STORMWATER TREATMENT BY NATURAL SYSTEMS

Final Report for STAR Project #84-026

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CHAPTER 1

INTRODUCTION

In the past few decades, it has become apparent that nonpoint source discharges of pollutants, primarily in the form of stormwater runoff, can contribute significantly to pollutant loadings in receiving water bodies. Nonpoint sources of pollution have been found to contribute significantly to receiving water loadings of nutrients and heavy metals (Wanielista 1982). As a result, efforts have been undertaken in the State of Florida to control nonpoint sources of pollution, particularly those associated with stormwater runoff.

As a means of protecting surface waters from further deterioration, several states have established regulations which require new developments to treat stormwater runoff before discharge from the property. In most cases, this treatment involves retention or detention of specified amounts of runoff volume in shallow ponds. Recently, a major interest has risen in the application of natural treatment systems, such as wetlands, for assimilation of stormwater pollutants in order to minimize the loss of valuable land in meeting these regulations.

Although numerous studies have been conducted on the treatment efficiency of controlled inputs of secondary effluent in wetland systems, with varying results, few detailed studies have been conducted on the feasibility of wetland systems in treating sporadic inputs of stormwater runoff in spite of the fact that numerous wetland areas are currently being used for this purpose. If natural systems such as isolated wetlands and bayheads could be effectively utilized in assimilating stormwater pollutants, then developers would have an incentive to preserve and incorporate them into their stormwater management systems. As a result, wetland areas may come to be viewed as valuable resources to developers rather than wasted land.

The purpose of this research was to investigate the fate and movement of runoffrelated inputs of nutrients and heavy metals in a hardwood wetland north of Orlando, Florida. This research, which began in August 1984 and continued until July 1986, was funded initially by a STAR grant from the Florida Institute of Government and later extended by a subsequent grant from the Florida Department of Environmental Regulation. The major objective was to determine the feasibility of using a hardwood wetland as a stormwater management system. To accomplish this, the following tasks were undertaken:

- 1. Characterization of rainfall and runoff inputs into the wetland system.
- 2. Monitoring of hydrologic inputs into and out of the wetland.
- 3. Characterization of surface and groundwaters along the wetland flowpath and in isolated control areas.
- 4. Investigate the horizontal and vertical migration of nutrients and heavy metals in wetland sediments.
- 5. Determine the chemical speciation of phosphorus and heavy metals in the sediments and the effect on the ability of the sediments to retain inputs of pollutants.
- 6. Determine the influence of pH and redox potential on the chemistry and stability of phosphorus and heavy metals in the sediments.
- 7. To examine the rate of uptake and removal of nutrients and heavy metals during flow through the wetland.

- 8. To examine the physical mechanisms and characteristics which enhance pollutant removal in the wetland to aid in development of specific design suggestions.
- 9. Examine changes in algal productivity on stormwater inputs during flow through the wetland using a series of algal bioassay experiments.

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CHAPTER 2

LITERATURE REVIEW

Introduction

The term "wetland" is a relatively new designation for marshes, bogs, swamps, and other low-lying land dominated by saturated soil conditions. Numerous efforts have been made to define wetlands in terms of function and characteristics. Most of these definitions reflect the fundamental role of water and hydrogeological factors in wetlands. Cowardin et al. (1979) established the following definition as part of the national wetlands inventory.

"Wetlands are lands transitional between terrestrial and aquatic systems where the water table is usually at or near the surface or the lane is covered by shallow water. For purposes of this classification, wetlands must have one or more of the following three attributes: (1) at least periodically the land supports predominantly hydrophytes, (2) the substrate is predominantly undrained hydric soil, and (3) the substrate is non-soil and is saturated with water or covered by shallow water at some time during the growing season of the year."

Natural wetlands are often classified into five major categories, according to hydrological factors: (1) riverine, (2) lacustrine, (3) palustrine, (4) brackish, and (5) tidal (salt marshes). Descriptions of these major classifications are listed in Table 2-1 (Tchobanoglous et al. 1980; Good et al. 1978; and Tourbier et al. (1976). In general, the highest plant productivity is found in systems with open stands of emergent vegetation and/or large open areas which allow algal growth. Therefore, palustrine freshwater

TABLE 2-1

CLASSIFICATION OF NATURAL WETLAND SYSTEMS

WETLAND SYSTEM	SYSTEM CHARACTERISTICS	VEGETATION TYPES	SENSITIVITIES
Freshwater Marshes - Riverine (associated with water channels)	Water circulation distributes dissolved and suspended materials through system. Good aeration and light penetration.	Emergent plants - cattails, reeds, sedges, bulrush, watercress; floating algae.	Subject to sedimentation, scouring and seasonally-changing water levels. Pollutant loadings vary with watershed.
Freshwater Marshes - Lacustrine (associated with ponds and lakes)	Temperature/oxygen stratification and light attenuation can cause major differences in top, middle and bottom layers. Circulation is often poor.	Floating plants - duckweed, water fern, water primrose, pondweeds and others. Emergent plants - see riverine system; submerged plants.	Closed or semi-closed systems. Pollutants enter food chain or accumulate in sediments.
Freshwater Marshes - Palustrine (not confined by channels or adjacent to lakes)	Surface layer has thick and/or porous deposits with high organic content. Marsh is fed by subsurface seepage/high groundwater.	Peat bogs, cypress, mangrove and papyrus swamps - vegetation types often specific to geographical area.	Isolation from open water bodies (streams, rivers and lakes) limits water exchange, forming potential pollutant sink.
Brackish Marshes - (salinity > 0.4 ppt)	Marsh fed by seasonal surface flows and/or seepage; may also be subject to tidal influences; can experience salinity fluctuations.	Emergent plants - sedges, bulrush, pickleweed, saltgrass, saltbush.	Evaporation can lead to salinities of 60-80 ppt and concentration of pollutants.
Salt Marshes - (subject to tidal influence)	 wetlands near streams lower wetlands - reversing flow lower wetlands - drained only at low tides upper wetlands - inundated only at high tides 	Emergent plants - pickleweed, cordgrass, sedges, saltgrass.	Salinity and sediment interactions can trap pollutants; however, low pH and oxidizing muds can re- release pollutants to system on a continuing basis.

SOURCES: Tchobanoglous et al. (1980); Good et al. (1978); and Tourbier et al. (1976).

marshes with peat-filled bogs or heavily shaded wooded swamps generally do not exhibit productivity as great as fresh or salt water marshes. Lacustrine marshes are largely regulated by water level in the system, and emergent plants are generally limited to pond and lake fringes where the water depth is less than 1 to 2 meters. Brackish marshes often occur within salt marsh areas near streams, and in many cases, can be considered as a type of salt marsh.

The Center for Wetlands at the University of Florida has developed a classification scheme based upon dominant species, hydroperiod, soils, and water regime. According to this method, the following wetland types exist in the State of Florida: (1) Hydric Hammock, (2) Mixed Hardwood Swamp, (3) Cypress Dome, (4) Bayhead, (5) Wet Prairie, (6) Shallow Marsh, and (7) Deep Marsh. Data for selected parameters of importance, including evapotranspiration, hydroperiod, water level, recharge potential, peat depth, and primary production associated with each wetland type are given in Table 2-2. These physical characteristics allow for the comparison of one wetland with the others and for comparison of individual functional characteristics between wetland communities.

By nature, most wetland systems receive surface runoff from adjacent lands and water bodies. To varying degrees, this provides treatment of runoff water inputs. In the past few years, serious attention has been given to capitalizing on wetland processes as a means of providing detention storage and treatment of stormwater flows.

Many wetlands have been receiving inadvertent as well as intentional inputs of stormwaters for a number of years. However, there have been only a few instances where stormwater has been specifically routed into natural or artificial wetlands for flood

TABLE 2-2

CHARACTERISTICS OF SELECTED WETLAND TYPES

PARAMETER	HYDRIC HAMMOCK	MIXED HARDWOOD SWAMP	CYPRESS DOME	BAYHEAD	WET PRAIRIE	SHALLOW MARSH	DEEP MARSH
Water Quality Enhancement, % Removal Phosphorus Nitrogen	40 40	90 98	98 92	85 85	40 60	98 97	30 30
Evapotranspiration (mm/day)	4.0	5.8	3.8	3.0	5.4	5.6	5.6
Hydroperiod (days)	100-150	200-250	250-300	200-250	150-200	365	365
High Water (m)	0.10	0.60	0.50	0.30	0.50	0.70	1.00
Low Water (m)	0	0	0	0	0	0	0.20
Maximum Level (m)	0.30	1.50	1.50	1.00	1.50	2.00	2.00
Recharge Potential (m ³ /m ² /day)	0.1	0.1	0.84	0.6	0.37	0.68	0.1
Peat Depth (m)	0.0-0.2	0.0-0.5	0.0-0.5	0.5-3.0	0-1.5	0.5-3.0	0.0-1.0
Gross Primary Productivity (g organic matter/m ² /day) during growing season	60	52.1	25.3	20.0	23.9	19.6	54.5

control or water quality management purposes. Where the practice has been intentionally employed, consistent reductions of BOD, suspended solids, and heavy metals have been generally observed. Current stormwater treatment through wetlands encompasses three main categories (Chan et al. 1982):

- 1. Systems planned primarily for flood control with treatment as an incidental benefit
- 2. Systems planned and operated with treatment of stormwater pollutants as a primary objective
- 3. Existing wetland systems providing detention and treatment of stormwater flows as an unplanned, natural function

<u>Physical and Chemical</u> <u>Removal Mechanisms in Wetlands</u>

In general, pollutants can be removed by a wetland system through three main mechanisms: loss to the atmosphere by volatilization, incorporation into the sediments or biota, and degradation. A summary of these major removal mechanisms, as modified from Chan et al. (1982), is given in Table 2-3.

Volatilization

In general, the atmosphere acts as a sink for pollutants in wetlands rather than a source. Pollutants enter the atmosphere primarily by evaporation (Elzerman et al. 1979), but may also enter by aerosol formation under windy conditions (Dilling et al. 1975). Common pollutants for which volatilization may be an important removal mechanism in wetlands includes oils (Shelton et al. 1974), chlorinated hydrocarbons (Dilling et al. 1975), and mercury (Sayler et al. 1976). The rate of volatilization in wetlands is affected

TABLE 2-3

PHYSICAL AND CHEMICAL POLLUTANT REMOVAL MECHANISMS IN WETLAND AND AQUATIC SYSTEMS

	POLLUTANT AFFECTED											
MECHANISM	SETTL FABLE SOLIDS	COLLOIDAL SOLIDAL	ORGANIC COMPOUNDS	PETROLEUM HYDROCARBONS	NITROGEN	SUJOHASOHA	HEAVY METALS	BACTERIA AND VIRUSES	HALOGENATED HYDROCARBONS	DESCRIPTION		
PHYSICAL												
Evaporation			X	X			X ¹		X	Volatilization and aerosol formation		
Sedimentation	x	Χ.		x	Х		X ²		x	Gravitational settling of particles and adsorbed pollutants		
Emulsification		х	x	х			X1		x	Suspension of chemicals that are sparingly soluble in water within an aqueous environment		
Adsorption		x	x	X			x	x	x	Electrostatic attraction, Van der Waals force		
Filtration	x	x						x		Mechanical filtration of particles through substrate, roots or animal systems		

TABLE2-3 -- CONTINUED

			P	OLLUT	ANT AF					
MECHANISM	SETTLEABLE SOLIDS	COLLOIDAL SOLIDS	ORGANIC COMPOUNDS	PETROLEUM HYDROCARBONS	NLTROGEN	PHOSPHORUS	HEAVY METALS	BACTERIA AND VIRUSES	HAL/OGENATED HYDROCARBONS	DESCRIPTION
CHEMICAL										
Chelation						x	x			Formation of metal complexes through ligands
Precipitation				х		x	x			Formation or coprecipitation of insoluble compounds
Decomposition			x	х	X	x	X	x	X	Alteration of less stable compounds by oxidation, reduction, hydrolysis or photochemical reaction
Chemical Adsorption			x	x	x	x	x		x	Covalent bonding, hydrogen bond formation, hydrophobic interaction

NOTES:

Significant only for mercury
 Not significant for manganese and mercury

SOURCE: Chan et al. (1982) by surface films which occur in both freshwater and marine environments. These surface films are composed of decomposition and metabolic byproducts such as fatty acids, esters, alcohols, lipids, and hydrocarbons (Elzerman et al. 1979). These films can both decrease the rate of volatilization by acting as a barrier to volatile solutes which are not soluble in the film with subsequent loss by evaporation. Elzerman et al. (1979) found concentrations of zinc, cadmium, lead and copper as high as 100 ppm in surface films of the Great Lakes. It was suggested that these surface films may allow easy access for metals to the food web through surface eating fish, insects and other organisms.

Sedimentation

Sedimentation is probably one of the most important mechanisms by which particulate pollutants are removed from the water column. Deposition of suspended matter and overall pollutant removal effectiveness in wetlands is affected largely by the nature of the flow patterns through the wetland. Tilton and Kadlec (1979) reported that sheet flow and meandering channels led to large effective flow rates and best deposition rates in a wetland receiving wastewater effluent. Agglomeration of small particles onto as well as into larger, more easily settleable solids is often the primary mechanism for removal of these finer particles from the water column. This process has been reported as important for removal of particulate nitrogen (McElroy et al. 1978), oils (Gearing et al. 1980), chlorinated hydrocarbons (Choi and Chen 1976), and heavy metals with the exceptions of manganese and nickel (Rohatgi and Chen 1975).

Adsorption

Adsorption onto suspended solids or bottom sediments is a principle mechanism for removal of dissolved pollutants in natural water. Bonding of ions to solids through adsorption occurs by three main mechanisms (Weber 1976):

1. Electrostatic attractions between oppositely charged particles

- 2. Physical attractions such as hydrogen bonds
- 3. Chemical reactions which form new molecules

Weber (1976) also concluded that adsorption rates were inversely related to the size of the sorbent particles and directly related to the organic content of both the particles and the soils.

