0.5 - 2' Deep pond <6 - 8'	6" (50% area) 6" - 1' (25% area) 3' (25% area)	6" (50% area) 0.5 - 1' (15% area) 2 -3' (15% area) 3' (20% area)
Surface Area	<70% open water	>3% watershed area	>1.5% watershed area
Side Slope	<6:1 to 2 -3' below permanent pool	--	<3:1
Short Circuiting	>3:1 length to width	>2:1 length to width	>3:1 length to width; 5:1 preferred
Soils	>6" depth	>4" depth	Use soil appropriate for species planted
Planting	Use native aquatic species	Use 2 aggressive species, 3 additional species; plant 30% of shallow area	Submit vegetation plan; use acceptable species which vary with depth or shoreline
Inlet Considerations	Use landscape retention areas and swales to promote infiltration; dissipate energy of entering water	Dissipate energy of entering water; use forebay to trap large sediments	Use oil spill control device or oil/water separator prior to forebay; use forebay
General Considerations	Provide capability to be completely drained	Use liner if needed to maintain pool level; include a frequently flooded area 10 - 20' from edge of normal water level	Use liner if needed to maintain pool level; use dense vegetation in forebay and near outlet to prevent erosion
Outlet Considerations	Use single or multiple stage control device; provide scour protection and emergency spillway for 100 yr storm	Site structure in deepest part of wetland; protect against outlet pipe blockage	--
Operation and Maintenance	Submit a plan; document species survival; remove nuisance species; remove trash, sediment; inspect vegetation; vary water level and control shoreline grass; maintain erosion	Remove accumulated solids in forebay and near outlet	Clean pretreatment devices; clean forebay once every five years or when sediment exceeds 6"; remove floatables annually; maintain shoreline to prevent erosion

Table 1.
Constructed Wetland Design Criteria Comparison

The Florida design criteria above are based on a wet detention pond and constructed wetland combination while Maryland criteria rest on a permanently pooled wetland concept. The Washington criteria are based on studies done on the east coast modified for local conditions (Kent, 1994:259).

Substrate Characteristics

Wetland soil is often described as hydric soil, soil saturated long enough during the growing season to develop anaerobic conditions in its upper parts (Mitsch and Gosselink, 1993:115). According to Mitsch and Gosselink, wetland soils are of two types: mineral or organic (1993:115). As one aspect of this research is concerned with metal transport and accumulation throughout the soil component of a wetland, chemical and physical properties of both mineral and organic soil are of interest. The following table compares the important mineral and organic physical and chemical properties commensurate with this research (Mitsch and Gosselink, 1993:117).

Property	**Mineral Soil**	**Organic Soil**
Organic Content (%)	Less than 20 to 35	Greater than 20 to 35
Bulk Density	High	Low
Porosity	Low (45 - 55%)	High (80%)
Hydraulic Conductivity	High (except clays)	Low to high
Water Holding Capacity	Low	High
Cation Exchange Capacity	Low, dominated by major cations	High, dominated by hydrogen ion
Typical Wetland	Riparian forest, some marshes	Northern peatland

Table 2.
Mineral and Organic Soil Comparison

These properties play a significant role in the behavior of metals in a wetland. It is apparent that the soil mixture in a natural or constructed wetland dictates to a large degree how a metal pollutant behaves once introduced to the system. Knowledge of this mixture is essential in order to effectively foresee any metal contamination problems. For instance, a highly organic soil will have a low bulk density and thus high porosity which allows it to hold more water. Depending on the hydraulic conditions, water can pass through at different rates. Organic soil also has a higher cation exchange capacity which makes it more favorable to metal reactions. A wetland composed of mainly organic soil then, gives the impression that it can become a more effective accumulator of metal than one containing mainly mineral soil. This may not necessarily be the case. Metal behavior within a wetland system is a function of many parameters, of which soil type is one. Vegetation type also plays an important role and is discussed below.

Plant Characteristics

One factor to consider when establishing a wetland system is whether to actively manage vegetation type and determine which species to plant or to allow naturally occurring vegetation to develop over time. Often, this debate is resolved by the decision of how fast the wetland needs to become operational. Regardless, little information exists about establishing vegetation in stormwater retention systems (Sediment and Stormwater Division, 1991:87). There is, however, information available on establishment of wetland vegetation for other purposes. Although there is evidence that underlying substrate influences vegetation type and distribution, the degree of influence is not clear. Other factors, such as water depth and temperature, turbidity, and competition from other species can also affect vegetation growing in wetland systems (Sediment and Stormwater, 1991:89). Furthermore, vegetation has the ability to modify the substrate in the root zone and rhizomes, the rhizosphere, by supplying oxygen and organic material. Thus, predominant vegetation type is often determined by a cyclical, interdependent relationship between substrate, water, and vegetation itself.

Many authors have attempted to delineate between shallow and deep water aquatic plants and terrestrial and semi-terrestrial plants. Little agreement has been reached and definitions often overlap. Hammer considers it simpler to include all these categories in a group labeled wetland plants (1992:33). Wetland plants are capable of growing in an environment continuously inundated for more than five days during the growing season. At one extreme, rooted, vascular plants may develop and survive in water depths of eight meters while at the other extreme, upland plants are only flooded, not necessarily yearly, for five days during the growing season. Plants are divided into rooted and floating forms. The rooted class can then be subdivided into emergent, floating, and submerged (Hammer, 1989:74). Whatever the classification, most research attention is commonly given to herbaceous, soft-stemmed plants rather than woody plants with rigid stems. Table 3 summarizes some of the plant species used in constructed wetlands (Mitsch and Gosselink, 1993:606).

Another important aspect related to vegetation in retention systems is its ability to influence water volume. Data from individual research studies conflict on whether vegetation increases or decreases water loss (Mitsch and Gosselink, 1993:100). The presence of vegetation retards evaporation from the water surface by offering shade, but disputes exist concerning whether loss through transpiration equals or exceeds the amount of water loss that would have occurred had vegetation not shaded the water. The point here is that vegetation can influence water loss in a constructed wetland. The degree of influence is determined by the type and quantity of vegetation as well as wetland classification. This is a significant design consideration when the purpose of the wetland is to treat stormwater runoff, as changes in water volume can change metal concentrations within the system.

Scientific Name	**Common Name**
Freshwater Marsh - Emergent	
Carex spp.	Sedges
Typha angustifolia	Narrow-leaved Cattail
Zinzania aquatica	Wild Rice
Freshwater Marsh - Submerged	
Elodea nuttallii	Waterweed
Vallisneria spp.	Wild Celery; Tape Grass
Freshwater Marsh - Floating	
Eichhornia crassipes	Water Hyacinth
Lemna spp.	Duckweed
Deepwater Swamp	
Toxodium distichum	Bald Cypress
Toxodium distichum var. nutans	Pond Cypress
Salt Marsh	
Spartina alterniflora	Cordgrass (eastern United States)
Spartina patens	Salt Meadow Grass

Table 3.
Selected Plant Species in Constructed Wetlands

As mentioned previously, vegetation also has the ability to influence system hydrology. Dense vegetation interferes with water flow velocities through the wetland and can dissipate inflow and outflow energies. As a result, turbulence is reduced and sedimentation increases. Rooted, emergent plants also stabilize the soil by physically binding it together with their root systems and by preventing erosion (by decreasing flow velocity) and subsequent export of particulate matter (Dunbabin and Bowmer, 1992:158).

Many studies have shown wetland plants exhibit the ability to absorb trace metals from stormwater runoff. Experiments performed in lakes and streams confirmed that concentrations of trace metals can be more than 100,000 times greater in plants than in the water (Albers and Camardese, 1993:959). Since wetland acidity can differ from that of lakes or streams, Albers and Camardese studied how metal concentrations might change by acidification in constructed wetlands. Their results indicated that little or no change in metal concentration was seen in wetland plants (1993:965). Another study performed by Gonzalez, Lodenius, and Otero declares similar results. Metal concentrations in water hyacinth growing in the Sagua la Grande river basin near a chlor-alkali plant and other industrial plants differed by location. Highest concentrations were found in the zone situated near Sagua city which receives urban and industrial runoff while the lowest concentrations were found upstream of the city. Water hyacinth downstream contained less metal than within the city zone but still indicated influence of pollution from city runoff (Gonzalez and others, 1989:911). These studies suggest that high potential exists for plants in constructed wetlands receiving metal laden stormwater runoff to accumulate large amounts of metal.

Ability to accumulate metal has a corollary. Although using wetland plants to intercept metal before it enters streams, lakes, or other water supply is an effective management practice, scenarios exist in which continued accumulation could become toxic to the plants. At this point, or likely just prior to this point, plants will cease to accumulate metal and possibly die. In either situation, though the latter could be more drastic, the efficiency of the wetland to remove metal from stormwater will diminish and the metal removal management practice will effectively fail. Toxicity assessments must be accomplished in order to ascertain the wetland plants will not succumb to metal accumulation. Many short-term assessments have been performed both in the laboratory and field and they offer reliable guidance. For instance, one assessment suggests that phytotoxicity tests be performed on runoff water samples to determine at what point the metal concentration becomes toxic. Samples can range from extremely toxic to slightly non-toxic and a pre-treatment industrial wastewater toxicity standard can be set at 61% of the perceived inhibition effects (Wang, 1990:109). This study and many like it prescribe how much metal a plant can accumulate before toxicity sets in and offer sound direction for short-term stormwater treatment. However, because these treatment practices are relatively new, no long-term studies have been accomplished. Long-term studies are necessary in order to determine chronic plant effects from metal accumulation as well as overall wetland behavior when exposed to metals for a period of decades. A system dynamics approach can incorporate wetland functions with stormwater metal effects and offer considerable foresight here. System dynamics modeling will be discussed later.

Metal Behavior

Many communities and Air Force installations are using constructed wetlands to filter organic and inorganic pollutants from their stormwater runoff and included among these pollutants are various types of metals. Sedimentation of these metals from the stormwater to the wetland bed appears to be the primary filtering process (Mesuere and Fish, 1989:125). Research indicates that these metals can accumulate in plants growing in constructed wetlands and in the solid matrix of decaying organic matter and soil. From 1978 to 1983, fifteen trace metals, among other pollutants, were studied during EPA's Nationwide Urban Runoff Program (NURP) project. Of these fifteen metals, copper, lead, and zinc were found in over 90 percent of the sites monitored. The following table presents the metal results from the NURP project (Sediment and Storm water Division, 1991:30).

Metal	Frequency of Detection(%)	Concentration Range(µg/L)
Antimony	14	6 - 23
Arsenic	58	1 - 50
Beryllium	17	1 - 49
Cadmium	55	0.1 - 14
Chromium	57	1 - 34
Copper	96	1 - 100
Lead	96	6 - 460
Mercury	16	0.5 - 1.2
Nickel	48	1 - 182
Selenium	19	2 -77
Silver	12	0.2 - 0.8
Thallium	10	1 - 14
Zinc	95	10 - 2400

Table 4.
Metals Results of the Nationwide Urban Runoff Program Study

The concentrations reported in the table above are given for total metal in the stormwater runoff. It must be noted that metal can be in different forms in the runoff. Specifically, metal can be in dissolved or particulate form. Further research done on the NURP metals in four different sites indicates that approximately 30% of the total copper and 20% of the total lead are dissolved. These percentages are strongly controlled by the amount of suspended solids in and the alkalinity of the runoff -- making adsorption of metals to suspended particles a key factor (Paulson and others, 1992:53). Thus, site specific conditions determine exactly how much metal is in the dissolved or particulate form.

Although many of these metals are essential in certain quantities for life, many others can cause toxic effects from seemingly minor exposure. All of these metals are toxic to aquatic life at low concentrations and exhibit potential to concentrate in the food chain. Copper is an essential element for life but excessive intake by mammals can result in accumulation in the liver. Lead can also accumulate in the liver and lead to loss of permeability of kidney, liver, and brain cells. Excess amounts of zinc cause metabolic dysfunction and although cadmium was not found in high concentrations in the NURP study, it is important by nature of its toxicity and ability to concentrate in the environment (Sediment and Stormwater Division, 1991:12). Sources of these metals encompass common, everyday practices. According to the Maryland Sediment and Stormwater Division, copper enters the watershed through the corrosion of copper plumbing, electroplating wastes, algicides, and oil and coal combustion. Lead primarily enters via combustion of gasoline, although this source has significantly decreased since the introduction of lead free gasoline. Lead based paints, stains, and pigments are other sources of lead. Zinc is also associated with roadway traffic as a common ingredient in road salt and a component of automobile tires. Cadmium is released into stormwater from the corrosion of alloys and plated surfaces, automobile tires, and from electroplating wastes (1991:12).

If metals such as these are allowed to accumulate in constructed wetlands, at some future time, the wetland plants and sediment will become toxic to organisms living in that wetland ecosystem. The danger from some of these metals is amplified by their persistence in the environment. For example, lead, a very persistent metal, has an estimated soil retention time from 150 to 5000 years (Kumar and others, 1995, 1232). Additionally, the estimated half-life of cadmium in soils varies between 15 and 1100 years, making cadmium pollution in soils potentially hazardous over an extended period of time (Yang and others, 1995:570). Scientists have researched the ability of metals to accumulate in plants, but very little research has been done to determine the rates at which metals are accumulated or the dynamics of such a process. The complexity of wetland processes and the difficulty in modeling these processes require integration of many specialized disciplines to understand and develop models that accurately reflect wetland behavior (Dixon and Florian, 1993, 2281). Subsequently, few general models exist to predict metal removal rates in constructed wetlands.

Common stormwater metals, such as those in Table 4, exhibit different properties when in an aquatic environment. Consequently, a wide range of metal behavior and plant uptake can be exhibited. For instance, literature suggests that lead has a tendency to bind tightly with soil and relatively low amounts of it actually get transported in plants (Kumar, et al, 1236). Copper, on the other hand, remains mostly dissolved in stormwater runoff and thus exhibits a greater phytoavailability where plant uptake is concerned (Mesuere and Fish, 1989:131). There are several reasons why each metal behaves differently in a particular wetland. Behavior depends, in part, on factors such as metal speciation at the time of input, water and soil chemistry, storm duration and intensity, and hydraulic retention time (Mesuere and Fish, 1989:125). Within a wetland, metal species are distributed in several different forms ranging in mobility and toxicity. The main pools are located in the subsurface, in colloidal material, in suspended particulate matter, and in the water column existing as a soluble fraction of hydrated ions and complexes (Dunbabin and Bowmer, 1992:152). According to Dunbabin and Bowmer, the majority of metal present in an aquatic ecosystem is found in the bottom sediments and in suspended particulate matter (1992:152). Metals can also be bound with a variety of organic matter via cation exchange, adsorption, precipitation, and complexation. Adsorbed, precipitated, and complexed metals are all considered bioavailable because they can be released back into solution, whereas metals bound by cation exchange are incorporated into mineral lattices and are considered unavailable. For these reasons a measure of concentration within the system cannot adequately reflect potential for plant uptake and toxicity (Dunbabin and Bowmer, 1992:153).

Soil conditions play a large part in metal behavior. Ordinarily, wetland soils are reduced and organically rich. The high organic content is the result of primarily decomposed plants that have accumulated in the wetland as a result of standing water (Mitsch and Gosselink, 1993:117). A wetland with highly organic soil has greater potential to bind metals through cation exchange, a process in which positive ions exchange sites between soil lattices and between soil and water. Reduced conditions are created as a consequence of water saturation, where water replaces air in the void spaces within the soil. This creates only a very thin boundary layer (1 to 5mm) at the soil/water interface that has adequate oxygen to maintain aerobic conditions (Hammer, 1992:30). Saturation and loss of oxygen also causes wetland soils to have negative oxidation-reduction potentials. Low oxidation-reduction potential combined with pH effects generally make wetland systems a reducing environment. As a reducing environment, wetlands are capable of being sinks for trace metals.

Often, water conditions are controlled by underlying sediment conditions and to the same extent, water conditions also determine metal fate within the system. Solution acidity, reducing power, salinity, and ligand concentration all affect metal behavior. With few exceptions, soluble metals dominate in acidic, low alkaline solutions with low amounts of suspended solids. Less soluble metals tend to favor neutral to alkaline, oxidizing conditions (Dunbabin and Bowmer, 1992:154).

It is apparent that a myriad of physical and chemical conditions determine metal fate in wetlands. These conditions vary in magnitude from one system to another, but generally, the conditions discussed above are the main drivers for metal accumulation in a wetland. Table 5 suggests the effectiveness of using wetland systems, either natural or constructed, to remove trace metals from stormwater runoff and why communities have begun to favor these systems over more expensive physical or chemical treatment systems (Kent, 1994:255).

Plant/Metal Interactions

Plant uptake of a solute depends on plant, soil, and soil water factors. Methods for predicting uptake should therefore account for interactions between these media. A great deal of research has been done regarding plant uptake of solutes. Many researchers describe uptake with mathematical equations. When it comes to metal uptake, most researchers default to using diffusion equations to describe metal incorporation into the plant root. For instance, Richard Corey states that trace metals move to the plant root through the soil primarily by diffusion, and therefore, diffusion equations should be used to describe uptake if all relevant variables are known (1983:443). However, the possibility exists that diffusion alone is not the only transport mechanism.

Wetland	**Monitoring Program**	**% Removal**		
Constructed		**Copper**	**Lead**	**Zinc**
DUST March, Freemont, CA	11 storms 17 months	31	88	33
Tampa Office Pond, Tampa FL	20 storms 2 years	-	-	33
McCarrons MWTA, Roseville, MN	25 storms 21 months	-	75	-
Orange Co. Orlando, FL	11 storms 2 years	-	81	62
Natural				
Island Lake, Orlando, FL	5 storms 2 years	87	83	67
Swift Run Wetland, Ann Arbor, MI	6 events 6 months	-	50	-
Wayzata Wetland, Wayzata, MN	multiple 1 year	73-83	90-97	78-86

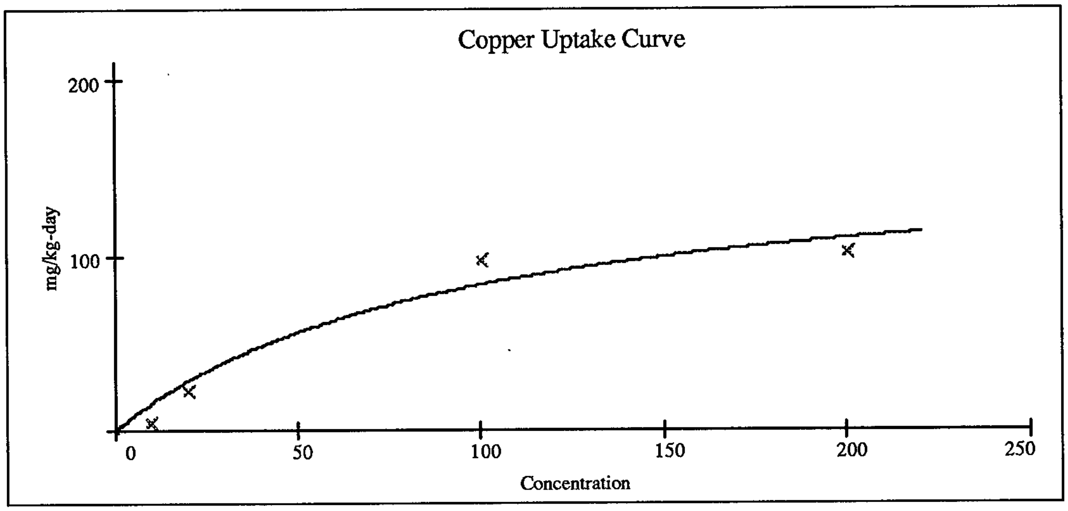
Table 5.
% Metal Removal in Constructed and Natural Wetlands

Barber and Claassen state that ion flux through the soil to the root occurs by diffusion and mass flow together and uptake of metal by the root depends on the metal ion concentration at the root surface (1975:358). More simply, only the metal ions that reach the root by mass flow and diffusion through the soil or those that the root moves to as it grows are available for uptake. If mass flow moves metal ions to a root faster than the root can absorb them, metal will accumulate around the root. On the other hand, if mass flow moves metals to the root slower than they can be absorbed, the metal concentration around the root is reduced to a lower level than originally present and a concentration gradient is established. Diffusion to the root occurs along this gradient. In such a fashion, mass flow and diffusion act simultaneously (Barber and Claassen, 1975:359).

Barber and Claassen developed a model to simulate metal uptake by plants. The model was based on radial flux of the metal through a thin-walled cylinder of soil surrounding the root. Parameter values of interest in this model consisted of the soil diffusion coefficient, concentration of metal in solution, root radius, initial root length, root growth rate, and the root uptake relation. The root uptake relation in the model was described as a rate limited process -- meaning that some theoretical maximum uptake value was approached as the concentration of metal around the root increased indefinitely. Such a technique allowed uptake to vary with the metal ion concentration in solution at the root surface. In this case, the uptake relation was defined with a Michaelis-Menten equation. The equation has three variables: Umax, the maximum uptake rate value; Km, the solution concentration corresponding to one-half Umax; and C, the metal ion solution concentration. Specifically, a Michaelis-Menten uptake equation can be given by:

$$\mathrm{Uptake} := \frac{\mathrm{Umax} \cdot C}{\mathrm{Km} + C}$$

Figure 1 shows a typical Michaelis-Menten uptake curve. Here, a maximum uptake rate of approximately 160 mg/kg-day is approached. The half-saturation constant, Km, is approximately 92 mg/L.



concentration in mg/L

Figure 1.
Typical Michaelis-Menten Uptake Curve

Barber and Claassen tested their uptake assumptions and model and acquired a high correlation ($r^2 = 0.87$) between predicted and observed uptake of potassium from four soils. Further tests were conducted to predict zinc uptake using parameter values taken from the literature. Once again, the predicted metal concentrations in the plant agreed with experimental results reported in the literature.

Conclusions made by Barber and Claassen, that metal uptake by the roots can be represented with Michaelis-Menten kinetics, invite further study of metal uptake. Given that root uptake is a saturable process, questions arise regarding many other things, including uptake efficiency, plant toxicity, and ecosystem effects. This project investigates some of these new questions.

Once nutrients, or metals in this case, are collected by the root system, some mechanism must move them into the rest of the plant. This mechanism is can be represented by Poiseuille's Law, which describes the volumetric movement of a fluid through a cylinder (Nobel, 1991:508). Nobel states that the volume of fluid moving along a cylinder is proportional to the fourth power of the cylinder radius and depends on changes in hydrostatic pressure within the cylinder (1991:508). The equation describing volumetric flow within a cylinder is given as:

$$\text{Flow} := \frac{-\pi \cdot r^4}{8 \cdot \eta} \cdot \frac{dP}{dX}$$

where r represents the cylinder radius, η represents fluid viscosity, and dP/dX represents the negative gradient of the hydrostatic pressure.

System Dynamics Modeling

Wetland modeling developed in the 1970's when sufficient data on wetland functions became available. Since then many wetland models have been published as knowledge and interest in the field became more prevalent (Mitsch and others, 1988:2). Of the published models, many address different aspects of wetland processes. Some focus on hydrology while others focus on biologic activity and production. Still others attempt to summarize large scale dynamics for wetland management.. The complexity of a model is often up for debate. Some argue that a more complex model should account for reactions in the real system, but this is not always true. Often a complex model contains more parameters which must be estimated or derived experimentally. These parameter values introduce a level of uncertainty that may not be acceptable. The most difficult component of modeling is deciding which parameters must be included and which can be left out without affecting system behavior (Jorgensen, 1991:23).

There are many schools of modeling based on unique techniques. They include linear programming, econometrics, stochastic simulation, and system dynamics modeling

(Randers, 1980:23). The underlying associations in each school are important and more or less determine how the modeling should be done and what results should be expected. Given that, one type of model may be appropriate for a given circumstance while another may not.

In the case of wetland modeling, system dynamics modeling may be the most appropriate to describe the extremely complex behavior exhibited by wetlands. Systems dynamics is a method of addressing questions about the dynamic tendencies of a complex system and the behavior it generates over time (Randers, 1980:31). By their nature, system dynamics models are commonly used at the general understanding stage of decision making. Relationships are often intuitive and easily understandable (Randers, 1980:34). As such, system dynamicists ordinarily are not preoccupied with exact numerical values of system variables at specific times. The general dynamic tendency of the whole system is of much more interest.

The underlying framework of system dynamics is the assumption of cause and effect relationships, i.e. two-way causation or feedback. Cause and effect feedback attempts to construct a boundary around a set of elements, the system, such that the cause of the behavior exhibited lies within this boundary. In essence, any behavior exhibited by the system is caused by an internal system element, not an exogenous variable. System dynamicists are commonly faced with the decision of which variables are internal to the system and which are external. The quest is to choose the simplest set of variables that can explain the system behavior. It is this causal structure framework concept, that the system as a whole exerts certain behavior, which commands this research.

3. Method

In order to effectively narrow the scope of this project and subsequently render the model more relevant, specific model structure, model parameters, plants, and metals must be considered. The ensuing discussion is devoted to the methods used in the modeling and experimental phases of this project. Explanations are given to defend model structure, parameter values, and experimental materials and techniques. Complete model diagrams and code are given in Appendix 1.

Wetland dynamics are very complex and vary from site to site. The parameters described below pertain to a hypothetical constructed wetland exposed to stormwater runoff contaminated with trace metals. Accordingly, many assumptions have been made to facilitate model construction. Special warrant is given to readers to understand the assumptions made in this design, recognize the hypothetical site specific conditions, and ascertain whether or not the model can be applied to their situations.

Modeling Phase

The intent of this model is to offer insight into the dynamics of metal uptake in wetland plants and offer environmental managers a quantitative understanding of behavior of wetlands chronically exposed to stormwater contaminated with trace metals. Consequently, the constructed wetland represented by this model must be characterized. Wetland compartments, flows between compartments, and parameter values used in this project correspond to a hypothetical wetland design. This design is typical of many wetland systems and model output is representative of typical behavior of wetlands with the similar parameter values.

Another important factor to consider in the model development and subsequent output analysis is the time horizon of interest. Since acute metal effects will most likely not be seen, effects produced by long-term, low concentration exposure are the focus of this model. Thus, a time horizon of between ten and twenty years is used. Such a time horizon allows behavior study, under certain conditions, over a period of time comparable to the lifespan of any long-term management practice.

In all cases, the hypothetical values for model parameters were taken from the literature. The model consists of three general sectors with respect to parameter estimation: wetland parameters, plant parameters, and metal uptake parameters. Figure 2 illustrates the conceptual structure of the model. In essence, the model is a collection of wetland compartments and flows between compartments. The compartments represent the surface water, sediment, soil water, and plant components of a wetland.

Wetland Parameters. The hypothetical model design incorporates a sediment bed of specified depth. The porosity in this bed can range from highly mineral (45 - 55%) to highly organic (80%). The extent of porosity determines the volume of soil and volume of water in the subsurface. The hypothetical wetland is also bound beneath by a clay liner to deter subsurface water from migrating to and prevent recharge from the groundwater aquifer. This is a typical design characteristic of constructed wetlands.

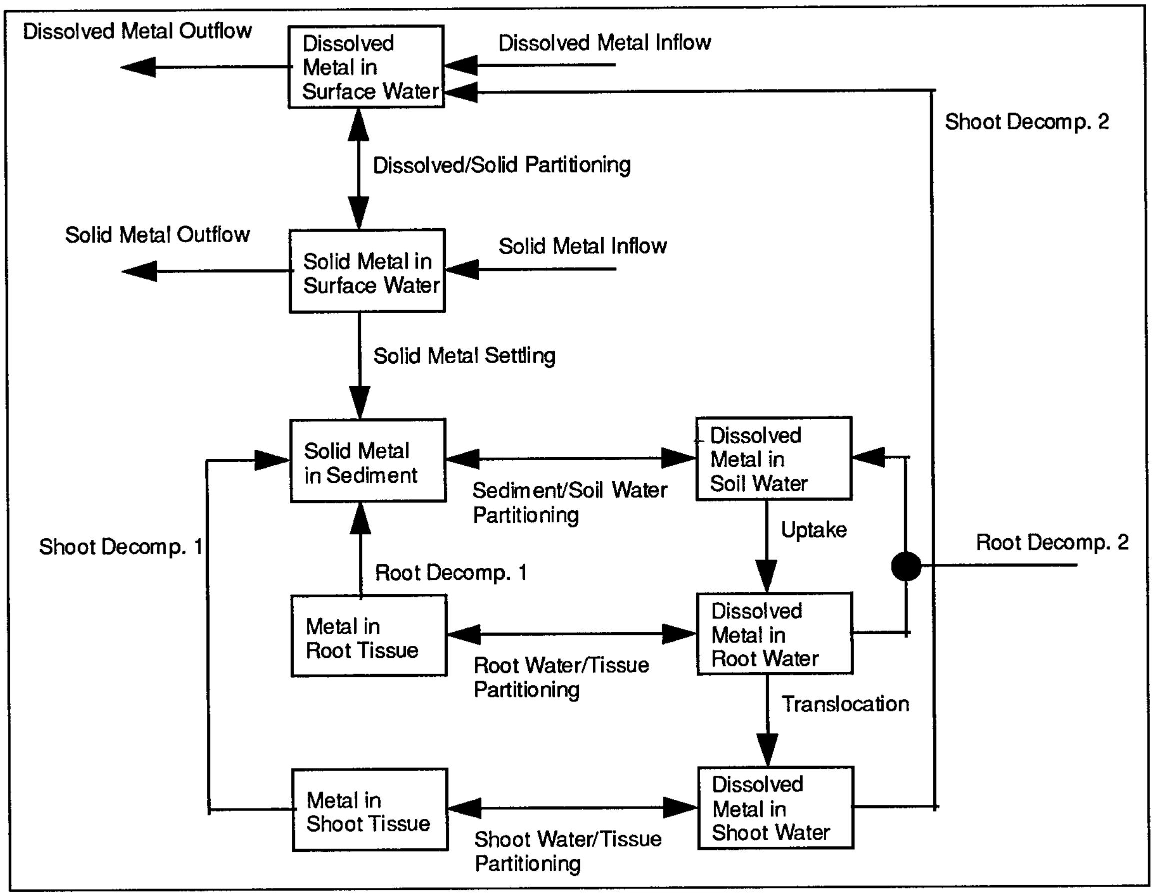


Figure 2.
Conceptual Model Structure

As stated previously, hydrology within a wetland system is a very important factor in determining overall system behavior. As such, water volume, evapotranspiration, precipitation, stream inflow and outflow, and soil porosity all require attention. In this design, surface water volume is controlled by four flows: influent, effluent, precipitation, and evapotranspiration. Influent is described by average stream channelized flow where the amount of water entering the wetland is the product of average stream velocity and stream cross sectional area (Mitsch and Gosselink, 1993:87). This flow takes into account the assumption that the wetland is fed by a stream which accumulates runoff from the surrounding community or Air Force installation. The surface water effluent rests on the same channelized flow concept as the influent. Here it is assumed that a stream approximately the same size as the inflow leaves the wetland and feeds a downstream water source such as a lake or river. The effluent is a function of water depth within the wetland. This function implies that until some maximum water depth is reached, no water will flow out of the wetland. This type of design is characteristic of many retention systems where the wetland is used to hold or slow water flows headed downstream. Once the maximum depth, and thus maximum volume of the wetland, is breached, water flow out of the wetland will approximately equal the difference between the evapotranspiration rate and the precipitation rate and water flow into the wetland.

Precipitation and evapotranspiration also control the surface water volume. The precipitation rate is taken from Mitsch and Gosselink and is indicative of average annual precipitation over the Great Lakes Coastal Marsh in northern Ohio (1993:78). The precipitation value is multiplied by wetland surface area to account for water added by precipitation over the entire wetland. Evapotranspiration is represented as a fraction, specifically 0.8, of the pan evaporation rate of a nearby open area (Hammer, 1989:26). Arguments exist that debate whether or not evapotranspiration increases or decreases with vegetation density. One side argues that more vegetation increases the total amount of transpiration and the other side argues that more vegetation decreases evaporation by offering more shade. For the purpose of this model, and considering the time horizon, magnitude changes in evaporation and transpiration caused by varying vegetation density are assumed to cancel each other out. The evapotranspiration rate is simply multiplied by the wetland surface area to account for water loss over the entire wetland.

The remaining wetland parameters are also site specific and can be changed to allow the model to represent a variety a different sites. For instance, retention time dictates to some extent how much particulate metal settles to the sediment. Intuition dictates that a longer retention time will allow more particulate metal to settle. Hammer suggests that typical wetland retention times vary from six to fourteen days (1989:334). Retention time is defined as the quotient of the water volume and effluent. As such, retention time is also a function of area. Given the same flow rates and water depths, a wetland with a larger surface area will have a longer retention time than one with a smaller surface area. Wetland area determines the magnitude of total precipitation and supportable plant biomass and thus total evapotranspiration. Hence, the size and shape of a wetland can determine how efficiently it performs its intended function. Size and shape are often determined by specified treatment volume and design guidance. Generally, design volumes coincide with retention times. Increased retention time usually indicates a larger treatment volume. Dimensions for the treatment volume are often determined by state guidance. Maryland and Florida wetland design standards specify a 2:1 length-to-width ratio for constructed wetlands (Hammer, 1989:257,260). These size and shape concepts are employed in the construction of this hypothetical model.

Plant Parameters. Attention is given to vegetation mass because it is a principal controlling factor on how much metal will be removed from the stormwater flow. The standing stock of plant biomass in this hypothetical design is governed by population dependent growth and death rates. Each rate is the product of a constant fraction multiplied by the existing biomass stock. Thus, as the amount of plant mass increases or decreases, the growth and death rates increase or decrease accordingly. The hypothetical vegetation mass is based on a maximum of ten kilograms per square meter (Smekrud, 1994:103). The root and shoot masses are described as fractions of the living vegetation mass. The respective fractions were determined from experimental dry weights. Since plant roots and shoots are composed of water and plant tissue, fractions of water and plant tissue within the roots and shoots were also determined experimentally. These fractions allow for breakdown of root and shoot mass into water and tissue components.

Metal Uptake Parameters. The parameters describing actual metal uptake in the plant biomass coincide directly with the wetland and plant parameters. The metal uptake parameters are divided conceptually into surface water, subsurface water, sediment, and plant compartments. As discussed previously, metal in the surface water, depending on the site conditions, can either be in dissolved or particulate form. Total metal in the surface water is controlled by seven flows: a mass inflow and outflow from both the dissolved metal and particulate metal stocks, a metal return from decomposing shoot biomass, an equilibrium relation between the dissolved and particulate metal stocks, and a settling flow from the particulate stock. The mass inflow and mass outflow rates for both the dissolved and particulate stocks are simply products of the influent and effluent rates described above and the respective dissolved or particulate stormwater and surface water concentrations. The equilibrium relation between the dissolved and particulate stocks accounts for partitioning between dissolved and particulate phases as site conditions vary. Possible conditions that could affect metal speciation in the surface water are changes in pH and alkalinity and changes in the amount of suspended solids. In each instance, the partitioning will be affected differently. The partition constant chosen for this model represents only one of many different possible situations. The particulate settling velocity is defined for a small (< 4 μm) clay particle which has a very slow settling velocity (Sediment and Stormwater Division, 1991:44). This allows a conservative approach to capturing all particles with settling velocities equal to or greater than this clay particle. The settling velocity is then multiplied by the product of the particulate metal concentration and wetland area. This flow represents metal settling to the sediment bed.

Metal in the sediment is governed by how much particulate metal settles from the surface water, how much metal partitions to the soil water, and how much particulate metal returns by decomposing root and shoot biomass. Here, it is assumed that the sediment and soil water are in an equilibrium state. An equilibrium partition coefficient governs the equilibrium partitioning between the media. Metal returning from the roots and shoots is controlled by the decomposition of plant material. Over the model time horizon, plant biomass will grow and decay. As it decays, metal incorporated into plant tissue will be released back into the sediment.

Dissolved metal in the soil water is controlled by partitioning between sediment and soil water, metal taken up by the root system, and metal returned from decomposing roots. As discussed in Chapter 2, metal taken up by the root system is described with Michaelis-Menten kinetics. The relation is governed by essentially two variables -- Umax, which defines the maximum uptake rate, and Km, which defines the concentration at which half-saturation occurs. These values were obtained from the experimental phase for *Zinzania aquatica*, wild rice. The entire Michaelis-Menten term is additionally multiplied by the existing root mass to account for uptake across the entire wetland. The flow returning dissolved metal from decomposing roots to the soil water is similar to the flow returning particulate metal to the sediment (as described above) but here, only metal dissolved in the water within the root is returned to the soil water.

Metal in the water within the roots is controlled by metal taken up from the soil water, metal returned to the soil water via decay, metal partitioning to root tissue, and metal translocated to the shoots. Very little, if any, literature exists about actual metal partitioning between plant water and tissue. Therefore, partitioning between root water and root tissue was estimated from the understanding that lead is a relatively immobile metal in the plant while copper is relatively more mobile. Here the assumption is made that lead is immobile solely because it is bound to the root tissue and not dissolved in the root water. The opposite assumption is made for copper. Partition constant estimations rest on these assumptions. In order to achieve these estimations, model runs were accomplished using differing values for the constants until the root and shoot metal concentrations were consistent with experimental observations. By doing so, the model is restricted to conditions involving specific metals and specific plants. For other plants, metals, and conditions, new values of the partition constants are warranted.

Translocation of metal from the roots into the shoots is described with a mass flow governed by Poiseuille's Law. It is simply represented as the product of Poiseuille's volumetric flow and metal concentration in the water within root. This term is then multiplied by the total number of plants within the wetland to account for translocation in all wetland shoots.

Metal in the plant shoots is governed very much the same way as it was in the roots. Dissolved metal enters the shoots via the mass flow described above. Partitioning occurs between the shoot water and shoot tissue. In the absence of harvesting practices, metal in the shoots remains until the plant dies. As the plant dies, metal incorporated into the shoot tissue returns to the sediment and metal dissolved in the shoot water returns to the surface water. It is important to note here and with the root metal return that the metal does not return to the subsurface instantaneously. Metal returns via microbial decay and other processes over an extended period of time. Given the model time horizon, this assumption does not appear to detract from the model.

Once the values from the experiment are entered into the model code, model behavior can be verified. Once the model is operational, baseline output cases will be used to study how the hydrology and plant biomass components behave. Further model runs and analysis will provide information about how and where metal accumulates in plants and other wetland compartments over different time horizons. These runs will incorporate varying wetland parameters such as stormwater runoff metal concentration, wetland area, and influent rate. Finally, the model will be run at extremely long time horizons to determine if any latent behavior exists in the wetland system that would otherwise not be seen in the shorter time horizon runs.

Experimental Phase

The experiment was designed to provide certain parameter values for the model. Most importantly, two Michaelis-Menten variables were determined, Umax and Km. Other important variable values such as soil/water partitioning constants, the fractions of water and plant tissue within the roots and shoots and root-to-shoot biomass ratio were also determined. Research and modeling time constraints dictated that this experiment be kept as simple as possible while still delivering sound data. Table 6 summarizes the equipment and materials used in the experimental phase of this project.

Essentially, five containers of plants, including one control container, were grown, subjected to varying concentrations of metals, harvested over a specified length of time, and analyzed for metal uptake. Water and soil samples were also taken from each container over the same time period. This time course data was then analyzed and concentration specific uptake rates were determined. The discussion below describes the methods used in each stage of the experiment.

Equipment/Material	Manufacturer	Model Number	Serial Number
Plastic Container	Small Pal	2 gallon	--
Wild Rice Seeds	Wildlife Nurseries, Inc.	--	--
Soil	--	Wright State University Research Wetland	--
Copper Acetate	Aldrich Chemical Co.	MF 05523LF	--
Lead Acetate	Aldrich Chemical Co.	BG 05821AG	--
Nitric Acid	Fisher	A-200 Reagent, ACS	169856
Laboratory Oven	Thelco	3M-9700	502155
Polypropylene Centrifuge Tubes	Elkay Products	50 mL, screwcap	--
Magnetic Stirrer	PMC	525A, 12.2 amp	1079
Magnetic Stir Bars	Spinbar	F37110-x	--
Plastic Syringe	Monoject	60 cc	--
Disposable Pipets	Falcon	7551 Serological, 10 mL 7520 Serological, 1 mL	-- --
Glass Fiber Filters	Gelman Sciences	A/E 124 mm	--
Atomic Absorption Spectrometer	Perkin Elmer	3030B	012553 University of Dayton
Analytical Balance	Ohaus	AP250D	1113270180

Table 6.
Equipment and Materials Used

Growth Stage. Soil for each container was taken from the Wright State University Research Wetland. The wetland soil appeared highly organic. However, there was a small fraction of clay present. This clay fraction caused the soil to adhere to the roots and made root washing and analysis difficult in the trial runs. Thus, in order to facilitate soil removal from the roots in later experiments, a 3:1 sand-to-wetland soil mixture was used in each container. The added sand decreased adhesion to the roots. Approximately 2600 cubic centimeters of sand/soil mixture and three liters of water were added to each two gallon plastic container.

Although there are many varieties of plants, certain plants share similar characteristics. This is the case with many wetland plants. Two types of aquatic plants exist, rooted and floating. According to the Maryland Sediment and Stormwater Division, metal pollutants tend to accumulate in the upper fifteen centimeters of sediment (1991:43). Since most metal pollutants in wetlands tend to accumulate in the upper layers of soil and since most metal uptake is accomplished in the rhizosphere, rooted, anchored aquatic plants were modeled. Thus, a similar plant type needed to be chosen for the experiment.

Wild rice, *Zinzania aquatica*, was chosen as the experimental plant because it is a typical rooted, anchored wetland plant and because it is a simple, vascular, herbaceous plant -- characteristics that facilitate analysis. Wild rice seeds were acquired from Wildlife Nurseries, Inc. in Oshkosh Wisconsin. Each container was planted with forty seeds, of which, approximately 50% germinated. The germinated plants were allowed to grow for seventy-one days before dosing. At this point, the plants were approximately thirty inches tall.

Dose Stage. As discussed previously, plant/metal interactions depend a great deal on site specific conditions. Also discussed earlier were the characteristic metals in stormwater runoff. These metals have different interactions with plants. Dunbabin and Bowmer found that, under contaminated conditions, some metals are not readily mobile within the plant while others are easily transported through the xylem (1992:155). Different plant/metal interactions call for different management practices. For instance, if a metal is readily mobile, frequent harvesting may be employed to remove the metal from the ecosystem. If a metal remains fixed in the rhizosphere, frequent harvesting would more than likely be a waste of time and money. This experiment determines interactions for two differently mobile metals, copper and lead. In a study observed by the Maryland

Sediment and Stormwater Division, copper showed relatively small differences, compared to lead, in root and shoot concentrations indicating that it moves through the xylem willingly -- possibly because it is an essential plant nutrient. Lead on the other hand showed the lowest relative concentrations in above ground parts which indicates it tends to remain fixed in the root system (1991:50). Experimental results from these two metals, used properly in the model, will offer managers more insight into correct management practices.

In order to construct the Michaelis-Menten curve discussed in Chapter 2, a wide range of concentrations for each metal was necessary. The intent here was to characterize the root uptake of metal at various solution concentrations. It was important to use low concentrations to characterize root uptake in the linear section of the Michaelis-Menten curve. Similarly, it was also important to use high concentrations in order to approach the point of saturation. At the same time, plant toxicity had to be addressed. A dosing solution of extremely high concentration could kill the plant -- resulting in erroneous uptake values. Therefore, it was important to dose at the high end with a large enough concentration to see the curve bend toward saturation, but not too high as to kill the plant. High end concentrations, then, were obtained through the combined knowledge from literature reviews and experimental trial runs. Table 7 indicates the concentrations used for each metal.