Adsorption mechanisms are enhanced by shallow water depths and long residence times which increase contact opportunities with the soil and generally increase the removal efficiencies for dissolved ions. Sutherland and Bevis (1979) found that the most effective removal of ionic species from wastewater occurred in seepage wetlands where inputs seep into the soil prior to discharging from the wetland. They reported nearly complete removal of phosphorus from wastewater effluents in seepage wetlands discharging to perimeter drainage ditches.

Rosenfeld (1979) reported that the primary removal mechanism for ammonium ions in wetlands was adsorption onto organic matter. He concluded that this adsorption process was both rapid and reversible and occurred primarily by ion exchange and enmeshment processes.

The adsorption of phosphate in freshwater sediments has been closely linked with concentrations of iron and aluminum by virtue of the tendency of phosphate ions to adsorb onto hydrous oxides of both metals. The stability of phosphorus in these associations is clearly sensitive to both pH and redox potential (Lijklema 1980). Under reduced conditions in deep sediments, hydrous oxides of iron become soluble and both phosphorus and iron diffuse toward the sediment/water surface. As oxic zones are encountered near the surface, iron becomes oxidized and phosphates are readsorbed onto the ferric complexes in the aerobic zone. This often leads to an enriched zone of both phosphorus and iron in the top sediment layers. However, if the upper sediment layers are primarily anoxic, this enriched zone will not form.

The adsorption of heavy metals onto organic matter in both the sediments and the water column is well documented. These adsorption processes are affected primarily by changes in pH, redox potential, temperature, ionic strength, soluble organic complexes, and competing ions. For example, Rohatgi and Chen (1975) found that cadmium is better adsorbed to suspended solids in low ionic strength water under aerobic conditions. However, under anoxic conditions, cadmium performs an exchange reaction with iron at the surface of ferrous sulfide substrates. Copper, unlike cadmium, is absorbed more strongly in high ionic strength water than in low ionic strength water. Saar and Weber (1980) reported a strong affinity of lead for organic complexes. Sayler and Colwell (1976) found that mercury is readily adsorbed onto solid particles, but is likely to originate from an initial oil association rather than water.

Complexation

Many inorganic molecules and ions can form stable complexes with metal species in natural waters. Reactions with hydroxides and carbonates are quite common, and

many hydroxy, carbonate and hydroxy-carbonate species are known to exist. Complexes with chlorides, sulfates, and phosphates, along with many other minor ions, can also be formed. The presence of complexing species will generally increase the solubility of slightly soluble metal salts.

Organic matter in natural waters includes a great variety of organic complexes which are usually present in minute concentrations. Organic materials appear to be present to some extent in most natural waters and, in some cases, are sufficiently concentrated to color the water yellow or brown. Most of the natural organic chemicals found in surface waters can be regarded as products of both synthesis and degradation of biological compounds. Humic substances and compounds, which are formed by transformation of biogenic substances within the soil and water, are believed to represent the most significant fraction of this organic matter. According to Forstner and Wittman (1979), about 60 to 80 percent of the dissolved organic carbon and particulate organic in fresh waters consists of humic substances.

Fulvic acids are generally considered to be degradation products of the more insoluble humic acids, and as a result of their higher solubility, are generally the most abundant humic acid occurring naturally in water. In addition to humic substances, tannins are often present in fresh waters where leaching of bark and leaf litter is abundant. Tannins have chemical properties similar to those of humic substances (Stumm and Morgan 1981). In addition to forming complexes, these acids also lower the pH, promoting dissolution of metals from solids, making them available for complexation. An investigation into the effects of complex organics, such as fulvic acid, on heavy metal speciation under aerobic conditions has been conducted by Yousef (1985). In this investigation, a computer program known as WATEQ2 was used to determine metal speciation of zinc, copper, cadmium, nickel, and lead with varying concentrations of fulvic acid between 1 and 50 mg/l. The results of this investigation indicated that zinc, nickel and lead formed no appreciable metal organic complexes, even at high concentrations of fulvate. Cadmium began to exhibit a metal organic complex at concentrations of fulvic acid greater than 10 mg/l. Both iron and copper, however, exhibit significant metal organic complexes even at low concentrations of fulvate.

Precipitation and Dissolution

Many ionic species, particularly metals, dissolve or precipitate in response to changes in the chemistry of the wetland environment. Metals, such as cadmium, copper, lead, mercury, silver, and zinc, form insoluble sulfides under reduced conditions commonly found in wetlands (Gambrell et al. 1980). Under oxidized conditions, metals such as aluminum, cadmium, chromium, iron, manganese, and zinc form insoluble oxides and hydroxides. Dissolution of formerly insoluble metal complexes commonly occurs in organic-rich sediments as a result of reductions in pH caused by release of organic acids during decomposition. A complete discussion of the effects of both pH and redox potential on metal solubility is given in Harper (1985).

Oxidation-Reduction Processes

The redox potential of a soil or water is a measure of the electrochemical potential or electron availability within these systems for oxidation-reduction type reactions. Oxidation is the loss of electrons and reduction is the gain of electrons. Since many redox reactions will be occurring simultaneously at any given time, a measurement of redox potential for a system is actually a mixed potential which reflects a weighted average of the potentials contributed by each of the redox couples present in the system (Bohn 1971). Since organic matter is continually being added or deposited in most natural systems, which can in turn be oxidized and serve as an electron donor, a redox equilibrium is almost never attained in a natural system (Bohn 1971).

Measurements of redox potential in aquatic systems are closely correlated with measurements of dissolved oxygen due to the fact that oxygen, when available, is used as the terminal electron acceptor by microorganisms according to:

$$O_2(g) + 4H^+ + 4e^- < ---- > 2H_2O$$

If the demand for oxygen exceeds the supply, facultative and then anaerobic organisms become active. As oxygen is depleted in the sediment along with the oxidized forms of many redox couples, the number of reduced compounds increases with a corresponding increase in electron activity. The degree of sediment reduction is then indicated by the magnitude of the redox potential.

Although oxidized environments are usually associated with the presence of free oxygen, oxidation reactions can occur in either the presence or absence of oxygen.

Oxidation of organic matter is constantly taking place in all wetland systems, much of which is biologically mediated. When oxygen is present, the degradation can proceed completely so that carbon dioxide and water are the end products. However, in wetland sediments having a high organic content, molecular oxygen is usually not present. Microbes can use nitrate or sulfate as a source of oxygen in these circumstances to oxidize organic matter. Usually, either nitrate or sulfate is the oxygen-rich agent that is reduced. Nitrate is reduced to nitrite, then to gaseous elemental nitrogen, while sulfate is reduced to hydrogen sulfide and iron sulfide. Some metals may also be reduced to lower oxidation states. Under each of these circumstances, methane and carbon dioxide are the final products of decomposition.

Biochemical Pollutant Removal in Wetlands

Vegetative systems have long been used as natural sinks for contaminants and as treatment systems for wastewater and other pollutant discharges, including stormwater. In general, wetland systems are characterized by: (1) high plant productivity and nutrient uptake, (2) high decomposition activity, (3) large adsorptive areas in sediment substrates, and (4) low oxygen content of the sediments. Each of these properties seem to provide vegetative systems with the ability to degrade and eliminate contaminants.

Vegetative systems possess a variety of mechanisms for obtaining nutrients and other elements from their environments under changing conditions. Through interaction with the various soil layers, water and air interfaces, plants can increase the overall capacity of a system to retain or remove pollutants. Since the primary mechanisms for pollutant removal in wetland systems are physical and chemical interactions that cause the contaminants to settle or be drawn out of the water column into the sediments, plant uptake of pollutants, particularly from the sediments, frees more exchange sites for further pollutant interaction and accumulation. Even if the major mechanisms for pollutant removal in wetlands are considered to be physical and chemical processes, plants provide surfaces for bacterial growth, filtration and adsorption of solids, attenuation of sunlight which retards algal growth, nutrient adsorption and uptake of heavy metals (Chan et al. 1982).

Uptake at the Plant-Soil Interface

Rooted plants actively absorb ions from the soil through the root system as well as through buried portions of shoots and leaves. In fact, the uptake capability of plants is generally directly proportional to the volume of below-ground roots. Upland vegetation generally develops in an aerated soil zone around the roots which shelters aerobic, nitrifying bacteria that convert ammonium ions into nitrate, the form most preferred by plants. However, wetland vegetation typically grows in a saturated and often anaerobic substrate. Under these conditions, ammonification and denitrification processes dominate and create an environment which is high in ammonium ions and low in nitrate ions. Wetland vegetation must, therefore, adapt to use primarily ammonium ions as well as nitrate (Chan et al. 1982).

As described previously, heavy metals as well as phosphorus are deposited in the upper sediment layers of wetlands by a variety of processes. This enriched layer is often within the root zone of plants and constitutes an abundant source for uptake by vascular plants. This process provides temporary removal of metals and phosphorus from the

sediments while they are retained in the plant tissue and provides renewed adsorption sites within the sediments for attraction of other ions. Ten species of emergent vascular plants absorbed 1-3 mg of nickel and 8-57 mg of boron per kg of dry plant weight in a study by Seidel (1976). Water hyacinths (<u>Eichornia crassipes</u>) and alligator weeds (<u>Alternanthera phileroxides</u>) were shown to adsorb lead at a rate of 0.176 mg/g dry weight per day and 0.1 mg/g day, respectively, in a study by Wolverton et al. (1976). In a study by Banus et al. (1975) on a Massachusetts wetland, 6-8 percent of lead inputs were adsorbed by live plants while over 50 percent of the zinc and cadmium was adsorbed by plants.

Uptake at the Plant-Water Interface

Although the majority of nutrient uptake by plants occurs within the rots, many species of wetland vegetation are able to absorb a limited amount of nutrients directly from the water by way of shoots and leaves. Of all nutrients, uptake of nitrogen by this method is the most significant (Boyd 1970), particularly for submerged plant species with poorly developed root systems.

Translocation Through Plant Vascular Systems

Translocation of nutrients and heavy metals from the roots to the shoots and leaves is an important process in the renewal of uptake sites in the roots which allows continued uptake. These translocation processes are generally the greatest during the growing season with peak uptake corresponding with the period of peak biomass production (Lindsley et al. 1976).

With the death of wetland vegetation in the fall, much of the nutrient loading in the leaves and stems is translocated into the roots. When the next growing season begins, the translocated nutrient mass is sent to the actively growing shoots, and additional uptake through the roots begins (Odum et al. 1975). However, unlike nutrients, heavy metals are often not translocated into the roots in the fall, but remain in the above-ground shoots and leaves. As this above-ground mass falls to the ground and decomposes, the accumulated pollutants are gradually released back to the sediments and water phase (Sidel et al. 1976).

Phosphorus Cycling in Wetlands

Physical and chemical removal mechanisms for phosphorus in wetlands includes: (1) sedimentation of particular matter, (2) precipitation and/or sorption onto solid surfaces (Spangler et al. 1976), (3) assimilation by plants and algae (Kitchens et al. 1975), (4) chelation, and (5) decomposition. Phosphorus can also be removed from the wetland surface water column by adsorption onto sediments. This type of removal is dependent upon the type of soils present, soil concentrations of Fe, Al and Ca, hydrologic conditions, pH, and redox potential. Under favorable conditions, high pH and dissolved oxygen, removal of phosphorus can be significant (Stumm and Morgan 1970), although Mortimer (1942), Patrick and Khalid (1974), and others have found that given unfavorable conditions of low pH and dissolved oxygen, the sediment layer can act as a phosphorus source and is able to release phosphates to the water column.

Phosphorus can enter a wet; land in a number of forms such as orthophosphorus, insoluble particulate phosphorus, or organic phosphorus. Under aerobic conditions,

aluminum and iron ions can form insoluble complexes with orthophosphorus, thereby removing the nutrient from the water column through precipitation (Stumm and Morgan 1970). When anaerobic conditions prevail, phosphate can become quite mobile and diffuse from the sediments into the overlying water column (Stumm and Morgan 1970; Patrick and Khalid 1974; and Wetzel 1975). A schematic of the phosphorus cycle in wetlands is given in Figure 2-1.

It is a well-established fact that the redox potential controls the oxidation state of iron and, thus, affects the ability of sediments to retain or release inorganic phosphorus. Mortimer (1941, 1942) showed that the disappearance of dissolved oxygen and the subsequent reduction of the sediment resulted in a several-fold increase of dissolved phosphorus and ferrous iron in the water column. Oxygenation of the sediment reversed the process and decreased the phosphorus concentration in solution. Mortimer (1971) conducted a study on redox potential profiles across the sediment-water interface of Lake Windermere in England. The results suggested that a progressive decline in oxygen concentrations from 2 mg/l to analytical zero at the interface was accompanied by a fall in electrode potential and this correlated with mobilization and transfer into the water of first manganese and then iron. There was also a concurrent release of large quantities of phosphorus previously held in a complex form. It was also found that an oxygen concentration of 1 to 2 mg/l at the sediment surface minimized exchange between the sediment and overlying water.

Patrick and Khalid (1974) observed that anaerobic soils release more phosphate to soil solutions low in soluble phosphate and sorbed more phosphate from solutions high in soluble phosphate than did aerobic soils. The difference in behavior of phosphate



Figure 2-1. Schematic Representation of the Phosphorus Cycle in Wetlands.

under the aerobic and anaerobic conditions was attributed to the change brought about in ferric oxyhydroxide by soil reduction. It was suggested that the probably greater surface area of the gel-like reduced ferrous compounds in an anaerobic soil results in more soil phosphate being solubilized where solution phosphate is low and more solution phosphate being sorbed where solution phosphate is high.