In order to establish these concentrations, copper acetate and lead acetate were dissolved in distilled water. The copper acetate $Cu(C_2H_3O_2)_2 \cdot H_20$ was 31.8% copper while the lead acetate $Pb(C_2H_3O_2)_2 \cdot 3H_20$ was 55.5% lead. Table 7 indicates how much of each acetate needed to be mixed with three liters of water in order to achieve the desired concentrations based on the fact that one liter of water is approximately one kilogram. No metal was added to control container V. All weights were determined on an Ohaus analytical balance. After the acetates were added to the distilled water, each solution was magnetically stirred for two hours. Meanwhile, the experimental containers were drained of all uncontaminated surface water and as much subsurface water as could be siphoned from the soil. Upon stirring completion, containers I, II, III, and IV were dosed with three liter solutions of increasing concentrations of copper and lead by evenly pouring the solutions into the containers, thereby distributing the metal among the void spaces and surface water as uniformly as possible.

Container	**Desired Concentration (mg/kg)**	**Acetate Required (mg)**	**Acetate Added (mg)**
	Copper		
I	10	94.3	94.6
II	20	189	190.8
III	100	943	945
IV	200	1887	1884
	Lead		
I	10	54	53.7
II	50	270	271
III	100	541	543
IV	500	2703	2704

Table 7.
Dosing Concentration Calculations

Harvest, Preparation, and Preservation Stage. The first harvest was taken three days after dosing. Similar harvests were taken at the ten day and seventeen day marks. Control harvests were taken at the three and seventeen day marks in order to determine background metal concentrations. Random surface water samples (10 mL each) from each container were taken using 10 mL disposable pipets. Surface water samples and all other samples throughout the experiment were contained in 50 mL polypropylene centrifuge tubes which were previously washed with 10% nitric acid. Once the surface water samples were taken, the surface water was drained and soil water samples were taken by employing a small scale sampling well field concept. Well screens were made by cutting small slits in a disposable 10 mL pipet at approximately root zone depth. These pipets were then placed in the soil at random locations. Ten milliliter soil water samples were then extracted through the slits in the 10 mL pipet using a 1 mL pipet. All surface water and soil water samples were preserved with 1 mL of concentrated nitric acid.

Soil samples were taken by depressing a sixty cubic centimeter syringe (with the tip cut off) into the soil down through the root zone. Pressure was applied to the syringe as it was depressed downward to compress any remaining soil water from the soil, allowing for a core sample near the root zone relatively free of excess soil water. Once the soil samples were dried in a laboratory oven at 100 °C for twenty-four hours, dry weights were recorded and each sample was immersed in 10 mL of concentrated nitric acid.

After all water and soil samples were taken, one-third of the standing plants were randomly selected and removed from each container. Plants were dissected into roots and shoots and dried in a laboratory oven along with the soil samples for one day at 100° C. Plant roots and shoots were weighed to determine dry weights and then digested in 15 mL of concentrated nitric acid. Acid from each plant and soil sample was filtered with glass fiber filters to remove all organic material. The resulting acid was analysis-ready.

Analysis Stage. All samples were analyzed with a Perkin-Elmer 3030B atomic absorption spectrophotometer located in the University of Dayton Chemistry Laboratory, room 401, Wohleban Hall. The atomic absorption theory relies on the excitation of atoms (metal atoms in this case) from their ground state to an excited state. Excitation occurs when the atom absorbs electromagnetic energy. A study of the radiation absorbed provides a means for characterizing the sample.

Atomic absorption spectroscopy essentially measures the radiation absorption and compares it to a calibrated concentration. In such a fashion, a curvilinear relation is constructed from which sample concentrations can be determined. The linear range for copper on this spectrophotometer is 0.0 mg/L - 5 mg/L. Likewise, the linear range for lead is 0.0 mg/L - 20 mg/L. For results expected below these values, the measurement-to-concentration relation is expected to be linear and no calibration is needed. However, the measurement-to-concentration relation above these linear ranges is no longer linear and calibration is required. Since analysis results for each metal in this experiment were expected to exceed their respective linear ranges, calibration standards were mixed for each metal and the machine was calibrated to these standards.

In order to account for viscosity differences in the samples, two different sets of standards were made. One set, which consisted of solutions of concentrated nitric acid, was used to calibrate for the plant and soil samples. Another set, which consisted of 10% nitric acid and 90% water, was made to calibrate for all water samples. Doing this allowed approximately equal amounts of standard and sample to be drawn by the machine nebulizer and measured. In all cases, standard concentrations over a range similar to expected result concentrations were used.

4. Results and Analysis

Results and data analysis from the experimental and modeling phases described in Chapter 3 are presented here. Preliminary data tables and graphs are embedded in this chapter. Graphs and data from further analyses are located in Appendices 2 and 3.

Experimental Results

All samples from the experiment were analyzed on an atomic absorption spectrophotometer. In all, there were seventy-one samples including the controls and a blank. Results given for the blank indicate there were no distinct abnormalities introduced by the sample preparation procedures. There were, however, cases when the atomic absorption reading exceeded the calibration standards. In such cases, the sample was diluted five times and the resulting atomic absorption readings were multiplied accordingly. The detection limit for copper in flame atomic absorption is approximately 0.002 mg/L while the limit for lead is 0.01 mg/L. In some cases the spectrophotometer did not detect any copper or lead in a sample. Non-detection is represented in the results table with the letters 'nd.'

Table 8 summarizes the weights and volumes of each sample taken from the sampling process. Table 9 indicates the atomic absorption results corresponding to these samples.

	Sample	Surface Water (mL)	Soil Water (mL)	Soil (g) DW	Root (g) DW	Shoot (g) DW
3 Day	I	10	10	5.64	0.511	1.21
	II	10	10	5.71	0.534	1.38
	III	10	10	5.78	0.460	1.05
	IV	10	10	5.95	0.908	1.87
	V	10	10	5.25	0.674	1.56
10 Day	I	10	10	5.08	0.535	1.00
	II	10	10	6.06	0.681	1.44
	III	10	10	5.27	0.965	1.69
	IV	10	10	5.44	0.547	1.41
17 Day	I	10	10	5.43	0.633	1.50
	II	10	10	5.87	1.16	1.40
	III	10	10	5.56	1.55	2.18
	IV	10	10	5.82	1.52	1.98
	V	10	10	5.27	0.569	1.07

Table 8.
Sample Size Summary

	Sample	Surface Water (mg/L)	Soil Water (mg/L)	Soil (mg/L)	Root (mg/L)	Shoot (mg/L)
Day 3 (Cu)	Container I	0.3 (0.01)	0.3 (0.01)	1.6 (0.05)	6.2 (0.2)	2.9 (0.08)
	Container II	0.5 (0.01)	2.1 (0.08)	6.1 (0.1)	15.1 (0.3)	6.9 (0.1)
	Container III	3.8 (0.1)	7.6 (0.1)	10.5 (0.3)	53.3 (0.5)	38.9 (0.9)
	Container IV	30 (0.9)	34.5 (0.5)	31 (0.9)	80 (2.0)	54 (1.6)
	Control V	0.1 (0.01)	nd	1.5 (0.05)	1.3 (0.02)	0.9 (0.05)
Day 10 (Cu)	Container I	0.1 (0.01)	0.5 (0.01)	3.3 (0.1)	8.4 (0.1)	8 (0.1)
	Container II	0.4 (0.02)	2.5 (0.1)	9.0 (0.2)	10.1 (0.3)	11.6 (0.3)
	Container III	1.4 (0.05)	2.2 (0.1)	33.4 (0.9)	113.75 (2.3)	89 (1.8)
	Container IV	1.5 (0.08)	6.1 (0.2)	47.3 (0.5)	122 (2.0)	121 (2.2)
Day 17 (Cu)	Container I	0.1 (0.01)	0.7 (0.05)	2.6 (0.1)	7.2 (0.3)	12.3 (0.3)
	Container II	0.1 (0.01)	0.4 (0.01)	7.9 (0.2)	16.5 (0.5)	13.8 (0.3)
	Container III	0.7 (0.02)	13.1 (0.2)	18.5 (0.5)	129.44 (2.7)	101.3 (2.2)
	Container IV	1.0 (0.02)	9.6 (0.1)	43 (0.9)	230 (3.1)	159.3 (2.7)
	Control V	nd	0.2 (0.01)	2.1 (0.05)	1.5 (0.02)	1.0 (0.05)
Day 3 (Pb)	Container I	nd	1.0 (0.06)	2.0 (0.04)	5.0 (0.2)	3.0 (0.2)
	Container II	1.0 (0.04)	5.0 (0.2)	13 (0.5)	40 (1.7)	14 (1.2)
	Container III	2.0 (0.07)	8.0 (0.2)	11 (0.8)	80 (2.5)	30 (1.7)
	Container IV	30 (1.2)	90 (2.0)	35 (1.1)	111.1 (3.4)	161 (3.4)
	Control V	nd	nd	2.0 (0.1)	1.0 (0.04)	nd
Day 10 (Pb)	Container I	nd	nd	3.0 (0.08)	7.0 (0.2)	6.0 (0.2)
	Container II	nd	5.0 (0.03)	18 (0.6)	20 (0.8)	23 (1.7)
	Container III	2.0 (0.04)	2.0 (0.2)	15 (0.6)	70 (1.2)	90 (3.6)
	Container IV	3.0 (0.03)	11.0 (1.2)	75 (3.0)	120 (4.8)	250 (9.4)
Day 17 (Pb)	Container I	nd	1.0 (0.04)	3.0 (0.2)	6.0 (0.3)	12 (1.7)
	Container II	nd	1.0 (0.04)	15 (1.0)	40 (1.5)	20 (0.8)
	Container III	1.0 (0.04)	13 (1.0)	19 (0.6)	113.3 (3.4)	166.7 (4.0)
	Container IV	3.0 (0.03)	17 (0.8)	35 (1.2)	200 (6.0)	333.3 (11)
	Control V	nd	1.0 (0.05)	2.0 (0.2)	nd	1.0 (0.04)

n.d. = not detected
() = std. dev.

Table 9.
Atomic Absorption Results

From these atomic absorption results, volume and mass concentrations were calculated based on the amount of mass and/or dilution volume in each sample. These concentrations, given in Table 10, were then used in determining metal uptake rates. Uptake rates were determined specifically from metal concentrations in the roots and shoots. The assumption being that all metal in the plant passed through the roots and after some period of time, metal in the shoots as well as the roots must be accounted for to properly describe uptake.

	Sample	**Surface Water**	**Soil Water**	**Soil**	**Root**	**Shoot**
Copper		**(mg/L)**	**(mg/L)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
Day 3	Container I	0.3 (0.01)	0.3 (0.01)	2.84 (0.05)	60.67 (0.2)	11.98 (0.08)
	Container II	0.5 (0.01)	2.1 (0.08)	10.68 (0.1)	212.08 (0.3)	25.00 (0.1)
	Container III	3.8 (0.1)	7.6 (0.1)	18.32 (0.3)	579.35 (0.5)	185.24 (0.9)
	Container IV	30 (0.9)	34.5 (0.5)	52.1 (0.9)	660.79 (2.0)	144.39 (1.6)
	Control V	0.1 (0.01)	–	2.86 (0.05)	19.29 (0.02)	4.33 (0.05)
Day 10	Container I	0.1 (0.01)	0.5 (0.01)	6.5 (0.1)	78.50 (0.1)	40 (0.1)
	Container II	0.4 (0.02)	2.5 (0.1)	14.85 (0.2)	111.23 (0.3)	40.28 (0.3)
	Container III	1.4 (0.05)	2.2 (0.1)	63.38 (0.9)	471.5 (2.3)	263.31 (1.8)
	Container IV	1.5 (0.08)	6.1 (0.2)	86.95 (0.5)	1115.17 (2.0)	429.08 (2.2)
Day 17	Container I	0.1 (0.01)	0.7 (0.2)	4.79 (0.1)	85.31 (0.3)	41 (0.3)
	Container II	0.1 (0.01)	0.4 (0.05)	13.46 (0.2)	106.68 (0.5)	49.29 (0.3)
	Container III	0.7 (0.02)	13.1 (0.01)	33.27 (0.5)	626.32 (2.7)	348.51 (2.2)
	Container IV	1.0 (0.02)	9.6 (0.2)	73.88 (0.9)	1134.87 (3.1)	603.41 (2.7)
	Control V	–	0.2 (0.1)	3.98 (0.05)	26.36 (0.02)	4.67 (0.05)
Lead						
Day 3	Container I	–	1.0 (0.06)	3.55 (0.2)	48.92 (0.2)	12.4 (0.2)
	Container II	1.0 (0.04)	5.0 (0.2)	22.77 (1.7)	561.8 (1.7)	50.72 (1.2)
	Container III	2.0 (0.07)	8.0 (0.2)	19.2 (2.5)	869.57 (2.5)	142.86 (1.7)
	Container IV	30 (1.2)	90 (2.0)	58.82 (3.4)	917.68 (3.4)	430.48 (3.4)
	Control V	–	–	3.81 (0.04)	14.84 (0.04)	–
Day 10	Container I	–	–	5.91 (0.2)	65.42 (0.2)	30 (0.2)
	Container II	–	5.0 (0.03)	29.70 (0.8)	220.26 (0.8)	79.86 (1.7)
	Container III	2.0 (0.04)	2.0 (0.2)	28.46 (1.2)	290.16 (1.2)	266.27 (3.6)
	Container IV	3.0 (0.03)	11.0 (1.2)	137.87 (4.8)	1096.89 (4.8)	886.52 (9.4)
Day 17	Container I	–	1.0 (0.04)	5.52 (0.3)	71.09 (0.3)	40 (1.7)
	Container II	–	1.0 (0.04)	25.55 (1.5)	258.62 (1.5)	71.43 (0.8)
	Container III	1.0 (0.04)	13 (1.0)	34.17 (3.4)	548.23 (3.4)	573.51 (4.0)
	Container IV	3.0 (0.03)	17 (0.8)	60.14 (6.0)	986.84 (6.0)	1262.5 (11.0)
	Control V	–	1.0 (0.05)	3.80 (0)	–	4.67 (0.04)

() = propogated uncertainty

Table 10.
Volume and Mass Concentrations Calculated from Atomic Absorption Results

The uptake rates were calculated by dividing the milligrams of metal in the total plant by the plant mass. This value was then divided by the time over which the metal was taken up. The concentration specific uptake rates are given in Table 11. For this project, each rate indicates the change in plant concentration over the first three days of the experiment. The three day mark was chosen as a cut-off point because it was necessary to ensure the soil water concentration remained relatively constant during the uptake process. The data shows significant fluctuations in soil water concentration after the three day mark, most likely due to competing effects of metal uptake and redistribution among the other media. For the first three days, however, competing effects between the media appeared small and rate estimations from changes in plant concentrations were more reliable.

Copper									
	Root AA Data (mg/L)	Cu in Roots (mg)	Shoot AA Data (mg/L)	Cu in Shoots (mg)	Total Cu in Plants (mg)	Total Cu Less Control (mg)	Plant Conc. (mg/kg)	Soil Water Conc. (mg/L)	Uptake Rate (mg/kg-day)
I	6.2	0.031	2.9	0.015	0.046	0.026	14.96	0.3	4.99
II	15.1	0.113	6.9	0.035	0.148	0.128	66.88	2.1	22.29
III	53.3	0.267	38.9	0.195	0.461	0.441	292.22	7.6	97.41
IV	80	0.600	54	0.270	0.870	0.850	306.07	34.5	102.02
V	1.3	0.013	0.9	0.007	0.020				
Lead									
	Root AA Data (mg/L)	Pb in Roots (mg)	Shoot AA Data (mg/L)	Pb in Shoots (mg)	Total Pb in Plants (mg)	Total Pb Less Control (mg)	Plant Conc. (mg/kg)	Soil Water Conc. (mg/L)	Uptake Rate (mg/kg-day)
I	5	0.025	3	0.015	0.040	0.030	17.43	1	5.81
II	40	0.300	14	0.070	0.370	0.360	188.09	5	62.70
III	80	0.400	30	0.150	0.550	0.540	357.62	8	119.21
IV	111.1	0.833	161	0.805	1.638	1.628	586.12	90	195.37
V	1	0.010	nd	–	0.010				

Table 11.
3 Day Uptake Rate Calculations

Figures 3 and 4 depict the soil water concentrations and associated plant metal concentrations derived from the experimental dosing concentrations of copper. Figures 5 and 6 illustrate the same results for lead. The following discussion refers to the first three days of uptake. At the three day mark, Figure 3 shows a dramatic difference in the highest and second highest soil water concentrations. The corresponding plant concentrations in Figure 4, however, do not change significantly. This fact offers evidence that metal uptake may have been limited because a large increase in soil water concentration had little effect on plant concentration. The same analysis and conclusions can be made in Figures 5 and 6 for lead. Here however, the differences in plant concentrations associated with the two highest soil water concentrations is relatively larger. This is expected because the highest soil water concentration for lead at day three is approximately eleven times higher than the next highest, as opposed to the copper case where the highest soil water concentration is only four times higher than the second highest.

Figures 7 and 8 illustrate lines fitted to the dose specific plant concentrations shown in Figures 4 and 6. The corresponding line fitting calculations are located on the Mathcad 6.0^{+} templates in Appendix 2. The correlation coefficients for each curve are high and thus the fit and Umax and Km calculations appear reliable. In these figures, it is again apparent that as soil water concentration increases, the rates of uptake decrease. These results are consistent with the Michaelis-Menten concept discussed in Chapters 2 and 3 and indicate the experimental phase of this project was successful in bounding the concentrations necessary to describe rate limited uptake.

The experimental uptake results for both metals and subsequent Michaelis-Menten curve fitting allow for calculation of Umax and Km values for each metal. Recall that the maximum uptake rate, Umax, and the half-saturation constant, Km, are the variables that determine the fit of the line. In Figure 7, copper Umax and Km values calculated from the Mathcad 6.0^{+} template are 124 mg/kg-day and 4.5 mg/L respectively. Likewise, in Figure 8, calculated Umax and Km values for lead are 218 mg/kg-day and 9.4 mg/L respectively.

These values are now available for use in the hypothetical constructed wetland model. Model analysis follows.

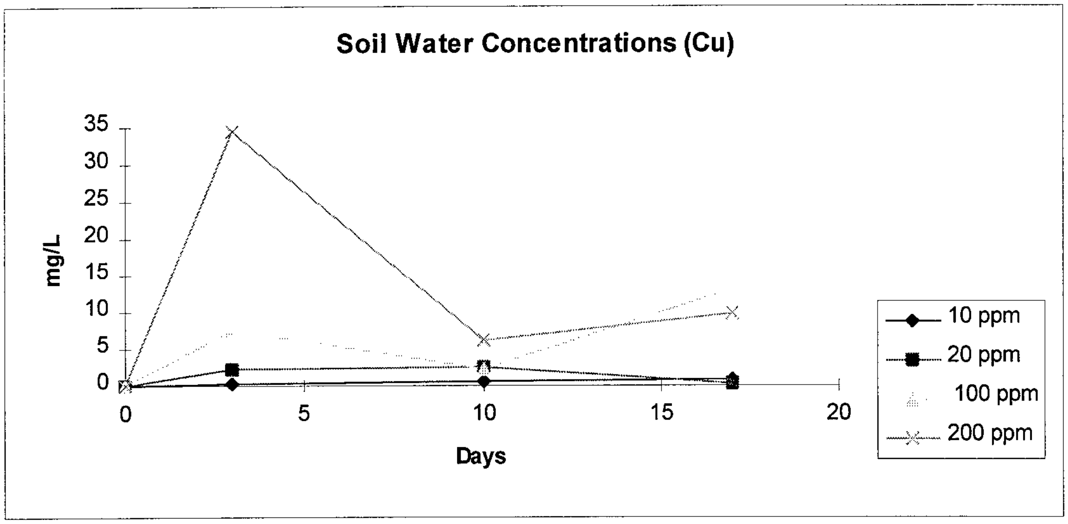


Figure 3.
17 Day Dose Specific Soil Water Concentration (Cu)

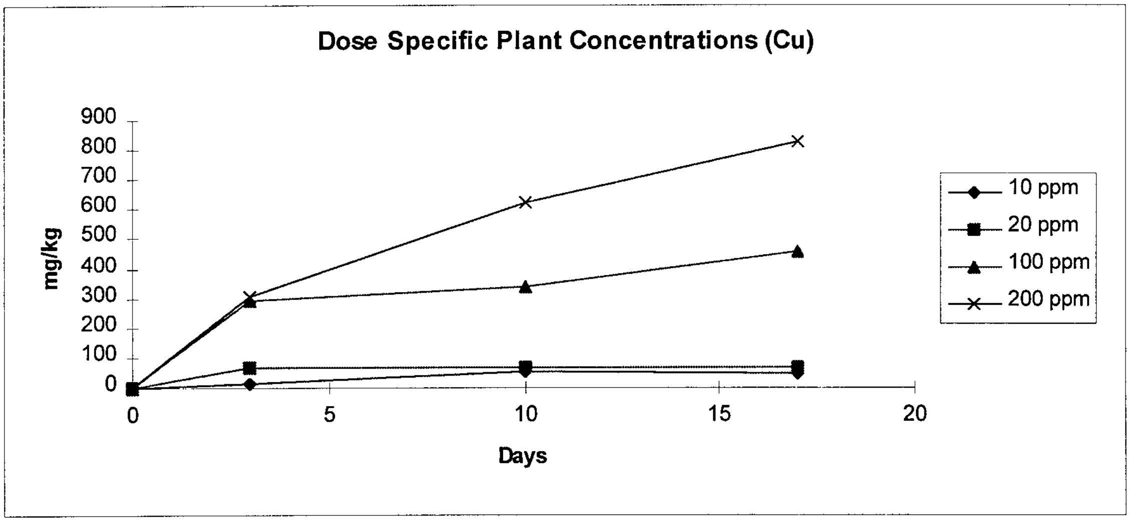


Figure 4.
17 Day Dose Specific Plant Concentration (Cu)

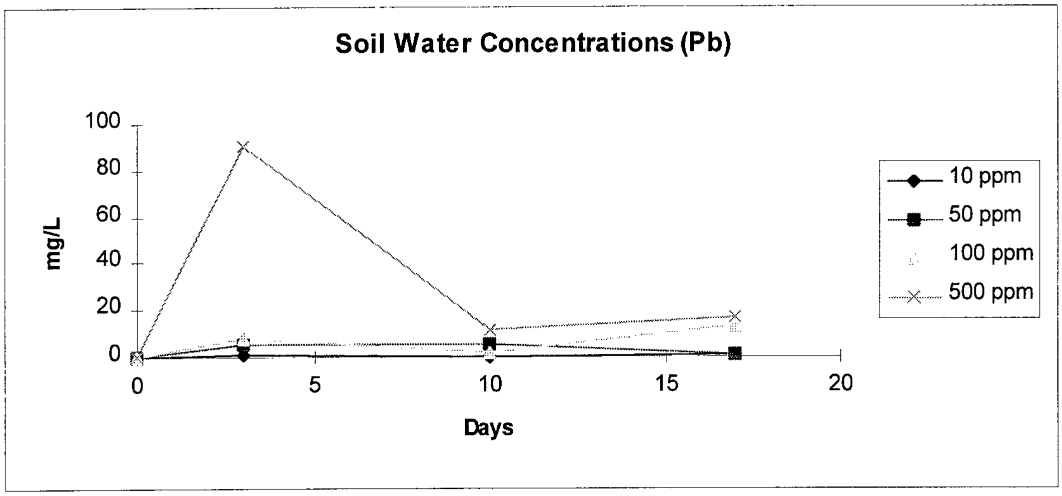


Figure 5.
17 Day Dose Specific Soil Water Concentration (Pb)

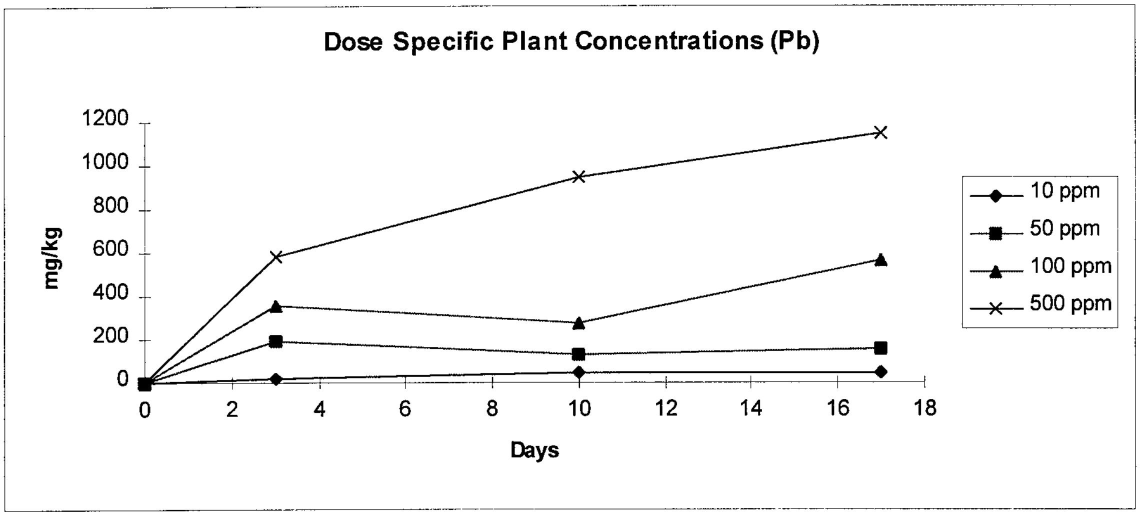
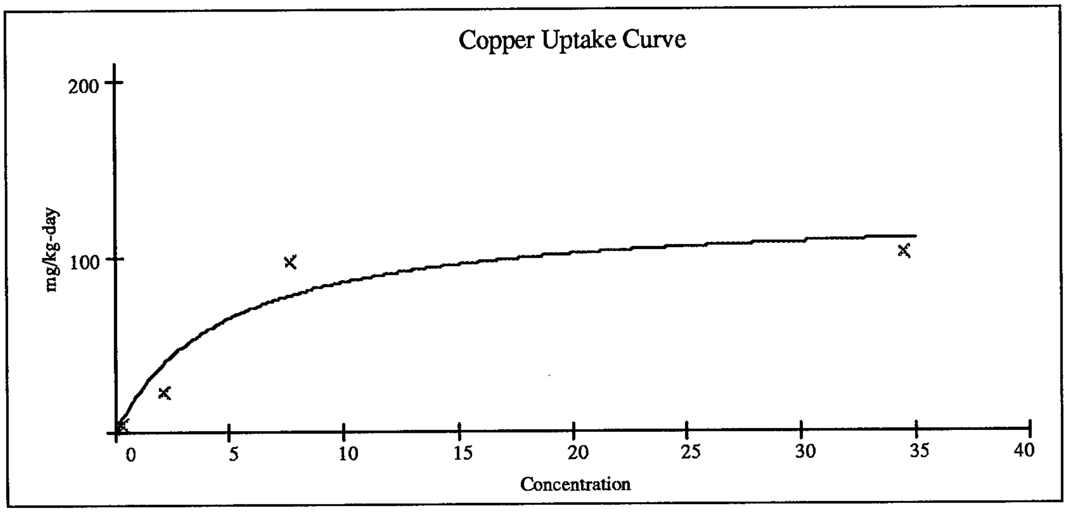
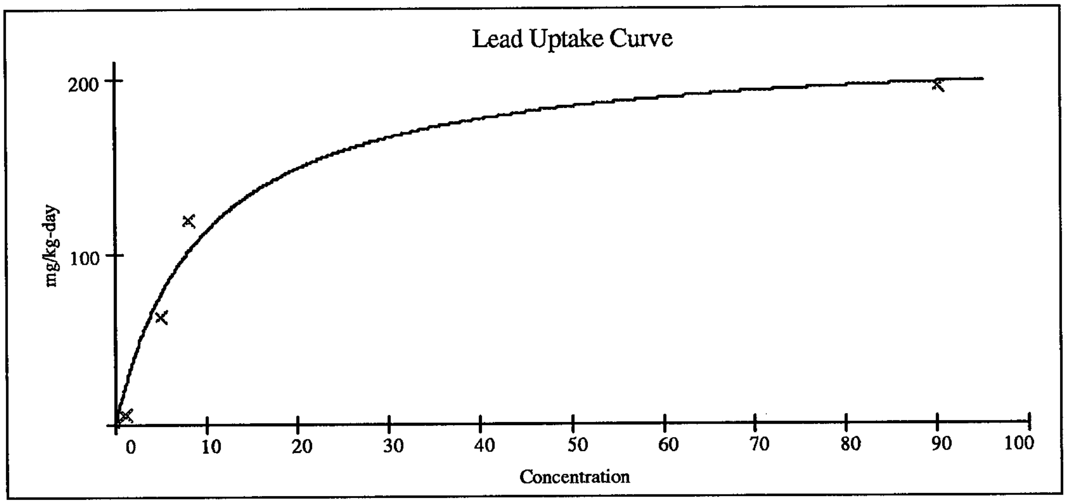


Figure 6.
17 Day Dose Specific Plant Concentration (Pb)



concentration in mg/L

Figure 7.
3 Day Copper Uptake vs. Soil Water Concentration



concentration in mg/L

Figure 8.
3 Day Lead Uptake vs. Soil Water Concentration

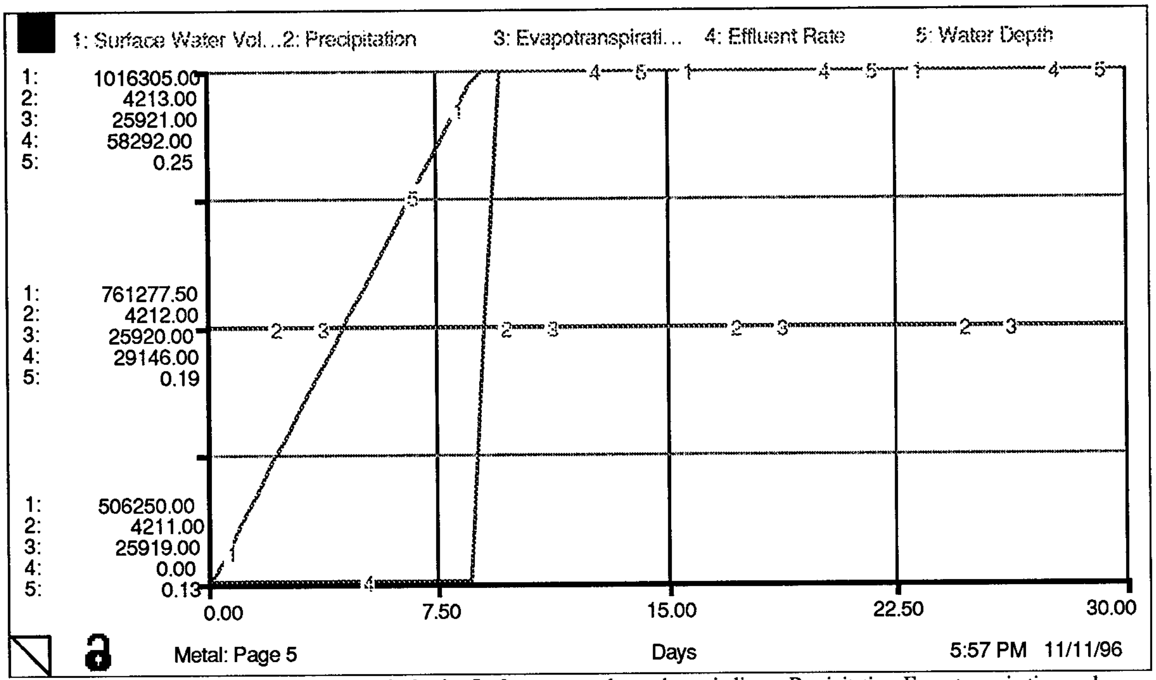
Model Analysis

Preliminary Analysis. In preliminary model analysis, it is necessary to ascertain the basic concepts defined in the model allow the model to calculate output associated with expected behavior. One of the most important components to check in any wetland model is the hydrology component. Figure 9 depicts the surface water volume and flows calculated by the model. Notice that the vertical axis is scaled for each entity. This format is typical for all other model graphs. All entities in the graph agree with the expected behavior dictated by the hypothetical design. It is evident that the surface water volume reaches a steady state value within the first month of operation. At this point, the actual water depth has reached its maximum design value and the amounts of water entering and leaving the wetland are equal. This can be demonstrated by multiplying the influent rate (80,000 L/day) by the number of days of input (30 days) and adding the product of the precipitation rate and input time to get a sum of 2,526,390 L. The opposing sum of the products of the effluent rate and evapotranspiration rate both multiplied by time also equals 2,526,390 L.

Agreement of calculated vegetation component output with expected output must also be verified. It is important to do so since the amount of vegetation in the wetland is a main controlling factor of metal uptake. Figure 10 illustrates the vegetation biomass calculated by the model. These values are indicative of expected behavior. For the purpose of these analyses, the vegetation biomass is held at a constant value. The assumption being that over an extended time horizon, a constructed wetland managed properly would have a relatively constant amount of biomass. Holding this value constant also facilitates further interpretation of model output. The value given in Figure 10 is based on a value of 10 kilograms of biomass per square meter. This value can be checked by multiplying the wetland area by 10 kg/m^2 to get 40,500 kg.

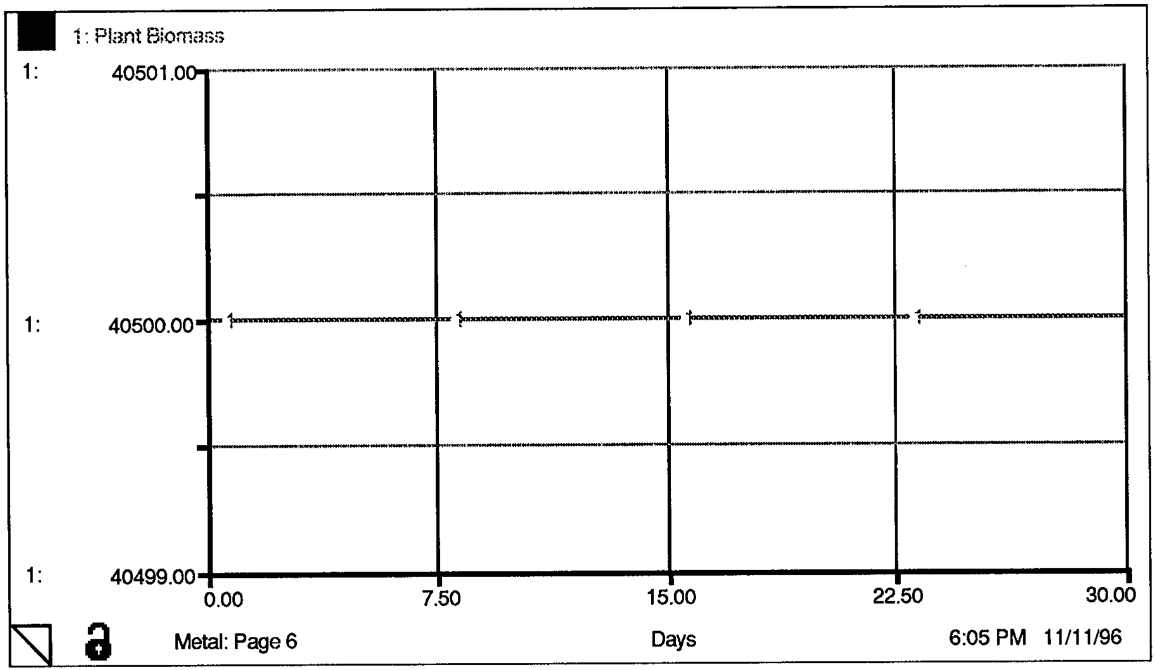
The values determining the hydrology and vegetation cases represented above will be used as baseline values for the rest of the model analysis. Holding these values at such a baseline facilitates further model analysis. Note, however, that these values can certainly be changed by future modelers to account for differing wetland characteristics.

Figure 11 depicts typical model behavior. This particular run incorporates a total copper runoff concentration of 0.1 mg/L. Note that the uptake rate increases dramatically at first and then transitions into an approximately linear relation. The soil water and sediment concentrations follow this same form. However, it is not apparent from this graph that uptake is a rate limited process. Therefore, it is necessary to verify the uptake mechanism is working correctly. To do so, it is desirable to see results which indicate that uptake is a saturable process. Hence, a saturating stormwater concentration is applied. Note that this saturating concentration is necessary to see the uptake curve increase at a decreasing rate. Any lower concentration simply depicts the linear range of the uptake curve. Notice in Figure 12 that as the soil water concentration continues to increase, the uptake rate increases at a decreasing rate -- as Michaelis-Menten kinetics prescribe. This particular run incorporates a total runoff copper concentration of 100 mg/L (which happens to be three orders of magnitude over the concentrations reported by the NURP study). Figures 14 and 15 in Appendix 3 show runs incorporating typical output and uptake verification for lead.



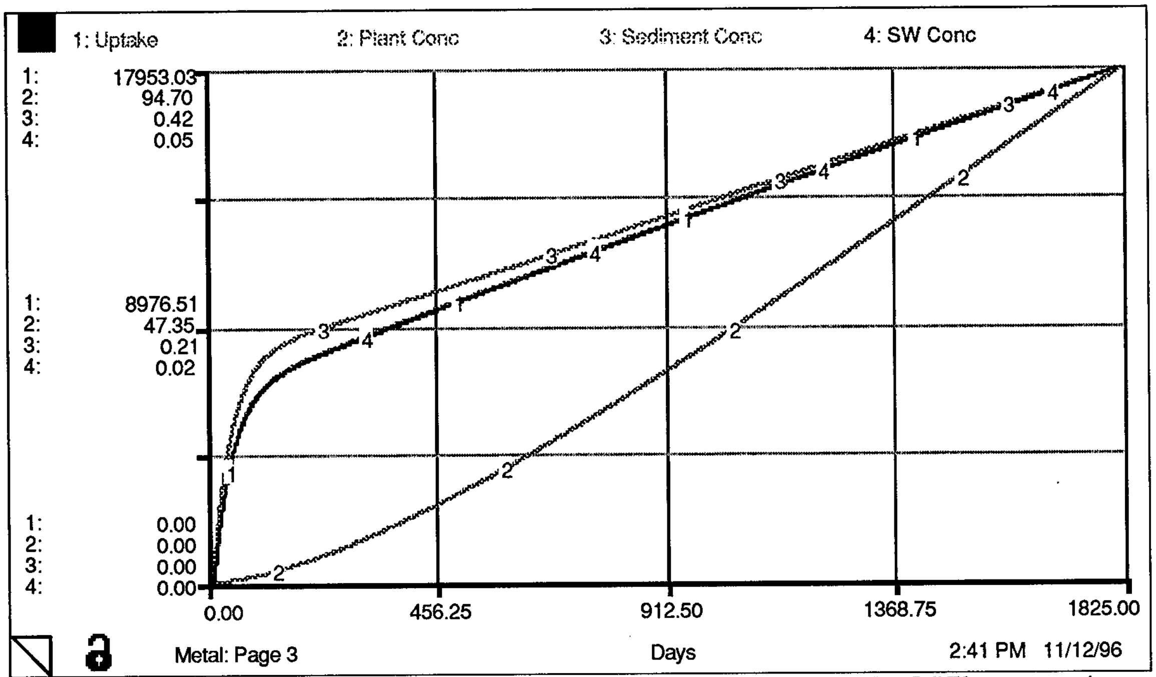
Curves correspond to respective scales on vertical axis. Surface water volume shown in liters. Precipitation, Evapotranspiration, and Effluent rates shown in liters/day. Water depth shown in meters.

Figure 9.
Hydrology Output



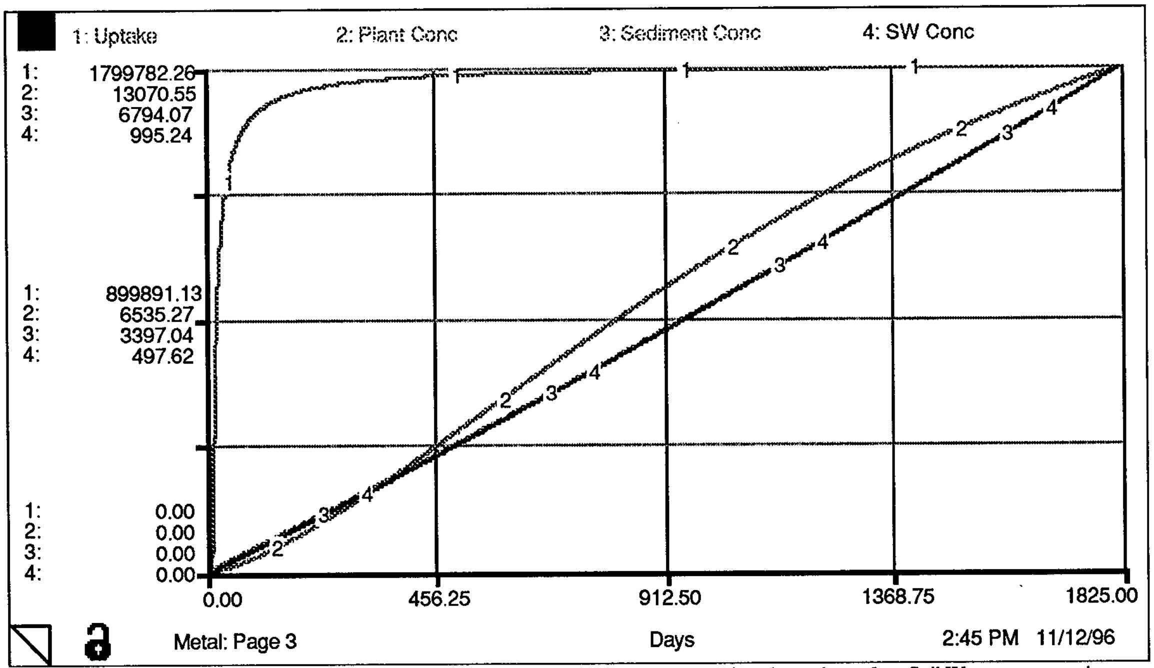
Plant mass shown in kg.

Figure 10.
Vegetation Output



Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 11.
5 Year Copper Uptake and Compartment Concentrations (@ 0.1 mg/L)

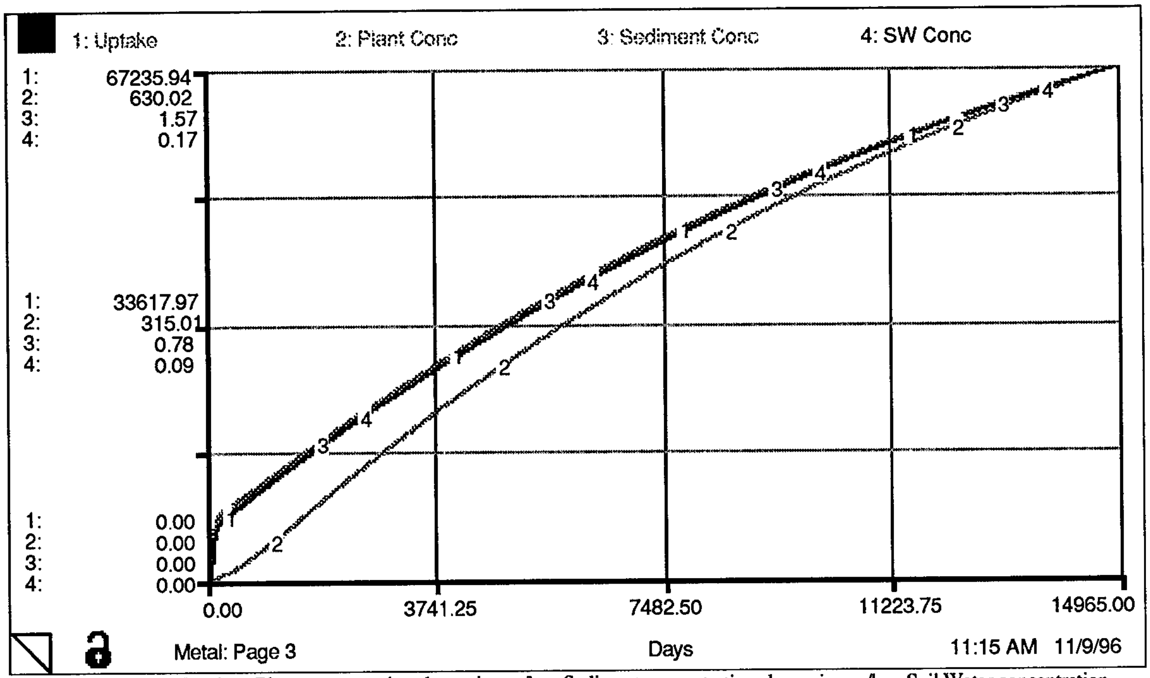


Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 12.
5 Year Copper Uptake and Compartment Concentrations (@ 100 mg/L)

Secondary Analysis. Note the model runs shown above indicate results over a relatively short time horizon and recall that the time horizon for this model extends beyond twenty years. The model runs above confirm the model behaves expectedly over small time horizons. It is also necessary to confirm behavior at the other extreme of the time horizon. Therefore, model runs over longer time horizons are necessary. Figure 13 shows the values of the uptake rate and plant, sediment, and soil water concentrations after the hypothetical wetland was exposed to a total copper runoff concentration of 0.1 mg/L for forty years. A similar run was accomplished for lead contaminated runoff and is shown in Figure 16 in Appendix 3. Notice in the figure below that after the initial quick rise the uptake rate and compartment concentrations increase at a decreasing rate. This behavior could not be seen in the five year run annotated in Figure 11. The behavior seen below offers evidence that long-term behavior can, in fact, differ from short-term behavior.