Changes in the pH of sediments also affect the exchange of phosphorus between sediments and the overlying waters. The form of phosphorus in solution is largely determined by the pH, as shown in Figure 2-2. The actual mechanisms for phosphate retention are also a function of the pH. In the acidic region, pH < 5.0, the solubility of iron and aluminum increases. Some soluble phosphate then reacts with the iron and aluminum to form insoluble precipitates. Much larger quantities of phosphate are adsorbed onto iron and aluminum hydrous oxides, this occurring over a wide pH range. Additional adsorption can occur on other clay materials. "Relatively available phosphorus" refers primarily to the availability to plants, but also indicates the availability for leaching from the soil. Maximum availability of phosphorus exists between pH 6.0 and 7.0.

Plants utilize orthophosphorus from the sediments during periods of growth (Klopatek 1975, 1978). Prentki et al. (1978) concluded from investigations on plant uptake that some of the stored phosphorus is transferred to underground structures during the fall, while the remainder returns to the water as litter. From studies conducted by mason and Bryant (1975), it was found that in the fall and early spring, surface waters in wetlands contain elevated concentrations of orthophosphorus due to the leaching of phosphorus from fresh litter. Although phosphorus is rapidly leached from fresh litter into the water, older fallen litter accumulates phosphorus due to microbial activity.


Figure 2-2. Variations in Forms of Dissolved Phosphorus and Phosphorus Retention Mechanisms with Changes in Soil pH.

Phosphorus is generally removed from water passing through wetlands during the growing season and released to some extent in the fall and early spring (Nichols 1983). Differences in hydroperiod, soils, vegetative species, and hydrologic regime have a major impact on the mobility of phosphorus as it migrates through the wetland area. It is, therefore, possible for a wetland to have different removal efficiencies in wet and dry years. Studies by Lee et al. (1975) and Bender and Correll (1974) indicated that wetlands are net exporters of phosphorus as well as nitrogen. However, other studies by Toth (1972), Turner et al. (1976), Nute (1977) and van der Valk et al. (1979) indicated a net retention of both nutrients. Unfortunately, most of these studies lacked detailed hydrologic data to allow examination of causative factors.

The distribution of phosphorus in wetlands varies widely during the year with respect to the major removal and input compartments including vascular plants, other organisms, sediments and hydrologic inputs from groundwater, rainfall and runoff, and base flow. Seasonal patterns are evident and the travel rates of phosphorus along pathways changes greatly. A schematic of the pathways along which phosphorus travels at various rates during the year is presented in Figure 2-3. Performing a mass balance on phosphorus in a wetland, similar to that done by Spangler et al. (1977), leads to the following relationships:

$$P_{o} = P_{I} - (P_{VPL} - P_{VPI}) - P_{PLS} - [(P_{LO} - P_{OI}) - (P_{TLS} - P_{SI})]$$
(2-1)

$$P_{I} = P_{GWI} + P_{RI} + P_{BFI}$$
(2-2)

$$P_{I} - P_{O} = Accumulation/Discharge Rate$$
 (2-3)



Figure 2-3. Pathways Along Which Phosphorus Travels at Various Rates During the Year.

2-23

P _{GWI}	_	rate of phosphorus input by groundwater
P _{BFI}	=	rate of phosphorus input by base flow
P _{RI}	=	rate of phosphorus input by stormwater runoff and precipitation
PI	=	the total rate of phosphorus that is input into the wetland system
P _{vpl}	=	rate of loss of phosphorus to vascular plants
P _{VPI}	=	rate of phosphorus input by vascular plants to the wetland surface water
P _{ls}	=	rate of permanent phosphorus loss to the wetland sediments
P _{lo}	=	rate of loss of phosphorus to organisms other than vascular plants
P _{oi}	-	rate of phosphorus input by other organisms to the wetland surface water
P _{tls}	=	rate of temporary phosphorus loss to the wetland sediments
P _{si}	=	rate of phosphorus input to the wetland surface water by the sediments
Po	-	rate of loss of phosphorus from the wetland surface water to the receiving stream

Nitrogen Transformations in Wetlands

Nitrogen transformations within wetlands are many and complex. Most nitrogen processes are biologically mediated and include ammonification, nitrification, denitrification, and vegetative uptake and release. These processes are affected by the hydrology of the wetland as well as environmental conditions such as substrate characteristics, pH, organic loading, redox potential, temperature, and the degree of bacterial activity. Important transformations of nitrogen in wetlands are shown in Figure 2-4. These processes are discussed in the following sections.



Figure 2-4. Transformations of Nitrogen in a Wetland System Receiving Runoff Inputs.

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Ammonification

Ammonification is the microbial conversion of organic nitrogen to inorganic nitrogen as ammonium. The ammonification process is represented as follows:

$$H_2CCOOH + 3/2 O_2 ----> 2 CO_2 + H_2O + NH_3$$

|
NH₂

This reaction is carried out by many different species of heterotrophic microorganisms (Alexander 1961; Tusneem and Patrick 1971; Hardy and Holsten 1972). In soils, ammonification may involve bacteria, fungi, and actinomycetes, with bacteria being predominant in neutral and alkaline conditions, and fungi in acidic conditions (Alexander 1961).

The amount of ammonium released during microbial decomposition is dependent on the C/N ratio of the material being decomposed (Alexander 1961; Bartholomew 1965; Power 1968; Tusneem and Patrick 1971; Keeney 1973). Ammonification is favored when the C/N ratio is less than 20:1 by weight (Enwezor 1976). The extent of ammonification also depends on the type of organic material being decomposed (Bartholomew 1965). The more stable the material being decomposed, the less ammonium will be released. Stanford and Smith (1972) have shown that only part of the organic-N in soils is subject to ammonification and this fraction is "extremely variable".

Chemical and physical properties of the soil or aquatic system also affect the rate of ammonification. Ammonification rates are more rapid at neutral pH values than under acidic conditions (Alexander 1961). The optimum temperature range for ammonification is in the thermophilic range of 40° to 60°C. Ammonification reactions will occur under both anaerobic and aerobic conditions. Although the ammonification process will be slower under anaerobic conditions (Tusneem and Patrick 1971; Keeney 1973), the net release of ammonium is greater than under aerobic conditions due to the lower nitrogen requirement of anaerobic microorganisms (Tusneem and Patrick 1971; Waring and Bremmer 1964).

Nitrification

Nitrification is the biologically mediated oxidation of nitrogenous compounds. This process can be carried out by both autotrophic nitrification and heterotrophic microorganisms, although autotrophic nitrification is generally considered the primary process in nature. In wetlands, nitrification of ammonium may be the limiting step in the loss of ammonium and organic nitrogen. Ammonium in the surficial sediments and overlying water is oxidized by nitrifying bacteria to nitrate, which then diffuses to underlying anaerobic sediments, where denitrification can occur (Patrick and Reddy 1976). Similarly, organic nitrogen can be converted to ammonium in anaerobic sediment layers where sequential nitrification-denitrification can occur (Patrick and Tusneem 1972).

Nitrification rates are very sensitive to environmental conditions, especially dissolved oxygen and pH. Oxygen is an obligate requirement for nitrification; therefore, if the oxygen supply is insufficient, there will be little nitrification. Although oxygen is an essential requirement, nitrification can occur down to about 0.3 ppm dissolved oxygen (Reddy and Patrick 1982). Since most nitrifying activity occurs within a thin aerobic surface sediment layer (EPA 1975), the development and thickness of this layer may be

a limiting factor to nitrification (Patrick and Tusneem 1972). In a waterlogged peat soil, Dickinson (1972) reported oxidized soil conditions to a depth of 3 cm.

Reddy et al. (1976) described the development of an oxidized layer in initially anaerobic soil-water columns amended with 200 μ g NH₄-N per gram of soil. In the first week, a thin aerobic layer developed which increased to 0.5, 1.25, 1.5, 1.6, and 2.0 cm after 7, 15, 30, 60, and 120 days, respectively. The rate of development and thickness of the aerobic layer depends on the oxygen supply and the amount of readily decomposable organic matter, with the layer being thinner with more organic matter due to increased microbial activity and higher oxygen demand (Engler and Patrick 1974; Patrick and Reddy 1976).

Another factor which greatly affects nitrification is pH. Alexander (1975, 1977) reported a significant relationship between nitrate production and pH. The optimum pH range for nitrate production has been reported from 6.6 to 9.0 (Alexander 1977; Keeney and Gardner 1970; EPA 1975). Although nitrification has been reported below pH 4.0, it generally does not occur at significant rates until a pH of 5.0 to 5.5 is reached (Alexander 1977; Tilsdale and Nelson 1975). In laboratory soil-water column studies, Erickson (1978) showed that the rate of nitrification occurring at the soil-water interface tripled when the pH was increased from 4.7 to 7.0 through the addition of lime.

The pH range for autotrophic nitrification is fairly restricted due to the toxicity of free ammonia and undissociated nitrous acid to <u>Nitrobacter</u>. The concentrations of ammonia and nitrous acid are pH-dependent (the pK_a for NH₃/NH₄⁺ is 9.3 and the pK_a for HNO₂/NO₂⁻ is 3.4). Based on these equilibria, Anthonisen et al. (1976) examined tolerance levels of ammonia and nitrous acid for the nitrification process. At ammonia

levels and nitrous acid levels above 150 and 40 mg N/liter, nitrification was found to be completely inhibited. However, if ammonia is removed, nitrification can proceed unaffected up to pH 11.2 (Prakasam and Koehr 1972).

Temperature also has an effect on nitrification. The optimum temperature range is between 25-35°C (Alexander 1977; Broadbent 1973). Nitrification becomes negligible above 40°C (Tilsdale and Nelson 1975) and below 17°C (White et al. 1977). Below 10°C, nitrification is completely inhibited (Chen 1974; Sharma and Ahlert 1977; Keeney 1973).

Temperature may also affect the availability of nitrogen for nitrification. During spring warming periods, organic and biomass nitrogen are rapidly converted to mineral forms (Focht and Verstraete 1977). The subsequent release of ammonia through ammonification stimulates the growth and metabolism of nitrifiers (Focht and Verstraete 1977).

Heterotrophic Nitrification

Although heterotrophic nitrification has been known for over half a century, not until the last 10-15 years has it been shown to be of quantitative significance in some environments. A variety of bacteria, fungi and actinomycetes can oxidize ammonium as well as other organic nitrogen compounds to form a variety of products (Eylar and Schmidt 1959; Hirsch et al. 1961; Verstraete and Alexander 1973; Tate 1977). The heterotrophic nitrifier <u>Arthrobacter</u> is reported to excrete hydroxylamine, a hydroxamic acid, nitrite, nitrate, and a compound tentatively identified as 1-nitrosoethanol (Verstraete and Alexander 1972). Tate (1977) showed that the populations of autotrophic nitrifiers was only sufficient to account for 0.1% of the nitrate present in a south Florida organic soil with a pH of 7.1. After selective culturing, Tate (1977) isolated large populations of <u>Arthrobacter</u>.

In acidic soils (pH \leq 4.5), many authors have suggested that heterotrophic nitrification may be responsible for nitrate formation. One piece of evidence supporting this hypothesis is that several authors have reported that in acid soils where nitrification has been observed, autotrophic nitrifiers cannot be isolated (Lemee 1967; Overrein 1975; Ishaque and Cornfield 1974; Cooper 1975; Verstraete and Voets 1976). A second point is that the optimum pH appears to be around pH 4.5. Ishaque and Cornfield (1972) noted that the addition of lime to an acidic Pakistan "tea" soil inhibited nitrification. Verstraete and Voets (1976) also noted that the optimum pH for acid forest soils was 4.5-5.0. A third fact is that the formation of nitrate is related to the amount of organicnitrogen present, and the addition of ammonium either inhibited or had no effect on nitrification (Weber and Grainey 1962; Verstraete and Voets 1976).

Autotrophic Nitrification

Autotrophic nitrification is a two-step process involving the sequential oxidation of ammonium to nitrite, and nitrite to nitrate. Ammonium is oxidized primarily by <u>Nitrosomonas</u>, although <u>Nitrosococcus</u>, <u>Nitrospira</u>, <u>Nitrosocystis</u> and <u>Nitrosogloea</u> are also capable of oxidizing ammonium (Alexander 1961, 1965). <u>Nitrobacter</u> is the primary organism responsible for the oxidation of nitrite in freshwater and sediments. The autotrophic nitrifiers, other than <u>Nitrosomonas</u> and <u>Nitrobacter</u>, tend to occur in much lower numbers and have narrower temperature and pH growth ranges (Focht and Verstraete 1977). The autotrophic nitrifiers utilize CO_2 as their carbon source and obtain energy by oxidizing ammonium and nitrite. The oxidation of nitrogen from -3 (NH₄⁺) to +5 (NO₃⁻) oxidation state covers a span of 8 electrons (Alexander 1965). Because the free energy charge ($\triangle F$) is about -65 versus -20 Kcal/mol for the oxidation of ammonium and nitrite, respectively, the nitrite oxidizing bacteria require approximately three times more nitrogen than the ammonium oxidizers (Focht and Verstraete 1977). However, in nature, the ammonium oxidizer populations are not always larger than the nitrite oxidizers. Morrill and Dawson (1967) showed that populations of <u>Nitrosomonas</u> were only slightly greater than <u>Nitrobacter</u> and varied depending on pH.