No other significant behavior changes are seen in any of the secondary analysis runs. The uptake and concentration magnitudes, however, are considerably larger. Model results given in the preliminary analysis and this secondary analysis offer evidence that the model performs properly.



Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 13.
40 Year Copper Uptake and Compartment Concentrations (@ 0.1 mg/L)

Sensitivity Analysis. Given that the model performs properly, sensitivity analysis on different model parameters can offer insight into which parameters affect model behavior significantly. Any one of the model parameters can be selected for sensitivity analysis if the scope of the project allows. The parameters selected for this project were selected because of their varying nature in a real system. For instance, stormwater concentrations in a real system could possibly change as the surrounding community and industry develop, while at the same time, wetland area in the system would most likely remain relatively constant.

The following data indicates how uptake and plant, water, and sediment concentrations change over time when exposed to different stormwater concentrations. The first two stormwater concentrations used for each metal (0.001 and 0.1 mg/L for copper and 0.006 and 0.46 mg/L for lead) are consistent with the range of concentrations reported by the NURP study. The final concentrations used for each metal (10 mg/L for copper and 46 mg/L for lead) are two orders of magnitude higher than the highest NURP concentration for each metal. Only the model behavior for these final concentrations differed significantly from the typical cases shown above. In these cases, the curves bend more dramatically toward their asymptotic values. Graphs corresponding to these analyses are shown as Figures 17 and 18 in Appendix 3.

The data in Table 12 shows a large increase in plant, soil water, and sediment concentrations over the first ten years. Over the next ten years, uptake and the plant, soil water, and sediment concentrations increase, but at a smaller rate than they did for the first ten years. This same behavior exists over the last ten year period as well.

Another observation in the data below and corresponding graphs is that the plant concentrations are much higher than all other concentrations making it seem as though most of the metal sinks into the plant stocks. Recall however, that the plant mass is relatively small compared to sediment and water volumes. Calculations for several cases indicate there is actually approximately five times more metal in the sediment than in the plant mass. This indicates that the sediment, as in a real system, is a large sink for metals.

Note that when exposed to the highest runoff concentrations for each metal, plant concentrations approach what would seemingly be toxic levels. Metal toxicity in plants is a very complex issue and no hard figures exist which correspond to this hypothetical model. The statement above is made based on knowledge gained from the literature review, experimental results, and other case specific toxicity studies. For instance, research has shown that copper in ash of a variety of plants is reported to range from 5 to

1,500 ppm and lead concentrations in plants can possibly reach as high as 2,714 ppm (DW) (Kabuta-Pendias and Pendias, 1992:106,198). Plant concentrations reported in the model output corresponding to the highest dosing concentrations are one order of magnitude higher than those reported in the literature and could certainly be toxic. However, these high plant concentrations are only seen when using a runoff concentration two orders of magnitude higher than the highest concentration reported by the NURP study. Note that plant concentration corresponding to the highest NURP concentrations (0.1 mg/L for copper and 0.46 mg/L for lead) are quite a bit smaller and do not suggest toxicity.

Model runs using runoff concentrations of 0.1 mg/L copper and 0.46 mg/L lead shown in Table 12 will be referred to as baseline cases throughout the remainder of the sensitivity analysis. They will serve as a benchmark to which further analyses can be compared. By doing so, output interpretation is facilitated. Figures 19 and 20 in Appendix 3 illustrate a comparison summary of all sensitivity analyses discussed below.

Metal @ Runoff Conc	Years	Uptake	Plant Conc	Sediment Conc	SW Conc	Surf Water Conc
		(mg/kg-day)	(mg/kg)	(mg/kg)	(mg/L)	(mg/L)
Cu @ 0.001 mg/L	1	90.18	0.10	< 0.01	< 0.01	< 0.01
	10	278.56	2.02	0.01	< 0.01	< 0.01
	20	441.69	3.79	0.01	< 0.01	< 0.01
	30	567.47	5.16	0.01	< 0.01	< 0.01
	40	664.46	6.21	0.02	< 0.01	< 0.01
Cu @ 0.1 mg/L	1	9,015.01	10.3	0.23	0.02	0.02
	10	27,841.51	201.62	0.65	0.07	0.04
	20	44,140.05	378.87	1.02	0.11	0.06
	30	56,706.99	515.53	1.32	0.15	0.08
	40	66,398.66	620.91	1.55	0.17	0.09
Cu @ 10 mg/L	1	842,861.71	939.41	33.89	3.93	1.6
	10	1,702,517.92	14,476.80	505.1	72.68	3.38
	20	1,774,995.72	17,272.60	1,661.03	242.59	3.75
	30	1,789,022.74	17,583.81	2,908.35	426.01	3.79
	40	1,794,681.07	17,665.57	4,159.61	610.01	3.81
Pb @ 0.006 mg/L	1	426.97	0.93	0.01	< 0.01	< 0.01
	10	1,120.57	14.71	0.03	< 0.01	< 0.01
	20	1,519.12	23.44	0.04	< 0.01	0.01
	30	1,720.18	27.85	0.05	0.01	0.01
	40	1,821.60	30.07	0.05	0.01	0.01
Pb @ 0.46 mg/L	1	32,712.67	71.27	1.09	0.1	0.19
	10	85,849.83	1,126.76	2.48	0.26	0.38
	20	116,396.55	1,795.97	3.34	0.36	0.5
	30	131,821.80	2,133.90	3.77	0.41	0.57
	40	139,614.22	2,304.59	3.99	0.43	0.6
Pb @ 46 mg/L	1	2,446,053.40	5,384.67	215.8	31.01	18.75
	10	3,134,240.19	49,224.55	3,107.72	556.38	27.05
	20	3,164,638.71	52,949.93	7,303.73	1,319.17	27.85
	30	3,172,908.59	53,253.79	11,535.88	2,088.64	27.91
	40	3,176,732.33	53,341.93	15,756.00	2,855.94	27.93

Table 12.
Forty Year Stormwater Concentration Sensitivity

If the metal concentrations reported in Table 12 are not acceptable to the community, plans may be set forth to double the wetland area and allow for more treatment area. Intuitively, given the same influent and effluent rates, doubling the wetland area increases the amount of plant biomass, sediment, and water available for treatment. Thus, plant, sediment, and water concentrations corresponding to model runs in which the wetland area was doubled would be expected to be about half of what they were in the baseline cases. Table 13 annotates the twenty year results corresponding to copper and lead runoff concentrations of 0.1 mg/L and 0.46 mg/L respectively. Notice that although the concentrations decrease somewhat, they are not, in fact, half of what they were in the baseline cases. Doubling the wetland area simply increases the amount of time it takes for each of these compartments to reach values comparable to those presented in the baseline cases. It appears then, that doubling the wetland area is a potential solution to reducing plant and sediment metal concentrations over a short time horizon. However, over a longer time horizon, plant and sediment concentrations will indeed reach baseline values -- indicating that doubling the wetland area is not necessarily an optimal long-term solution.

Runoff Conc	Year	Uptake (mg/kg-day)	Plant Conc (mg/kg)	Sediment Conc (mg/kg)	SW Conc (mg/L)	Surf Water Conc (mg/L)
Cu @ 0.1 mg/L	1	9,828.98	5.61	0.12	0.01	0.01
	10	32,734.83	115.84	0.38	0.04	0.02
	20	56,125.18	234.93	0.65	0.07	0.04
Pb @ 0.46 mg/L	1	40,394.55	43.73	0.67	0.06	0.13
	10	124,258.93	778.25	1.8	0.19	0.31
	20	195,380.74	1,440.80	2.81	0.3	0.48

Table 13.
Increased Wetland Area Concentrations

The community might also be interested in what effects would emerge by increasing the influent stream feeding the wetland. Model runs with increased influent flows and the same runoff concentrations as above show that doubling the influent increases the plant, sediment, and water concentrations from their baseline values. Notice that doubling the influent did not necessarily double these concentrations as might have been expected. Increasing the influent rate simply increased the rate which these compartments accumulate metal.

Runoff Conc	Year	Uptake (mg/kg-day)	Plant Conc (mg/kg)	Sediment Conc (mg/kg)	SW Conc (mg/L)	Surf Water Conc (mg/L)
Cu @ 0.1 mg/L	1	15,585.64	17.87	0.4	0.04	0.02
	10	42,972.88	322.12	1.01	0.11	0.05
	20	61,332.36	545.4	1.43	0.16	0.08
Pb @ 0.46 mg/L	1	51,090.32	112.07	1.71	0.15	0.24
	10	116,070.02	1,589.00	3.36	0.36	0.41
	20	140,755.81	2,244.82	4.04	0.43	0.49

Table 14.
Increased Influent Flow Concentrations

These observations and the observations made above by doubling the wetland area offer important insight for communities considering wetland modification in response to increased community development. It seems as though increases and decreases in concentrations resulting from doubling both the influent and wetland area respectively do not necessarily cancel each other out in the short-term. This information is crucial to developing communities considering how to treat an increase in stormwater volume. Once the wetland system reaches a steady state, the effects of doubling the influent and doubling the wetland area may very well cancel each other out. However, systems might not reach a steady state for a long time (in excess of twenty years in this case). The results above indicate that doubling the wetland area may not be the best short-term response to an increase in stormwater flow.

A further parameter sensitivity inspection can be directed at the metal speciation within the surface water. As stated previously, speciation can be governed by many entities including water pH, alkalinity, and amount of suspended solids. The distribution coefficients used in this model represent a specific case from the literature encompassing values of these entities which result in a dissolved copper concentration 1.9 times higher than the suspended copper concentration. Likewise, the dissolved lead concentration is 5 times higher than the suspended lead concentration. Investigation into how changes in these values affect the model behavior follows.

The results given in Table 15 show that decreasing the distribution coefficient (Kd) for each metal and changing the speciation from mostly dissolved to mostly particulate actually decreases the total amount of metal in the surface water as more particulate metal is available for settling. Hence, the plant and subsurface matrix concentrations increase. Typical variable changes that could cause such a change in Kd are a possible increase in pH and increase in the amount of suspended solids. Therefore, for the purpose of metal removal from stormwater, a higher pH and total suspended solids (TSS) value might prove beneficial. On the other hand, if toxicity in the subsurface and plant components is of concern, keeping the metal in solution with a lower pH and lower TSS value might be a better course of action.

Runofff Conc	Year	Uptake (mg/kg-day)	Plant Conc (mg/kg)	Sediment Conc (mg/kg)	SW Conc (mg/L)	Surf Water Conc (mg/L)
Cu @ 0.1 mg/L	1	9,601.44	10.98	0.24	0.02	0.01
	10	31,521.68	224.07	0.74	0.08	0.02
	20	53,271.64	447.82	1.25	0.14	0.02
Pb @ 0.46 mg/L	1	43,711.44	95.47	1.46	0.13	0.03
	10	146,077.11	1,787.02	4.3	0.45	0.08
	20	250,826.90	3,599.69	7.45	0.8	0.08

Table 15.
Decreased Distribution Coefficient Concentrations

Sensitivity analysis is also required on the parameters taken from the experiment. Recall that the partition constants describing the equilibrium between plant tissue and water within the plant were determined from matching successive model runs against experimental data. Recall also that the soil/soil water partition constants were taken from the experiment. It is essential to determine how model behavior is affected by changes in all these constants. Table 16 shows data from model runs in which the plant tissue/plant water partition coefficients were doubled. Notice that after a twenty year run, all concentrations except the plant concentrations are similar to those in the baseline case. The plant concentrations are significantly lower -- indicating that the plant compartments in the model are sensitive to changes in the plant tissue/plant water partition coefficients over a short time horizon. Again, since very little literature exists describing these partitioning values, further research is recommended. Since these values may be plant dependent, experimentation to find them should not be ruled out.

Table 17 shows data from model runs in which the soil/soil water partition constants for each metal were doubled. Notice here that the sediment concentrations reported are significantly different from those in the baseline case. Doubling the partition constant effectively increases the amount of metal that can bind to the soil at steady state conditions. Thus, higher sediment concentrations are expected. As more metal is bound to the sediment, less is available in the soil water for plant uptake. Therefore, lower soil water and plant concentrations are expected.

Runoff Conc	Year	Uptake	Plant Conc	Sediment Conc	SW Conc	Surf Water Conc
		(mg/kg-day)	(mg/kg)	(mg/kg)	(mg/L)	(mg/L)
Cu @ 0.1 mg/L	1	9,012.38	5.39	0.23	0.02	0.02
	10	27,591.03	106.6	0.64	0.07	0.04
	20	43,370.08	198.77	1.01	0.11	0.07
Pb @ 0.46 mg/L	1	32,680.49	38.16	1.09	0.1	0.19
	10	82,595.64	606.49	2.37	0.25	0.4
	20	108,644.87	937.6	3.09	0.33	0.52

Table 16.
Increased Plant Tissue/Plant Water Partition Constant Concentrations

Runoff Conc	Year	Uptake	Plant Conc	Sediment Conc	SW Conc	Surf Water Conc
		(mg/kg-day)	(mg/kg)	(mg/kg)	(mg/L)	(mg/L)
Cu @ 0.1 mg/L	1	8,570.99	8.88	0.44	0.02	0.02
	10	27,063.91	195.29	1.26	0.07	0.04
	20	43,147.60	369.76	2	0.11	0.06
Pb @ 0.46 mg/L	1	30,496.11	59.07	2.06	0.09	0.19
	10	83,715.30	1,092.33	4.84	0.25	0.37
	20	114,628.42	1,763.74	6.57	0.35	0.5

Table 17.
Increased Soil/Soil Water Partition Constant Concentrations

As described in Chapter 3, metal moves into the shoots from the roots by a mass flow process. The volumetric flow of water is a function of the xylem vessel radius. As the radius increases, more water can flow into the shoots. Subsequently, more metal enters the shoots. Table 18 shows data from model runs in which the xylem vessel radius was doubled. Notice that although the uptake rate is smaller than the baseline cases, the plant concentrations are actually higher. Again, the model offers insight into this counter-intuitive behavior and suggests that metal uptake and plant concentrations are significantly affected by changes in the xylem vessel radius, a characteristic most likely related to plant size and type. As a result, the model indicates that vegetation type within a wetland has a direct effect on metal uptake and wetland ecosystem behavior.

Two final parameter considerations relating to both plant and experimental values concern the values of Umax and Km. The values used in the model for these two parameters relate directly to a specific plant under specific experimental conditions. However, different plants may possibly be more tolerant to metal contamination or simply not as efficient at metal accumulation. Plants such as these most likely exhibit significantly smaller uptake rates. To investigate this concept, the model was run with lower maximum uptake rates (Umax). Table 19 contains data from model runs in which Umax was decreased by 75%. Note that the uptake rate and plant concentrations are smaller than their corresponding baseline values -- as might be expected. Also note the significant rise in sediment concentration. The model output indicates that the sediment concentration increases faster as a result of a smaller plant Umax. Again, evidence is offered that indicates vegetation type chosen for a constructed wetland can have considerable effects on wetland ecosystem behavior. These are important results because wetlands commonly contain several species of plants. Some of these plants may have low saturation values and/or high uptake rates, which can lead to rate limited uptake. On the other hand, plants with a higher tolerance and/or lower uptake rates would not become saturated as quickly, if at all. These concepts should be considered when constructing and operating a constructed wetland.

Runoff Conc	Year	Uptake	Plant Conc	Sediment Conc	SW Conc	Surf Water Conc
		(mg/kg-day)	(mg/kg)	(mg/kg)	(mg/L)	(mg/L)
Cu @ 0.1 mg/L	1	8,752.99	29.04	0.24	0.02	0.02
	10	24,390.99	304.25	0.66	0.06	0.06
	20	35,800.30	505.03	0.97	0.09	0.09
Pb @ 0.46 mg/L	1	30,708.33	164.32	1.12	0.09	0.22
	10	63,805.39	1,376.79	2.32	0.19	0.48
	20	76,523.70	1,842.83	2.79	0.23	0.58

Table 18.
Increased Xylem Vessel Radius Concentrations

Runoff Conc	Year	Uptake	Plant Conc	Sediment Conc	SW Conc	Surf Water Conc
		(mg/kg-day)	(mg/kg)	(mg/kg)	(mg/L)	(mg/L)
Cu @ 0.1 mg/L	1	7,646.39	7.14	0.59	0.08	0.02
	10	25,540.86	183.36	1.99	0.27	0.04
	20	41,027.35	350.83	3.3	0.45	0.06
Pb @ 0.46 mg/L	1	27,362.31	49.67	2.34	0.33	0.19
	10	80,076.20	1,037.99	6.77	1.05	0.36
	20	111,116.23	1,702.90	9.71	1.52	0.49

Table 19.
Decreased Umax Concentrations

Conclusions

The parameters analyzed in this section are by far not the only parameters that can change in a real system. They are however, some of the most prominent and obvious parameters associated with wetlands. As such, the opportunity for them to be changed either by the wetland managers or by natural processes is high. It is sufficient to say then, that the model runs discussed above offer understanding about how a particular wetland may behave when these parameters change.

Several conclusions are suggested by this research. Evidence is given that doubling the wetland area in response to increased stormwater flow does not produce expected short-term results. This type of response is better suited as a long-term solution. Evidence is also given that when exposed to normal stormwater runoff metal concentrations, plant toxicity due to high concentrations of copper or lead is unrealized. Lastly, when exposed to normal runoff metal concentrations, the rate of metal accumulation in wetland plants and sediment is highly dependent on plant characteristics which possibly differ between plant species. These conclusions contain important information about wetland behavior.

This information is vital to community planners in that it allows them to discern among many design options when considering a constructed wetland design. Information presented here indicates that metal accumulates in a wetland differently based on hydrologic design, extent of vegetation, vegetation type, and system chemistry.

5. Conclusions and Recommendations

The purpose of this project was to develop quantitative concepts for understanding the dynamics of metal uptake in constructed wetland plants. Throughout the course of the research, behavior associated with certain wetland characteristics brought additional facets into the research. This chapter presents the overall summary, conclusions, and recommendations associated with the research objectives presented in Chapter 1.

Summary and Conclusions

There were two phases in this project, a modeling phase and an experimental phase. The experimental phase established specific parameters which were used in the modeling phase. It was shown in the experiment that plant uptake of metal does, in fact, coincide with a rate limited process. The uptake rate data taken from the experiment clearly illustrate that as the metal exposure concentration increases indefinitely, the pace at which the plant incorporates metal decreases asymptotically. Experimental results also showed that metal accumulates in the sediment and does not necessarily remain in the surface water for any extended period of time. These results are consistent with literature reviews.

Model analysis using this experimental data revealed certain latent behavior in the hypothetical constructed wetland when it was exposed to metal contaminated stormwater. The results of the analysis indicate that metal can accumulate at a greater rate in wetland plants and other wetland components in the early years of wetland operation as compared to the later years. Changes in different wetland parameters affect the rate at which metal is taken up by wetland plants. For instance, changing parameters that affect water chemistry and amount of suspended solids can change metal speciation in the surface water. As metal speciation changes, different amounts of dissolved and particulate metal are available for mass outflow and settling, which can ultimately affect metal concentrations in the system. Another notion uncovered by the model is the unrealized potential for toxicity in wetland plants due to high metal concentrations in the system when exposed to typical stormwater runoff concentrations. Model analysis using the highest stormwater metal concentrations reported by EPA's Nationwide Urban Runoff Program project indicate seemingly non-toxic metal concentrations in the system after an extended period of time. Potentially toxic concentrations were reached only when the model was run with stormwater concentrations two orders of magnitude higher than the NURP concentrations.

Understanding of plant and wetland characteristics is necessary for communities operating constructed wetlands for stormwater treatment. Model analysis attests that certain behavior results when parameters are manipulated. As such, communities interested in preserving the efficiency and extending the life of their wetlands might consider modeling parameter changes before executing them in a real system.

Recommendations

Several recommendations for further research stem from this project. Many of these recommendations pertain to the modeling phase. Time constraints and the complexity of this project dictated that the model not be too complex. Consequently, some factors were not addressed fully.

Primarily, the model in this project operates under the continuously stirred tank reactor (CSTR) assumption. It is assumed that the wetland is a well-mixed system and metal distributes in the system evenly. In reality, this is most likely not the case. In fact, a concentration gradient most likely exists between where the influent enters and effluent exits. Presumably, more metal will settle near the influent or center where metal concentrations are highest and water velocities are slowest.

Additionally, atmospheric deposition of metal, which can be a significant source of metal over time, was not addressed. Further research into the speciation of atmospherically deposited metal and affects caused by deposition is warranted.

No toxicity mechanism exists in the model. Research into plant toxicity and inclusion of a toxicity mechanism in the model would provide communities with insight into wetland behavior if their stormwater metal concentrations happen to be very large. At the same time, competing and antagonizing affects of different metals must be studied with respect to accumulation, plant uptake, and toxicity. It is possible that varying concentrations of different metals applied to the wetland at the same time could bring about entirely different effects.