Role of Plants in Nitrification

The role of plants on nitrification is not well understood at present. In one study, White et al. (1977) suggested the coupling of photosynthetic oxygen with nitrification since nitrification rates were higher at mid-day than morning, and higher in July and August than any other months. Other work by White et al. (1977) shoed daytime nitrate production three times greater than at night. On the other hand, Rice and Pancholy (1973) have suggested that the production of tannins by plants may inhibit nitrification. Based on evidence that many plants, particularly wetland plants, can use ammonium more effectively than nitrate (Allison 1931; Cramer and Myers 1948; Ferguson and Bollard 1969; McFee and Stone 1968; Moore and Keraitis 1971; Oertli 1963; Shen 1969), the inhibition of nitrification would make good biological sense. In their study, Rice and Pancholy (1973) found that the presence of as few as 2 ppm of tannins inhibited oxidation of ammonium by <u>Nitrosomonas</u>.

Denitrification

Denitrification is one of the major mechanisms by which nitrogen is lost from wetland systems. It involves the biological reduction of nitrate to nitrogen gas. Many heterotrophic bacteria and a small number of autotrophic bacteria are capable of nitrate reduction (Payne 1973). Because of the wide diversity of the denitrifying bacteria, denitrifiers are found in high numbers in nearly all soils. Of these, species of the genera <u>Alcaligenes</u> (including <u>Actoromobacter</u>) and <u>Pseudomonas</u> are the most common (Valera and Alexander 1961; Vives and Paris 1975).

In the absence of oxygen, denitrifiers utilize nitrate as the terminal electron acceptor. Electrons are transferred directly to nitrate from cytochrome C via an iron-molybdenum complex (Fewson and Nichols 1961; Forget and Dervastanian 1973) as opposed to being transferred to cytochrome oxidase A_3 in the presence of oxygen (Payne 1973). The denitrification pathway is now regarded as a four-step process as follows (Payne 1973):

$$NO_3^- ---> NO_2^- ---> NO ----> N_2O ----> N$$

The rate of denitrification as with most biochemical processes tends to increase with increasing temperature until enzyme deactivation occurs (Focht 1974). In their review of denitrification, Focht and Verstraete (1977) concluded from the literature that the kinetic effect of temperature can be related to the Arrhenius equation between 12° and 35°C. Below 10-12°C, denitrification rates decrease rapidly although slow denitrification has been reported down to 3°C (Nommik 1956). Rates increase slowly

above 35°C to about 60-65°C, dropping off rapidly at higher temperatures (Nommik 1956; Bremmer and Shaw 1958).

Organic matter may be the single most important factor affecting denitrification. Several authors have studied the effect of organic matter on denitrification (McGairity and Meyers 1968; Stefanson 1972; Engler and Patrick 1974). Because organic matter in soils is generally humified, and thus resistant to microbial decomposition, a measure of available carbon is a better indicator of denitrification rates (Bremmer and Shaw 1958; Reddy et al. 1978).

In a study of 30 widely varying soils, Stanford et al. (1975) obtained an r^2 value of 0.82 for extractable carbohydrate versus apparent first-order denitrification rates while total organic carbon versus apparent first-order denitrification gave an r^2 of 0.69. In another study, Burford and Bremmer (1975) obtained an r^2 value of 0.99 for zero-order denitrification rate versus "mineralization" carbon, as determined by CO₂ evolution for 17 soils, while total organic carbon yielded an r^2 value of 0.59. Graetz et al. (1980) studied 15 Florida wetland soils and developed a predictive equation for denitrification rates based on soil organic carbon content and soil pH. The equation ($r^2 = 0.864$, d.f. = 13) is given below:

$$K_1 = [8.9 \times 10^4 \text{ (OCW)} - (3.9 \times 10^4) \text{ (OCW)} (pH_{6.5}) + 0.002]^{0.5}$$

where:

- K_1 = apparent first-order denitrification rate constant, day⁻¹
- OCW = organic carbon content by weight %, as determined by the Walkley-Blacke method
- $pH_{6.5} =$ the pH-deficit (in pH above 6.5 = 0; below pH of 6.5 = 6.5 observed pH)

Effect of Soil pH on Denitrification

Denitrification is also greatly influenced by soil pH. Several reports indicate that the optimum pH for denitrification is between pH 7 and 8, and drops off considerably below pH 6 (Wijler and Delwiche 1954; Nommik 1956; Bremmer and Shaw 1958). However, several authors have reported rapid denitrification rates near pH 5.0 (Van Cleemput et al. 1975) and below pH 5.0 (Ekpete and Cornfield 1965; Erickson 1978; Gilliam and Gambrell 1978). These discrepancies in optimum pH range may be due to the lack of adapted microbial populations in some of the earlier studies (Brezonik 1977).

Effect of Oxygen on Denitrification

Since oxygen is always used in preference to nitrate by denitrifying bacteria, the reduction of nitrate does not occur until oxygen becomes limiting. Wuhrmann (1964) and Chance (1957) reported that oxygen consumption shifts from zero-order to first-order at about 0.1 to 0.2 mg/l. However, denitrification has been observed to occur under well-aerated conditions (Focht and Verstraete 1977). This is due to the presence of many small anoxic microsites, which are usually too small to measure with an oxygen probe or platinum electrode. The existence of these anoxic microsites is dependent on three factors: (1) the oxygen consumption rate, (2) the oxygen diffusion rate, and (3) the geometry (Focht and Verstraete 1977). Greenwood (1961) showed that anoxic microsites could exist in a well-aerated soil crumb having a 200 μ m diameter.

In wetland systems, where sediments are frequently flooded, two distinct soil layers develop: (1) a surface oxidized layer and (2) an underlying reduced layer. For denitrification to occur, nitrate must be present in the reduced layer. Therefore, where

an oxidized layer is present, the diffusion of nitrate into the reduced layer affects the rate of denitrification (Phillips et al. 1976; Reddy et al. 1976).

Effect of Plants on Denitrification

Plant roots have been widely reported to enhance denitrification, particularly in soils with low endogenous carbon (Stefanson 1972; Bailey 1976). This has been attributed to increased organic matter content and lower oxygen levels in the root zone, or both (Volz et al. 1976; Alexander 1977).

Sherr and Payne (1978) conducted a study on the effect of <u>Spartina alterinflora</u> roots on denitrification. The above-ground parts of the plants were cut back and the roots were pruned in order to reduce the below-ground effects of the plants. They observed that the denitrifying activity was unaffected after 5 months, but significantly lowered after 18 months. Thus, they concluded that the effect of root exudates was relatively unimportant over the short-term and that the main effect of the roots was due to long-term maintenance of underground biomass.

Dissimilatory Reduction of NO₃⁻ to NH₄⁺

Dissimilatory reduction of nitrate to ammonium is analogous to denitrification except that ammonium is the final product rather than N_2 or N_2O gas. As in denitrification, the reduction of nitrate is for the purpose of obtaining respiratory energy rather than obtaining cell nitrogen. The pathway for the reduction may involve the following sequence of reductions (Campbell and Lees 1967):

$$H_2N_2O_2 - \cdots > N_2$$
(Pathway 1)
$$2NO_3^- - \cdots > 2[HNO]$$

$$2NH_2OH - \cdots > 2NH_4^+$$
(Pathway 2)

The assimilation of hydroxylamine and ammonium by microbial cells may be considered an extension of pathway 2 while pathway 1 is the denitrification pathway.

Verhoeven (1956) was the first to describe the reduction of nitrate to ammonium. In his studies, Verhoeven (1956) observed the copious production of ammonium and gaseous products by <u>Bacillus licheniformis</u>, however other commonly known denitrifiers (e.g., <u>Micrococcus denitrificans and Pseudomonas aeruginosa</u>) produced only N₂ and N₂O. The reduction of nitrate to ammonium is favored by strict anaerobic conditions and large quantities of readily oxidizable organic matter (Nommik 1956; Stanford et al. 1975a,b; Terry and Nelson 1975; Chien et al. 1977; Buresh and Patrick 1978). Because of the highly anaerobic conditions required for the reduction of nitrate to ammonium, Buresh and Patrick (1978) suggested that the diffusion of nitrate into a highly reduced soil zone may be a limiting factor in nature.

In wetland systems, the diffusion through less reduced soil zones and the thickness of these zones probably affects the proportion of nitrate which is reduced to ammonium or denitrified to N_2 or N_2O . In ¹⁵N labeled denitrification studies, various amounts of ammonium and organic-N have been formed from ¹⁵NO₃-N. A summary of the final conversion products of denitrification in various studies is given in Table 2-4. The

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SUMMARY OF FINAL PRODUCTS OF DENITRIFICATION IN SELECTED STUDIES

REFERENCE	PRODU	CTS OF DENITRIE (%)	COMMENTS	
	NH4 ⁺	N ₂ or N ₂ O	Organic N	
Chen et al. (1972)	7	90	3	Lake sediments after 2-day incubation
Chen et al. (1972)	0	89.5	10.5	Under aerobic conditions
Somponyse (1982)	< 3	95.5	< 1.5	Cypress wetland after 2- to 6-day incubation period
Brinson et al. (1981)	30			Isolation chambers in North Carolina riverine swamp
Buresh and Patrick (1978)	35.7	30.3	34.0	Crowley silt loam pre-incubated for 1 day with glucose
Stanford et al. (1975b)	19.4	62.4	18.2	Timrik silt loam incubated after 24 hours

considerably different reduction of ${}^{15}NO_{3}$ to ${}^{15}NH_{4}$ in studies summarized in Table 2-4 soils may reflect different soil properties and experimental conditions, such as levels of incubation of glucose and NO_{3} , degree of anaerobiosis, length of pre-incubation, temperature and different types of organisms involves.

Of the factors listed above, the length or presence of pre-incubation may be the most important. Caskey and Tiedje (1979) suggest that fermentative anaerobes, such as <u>Clostridium</u>, are responsible for the reduction of nitrate to ammonium in soils. Since <u>Clostridium</u> form spores and require intensely reduced soil conditions, their populations may not reach significant numbers in studies with short or no pre-incubation period.

Water Quality Parameters in Wetlands

Within the water column of a wetland, variations in pH, specific conductivity, dissolved oxygen, redox potential, and color are the most evident under different wetland conditions. Each of these parameters will be discussed briefly with the exception of redox potential which was addressed in an earlier section.

pН

The two most important factors affecting the pH level in a wetland area: (1) the pH and characteristics of the inflow waters and (2) the type and magnitude of metabolic activity within the wetland (Verry 1975). In a comparison of a groundwater fed and a perched wetland in Minnesota, Verry found the isolated perched bog to have a pH value in the range of 3.1 to 4.2. He theorized that the hydrogen ions were produced during the dissociation of sulfuric acid derived from hydrogen sulfide gas. By contrast, the

groundwater fed wetland had a mean pH value near 6.5. Lee et al. (1969) found diurnal fluctuations in pH values in marshes as a result of algal productivity and reported higher values of pH in the summer and decreased values in the winter.

Dissolved Oxygen

In addition to diurnal fluctuations in pH, Lee et al. (1969) also reported diurnal fluctuations in dissolved oxygen concentrations in marshes. During winter months, D.O. levels in the range of 6 to 9.5 mg/l were found, while a range of 0 to 8 mg/l was reported in the summer months. However, regardless of the time of year, D.O. levels were almost always at 50 percent saturation or less. Sparling (1960) conducted a detailed study on reaeration in bog waters. He found that the primary mechanisms for input of oxygen into the water column were reaeration during water movement and circulation around vegetation. He reported that a water velocity of 1 cm/sec was necessary to maintain an agitated and saturated water column. At water velocities less than 0.4 cm/sec, reaeration rates were insufficient to offset sediment consumption and root respiration, leading to depletion of D.O. levels even in shallow waters.

Specific Conductivity

Specific conductivity is used primarily as an indicator of dissolved solids content and degree of treatment in a wetland system. Verry (1975) suggests that specific conductivity can also serve as a good indicator of the source of freshwater in wetlands. Values of specific conductivity less than 80 μ mho/cm are indicative of an isolated or perched condition, whereas values greater than 80 indicate a continuous surface or groundwater input.

Color

As discussed previously, color is indicative of the presence of decomposition products such as humic acids. Wetlands exhibit large variations in water color due to interactions between sediments, microorganisms, and decaying plant matter. Verry (1975) found that color values were inversely proportional to the amount of surface inflow in a Minnesota wetland. Lee et al. (1969) reported higher color values at the end of the growing season as a result of the breakdown of plant matter.

Characteristics of Urban Stormwater Drainage

During the past few years, it has been recognized that urban stormwater runoff is not just "rainwater" in terms of quality. Stormwater runoff typically contains substantial quantities of impurities, and in some locations it has become a more serious source of pollutants than municipal wastes (Sartor et al. 1974). Street litter, gas combustion products, ice control chemicals, rubber and metals lost from vehicles, decaying vegetation, domestic pet wastes, fallout from industrial and residential combustion products, and chemical applied to lawns and parks may be sources of contaminants in urban runoff.

One of the first comparisons of area yields of pollutants from varying land uses was performed by Loehr (1974). A summary of mean area loading rates from 12 urban and rural sites is presented in Table 2-5. Urban runoff was found to produce higher concentrations of every parameter measured, and in the case of total PO₄, urban runoff loadings were approximately 19 times that found in rural runoff. Loehr (1974) also concluded that runoff from residential streets contained the highest concentrations of total

AREA YIELDS OF SELECTED CONSTITUENTS FROM URBAN AND RURAL RUNOFF SOURCES

	AREA YIELD (kg/ha/yr)				
	URBAN RUNOFF	RURAL RUNOFF			
тос	345	144			
Total PO₄	150	7.8			
TKN	7.5	1.9			
Nitrate-N	13.3	5.0			
Sodium	235	42.5			
Potassium	133	21.7			
Calcium	960	628			
Magnesium	290	290			

SOURCE: Loehr (1974)

phosphorus, whereas runoff from arterial streets contained the highest concentrations of orthophosphorus. The quantity of pollutants per unit length of street was also shown to increase as the time interval since the last rain event or street sweeping increased, with the greatest quantity of contaminants located within 6 inches of the curb.

Mass loadings of urban runoff from residential and commercial areas surrounding Lake Eola, Orlando, Florida, are presented in Table 2-6 (Wanielista et al. 1982). Measured loading rates of total phosphorus and nitrate-nitrogen at the Lake Eola site are substantially lower than those measured in similar areas by Loehr (1974). The differences can possibly be attributed to the large number of storm events and higher runoff volumes during much of the year that the Orlando area experiences.

Sartor et al. (1974), in an investigation of the water pollution aspects of street surface contaminants, found that the major constituent of street surface contaminants was consistently inorganic mineral-like matter, similar to common sand and silt. One of the most significant findings of the study is that a great portion of the overall pollutional potential was associated with the fine solids fraction of the street surface contaminants. The fines accounted for only a minor portion of the total loading of street surfaces. Yet, as shown in Table 2-7, the very fine silt material (< 43 microns) accounts for only 5.9 percent of the total solids, but about one-fourth of the oxygen demand and 56.2 percent of the phosphate concentration. This fraction also accounts for over half of the heavy metals, nearly three-fourths of the total pesticides, and one-third to one-half of the algal nutrients.

A study of stormwater characteristics in Boca Raton, Florida, was conducted by Cullum (1985) on a 122-acre single-family residential development containing 311

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MASS LOADINGS FROM URBAN STORMWATER RUNOFF FROM A 28-ACRE COMMERCIAL AREA AND A 16.1-ACRE RESIDENTIAL AREA IN THE LAKE EOLA DRAINAGE BASIN

	AVERAGE MASS LOADING (kg/ha/yr)				
CONSTITUENT	28-ACRE COMMERCIAL	16.1-ACRE RESIDENTIAL			
SS	338	195			
BOD	50	74.6			
COD	296	442.3			
TOC	123	138.5			
TKN	4	1.8			
NO3-N	6	2.2			
OP-P	2	0.8			
TP-P	3.5	2.2			

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SOURCE: Wanielista et al. (1977)

POLLUTANT FRACTIONS ASSOCIATED WITH PARTICLE SIZE

PARAMETER	FRACTION OF TOTAL (% by Weight)				
	< 43 μ	43 μ - 246 μ	> 246 µ		
TS	5.9	37.5	56.5		
BPD ₅	24.3	32.5	43.2		
COD	22.7	57.4	19.9		
vs	25.6	34.0	40.4		
Phosphates	56.2	36.0	7.8		
Nitrates	31.9	45.1	23.0		
TKN	18.7	39.8	41.5		
All Heavy Metals	51	48.7			
All Pesticides	73	27.0			
РСВ	34	ł.0	66.0		

SOURCE: Sartor et al. (1974)

residences with a population density of 2.5 persons/acre. The drainage system consisted of grassed swales, catch basins, and 7.9 acres of interconnected lakes. Stormwater runoff samples were collected over an 18-month period. Total phosphorus concentrations averaged 136 μ g/l, while orthophosphorus averaged 84 μ g/l. Concentrations of total nitrogen averaged less than 1 mg/l with approximately 75% in the organic form. A comparison of stormwater quality characteristics at the South Florida site with mean values from the National Urban Runoff Program (NURP) database is given in Table 2-8. In general, concentrations of measured parameters at the South Florida site were substantially less than those reported in the NURP study. Only the mean total Kjeldahl nitrogen (TKN) and orthophosphate levels at the residential site studied were within the range of those reported from NURP, and both were at the extreme lower end. Mean concentrations of TSS, TP and NO_x measured at the Boca Raton site were lower than even the minimum values reported in the NURP study.

A comparison of mean stormwater concentrations in a 28-acre commercial area and a 16.1-acre residential area in the Lake Eola drainage basin is given in Table 2-9. In contrast to the findings at the Boca Raton site by Cullum (1985), concentrations of TSS, TP, ortho-P, NO_x, and TKN at both the commercial and residential sites were within the range of values measured in the NURP study for these parameters. In fact, concentrations of TKN, NO_x, and TP at the commercial and residential sites at Lake Eola were very close to the mean values reported in the NURP study.

Stormwater runoff studies of three small basins (residential, commercial, and highway) were conducted in Ft. Lauderdale, Florida, between 1974 and 1978 by Miller et al. (1982). They found the greatest total phosphorus loadings to be located in the

COMPARISON OF SELECTED STORMWATER RUNOFF QUALITY CHARACTERISTICS BETWEEN A SOUTH FLORIDA RESIDENTIAL COMMUNITY AND THE NATIONAL URBAN RUNOFF PROGRAM AVERAGE

	BOCA RATON,	NATIONAL URBAN RUNOFF PROGRAM (NURP)				
PARAMETER	FLORIDA EVENT MEAN	EVENT MEAN	RANGE	SITES		
TSS (mg/l)	20.6	249	22 - 2,216	35		
TP (µg/l)	136	640	210 - 4,100	34		
Ortho-P (µg/l)	84	182	69 - 313	16		
NO _x (µg/1)	180	1,560	330 - 7,840	24		
TKN (µg/l)	750	2,710	480 - 10,790	32		

SOURCE: Cullum (1985)

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COMPARISON OF STORMWATER CHARACTERISTICS IN A 28-ACRE COMMERCIAL AREA AND A 16.1-ACRE RESIDENTIAL WATERSHED IN THE LAKE EOLA DRAINAGE BASIN

	UNITS OF	RUNOFF CONCENTRATION		
	MEASUREMENT	COMMERCIAL	RESIDENTIAL	
pH	units	7.39	7.72	
Spec. Cond.	µmho/cm	195	128	
Alkalinity	mg /1	57.1	67.3	
Turbidity	NTU	39	24	
S.S.	mg/1	157	80	
V.S.S .	mg /1	62	46	
BOD	mg/1	16.2	9.4	
TOC	mg/1	133	72	
NO3-N	mg/1	1.69	2.56	
nh ₃ -n	mg /1	0.22	0.25	
TKN	mg/l	3.56	2.52	
Diss. OP	mg/ 1	0.41	0.23	
Total P	mg/1	0.80	0.59	
Total Zinc	mg/1	0.42		
Total Lead	mg/1	1.42		
Total Copper	mg/1	0.513		
Total Chromium	mg/1	0.042		
Total Nickel	mg /1	0.031		
Total Iron	mg/l	1.39		

SOURCE: Wanielista et al. (1982)

residential drainage basin, possibly due to lawn fertilizer being blown onto hydraulically effective impervious areas and also to pet wastes. Typical daily loading rates for total phosphorus averaged 0.0216, 0.0168 and 0.033 pounds/day for the residential, highway and commercial land-use areas, respectively.

Mattraw and Miller (1981) conducted a systematic collection of rainfall, runoff and water quality samples from three small urban areas of Broward County, Florida, between 1974 and 1977. A summary of stormwater characteristics measured at an 18.5-hectare residential area with 5.9 percent impervious is given in Table 2-10. Mean concentrations of most parameters appear to be similar to values measured at Lake Eola, Florida, and are within the range of values reported in the NURP study.

Wetland Treatment of Stormwater Runoff

Wetlands have come into focus in the last decade as natural systems which may have the potential to improve water quality of both stormwater runoff and secondary wastewater effluent. Wastewater effluent has been applied to various natural wetlands throughout North America. In many of the studies, wetlands have acted to improve water quality, including uptake of nitrogen and phosphorus, to some extent. However, pollutant removal efficiencies in other studies were extremely variable, and a more quantitative assessment is needed of the capabilities and limitations of wetlands to remove nutrients (Nichols 1983). In addition, concentrations of nitrogen and phosphorus in wastewater effluent are generally much greater than values measured in stormwater runoff, especially in the Central Florida area, where nutrient concentrations in typical wastewater effluent and stormwater runoff may easily differ by a factor of 10 or more.

MEAN STORMWATER QUALITY CHARACTERISTICS AT AN 18.5-HECTARE RESIDENTIAL AREA IN BROWARD COUNTY, FLORIDA DURING 1974-1977

	CON	NO. OF		
PARAMETER	MINIMUM	MAXIMUM	AVERAGE	SAMPLES
Conductivity (µmho/cm)	34	350	96	452
NH3-N	0.00	2.60	0.33	379
NO3-N	0.00	2.09	0.46	380
Organic N	0.14	9.4	1.2	379
Total N	0.29	11.5	2.0	380
Diss. OP	0.03	1.8	0.21	380
Total P	0.06	2.4	0.31	380
TOC	0	104	14	366
BOD	2	289	41	377
Color (Pt-Co Units)	5	160	31	348
Turbidity (JTU)	3	70	13	380
Total Residue	9	625	113	367
Suspended Solids	0	249	26	367
Total Cd (µg/l)	0	6	0.8	96
Total Cu (µg/l)	0	41	8.0	96
Total Fe (μ g/l)	0	5,300	298	300
Total Pb (μ g/l)	30	1,100	167	96
Total Zn (µg/l)	10	560	86	96

SOURCE: Mattraw and Miller (1981)

Therefore, studies of the treatment efficiency of wetlands for wastewater effluent may not be applicable to treatment of stormwater, even in the same wetland.

Investigations concerning the use of wetlands for treatment of stormwater runoff have been extremely limited. The few studies undertaken reveal that: (1) a wide disparity exists in the capability of wetlands to remove nonpoint source pollution, particularly with respect to nutrients; (2) the nature of flow and seasonal factors are major influences on pollutant removal capabilities in certain wetlands; and (3) the greatest consistency in pollutant reduction appears to be for BOD, suspended solids, and heavy metals (Morris 1980; Nichols 1983; Hickok et al. 1977; McCuen 1978). A summary of pollutant removal efficiencies obtained in four wetland stormwater treatment systems is given in Table 2-11.

In one of the few previous studies on the feasibility of treating stormwater in wetland systems, the Wayzata Wetland in Wayzata, Minnesota, was investigated by Hickok et al. (1977) to evaluate the interactions of stormwater runoff in a wetland area and determine the potential usefulness of such areas for water quality management. The study site was a 3.06 ha peat wetland with a contributing watershed (26.3 ha) of mixed urban, sparsely developed, and open wooded land uses. Phosphorus was found to be the limiting plant nutrient in the system. Microbial activity in the wetlands appeared to be the initial and most important mechanism for removing phosphorus from the soil-water solution. The removal efficiency of phosphorus (on a concentration basis) averaged 78 percent on an annual basis. Under submerged, anaerobic conditions, the microbial activity was found to decrease dramatically, suggesting a similar decrease in phosphorus removal capability.

OBSERVED POLLUTANT REMOVAL EFFECTIVENESS OF WETLAND-STORMWATER TREATMENT SYSTEMS

SYSTEM/ LOCATION	WETLAND TYPE	HYDRAULIC/ HYDROLOGIC FACTOR	APPLICATION CONCENTRATION (annual average)		REMOVAL EFFICIENCY		COMMENTS
Wayzata, Minnesota	Peatland	28.3 ha watershed	NH₃-N	3.94 mg/l	Net Increase	-	Nutrient discharge from wetlands related to seasons
(existing runoff		2.8 ha wetland area	Total P	0.92 mg/l	78%		
situation) Hickok et al. (1977)		<u>Inputs</u> :	SS	701 mg/l	94%	-	P seems to be limited to plant nutrients. Microbial activity appears to be initial and most important
		Precipitation: 2.38 ha-m	Cd	0.4-1.4 μg/l	25-80%	ľ	mechanism for P removal.
		Groundwater: 1.20 ha-m	Cu	12-19 µg/l	73-83%	-	Heavy metal inflow concentrations and removal efficiencies varied according
		Runoff: 3.19 ha-m	Pb	26-71 μg/l	90-97%		to contributing land uses. Greatest
			Zn	10-15 µg/l	78-86%		reduction values for commercial area runoff.
Lake Tahoe, California	High Altitude	Several sites investigated with watersheds of several	NH3-N	0.02-0.44 mg/l	Up to 67%	-	Extreme variability in nutrient removal. Many instances of increase
(natural system)	Meadows	hundred to 14.350 ha.	NO3-N	0.02-0.57 mg/l	Up to 96%		through wetland. Most significant reductions during storm episodes.
		Wetland slopes of 2-7%.	TKN	0.6-6.6 mg/l	Up to 76%		
Morris et al. (1980)			Total P	0.018-1.9 mg/l	Up to 93%	-	during spring snowmelt runoff.
			SS	1-2,978 mg/l	Up to 99%	-	SS removal greatly enhanced by sheet flow conditions.

HYDRAULIC/ APPLICATION SYSTEM/ WETLAND REMOVAL HYDROLOGIC CONCENTRATION COMMENTS LOCATION TYPE EFFICIENCY FACTOR (annual average) Palo Alto, California Brackish 248 ha marsh Total N 3.67 mg/l 37% Inflow/outflow pollutant relationships _ extremely variable from storm to (flood control basin) 72 km² watershed Total P 0.36 mg/l Net Increase storm. Hickok et al. (1977) 224,000 m³ dead storage SS 290 mg/l 87% Outflow SS exhibited less variability than inflow levels. Because of Mainly channelized flow, VSS 62.9 mg/l 85% hydraulics, very little solids high marsh areas deposition appears to occur in high inundated infrequently. BOD 54% 12.2 mg/l marsh areas. Heavy metals inflow and outflow Cd 0.5 mg/l NA _ levels were at limits of detectability. Cu < 0.01 mg/lNA Consistent decrease of Pb measured Ni 0.07 mg/l NA across marsh. Pb 0.16 mg/l NA 9.76 ha watershed, with University of Total N 95% Slow moving, circuitous flow allows Cypress 45 kg/yr Central Florida Stand 67% impervious area particulate matter to settle and 97% accumulate rapidly. Total P 8 kg/yr Lynard et al. (1980) SS 22,580 kg/yr 99% BOD. 145 kg/yr 89%

TABLE 2-11 -- CONTINUED

Consistent removals of approximately 80% or more were observed for total P, SS, Cu, Pb, and Zn in the Wayzata Wetland. However, as seen in Table 2-11, concentrations of total P were near 1 mg/l and SS were near 700 mg/l. Even after the removals listed in Table 2-11, concentrations of total P still averaged greater than 0.2 mg/l and SS averaged 42 mg/l. The peatland was not effective in removal of ammonia, and many times increases were noted during travel through the system. Removal of heavy metals was found to be greatest for the commercial runoff. This result is not surprising since concentrations of metals in this runoff were much greater than those reported for the other land uses.