Finally, further research into the actual uptake mechanism in plants is required. This project showed that plant uptake can be described mathematically with Michaelis-Menten kinetics. However, no studies were done on the actual physical and chemical processes that control metal uptake. Knowledge of the actual uptake mechanism can provide insight into the statistical differences in maximum uptake rates offered by Michaelis-Menten kinetics. It is possible that uptake rates of copper and lead are statistically different from the rates of two other metals. If the actual uptake mechanism were known, this difference could possibly be attributed to some physical or chemical parameter.

The conclusions and recommendations presented in this research are vital to further understanding of the behavior of wetlands exposed to metal contaminated stormwater. Only through proper understanding of this behavior can we hope to achieve effective environmental management of constructed wetlands.

Appendix 1. Model Code and Structure

Code

Concentrations of Interest

```
Dis_Water_Conc = IF (Surface_Water_Volume>0) THEN (Surface_Water_Dis_Metal/Surface_Water_Volume) EISE 0
{milligrams per liter}

Part_Water_Conc = IF(Surface_Water_Volume>0) THEN (Surface_Water_Part_Metal/Surface_Water_Volume) ELSE 0
{milligrams per liter}

Plant_Conc = (Root_Tissue_Metal+Shoot_Tissue_Metal)/(Root_Tissue_Mass+Shoot_Tissue_Mass)

Root_Tis_Conc = Root_Tissue_Metal/Root_Tissue_Mass {milligrams per kilogram}

Root_Water__Conc = Root_Water_Metal/Root_Water_Vol {milligrams per liter}

Sediment_Conc = Part_Metal_in_Sed/Solid_Volume {milligrams per liter}

Shoot_Tis_Conc = Shoot_Tissue_Metal/Shoot_Tissue_Mass {milligrams per kilogram}

Shoot_Water_Conc = Shoot_Water_Metal/Shoot_Water_Vol {milligrams per liter}

SW_Conc = Dis_Metal_in_SW/Subsurface_Water_Vol
{milligrams per liter}

Total_Water_Conc = Dis_Water_Conc+Part_Water_Conc {mg/L}
```

Metal Flows

```
Dis_Metal_in_SW(t) = Dis_Metal_in_SW(t - dt) + (Root_Decomp_2 + SW_Dist - Uptake) * dt
INIT Dis_Metal_in_SW = 0 {milligrams}

Root_Decomp_2 = Root_Death*Root_Water_Frac*Root_Water__Conc
{milligrams per day}

SW_Dist = (SW_Goal-Dis_Metal_in_SW)*.25 {milligrams per day}

Uptake = ((Umax*SW_Conc)/(SW_Conc+Km))*Root_Mass {milligrams per day}

Part_Metal_in_Sed(t) = Part_Metal_in_Sed(t - dt) + (Settling + Root_Decomp_1 + Shoot_Decomp_1 - SW_Dist) * dt
INIT Part_Metal_in_Sed = 0 {milligrams}

Settling = (Settling_Velocity*Part_Water_Conc*Wetland_Area)*1000 {milligrams per day}
DOCUMENT: Design settling velocity is given by Sediment and Stormwater Division (1991:37). The expression is converted
to milligrams per day.

Root_Decomp_1 = Root_Death*Root_Tissue_Frac*Root_Tis_Conc {milligrams per day}

Shoot_Decomp_1 = Shoot_Death*Shoot_Tissue_Frac*Shoot_Tis_Conc
{milligrams per day}

SW_Dist = (SW_Goal-Dis_Metal_in_SW)*.25 {milligrams per day}

Root_Tissue_Metal(t) = Root_Tissue_Metal(t - dt) + (Root_Tissue_Dist - Root_Decomp_1) * dt
INIT Root_Tissue_Metal = 0 {milligrams}

Root_Tissue_Dist = RT_Goal-Root_Tissue_Metal {milligrams per day}

Root_Decomp_1 = Root_Death*Root_Tissue_Frac*Root_Tis_Conc {milligrams per day}
```

Root_Water_Metal(t) = Root_Water_Metal(t - dt) + (Uptake - Translocation - Root_Decomp_2 - Root_Tissue_Dist) * dt
INIT Root_Water_Metal = 0 {milligrams}

Uptake = ((Umax*SW_Conc)/(SW_Conc+Km))*Root_Mass {milligrams per day}

Translocation = Transport*Root_Water__Conc*No_of_Plants
{milligrams per day}
DOCUMENT: Transport into the shoots occurs in water within the plant. The flow rate is given by the transport flow and the concentration is that concentration in the root water.

Root_Decomp_2 = Root_Death*Root_Water_Frac*Root_Water__Conc
{milligrams per day}

Root_Tissue_Dist = RT_Goal-Root_Tissue_Metal {milligrams per day}

Shoot_Tissue_Metal(t) = Shoot_Tissue_Metal(t - dt) + (Shoot_Tissue_Dist - Shoot_Decomp_1) * dt
INIT Shoot_Tissue_Metal = 0 {milligrams}

Shoot_Tissue_Dist = ST_Goal-Shoot_Tissue_Metal {milligrams per day}

Shoot_Decomp_1 = Shoot_Death*Shoot_Tissue_Frac*Shoot_Tis_Conc
{milligrams per day}

Shoot_Water_Metal(t) = Shoot_Water_Metal(t - dt) + (Translocation - Shoot_Decomp_2 - Shoot_Tissue_Dist) * dt
INIT Shoot_Water_Metal = 0 {milligrams}

Translocation = Transport*Root_Water__Conc*No_of_Plants
{milligrams per day}
DOCUMENT: Transport into the shoots occurs in water within the plant. The flow rate is given by the transport flow and the concentration is that concentration in the root water.

Shoot_Decomp_2 = Shoot_Death*Shoot_Water_Frac*Shoot_Water_Conc
{milligrams per day}

Shoot_Tissue_Dist = ST_Goal-Shoot_Tissue_Metal {milligrams per day}

Surface_Water_Dis_Metal(t) = Surface_Water_Dis_Metal(t - dt) + (Dis_Mass_Inflow + Shoot_Decomp_2 - Dis_Mass_Outflow - Dist) * dt
INIT Surface_Water_Dis_Metal = 0 {milligrams}

Dis_Mass_Inflow = Influent_Rate*Dis_Runoff_Conc {milligrams per day}

Shoot_Decomp_2 = Shoot_Death*Shoot_Water_Frac*Shoot_Water_Conc
{milligrams per day}

Dis_Mass_Outflow = Effluent_Rate*Dis_Water_Conc {milligrams per day}

Dist = if (Surface_Water_Part_Metal>0) then (Dist_Goal-Surface_Water_Part_Metal)*1.9 else 0

Surface_Water_Part_Metal(t) = Surface_Water_Part_Metal(t - dt) + (Part_Mass_Inflow + Dist - Part_Mass_Outflow - Settling) * dt
INIT Surface_Water_Part_Metal = 0 {milligrams}

Part_Mass_Inflow = Influent_Rate*Part_Runoff_Conc {milligrams per day}

Dist = if (Surface_Water_Part_Metal>0) then (Dist_Goal-Surface_Water_Part_Metal)*1.9 else 0

Part_Mass_Outflow = Effluent_Rate*Part_Water_Conc {milligrams per day}

Settling = (Settling_Velocity*Part_Water_Conc*Wetland_Area)*1000 {milligrams per day}
DOCUMENT: Design settling velocity is given by Sediment and Stormwater Division (1991:37). The expression is converted to milligrams per day.

Dis_Runoff_Conc = .3*Total_Runoff_Conc {milligrams per liter}
DOCUMENT: Paulson and others indicate that 30% of total copper (20% for lead) in runoff is in dissolved form (1992:53). These values, however, can vary greatly from site to site.

Km = 4.5 {milligrams per liter}

Part_Runoff_Conc = .7*Total_Runoff_Conc {milligrams per liter}
DOCUMENT: Paulson and others indicate that 70% (80% for lead) of copper is in particulate state in runoff (1992:53). These values, however, can vary greatly from site to site.

Settling_Velocity = 0.35 {meters per day}
DOCUMENT: This value is taken from Sediment and Stormwater Division (1989:44). It is representative of a particle with diameter < 4 microns.

Total_Runoff_Conc = .1 {milligrams per liter}
DOCUMENT: Total runoff metal concentration is taken from the NURP data. Cu ranges from 0.001 to 0.1 ppm while lead ranges from 0.006 to 0.46 ppm (Sediment and Stormwater Division, 1991:30)

Umax = 124 {milligrams per kilogram per day}

Partitioning Parameters

Dist_Goal = Surface_Water_Volume*(Dis_Water_Conc/Kd)

Kd = 1.9
DOCUMENT: Data taken from Meseure and Fish indicates that a typical distribution coefficient describing dissolved/particulate metal concentrations is 1.9 for Cu and 5 for Pb (1989:131).

Krwt = 3.5

Kssw = 6.8
DOCUMENT: This value was determined experimentally. Typical values for copper and lead are 6.8 and 5.5 respectively.

Kswt = 2.5

Root_ratio = Root_Water__Conc/Root_Tis_Conc

RT_Goal = Root_Tissue_Mass*(Root_Water__Conc/Krwt)

Shoot_ratio = Shoot_Water_Conc/Shoot_Tis_Conc

ST_Goal = Shoot_Tissue_Mass*(Shoot_Water_Conc/Kswt)

SW_Goal = Subsurface_Water_Vol*(Sediment_Conc/Kssw)

Total_Root_Conc = (Root_Tissue_Metal+Root_Water_Metal)/Root_Mass {milligrams per kilogram}

Total_Shoot_Conc = (Shoot_Tissue_Metal+Shoot_Water_Metal)/Shoot_Mass {mg/kg}

Plant Parameters
Plant_Biomass(t) = Plant_Biomass(t - dt) + (Growth - Death) * dt
INIT Plant_Biomass = (Wetland_Area*10) {kilograms}
DOCUMENT: Based on maximum value of 10Kg per square meter over the entire wetland (Smekrud, 1994:103).

Growth = Growth_Frac*Plant_Biomass

Death = Death_Frac*Plant_Biomass {kilograms per day}

Death_Frac = .001

Growth_Frac = .001

Mass_per_Plant = .0024 {kilograms}

No_of_Plants = Plant_Biomass/Mass_per_Plant {plants}

Organic_Sedimentation = ((Root_Death*Root_Tissue_Frac)+(Shoot_Death*Shoot_Tissue_Frac))*.1*TIME

Pressure_Gradient = -0.03E6 {kg/sq. m sq s}
DOCUMENT: Pressure gradient in transpiring plants (Nobel, 1991:510).

Transport = ((((-PI*(Xylem_Vessel_Radius^4))/8*Water_Viscosity)*Pressure_Gradient)*60*60*24)*1000 {liters per day}
DOCUMENT: Volumetric flow in plants can be described by Poiseulle's Law as noted below (Nobel, 1991:508). The expression is converted from cubic meters per second to liters per day.

Root_Death = Root_Mass_Frac*Death

Root_Mass = Root_Mass_Frac*Plant_Biomass {kilograms}
DOCUMENT: This parameter indicates the amount of root mass in the wetland.

Root_Mass_Frac = .36
DOCUMENT: 36% of the total plant biomass is attributed to the root. This value was determined experimentally.

Root_Tissue_Frac = .07
DOCUMENT: This value indicates what percentage of the total root mass is actually tissue. The value was determined experimentally.

Root_Tissue_Mass = Root_Tissue_Frac*Root_Mass {kilograms}

Root_Water_Frac = .93
DOCUMENT: This value indicates what percentage of the total root mass is water. The value was determined experimentally.

Root_Water_Vol = Root_Water_Frac*Root_Mass {liters}
DOCUMENT: Assumption: 1 kg water = l liter

Shoot_Death = Shoot_Mass_Frac*Death

Shoot_Mass = Shoot_Mass_Frac*Plant_Biomass {kilograms}
DOCUMENT: This value indicates the total amount of shoot mass in the wetland.

Shoot_Mass_Frac = .64
DOCUMENT: 64% of the total plant biomass is attributed to the shoot. This value was determined experimentally.

Shoot_Tissue_Frac = .27
DOCUMENT: 27% of the shoot is tissue. This value was determined experimentally.

Shoot_Tissue_Mass = Shoot_Tissue_Frac*Shoot_Mass {kilograms}
DOCUMENT: This value indicates the amount of shoot that is actually tissue.

Shoot_Water_Frac = .73
DOCUMENT: 73% of the shoot is water. This value was determined experimentally.

Shoot_Water_Vol = Shoot_Water_Frac*Shoot_Mass {liters}
DOCUMENT: Assumption: 1 kg water = 1 liter

Water_Viscosity = 1.002E-3 {kg/m s}
DOCUMENT: Water viscosity value at 20 C (Nobel, 1991:509).

Xylem_Vessel_Radius = 175E-6 {meters}
DOCUMENT: Nobel indicates that xylem vessel radii range from 8 to 500 microns (1991:507).

Wetland Parameters
Surface_Water_Volume(t) = Surface_Water_Volume(t - dt) + (Influent_Rate + Precipitation - Effluent_Rate - Evapotranspiration) * dt
INIT Surface_Water_Volume = Wetland_Area*Max_Water_Level*1000*.5 {liters}
DOCUMENT: Initial volume is that volume at .5 maximum depth
(Area x Max Water Level).

Influent_Rate = 80000 {liters per day}
DOCUMENT: Surface water inflow is represented by average annual stream channelized flow (Mitsch and Gosselink, 1993:87). The whole expression is then converted to liters per day.

Precipitation = (.00104*Wetland_Area)*1000 {liters per day}
DOCUMENT: This precipitation value is taken from Mitsch and Gosselink (1987:78) and is indicative of precipitation over the Great Lakes Coastal Marsh in Ohio. The value of 38 cm/yr has been converted to .00104 m/day. The whole expression then is converted to liters per day.

Effluent_Rate = IF (Water_Depth>Max_Water_Level) THEN (Influent_Rate+Precipitation-Evapotranspiration) ELSE (0) {liters per day}
DOCUMENT: The wetland is designed with a maximum volume based on water depth. If water depth exceeds its maximum value, the outflow will equal the inflow (channelized). No water will flow out until this point is reached.

Evapotranspiration = (.8*.008*Wetland_Area)*1000 {liters per day}
DOCUMENT: The evapotranspiration rate can be represented by .8 of the pan evaporation rate of a nearby open area (Hammer, 1989:26). A pan evaporation value of 8 mm/day (Mudgett, 1995) has been converted to .008 m/day. The whole expression is then converted to liters per day.

Bulk_Density = 900 {kilograms per cubic meter}
DOCUMENT: Vymazal, 1995:189

length = 90 {meters}

Max_Water_Level = .25 {meter}
DOCUMENT: This is the maximum water level in the wetland. Its value determines surface water volume and effluent rate. A common water depth ranges between 6 and 18 inches.

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

Retention_Time = IF (Surface_Water_Volume>0) AND (Effluent_Rate>0) THEN Surface_Water_Volume/Effluent_Rate ELSE 14 {days}
DOCUMENT: (Sediment and Stormwater Division 1989:37).

solid_depth = 1 {meters}
DOCUMENT: This wetland has a specified bed depth above a clay liner which keeps water from exiting the system via groundwater flow. -

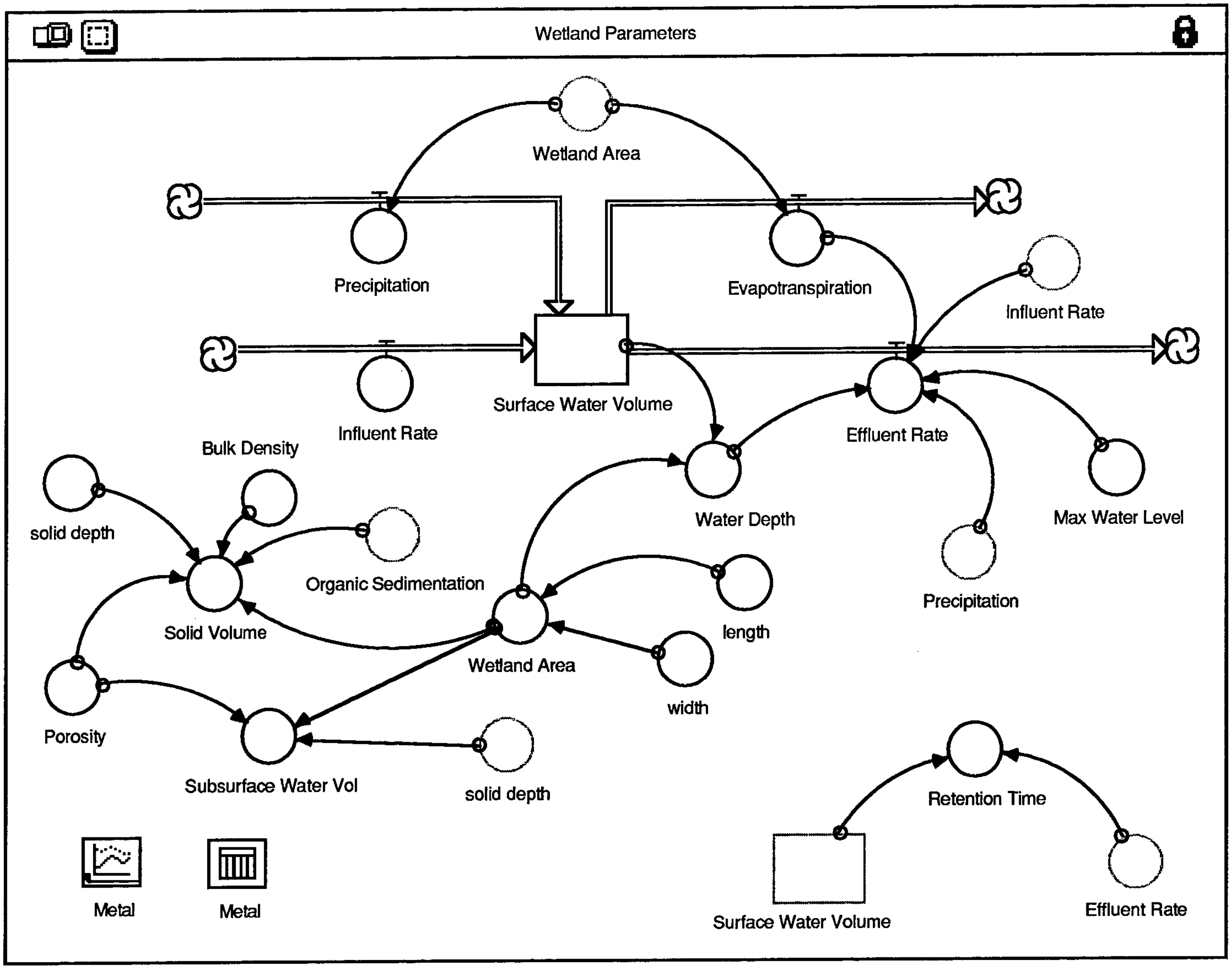
Solid_Volume = (Wetland_Area*solid_depth*(1-Porosity)*Bulk_Density)+Organic_Sedimentation {kg}

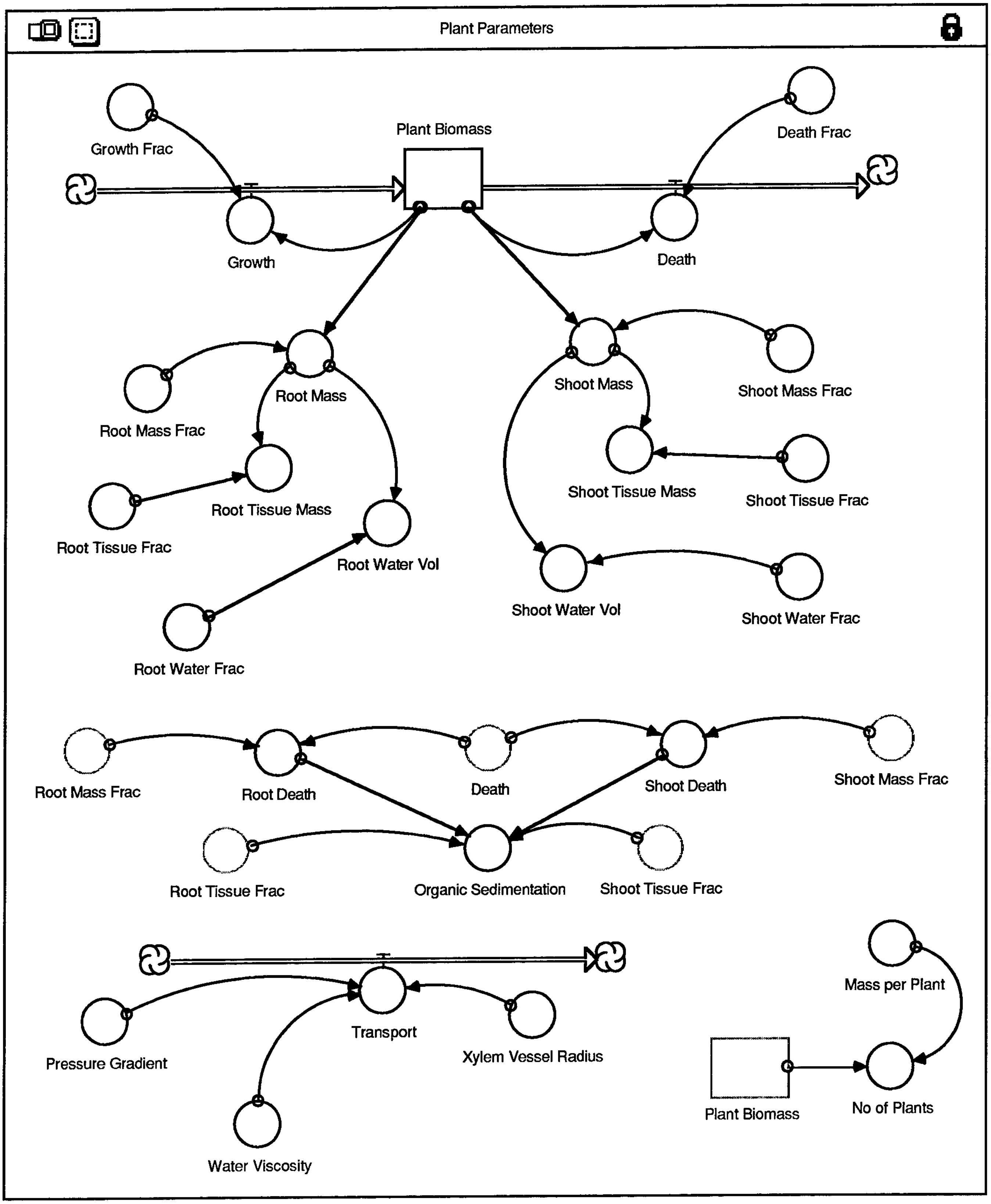
Subsurface_Water_Vol = Porosity*solid_depth*Wetland_Area*1000 {liters}