Morris et al. (1980) recently conducted a one-year field investigation of the effectiveness of natural marsh and meadowlands to provide treatment of surface runoff in the Lake Tahoe Basin. Seven systems consisting of four streams and three tributary drainage areas were investigated. The contributing watershed consisted of a mix of urban, rural residential, pasture, and forested lands. Results indicated an extreme seasonal variability in the nutrient removal capacities of the marsh. There were many instances of nutrient concentration increases through the wetland, with the most significant reductions occurring during storm events. On an annual basis, phosphorus concentrations were found to have increased, over background levels, in 64% of the sampling areas. Both nitrate and ammonia were found to be removed from the wetland on some occasions and added to the flow on others. Maximum removals occurred during storm events at concentrations near the upper range of measured values, while little removal was observed for runoff with low concentrations.

The nature of flow through wetlands is considered to be a critical factor affecting nutrient removal. Morris et al. (1980) found the extent to which runoff followed a sheet flow pattern to be the most significant factor distinguishing pollutant removal efficiencies at different sites. In a Palo Alto study of a 248 ha tidal marsh by the Association of Bay Area Governments, widespread sheetflow did not occur. Rather, the flow remained confined to well-defined channels traversing the marsh. The resultant effect was a net increase in the concentrations of phosphorus during flow through the marsh. Mean input concentrations of phosphorus were 0.36 mg/l. Removal of total N, which averaged 3.67 mg/l in the inflow, was extremely variable, but a net removal of 37% was observed. Concentrations of heavy metals in both the inflow and outflow were near detection limits.

The influence of the seasons has also been observed to also be an important factor. Nutrient discharges in particular were related to the seasons in the Wayzata wetlands (Hickok et al. 1977). The flushing and leaching effects of spring snow melt appeared to be the cause for higher TKN and organic carbon discharges in the Lake Tahoe meadowlands as well.

The final study summarized in Table 2-9 was conducted at the University of Central Florida by Lynard et al. (1982). This study examined the removal effectiveness of an isolated cypress dome approximately 2.5 ha in size. The contributing watershed was 9.76 ha and was largely impervious parking areas. Since the wetland was isolated, the majority of inputs remained within the system. Loading rates of nutrients and solids were relatively high (Table 2-11), but excellent removals from the water column were observed for total N, total P, SS, and BOD. Removal efficiencies for all four parameters

were thought to be a result of the slow moving circuitous flow which optimized settling of particulate matter.

An 8.5-hectare wetland treatment system was also investigated was part of the recent NURP study. Five rain events and one snow melt event were monitored at the Swift Run Wetland in Michigan. This study is one of the few wetland studies to attempt measurements of both inputs and outputs so that pollutant removal efficiencies could be calculated on a mass basis as well as a concentration basis. Land use in the 549-hectare drainage basin was a mixture of rural and pasture (42%), residential (12%), commercial and industrial (1%), parkland (15%), and agricultural land (30%). A summary of inlet and outlet concentrations for selected parameters measured at the Swift Run site are given in Table 2-12.

Summaries of the pollutant loadings into and out of the wetland system are given in Table 2-13. These loadings represent the total measured load during each event which includes both the baseflow and runoff volumes. As seen in Table 2-13, the removal efficiency of the wetlands for most parameters monitored was very good. Removal of total suspended solids ranged from 76 to 93 percent for the five rain events. Removal of total iron and lead was also good with most removals in excess of 50 percent and some as high as 87 percent. The observed removal efficiencies for iron and lead were found to be closely associated with the removal of suspended solids as well as with detention time.

In general, nutrient removals by the wetland system were lower and more variable than those observed for TSS, lead, and iron. Removal of total phosphorus ranged between 0-62%, with a mean removal efficiency of 42%. Removal of organic nitrogen,

RANGE OF INLET AND OUTLET EVENT MEAN CONCENTRATIONS AT SWIFT RUN WETLAND

PARAMETER	STATION	MINIMUM	MAXIMUM	AVERAGE	NUMBER OF EVENTS
TSS	Inlet	17	139	74	6
(mg/l)	Outlet	4	46	18	6
TKN	Inlet	1.0	1.7	1.2	6
(mg/l)	Outlet	0.8	1.7	1.0	
T-P	Inlet	0.05	0.42	0.18	6
(mg/l)	Outlet	0.04	0.26	0.10	6
T-Fe	Inlet	0.5	2.3	1.4	6
(mg/l)	Outlet	0.1	1.7	0.7	6
T-Pb	Inlet	< 0.006	0.02	0.01	5
(mg/l)	Outlet	< 0.001	0.009	0.003	6

SOURCE: National Urban Runoff Program (1983)
TABLE 2-13

SUMMARY OF POLLUTANT LOADS AT SWIFT RUN WETLAND, WASHTENAW COUNTY, MICHIGAN

STATION	DATE	RAIN (cm)	RUNOFF VOLUME (10 ⁴ m ³)	AVERAGE DETENTION TIME (hours)	RUNOFF COEFFICIENT	TSS (lbs)	T-P (lbs)	TKN (lbs)	T-Fe (lbs)	T-Pb (lbs)
Inlet Outlet % Removal	08/22/80	8.45	3.4 3.7	33	0.16	5,300 390 93	13 7 46	75 73 3	110 20 82	1.3 < 0.2 > 85
Inlet Outlet % Removal	02/81	Snow Melt	10.8 10.8	12		20,000 11,000 45	100 60 40	420 420	550 410 25	3.2 2.1 34
Inlet Outlet % Removal	04/11/81	2.79	1.6 1.6	67	0.11	2,900 500 83	4.9 2.2 55	36 26 28	38 15 60	0.34 0.08 76
Inlet Outlet % Removal	04/13/81	2.01	2.5 2.5	53	0.26	7,800 1,700 78	10 5 50	74 56 24	110 50 55	0.68 0.09 87
Inlet Outlet % Removal	04/22/81	2.24	3.4 3.4	48	0.30	4,100 770 81	8 3 62	79 59 25	97 53 45	< 0.4 < 0.08
Inlet Outlet % Removal	05/29/81	1.50	1.6 1.6	82	0.21	600 150 75	2 2	45 33 27	19 4 79	< 0.08 < 0.04 50

most of which was present in a soluble form, was even more variable than phosphorus, with a range of 0-28% and a mean value of 18%.

The extreme variability of treatment efficiencies observed in most studies strongly points to the need to carefully examine each individual wetland system prior to predicting its usefulness in stormwater runoff management. In addition to flow regime, vegetative communities and species, sediments, wetland slope, redox potential, and pH should be examined very carefully since each of these factors are important in regulating the nutrient removal capacity of a wetland.

CHAPTER 3

FIELD AND LABORATORY INVESTIGATIONS

Site Description

The natural wetland site investigated during this research is part of a 48.4 hectare hardwood wetland hammock located just south of Sanford, in Seminole County, Florida (Figure 3-1). The wetland lies adjacent to and partially encloses Hidden Lake, which is the ultimate receiving waterbody for the surrounding wetland. The wetland is surrounded on the north and east by a residential community of single-family and multi-family residences. A small portion of the wetland, approximately 1.0 hectare in area, has been receiving stormwater runoff from a 22.4 hectare residential drainage basin since 1975 and was selected for study in these investigations. A schematic of the study site is given in Figure 3-2.

General Characteristics of the Wetland Community

The wetland study area, which constitutes the major flowpath for stormwater inputs, occupies only approximately 1.0 hectare of the total 48.4 hectare in the hardwood hammock (Figure 3-2). Vegetation along the flowpath is both abundant and diverse, with the hydrologic regime, primarily the duration and depth of flooding, being the major factors affecting the spatial diversity in the community. Since the ground slopes in study areas are steepest along the upland boundary and gradually decrease toward Hidden



Figure 3-1. Study Site Selected in Seminole County, Florida.



Figure 3-2. Study Site at Hidden Lake, Florida.

Lake, the species composition changes are much more rapid along the upland boundary and become less distinct as one moves toward the lake.

The wetland itself exists on land slopes which are nearly level to gently sloping with a slight positive gradient from the inflow canal to Hidden Lake. This slight gradient appears to be a dominant factor influencing both the hydroperiod and the vegetative species composition. The slightly higher areas of the path near the inflow canal were observed to have a hydroperiod of approximately 250 days with dominant canopy species such as red maple and swamp ash. The understory in this area of the flowpath is dominated by strands of greenbriar, blackberry, grapevine, galactica, lizard's tail, royal fern and cinnamon fern. This type of vegetative association has been termed a hardwood wetland by Brown and Starwes (1983).

In areas closer to Hidden Lake near the control site, which are subjected to hydroperiods in excess of 300 days per year, the dominance of red maple and swamp ash decreases while sweet bay and sweet gum become the dominant species. Ferns become the dominant understory plant species in this part of the wetland and include species such as cinnamon fern, Virginia chain fern, and royal fern. This type of vegetative association has been termed a bayhead wetland by Brown and Starwes. In numerous areas throughout the wetland, the vegetative species form a thick foliage that appears to be impenetrable.

Characteristics of Soils in the Wetland Community

Soils associated with the Hidden Lake wetland are organic soils, primarily histosols, which are commonly called peats and mucks. The histosols are primarily

composed of decayed and partially decayed plant tissue and contain approximately 80-90% organic material by weight. These organic soils are characterized in general by: (1) a very low bulk density; (2) high water holding capacity and content by percent volume; (3) low hydraulic conductivity; (4) low percent ash; (5) high organic matter content; and (6) high organic nutrient content.

The soils in the wetland are nearly always moist, with the water table at or near the surface during much of the year. Soil moisture during non-storm periods is provided by groundwater seepage from surrounding upland areas. The surface soils in the study area are characteristic of wetland soils associated with the different wetland communities. In the mixed hardwood region, the surface sediments are dark brown and reddish-brown muck 10-30 cm thick overlying a loose peat layer 1-2 m thick. In the bayhead region near the lake, soils are almost entirely peat to depths over 1.5 m. The entire wetland appears to be underlain by a dense sand or clay layer at 1-2 m deep which acts as an aquatard for vertical seepage.

Groundwater

The groundwater table in the hardwood hammock varies seasonally with wet and dry months. During the winter and spring months (December through June), the piezometric surface ranges from near the surface to as much as one meter beneath the wetland surface, although the upper soil layers remain damp. Stormwater inputs during this period usually infiltrate into the groundwaters and do not discharge directly to Hidden Lake. However, during the summer months, standing water, ranging from 1-20 cm, is common in all areas of the wetland. Vertical movement of groundwater is retarded by the underlying clay liner, and as a result, the dominant groundwater flow is horizontal. The groundwater table in the upland areas contributes a continuous but variable subsurface input to the wetland. Groundwater seepage into the inflow canal from upland areas also contributes a continuous but variable surface inflow to the wetland during much of the year. This background flow through the canal into the wetland is greatest during the summer and fall, decreases during the winter months, and usually stops completely during spring. Virtually no direct surface runoff was observed from adjacent upland areas into the wetland.

The groundwater regime in the study area is regulated to a large degree by water elevations in Hidden Lake. As the water elevations in the lake change, the groundwater gradient between the wetland and the lake also changes. From October to March, the piezometric surface in the wetland is generally higher than that of Hidden Lake, and a positive gradient exists for groundwater movement into Hidden Lake. However, from April to September, elevations in Hidden Lake are higher than the piezometric surface in the wetland and the lake appears to recharge the wetland groundwaters.

Hidden Lake

Hidden Lake is located near the center of the wetland community. Physical and morphometric characteristics of Hidden Lake are listed in Table 3-1. In most areas, the shoreline of Hidden Lake exists in an undeveloped and natural state. The lake maintains a constant population of Nuphar luteum (yellow water lilies) which normally peak in numbers during the summer, covering 25-40% of the pond surface. However, during the winter months, these plants retreat to a coverage of less than 10%. Numerous

TABLE 3-1

PHYSICAL CHEMICAL CHARACTERISTICS FOR HIDDEN LAKE, FLORIDA

PARAMETER	QUANTITY
Approximate Surface Area	44,400 m ² 4.44 hectares (10.97 acres)
Approximate Volume	66,500 m ³ 17.6 x 10 ⁶ gallons
Mean Depth	1.5 m (4.9 ft)
Maximum Depth	2.5 m (8.2 ft)
Length of Shoreline	1760 m (5770 ft)
Shoreline Development	2.36
Volume Development	1.80

patches of other rooted emergent macrophytes have been noted in the lake. Hidden lake appears to be geologically old and in an advanced state of natural eutrophication. As a result, sediment material, which is predominantly organic in nature, has accumulated to a depth of several meters within the lake. In general, the water can be characterized as acidic, highly colored, and relatively high in dissolved phosphorus and organic nitrogen.

Hydrologic inputs into the lake originate as overland flow from the surrounding wetland as well as direct inputs of runoff from the developed residential areas. The piezometric surface of the lake is variable and fluctuates in excess of 1 m with seasonal precipitation. Hidden Lake discharges to the south during the wet season through a series of vegetated canals which eventually flow into Lake Minnie. The two lakes, as well as the wetland, become hydraulically connected as the wet season progresses and the quantities of rainfall and runoff increase.