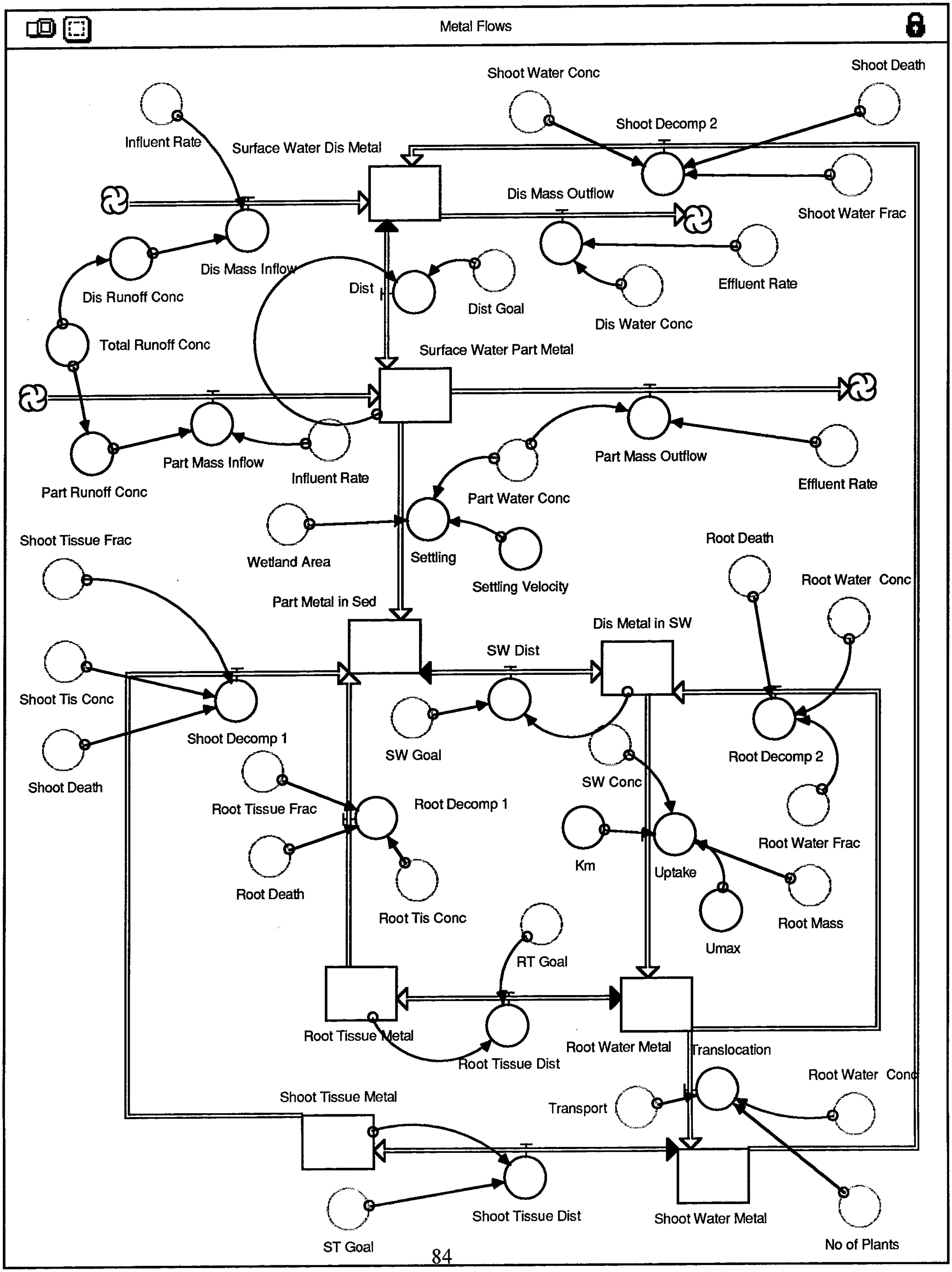
Water_Depth = (Surface_Water_Volume/1000)/Wetland_Area {meters}
DOCUMENT: Note: surface water volume is converted back to cubic meters here.

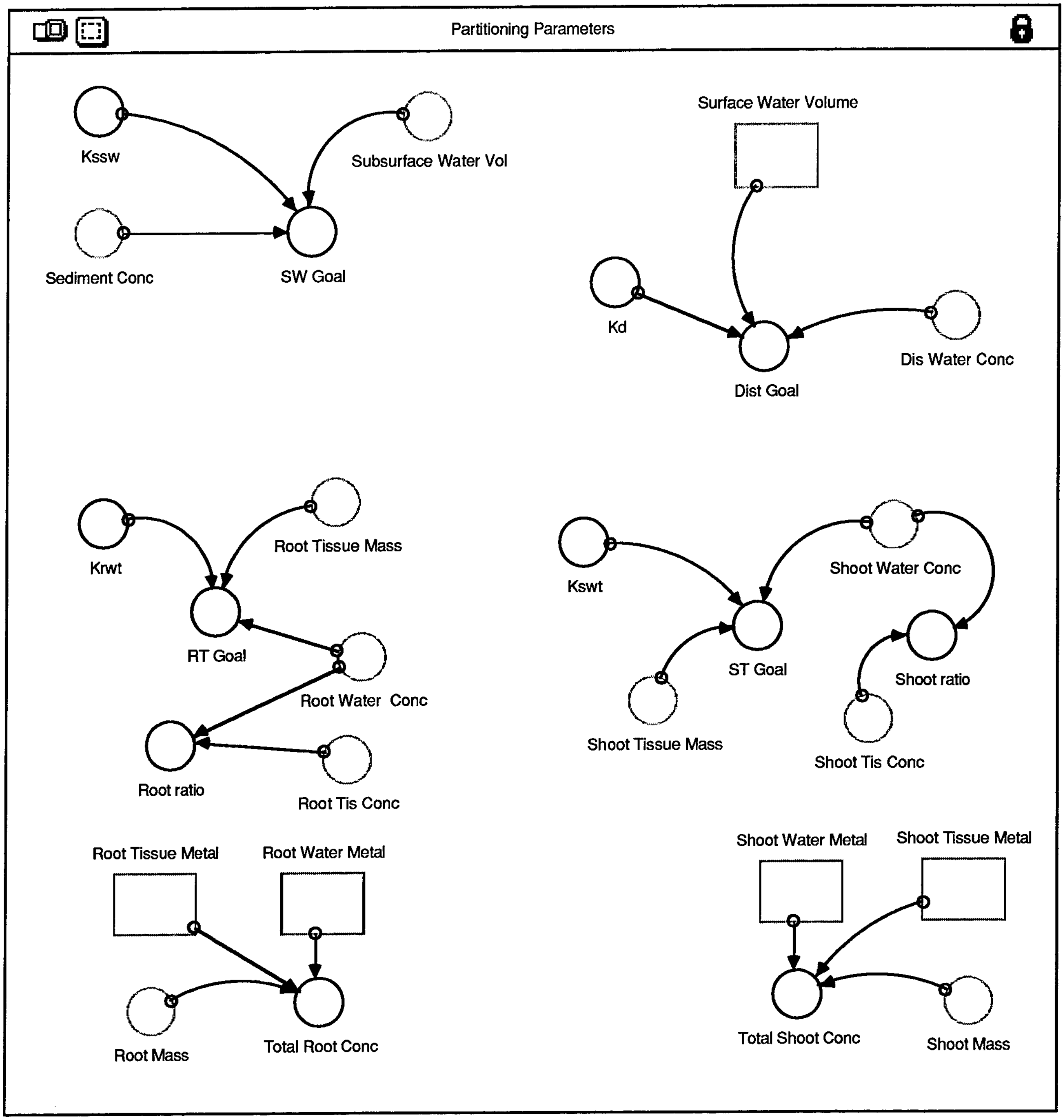
Wetland_Area = width*length {square meters}
DOCUMENT: Hammer recommends a 2:1 length-to-width ratio in constructed wetlands (Hammer, 1989).

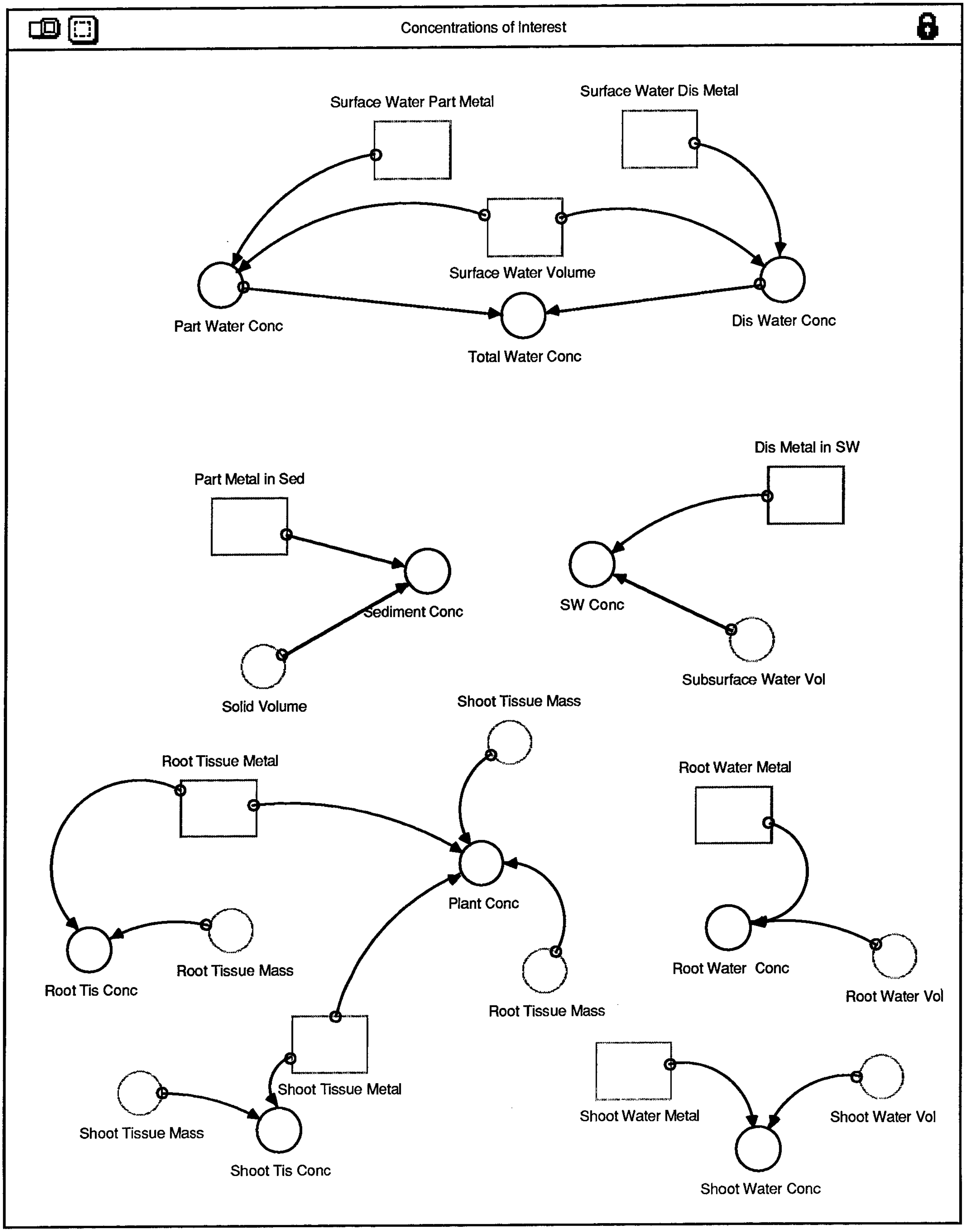
width = 45 {meters}


Wetland Parameters
Wetland Area
Precipitation
Evapotranspiration
Influent Rate
Influent Rate
Surface Water Volume
Effluent Rate
Bulk Density
solid depth
Organic Sedimentation
Water Depth
Max Water Level
Precipitation
Solid Volume
Wetland Area
length
width
Porosity
Subsurface Water Vol
solid depth
Retention Time
Metal
Metal
Surface Water Volume
Effluent Rate


Plant Parameters
Growth Frac
Plant Biomass
Death Frac
Growth
Death
Root Mass
Shoot Mass
Root Mass Frac
Shoot Mass Frac
Root Tissue Mass
Shoot Tissue Mass
Shoot Tissue Frac
Root Tissue Frac
Root Water Vol
Shoot Water Vol
Shoot Water Frac
Root Water Frac
Root Mass Frac
Root Death
Death
Shoot Death
Shoot Mass Frac
Root Tissue Frac
Organic Sedimentation
Shoot Tissue Frac
Mass per Plant
Transport
Pressure Gradient
Xylem Vessel Radius
Plant Biomass
No of Plants
Water Viscosity


Metal Flows
Shoot Water Conc
Shoot Death
Shoot Decomp 2
Influent Rate
Surface Water Dis Metal
Shoot Water Frac
Dis Mass Outflow
Dis Mass Inflow
Dist
Dist Goal
Effluent Rate
Dis Runoff Conc
Dis Water Conc
Total Runoff Conc
Surface Water Part Metal
Part Mass Outflow
Part Mass Inflow
Influent Rate
Effluent Rate
Part Runoff Conc
Part Water Conc
Shoot Tissue Frac
Wetland Area
Settling
Root Death
Settling Velocity
Root Water Conc
Part Metal in Sed
Dis Metal in SW
SW Dist
Shoot Tis Conc
Shoot Decomp 1
SW Goal
Root Decomp 2
Shoot Death
SW Conc
Root Tissue Frac
Root Decomp 1
Root Water Frac
Km
Uptake
Root Death
Root Mass
Root Tis Conc
Umax
RT Goal
Root Tissue Metal
Root Water Metal
Translocation
Root Tissue Dist
Root Water Conc
Shoot Tissue Metal
Transport
Shoot Tissue Dist
Shoot Water Metal
ST Goal
No of Plants


Partitioning Parameters
Kssw
Subsurface Water Vol
Sediment Conc
SW Goal
Surface Water Volume
Kd
Dis Water Conc
Dist Goal
Krwt
Root Tissue Mass
RT Goal
Root Water Conc
Root ratio
Root Tis Conc
Kswt
Shoot Water Conc
ST Goal
Shoot ratio
Shoot Tissue Mass
Shoot Tis Conc
Root Tissue Metal
Root Water Metal
Root Mass
Total Root Conc
Shoot Water Metal
Shoot Tissue Metal
Total Shoot Conc
Shoot Mass


Concentrations of Interest
Surface Water Part Metal
Surface Water Dis Metal
Surface Water Volume
Part Water Conc
Total Water Conc
Dis Water Conc
Dis Metal in SW
Part Metal in Sed
Sediment Conc
SW Conc
Solid Volume
Subsurface Water Vol
Shoot Tissue Mass
Root Tissue Metal
Root Water Metal
Plant Conc
Root Tis Conc
Root Tissue Mass
Root Water Conc
Root Water Vol
Root Tissue Mass
Shoot Tissue Metal
Shoot Water Metal
Shoot Water Vol
Shoot Tissue Mass
Shoot Tis Conc
Shoot Water Conc

Appendix 2. Curve Fitting Calculations

Copper Fitting

This template finds the values of Umax and Km that give the best fit of a Michaelis-Menten curve to experimental data. First, the Michaelis-Menten equation is defined and partial derivatives with respect to Umax and Km are found.

$$f(umax, km, c) := \frac{umax \cdot c}{km + c} \qquad \frac{d}{d\,umax} f(umax, km, c) \rightarrow \frac{c}{(km + c)} \qquad \frac{d}{d\,km} f(umax, km, c) \rightarrow -umax \cdot \frac{c}{(km + c)^2}$$

Next, a matrix consisting of the Michaelis-Menten function and its derivatives and the concentration and experimental data vectors are defined.

$i := 0..4 \qquad C := 0, .1..35$

$$F(c, guess) := \begin{bmatrix} \dfrac{guess_0 \cdot c}{guess_1 + c} \\ \dfrac{c}{\left(guess_1 + c\right)} \\ -guess_0 \cdot \dfrac{c}{\left(guess_1 + c\right)^2} \end{bmatrix} \qquad conc := \begin{bmatrix} 0 \\ .3 \\ 2.1 \\ 7.6 \\ 34.5 \end{bmatrix} \qquad rates := \begin{bmatrix} 0 \\ 4.99 \\ 22.29 \\ 97.41 \\ 102.02 \end{bmatrix}$$

Next, guesses for Umax and Km are supplied and the fitting functinon is defined. The fitting function uses a vector returned by Mathcad's genfit function. This vector contains the optimal values for Umax and Km. The fitting function is plotted against the actual data.

$$guess := \begin{pmatrix} 115 \\ 10 \end{pmatrix} \qquad bestfit := genfit(conc, rates, guess, F) \qquad fit(C) := F(C, bestfit)_0$$

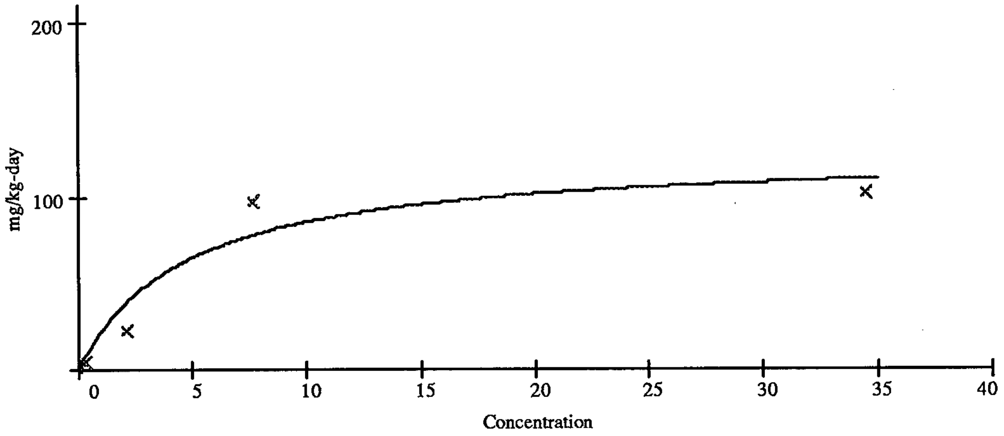
$$bestfit = \begin{pmatrix} 124.032 \\ 4.523 \end{pmatrix}$$

Next, a vector containing the data points given by the fitted line is defined. These points will be compared to actual data to determine the correlation coefficient.

$$\text{linedata} := \begin{bmatrix} \text{fit}(0) \\ \text{fit}(.3) \\ \text{fit}(2.1) \\ \text{fit}(7.6) \\ \text{fit}(34.5) \end{bmatrix} \qquad \text{linedata}^T = (\,0 \quad 7.715 \quad 39.328 \quad 77.757 \quad 109.656\,)$$

Finally, the correlation coefficient is calculated. $r := \text{corr}(\text{rates}, \text{linedata}) \quad r = 0.964 \quad r^2 = 0.929$

Copper Uptake Curve



Lead Fitting

This template finds the values of Umax and Km that give the best fit of a Michaelis-Menten curve to experimental data. First, the Michaelis-Menten equation is defined and partial derivatives with respect to Umax and Km are found.

$$f(\mathrm{umax},\mathrm{km},c) := \frac{\mathrm{umax}\cdot c}{\mathrm{km}+c} \qquad \frac{d}{d\mathrm{umax}}f(\mathrm{umax},\mathrm{km},c) \rightarrow \frac{c}{(\mathrm{km}+c)} \qquad \frac{d}{d\mathrm{km}}f(\mathrm{umax},\mathrm{km},c) \rightarrow -\mathrm{umax}\cdot\frac{c}{(\mathrm{km}+c)^2}$$

Next, a matrix consisting of the Michaelis-Menten function and its derivatives and the concentration and experimental data vectors are defined.

$$i := 0..4 \qquad C := 0,.1..95$$

$$F(c,\mathrm{guess}) := \begin{bmatrix} \dfrac{\mathrm{guess}_0\cdot c}{\mathrm{guess}_1+c} \\ \dfrac{c}{\left(\mathrm{guess}_1+c\right)} \\ -\mathrm{guess}_0\cdot\dfrac{c}{\left(\mathrm{guess}_1+c\right)^2} \end{bmatrix} \qquad \mathrm{conc} := \begin{bmatrix} 0 \\ 1 \\ 5 \\ 8 \\ 90 \end{bmatrix} \qquad \mathrm{rates} := \begin{bmatrix} 0 \\ 5.81 \\ 62.7 \\ 119.21 \\ 195.37 \end{bmatrix}$$

Next, guesses for Umax and Km are supplied and the fitting functinon is defined. The fitting function uses a vector returned by Mathcad's genfit function. This vector contains the optimal values for Umax and Km. The fitting function is plotted against the actual data.