Characteristics of the Contributing Watershed

The hydrologic regime of the hammock was modified in 1975 when it began receiving stormwater runoff from the adjacent 22.4 hectare drainage basin of newly constructed single-family and high-density multi-family residences. Prior to development, this area was primarily a pine flatwood community. Watershed characteristics of the drainage basin are given in Table 3-2. Curb and gutter, grasses swales, and stormsewers are used to convey runoff to a small vegetated canal, 1-2 m in width, which flows into the wetland (Figure 3-2). Other residential areas outside the drainage basin discharge runoff into the perimeter of the hammock at various locations.

TABLE 3-2

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WATERSHED CHARACTERISTICS OF THE HIDDEN LAKE STUDY SITE

PARAMETER	QUANTITY
Drainage Basin	22.36 hectares 55.22 acres
Percent Impervious	26.0
Impervious Area That Is Directly Drained	68.0%
Time of Concentration	26.5 minutes
Weighted Runoff Coefficient, C	0.11
Mean Slope (ft/ft): Watershed Inflow Canal	0.0050 0.0049
Mean Yearly Rainfall	132 cm 52 inches

However, these inputs are relatively small and are not hydraulically connected with the study area.

Runoff Flow Regime

Upon entering the wetland, runoff from ordinary rain events as well as baseflow generally follow a shallow well-defined flow channel to the south for the first 25 m before gradually spreading out over the entire flowpath. During extreme or high intensity rain events, the capacity of the shallow inflow channel can be exceeded, and the inflow has been observed to travel not only south but north and west as well. However, even though some variation is possible in the initial flow regime for inputs to the system, the dominant flow regime remains through the 1.0 ha study area in the direction of Hidden Lake.

Field Investigations

Field investigations conducted at the Hidden Lake site during 1984-85 were divided into the following tasks: (1) assessment of the quantity of nutrients and heavy metals entering the wetland by way of stormwater runoff; (2) characterization of water quality in surface waters in the wetland; (3) monitoring the accumulation and movement of nutrients and heavy metals in groundwater; (4) measurement of the accumulation of nutrients and heavy metals in the sediments of the wetland; and (5) changes in productivity of runoff water during flow through the wetland. Each of these tasks is described in the following sections.

Characterization of Hydrologic Inputs

A 90-degree V-notch weir was installed across the inflow canal adjacent to the trailer to monitor direct hydraulic inputs into the wetland. Surface water flow through the weir into the wetland was monitored continuously for both baseflow and runoff flow using a programmed ISCO flowmeter and flow totalizer from December 1984 to April 1986. All water entering the wetland through the V-notch weir was totaled and recorded on an hourly basis.

Characterization of Rainwater

Direct precipitation was monitored in the Hidden Lake wetland from March 1985 through December 1985. A wet/dry fallout collector was mounted on the roof of the research trailer and used to collect rainfall samples. A tygon sample tube was inserted through the bottom of the wet collection bucket and was routed to a 4-liter polyethylene storage bottle located inside the trailer. The initiation of a rain event would cause the wet collection bucket to be uncovered. A composite rainfall sample would then begin to collect in the bucket and drain through the tygon tubing into the storage bottle in the trailer. At the completion of a rain event, a sensor would signal the cover to return over the wet collection bucket. Immediately following storm events, the collected sample was returned to the Environmental Engineering Laboratory at the University of Central Florida for water quality analysis.

Stochastic monitoring of storm events in the study area was also performed during the study period. A Texas Electronics Model TR-6118 "Tipping Bucket" rainfall collector was placed on the roof of the research trailer and was connected to a Model 1014-P Rainfall Sensor/Strip Chart Recorder located inside the trailer. A permanent record of direct precipitation, antecedent dry period, rainfall volume, and intensity were collected throughout the project.

Characterization of Stormwater Runoff

To determine the quantity of nutrients and heavy metals entering the wetland by way of stormwater runoff, an ISCO automatic refrigerated sampler was installed in the trailer adjacent to the weir. A tygon sample tube was extended from the ISCO sampler in the trailer to the inflow canal. A 5-cm PVC rod was driven into the sediments approximately 1 m upstream of the 90-degree V-notch weir. The sample collection tube and a sample initiation actuator were attached to the PVC rod. The stormwater sample collection tube was positioned near the baseflow water level while the sample actuator was attached approximately 2 cm above the baseflow level. A sudden increase in water level would wet the actuator, causing the sample collection program to begin. Water elevations discharging through the V-notch weir were monitored by an ISCO pressure transducer attached to the weir and converted to a volumetric flow rate by a preprogrammed ISCO flow meter. A record of stormwater volumes entering the wetland was made on an hourly basis for each storm event as well as for baseflow during dry periods.

Flow-weighted composite samples were collected with the automatic refrigerated sampler over a 12-month period for 24 separate storm events, representing a wide range of rainfall intensities and antecedent dry periods. After rising water levels reached the flow actuator, the automatic sampler was programmed to collect a 0.5-liter sample of stormwater runoff every 5 minutes during the elevated flow conditions of a storm event. The ISCO refrigerated sample used in this research had a capacity of 28 one-liter samples or 56 half-liter samples. This sampling scheme constituted a possible sampling period of 280 minutes or until the water level dropped below the sample actuator. Since approximately 3 liters of runoff sample was required to perform all the desired laboratory analyses, collected samples were combined in groups of seven (bottles 1-7, 8-14, 15-21 and 22-28) to produce a potential of four composite samples per runoff event. Samples were collected as soon as possible following storm events and returned to the Environmental Engineering Laboratory at the University of Central Florida for water quality analyses.

Characterization of Hidden Lake Water

Water samples were collected periodically from Hidden Lake from April 1985 through November 1985. Since physical access to Hidden Lake was extremely difficult due to the dense wetland which surrounded it, it was necessary to pump water samples from Hidden Lake for analysis. A 2.5-cm diameter schedule 40 PVC pipeline was installed from Hidden Lake to the research trailer, a distance of approximately 300 m, in order to collect samples for water quality analysis. The PVC pipe was submerged near the center of Hidden Lake at a depth of 1.0 m from the water surface at time of installation. The pipeline was attached to a 1 HP centrifugal pump in the research trailer. On sampling days, the pump was turned on and allowed to run for 30 minutes before a sample was taken in order to purge water that had been stored in the pipeline previously. The sample was placed in a 4-liter polyethylene sampling bottle and returned as soon as possible to the Environmental Laboratory at the University of Central Florida for water quality analysis.

Wetland Surface Water Monitoring

Surface water sampling sites were established within the wetland based on observations of the flow of runoff throughout the wetland during rain events. Surface water sampling sites were established at seven fixed stations along the flowpath within the wetland beginning at the inflow canal, then at a distance of 10 m along the flowpath followed by stations at 25 m intervals along the dominant flowpath to a distance of 150 m as indicated in Figure 3-3. This distance was observed to be the extent of runoff movement into the wetland during most storm events. A fixed "control" station was also established in an area of the wetland west of the dominant flowpath which was removed from runoff influence.

Fixed sample ports were installed in the wetland at the locations indicated in Figure 3-3. Sample collection devices were constructed from 5-cm PVC pipe with a sampling port attached into one side of the apparatus. The port was plugged with a one-hole neoprene stopper and covered with a plastic mesh screen to prevent debris from plugging the sample port. Five millimeter polyethylene tubing was then inserted into the neoprene stopper hole to complete the sampling device. A schematic diagram of the surface water collection device is given in Figure 3-4. Collection devices were placed along the major flowpath at each of the designated stations with polyethylene sample tubing extending to areas away from the flowpath. By collecting samples in this manner, it was not necessary to cross or disturb the flow of water during sample collection.



Figure 3-3. Sample Collection Sites for Surface Water, Groundwater, and Sediment Cores in the Hidden Lake Wetland.



Figure 3-4. Schematic Diagram of Sample Collection Devices for Groundwaters and Surface Waters.

Samples were collected from all seven locations for analysis on a bi-weekly basis beginning in December 1984 and ending in December 1985. A Turner portable battery powered peristaltic pump was connected to the end of the extended polyethylene tubing and used to slowly pump the surface water samples into collection bottles. Samples were collected in 4-liter polyethylene bottles which were pumped directly into a flow-throughcell connected to a Hydrolab System 8000 Water Quality Monitor which was placed inline before the sample bottle. This technique allowed direct field measurement of temperature, conductivity, pH, dissolved oxygen and redox potential as the sample was being collected. Field measurements collected in this manner are more accurate for certain parameters such as pH, dissolved oxygen and redox potential which are subject to rapid change during storage. Collected samples were returned to the Environmental Engineering Laboratory at the University of Central Florida for analysis of nutrients, heavy metals, and other water quality parameters.

Groundwater Monitoring

To investigate the possibility of groundwater contamination by leaching of nutrients and heavy metals, four multi-port monitoring wells were installed at locations indicated in Figure 3-3. Well #1 was located in the upland area of the wetland, approximately 30 m south-southwest of the research trailer, in order to characterize groundwater quality in an area upgradient of the wetland site. Wells #2 and #3 were installed in the major flowpath of the wetland at distances of 25 m and 150 m, respectively, in order to monitor areas which receive continuous flows of baseflow and stormwater. Well #4 was installed in the control section of the wetland, near Hidden

Lake, in an area which receives no direct stormwater discharges and exhibits generally stagnant surface water conditions.

The well design was a multi-port approach with all sample ports housed in a single 5-cm Schedule 40 PVC pipe. A schematic of the multi-port sampling device was given in Figure 3-4. It was felt that this design would minimize soil disturbance and reduce groundwater recovery time for obtaining representative samples when compared to other monitoring well designs. Sample ports were constructed from one-hole neoprene stoppers with a 5 mm semi-rigid polyethylene tube inserted in the hole. The stopper was covered with a small plastic mesh screen to prevent particles from entering the tubing. Sample ports were inserted in the casing at depths of 0.1 m, 0.5 m, and 1.0 m below the soil surface at the time of placement. Polyethylene tubing was extended from each of the sample ports through the PVC casing to the surface where the ends were permanently marked for identification of sample ports during sample collection.

Bore holes for the multi-port wells were dug to a depth of approximately 1.25 m using a 13-cm diameter hand auger. A 30-cm PVC casing was used as the drilling progressed to hold the bore hole open. Upon completion of the bore hole, the multi-port device was inserted and back-filled with clean silica sand (20-30 grade). A removable end cap was placed on each well in order to protect the sample tubes. A 30-cm Casagrande type piezometer tip was also installed in each bore hole with the monitoring well. A 1.3-cm diameter PVC pipe was extended from the piezometer tip to the surface for measurement of the piezometric level. Piezometric measurements were collected on a monthly basis with the groundwater samples.

After construction was complete in September 1984, no samples were collected for approximately 60 days to allow for groundwater disturbances created during the installation process to subside. In addition, during this 60-day period, each port on each well was pumped for 15 minutes on a weekly basis with a peristaltic pump to remove any dissolved solids and sand which may have been disturbed during the installation of the multi-port wells. This process removed approximately 10 liters from each port on a weekly basis.

Groundwater samples were collected for analysis on a monthly basis beginning in November 1984. Samples were collected using a Turner portable battery-powered peristaltic pump. Groundwater samples were collected in 2-liter polyethylene bottles which were allowed to overflow one volume before a sample was taken. All groundwater samples were pumped through a flow cell connected to a Hydrolab System 8000 Water Quality Monitor which was placed in-line before the sample bottle. This technique allowed direct field measurement of temperature, conductivity, pH, dissolved oxygen, and redox potential as the sample was being collected. Collected samples were returned to the Environmental Engineering Laboratory at the University of Central Florida for analysis of nutrients, heavy metals, and other water quality parameters.

Characterization of Sediments

Sediment analyses were conducted on core samples collected near each of the surface water sample stations and in an isolated control area not subject to stormwater influence to characterize the deposition and attenuation of heavy metals and nutrients. The location of the isolated control area was indicated in Figure 3-3.

A "split-spoon" core collection device was used in the retrieval of the sample cores from the wetland soils. The collection device was constructed of a split Schedule 40 PVC pipe, approximately 75 cm in length, with a beveled edge on one end for ease in sediment penetration. A schematic of the "split-spoon" sediment core sampler is given in Figure 3-5. A pair of hose clamps were used to hold the split-spoon sampler in place as it was inserted into the sediments. In some locations, the collection tube could be pushed into the sediments by hand, while at other locations a hammer was used. The sediment removal technique consisted of inserting the sample collection device into the sediments to a depth of approximately 40 cm and then removing it using an upward twisting motion.

Core samples were collected at the eight surface water sample stations on March 12, 1985 and May 15, 1985, and in the isolated control area on March 12, 1985. At the time of collection for the March samples, standing water was present at most locations in the wetland and the soil was completely saturated. However, the period from March to May was extremely dry, and by the time of collection for the May samples, the water table had dropped to approximately 1 m below the surface. The soils on this date were moist but were not inundated.

Upon removing the split-spoon sampler from the sediments, each core sample was immediately divided into the following layers: (1) 0-1 cm; (2) 1-5 cm; (3) 5-10 cm; (4) 10-15 cm; and (5) 15-20 cm. After separation of the sample into layers, each of the horizons were stored in polyethylene bottles and labeled appropriately. Three 5.0-cm diameter core samples were collected at each site and combined to form a single composite sample for each site. The technique of sampling near the surface water

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SAMPLER PUSHED INTO SOIL



CORE SAMPLE AFTER COLLECTION WITH TOP OF SPLIT-SPOON REMOVED

Figure 3-5. Modified Split-Spoon Apparatus Used for Collection of Sediment Cores.