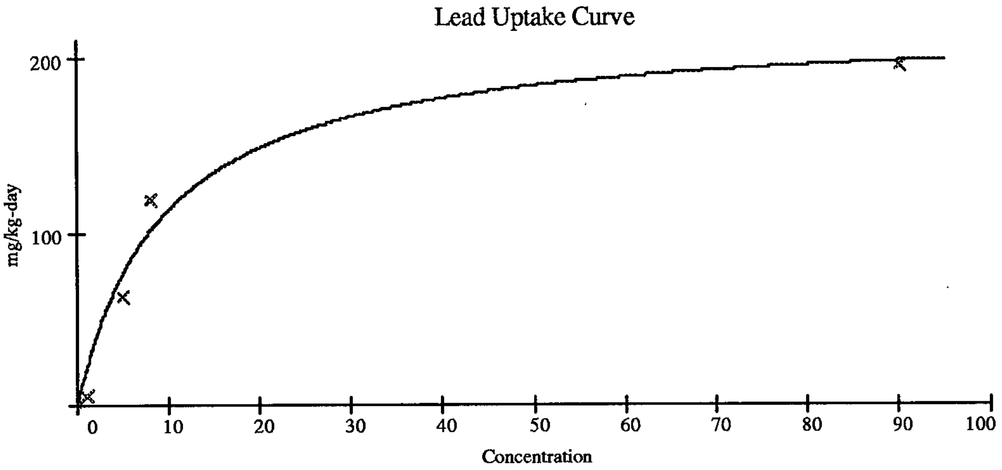
$$\mathrm{guess} := \begin{pmatrix} 220 \\ 10 \end{pmatrix} \qquad \mathrm{bestfit} := \mathrm{genfit}(\mathrm{conc},\mathrm{rates},\mathrm{guess},F) \qquad \mathrm{fit}(C) := F(C,\mathrm{bestfit})_0$$

$$\mathrm{bestfit} = \begin{pmatrix} 218.664 \\ 9.375 \end{pmatrix}$$

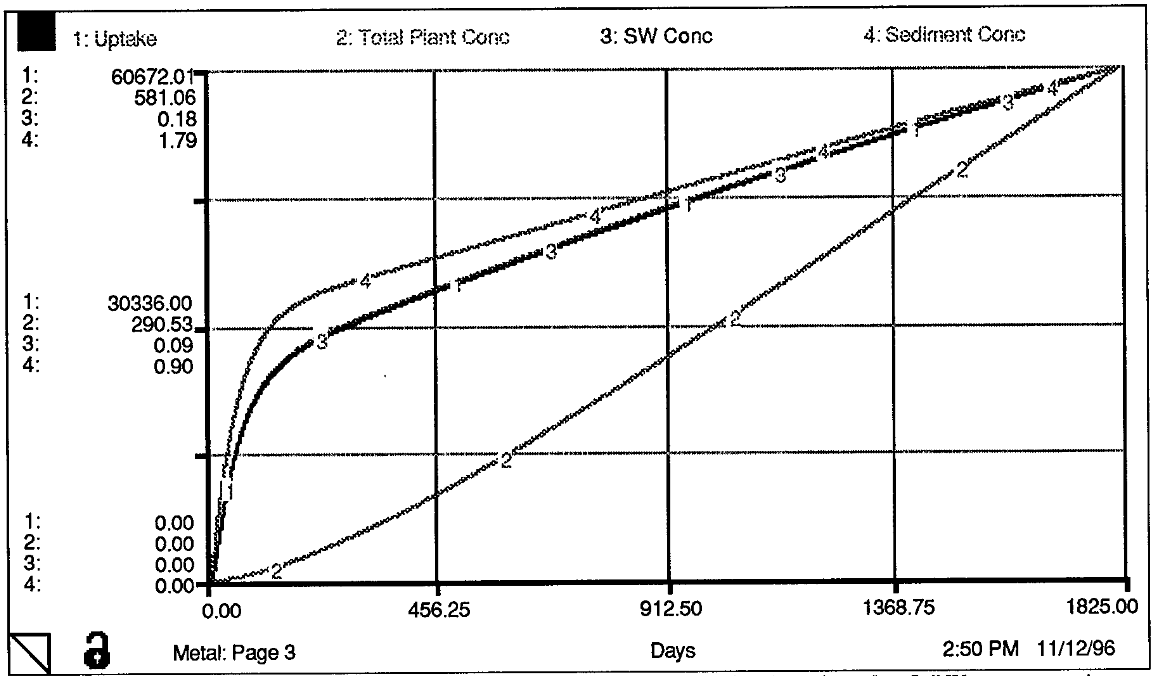
Next, a vector containing the data points givne by the fitted line is defined. These points will be compared to actual data to determine the correlation coefficient.

$$\text{linedata} := \begin{bmatrix} \text{fit}(0) \\ \text{fit}(1) \\ \text{fit}(5) \\ \text{fit}(8) \\ \text{fit}(90) \end{bmatrix} \qquad \text{linedata}^{T} = (\, 0 \quad 21.077 \quad 76.059 \quad 100.682 \quad 198.036 \,)$$

Finally, the correlation coefficient is calculated. $r := \text{corr}(\text{rates}, \text{linedata})$ $r = 0.987$ $r^2 = 0.975$

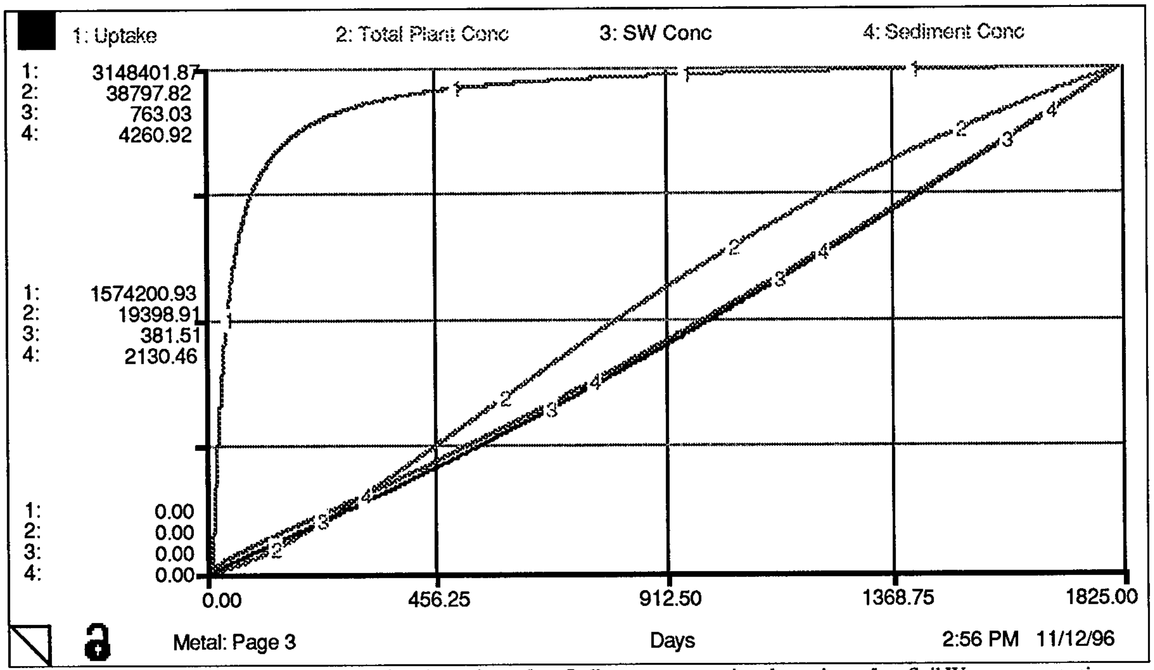

Lead Uptake Curve

Appendix 3. Model Analysis



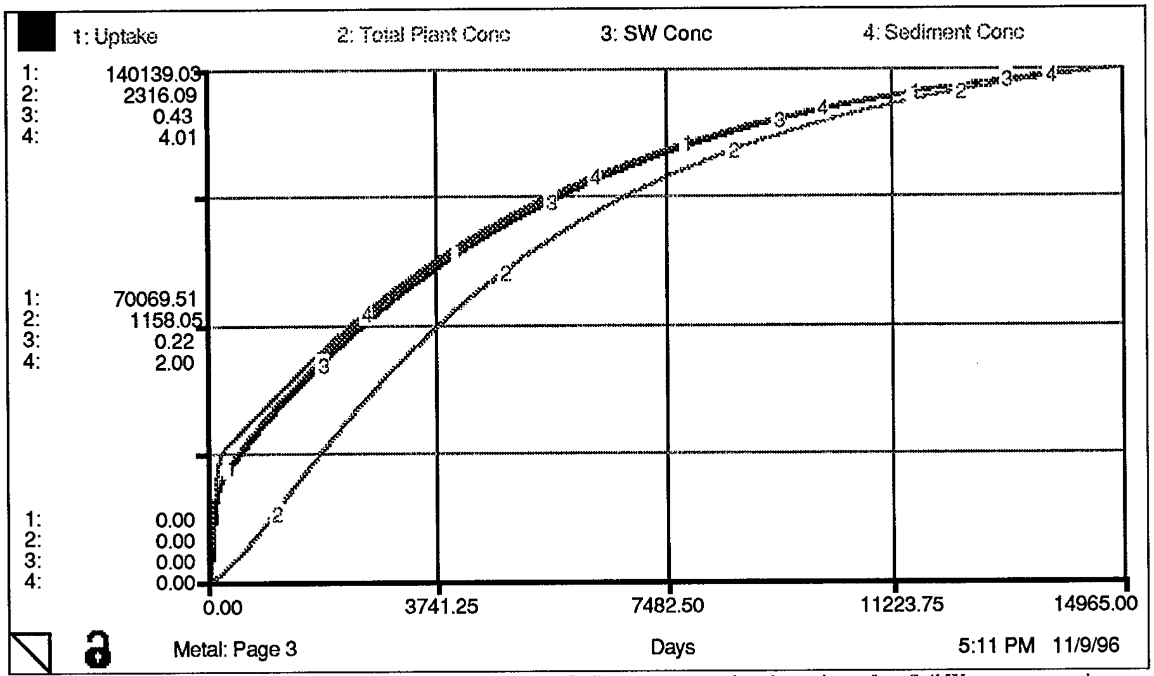
Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 14.
5 Year Lead Uptake and Compartment Concentrations (@ 0.46 mg/L)



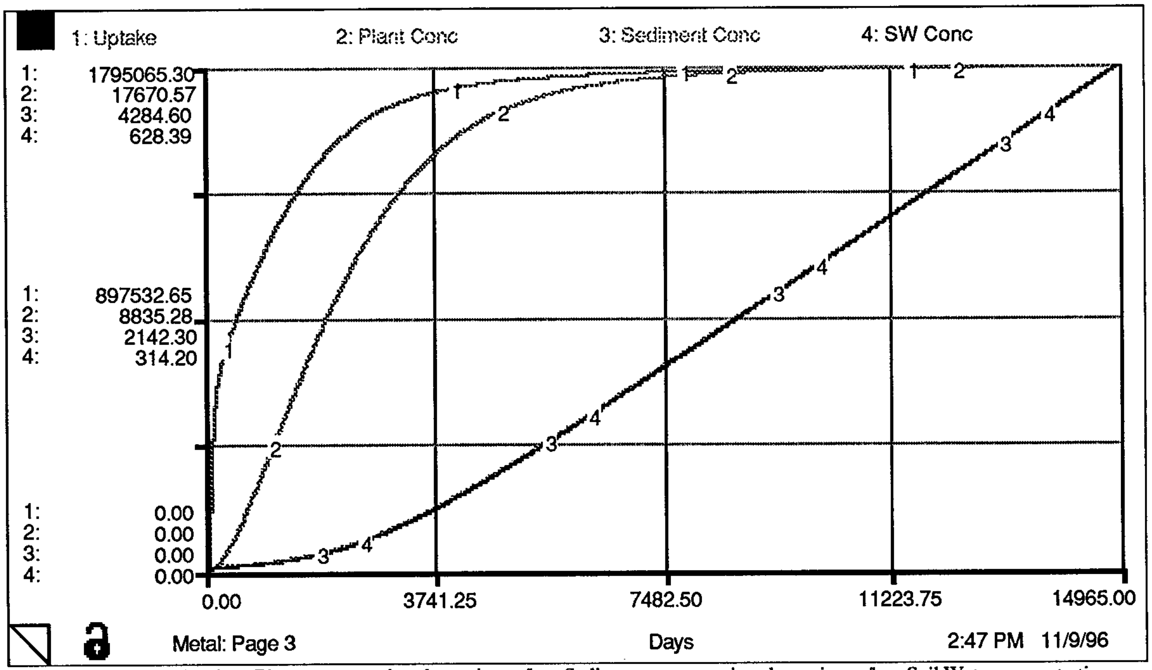
Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 15.
5 Year Lead Uptake and Compartment Concentrations (@ 100 mg/L)



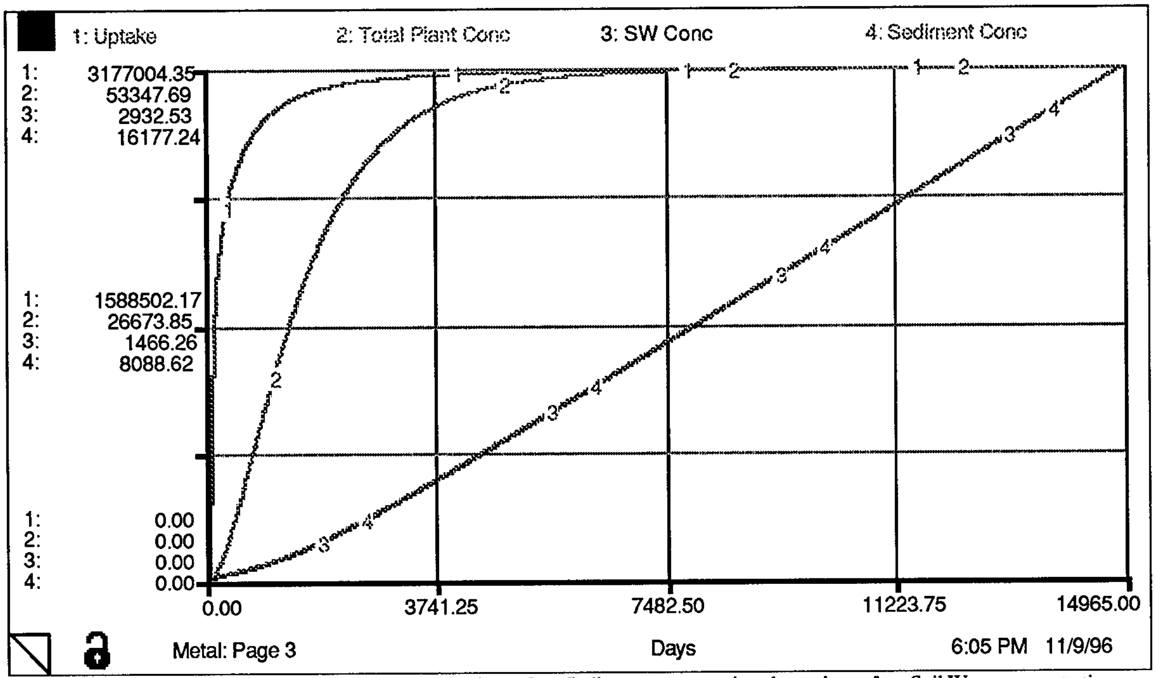
Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 16.
40 Year Lead Uptake and Compartment Concentrations (@ 0.46 mg/L)



Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 17.
40 Year Copper Uptake and Compartment Concentrations (@ 10 mg/L)



Uptake shown in mg/kg-day. Plant concentration shown in mg/kg. Sediment concentration shown in mg/kg. Soil Water concentration shown in mg/L.

Figure 18.
40 Year Lead Uptake and Compartment Concentrations (@ 46 mg/L)

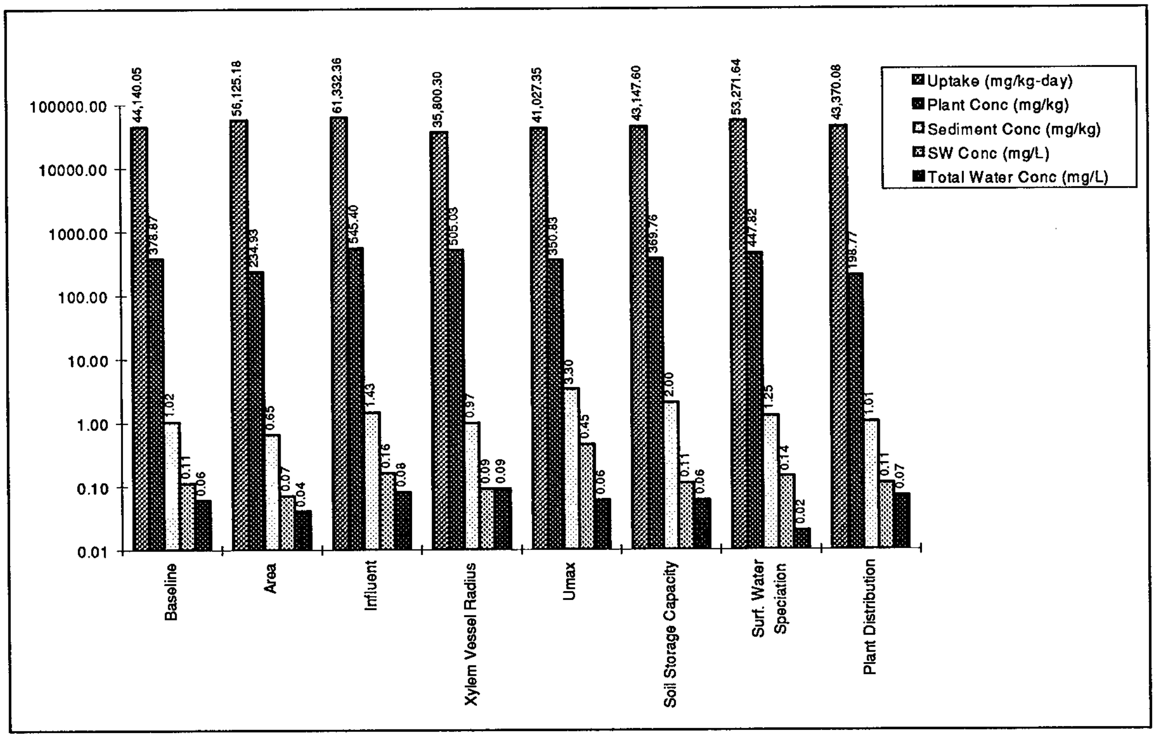


Figure 19.
Sensitivity Analysis Comparison Summary (Cu)

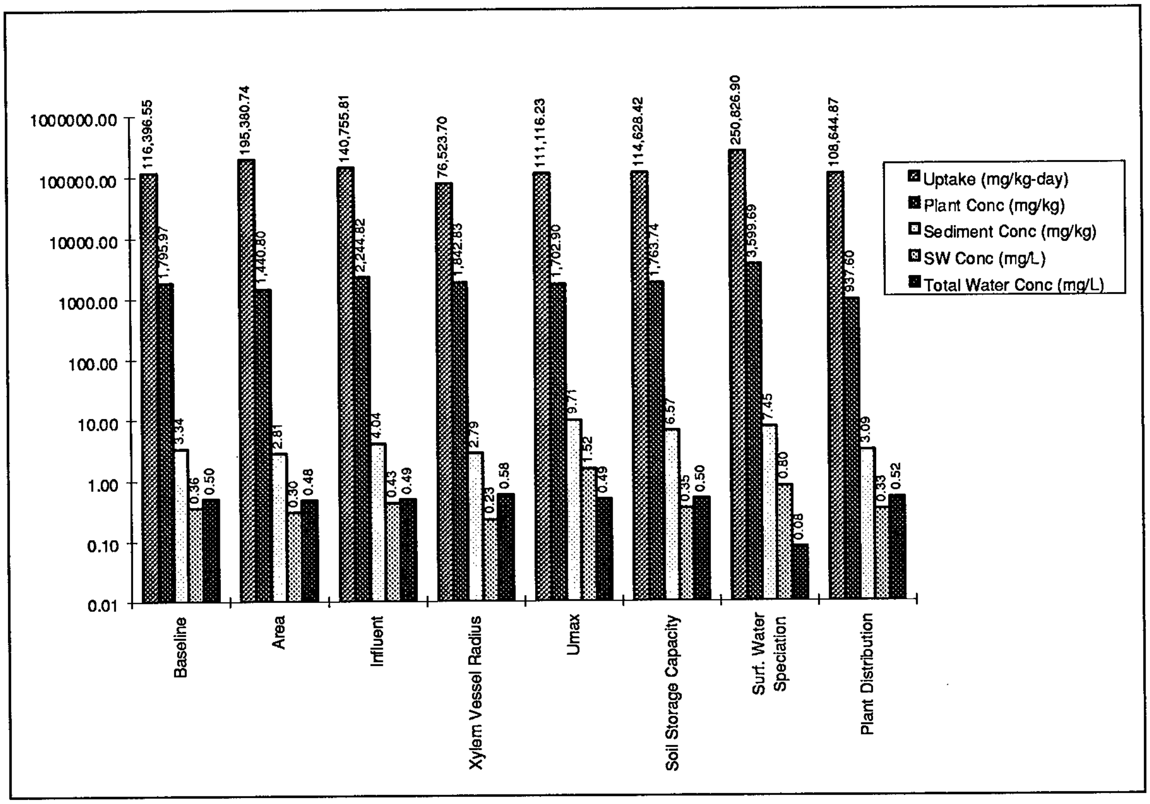


Figure 20.
Sensitivity Analysis Comparison Summary (Pb)

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13. ABSTRACT *(Maximum 200 words)*

Many communities and Air Force installations are using constructed wetlands to filter trace metals from their stormwater runoff. Constructed wetlands are attractive to industry for runoff mitigation because they are relatively cheap to build and operate and require little or no energy for operation. The purpose of this research project is to develop quantitative concepts for understanding the dynamics of metal uptake in constructed wetland plants by constructing a system dynamics model supported by experimental observation and offer environmental managers a tool to simulate, under a broad range of conditions, long-term wetland exposure to stormwater runoff contaminated with trace metals. There are two phases in this project, a modeling phase and an experimental phase. Greater emphasis was given to model development initially in order to determine aspects of the experimental design. The results of the study indicate that metal can accumulate in wetland plants and sediment. Changes in different wetland parameters affect the rate at which metal accumulates in wetland plants and other components. A complete understanding of which wetland parameters to manipulate is essential for proper management of constructed wetlands for stormwater treatment.

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