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stations allowed for further collections at a later date in the same area and also provided concurrent sediment and water quality data at various locations in the wetland. Upon return to the Environmental Engineering Laboratory at the University of Central Florida, the core analyses were begun. Analyses for moisture content, organic content, total phosphorus, organic nitrogen, and heavy metals were conducted in triplicate on each layer collected at each station. Concentrations of nutrients and heavy metals in the 0-1 cm layer were used to investigate the horizontal movement of heavy metals after discharge to the wetland. The extent of vertical migration of nutrients and heavy metals was determined using all five sediment core layers.

Rate Experiments

Five isolation experiments were conducted to provide information on the rates of nutrient and heavy metal exchange in flow-through and stagnant systems with and without sediment contact. Three 1.0 m diameter and 30 cm tall isolation chambers were constructed from 5 mm thick semi-rigid polyethylene sheets by forming a ring which was fastened using teflon bolts and silicon glue to ensure a watertight seal. The rings were then inserted approximately 15 cm into the sediments near groundwater monitoring well #2 to completely isolate an area of sediments and the overlying water column from the rest of the wetland.

The chambers were placed close together to ensure similar sediment conditions and efforts were made to duplicate as closely as possible the vegetation patterns and plant species enclosed within each chamber. A thin polyethylene sheet was placed over the sediments in one of the chambers (A) so that test waters could be isolated from the sediments. The other two chambers (B and C) were not modified to allow free contact with the sediments. Simulated stormwater solutions were then placed inside each chamber, and changes in concentrations were monitored under various conditions.

At the initiation of each experiment, a simulated stormwater solution was prepared by adding small amounts of concentrated solutions of nutrients and heavy metals to 300 liters of baseflow pumped from the initial canal into a nalgene barrel. Sufficient nutrient and heavy metal spikes were added so that concentrations of the solution in the barrel were similar to those measured in residential runoff. After the solution was mixed, all of the standing water inside the isolation chambers was removed by hand with a nalgene beaker. Approximately 100 liters of the simulated stormwater solution was slowly siphoned into each of the isolation tanks with every effort taken not to disturb sediments. The volume of water siphoned into each chamber was sufficient to fill it to a height of approximately 10-12 cm. Since the mean water level in the wetland during these experiments was approximately 6-8 cm, the additional water added to the chambers infiltrated into the sediments, usually within 30 minutes. This process insured that the water column and pore water in the surface sediments would be initially similar in chemical characteristics and that no wetland water would enter the chamber. Two sample ports, similar to those described previously for collection of surface water samples, were permanently inserted inside each chamber with tubing extending to a location away from the chambers. Sample ports in the control chamber, which was isolated from the sediments with plastic, were placed on top of the plastic.

A total of three long-term and two short-term experiments were conducted. In the first long-term experiment, chamber B was established to simulate slow movement

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of the water through the wetland with a residence time of 4.6 days using a small pulse pump to circulate the water inside the chamber. Tubing from one of the sample ports was connected to the suction side of the pump with the remaining sample port connected to the discharge side. Water within the chamber was then pumped out of one sample port and back into the other to create a circulation. Chamber C was set up to simulate a stagnant water system, and chamber A was the control system with no sediment contact. Samples were collected from each isolation chamber immediately after addition of the simulated stormwater mixture and then periodically during the 18-day experiment generally at 1-2 day intervals. Field measurements of water temperature, pH, dissolved oxygen, specific conductivity, and ORP were also made at the time of sample collection by pumping the sample through a flow-through cell attached to a Hydrolab Model 8000 as described previously.

The second long-term experiment was set up in the same manner as the first with the exception that chamber C was converted to the circulation system with chamber B the stagnant system. The third experiment was run using the same experimental set-up as the second experiment with the exception that the residence time was decreased by one-half to 2.3 days.

The last two experimental runs were designed to examine short-term removal kinetics for pollutant concentrations over a 24-hour period. Only chambers A and B were used in the simulations. In order to investigate the initial rapid uptake by sediments, two refrigerated ISCO automatic sequential samplers were used in the sampling process. After the initial input of the stormwater solution, a sample was collected. Another sample was collected after 15 minutes in an effort to look at rapid

uptake by sediments. The ISCO sampler was then set to take samples every two hours up to a maximum of 25 hours.

All rate experiment samples were returned to the Environmental Engineering Laboratory at the University of Central Florida for analysis of nutrients, heavy metals and other water quality parameters. Samples were filtered through a 0.45 micron glass fiber filter prior to analysis.

Channel Experiments

An early objective of this research was to investigate the relationships between characteristics of runoff inputs and removal efficiencies for various pollutants. It was decided to isolate a well-defined flow channel area within the wetland, pump a simulated stormwater solution through this section, and measure reductions in pollutant concentrations during travel through the channel. The first channel design was constructed in an area of the wetland adjacent to the dominant flowpath area so that it would not be disturbed by runoff inputs. This area is indicated on Figure 3-3 as the Isolated Control Area for sediment cores. A continuous length of rigid polyethylene. The sections were overlapped approximately 15 cm, coated with a silicone sealant on the two contact surfaces, and then bolted together with four 0.5 cm diameter plastic bolts to form watertight seals at all connections. Two long sections, each approximately 55 cm in length, were made in this fashion.

The prepared sections were stretched out throughout the chosen area in an irregular path to avoid trees and larger subcanopy shrubs. A continuous narrow slit was

made along this path into the soil with a flat-head shovel to break through roots and debris. One of the 55 cm sections was placed in the silt and hammered vertically into the soil so that approximately 20 cm were below the soil surface and 10 cm above the soil surface. A second narrow slit was made exactly 1 m from the first inserted section, carefully following the pattern of the initial section. The second 55 cm section was inserted similar to the first to form an isolated channel 1 m in width, 55 m in length, with 10 cm high side walls.

Upon completion of the channel section, a source of water was sought for pumping into the channel during experimentation. Initially, it was decided that the inflow canal, which maintained a continuous flow into the wetland, would be used as the source of raw water. A 1-HP centrifugal pump was installed in the trailer with the suction line in the canal and the discharge extended to the channel area. A concentrated solution of nutrients and heavy metals was prepared in a 200 liter nalgene barrel and was pumped into the suction side of the pump at a slow controlled rate to provide the desired concentrations of nutrients and heavy metals after mixing with the canal water. However, after 3 days of pumping into the channel, it became apparent that the inflow canal could not supply an adequate amount of raw water.

After careful re-evaluation, it was decided that the only resource available that could meet the pumping demand for our experiments was Hidden Lake. During March 1985, a 3.8 cm diameter PVC pipeline was installed through the wetland from the research trailer to the center of Hidden Lake, a distance of approximately 200 m. The suction end was equipped with a screened entrance and check valve and then positioned at a fixed distance of 0.5 m from the lake bottom. This piping, combined with the 1-HP pump, could deliver approximately 30 gallons of spiked water per minute into the channel.

From March through October 1985, attempts were made to obtain experimental data from the channel with very little success. The first problems which were encountered involved priming of the pump. Approximately 2-4 hours were required to remove all air pockets from the 200 m long pipeline and obtain a continuous pumped flow of water. The check valve was designed to prevent loss of this prime during power failures. However, the check valve would invariably become clogged with some of the small debris common in Hidden Lake and even short power failures, which were virtually a daily occurrence, resulted in a loss of prime. Damage by fallen trees, animals or vandalism was also a problem. Countless hours were spent attempting to maintain a prime on this pump. Attempts were made to modify the check valve design, increase the number of check valves, and even to install electrically operated solenoid valves. However, none of those designs were totally satisfactory.

During times when a prime could be maintained, other problems arose. Frequently, the flow would continue for a few days, then a small depression would open up somewhere along the channel and all the water would seep into the groundwaters. Attempts to move the channel in these areas were generally only temporarily successful. Loss of flow under the channel walls and washout of soil under the channel was also a common problem. After 8 months of largely futile efforts, these experiments were discontinued.

After careful reconsideration of the persistent problems and potential solutions, it was decided that the desired degree of experimental control could only be achieved in

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a man-made design. A plywood channel, 30 m long, 0.45 m wide and 0.38 m tall, was constructed near the University of Central Florida wastewater treatment facility. The channel was supported with concrete blocks and leveled using a transit. Two layers of 5 mil polyethylene film were placed in the channel, smoothed out along the bottom and inside walls, wrapped over the outside wall and stapled to hold it in place. The inlet end of the channel was enclosed with a 0.15 m high weir. A stilling well was constructed at the inlet end by placing a plywood wall, 0.15 m high, across the channel approximately 0.25 m from the inlet. Inputs of simulated stormwater solutions would be initially discharged into this basin. The basin served to eliminate the turbulence in the flow, and the solution flowed gently over the wall and into the channel. This minimized sediment disturbance in the channel during experimentation.

After the channel was constructed and lined with polyethylene, it was filled to a depth of 0.15 m with soils from the Hidden Lake wetland. Approximately 2100 liters of wetland soils were collected from various locations in the wetland and transported in large polyethylene barrels to the channel site. Soils were only collected within the first 0.15 m from the soil surface. After returning to the channel, the soils were mixed and spread out evenly over the channel, at a depth of 0.15 m. Native wetland vegetation was also collected along with the soils, and planted in the channel at the same approximate density as was found in the wetland. It was originally intended that the polishing pond for the wastewater treatment plant would be used as a source of raw water for flow through the channel. However, chemical analyses indicated that concentrations of nitrogen and phosphorus were approximately 10-100 times that found in the stormwater at Hidden Lake. It was then decided to use a mixture of potable water and wastewater

effluent to obtain the desired pollutant concentrations. A large 225 liter polyethylene barrel was placed near the channel input and a hose was extended from a faucet to the barrel. The faucet was partially opened to provide the desired flow into the barrel and a pulse pump was used to inject the desired volumes of wastewater flow into the barrel. A submersible pump was placed in the bottom of the barrel and operated continuously to circulate and mix the two inputs. A gravity overflow was then provided from the barrel to the stilling well on the channel. Retention time in the barrel ranged between 0.5 and 10 hours, depending on the experiment design. Periodic tests of chlorine residual indicated that these times combined with the vigorous circulation were sufficient to reduce chlorine levels to near zero.

Construction of the channel and addition of the soil was completed in November 1985. The channel was allowed to equilibrate and plants allowed to establish until March 1986 when collection of data began. A slow flow was maintained in the channel during this equilibration period. Virtually all of the initial plantings survived and were multiplying by this time.

Sample ports were installed along the channel at the inlet as well as 10 m, 20 m, and 30 m along the flowpath. Sample ports consisted of a 5 mm rigid polyethylene tube inserted midway between the water surface and the soil surface at each of the four locations. The tubing was extended from each sample point to the midpoint of the channel and connected to two dual-head peristaltic pumps. The pumps were connected to tachometers so that each could be set to pump at the same number of revolutions per minute. A timer was used to supply power to the pumps so that each pump would come on every 2 hours for 90 seconds. Each pump would discharge approximately 200 ml of sample at every 2-hour interval. The discharge line from the pumps were connected to separate 8-liter collection bottles inside a refrigerator along the channel. Each bottle would, therefore, collect a composite sample from each sample point which reflected samples collected every 2 hours at each point.

Beginning in March, a series of six experiments at different flow rates were started. Each experiment would begin by setting an initial flow rate through the channel. This flow rate would be maintained for 7-10 days without sample collection to allow equilibration to occur. After the equilibration period, samples were collected every 2 hours as described previously. Each separate experiment was conducted for 7 days after equilibration. A sub-sample of the total sample collected over this period at each station was returned to the laboratory for analysis. A summary of the hydrologic characteristics of the channel experiments is given in Table 3-3. At the end of an experiment, a new flow rate would be set, the channel would be allowed to equilibrate again for 7-10 days, and a new 7-day sample period begun.

All samples were returned to the University of Central Florida laboratory for analysis. Prior to analysis, samples were filtered through a 0.45 micron glass fiber filter.

Laboratory Investigations

Laboratory investigations during this research were divided into the following tasks: (1) water quality analyses; (2) a series of algal bioassay experiments to examine changes in productivity in stormwater runoff during wetland flow; (3) extraction process which allowed determination of the chemical speciation of heavy metals and phosphorus in sediment core samples; (4) a series of investigations to determine the influent of pH

TABLE 3-3

HYDROLOGIC CHARACTERISTICS OF UPTAKE EXPERIMENTS IN THE ARTIFICIAL CHANNEL

EXPERIMENT NUMBER	INPUT FLOW RATE (L/min)	MEAN FLOW VELOCITY (m/min)	MEAN RETENTION TIME (hours)	MEAN HYDRAULIC DEPTH (cm)
1	7.00	0.36	1.39	3.20
2	5.11	0.26	1.92	3.10
3	3.22	0.16	3.13	3.00
4	2.27	0.12	4.17	3.00
5	1.32	0.07	7.14	2.95
6	0.38	0.02	25.0	2.90

and redox potential on the chemistry of phosphorus and heavy metals in sediments; and (5) series of column studies to quantify removal efficiencies for pollutants during infiltration into wetland soils. Each of these procedures is described in the following sections.

Water Quality Analysis

A summary of the various water quality analyses performed on water samples collected during this research is given in Table 3-4. All water quality analyses were determined as described in <u>Standard Methods</u>, 14th Edition (APHA 1976) and within the time limits specified by <u>U.S. EPA Methods for Chemical Analysis of Water and Wastes</u> (1976). Determinations of dissolved orthophosphorus and total phosphorus were performed using the Ascorbic Acid Digestion Method (425 F) on a filtered sample and the Persulfate Digestion Method (425 C.III) on an unfiltered sample as described in <u>Standard Methods</u>. A Bausch and Lomb Spectronic 70 spectrophotometer was used in the colorimetric determinations of the phosphorus species. Carbon analyses were performed using the Combustion-Infrared Analysis Technique with a Beckman Model 915-B Total Organic Carbon Analyzer. Determinations of total carbon and inorganic carbon were made directly with organic carbon determined by difference.

Ammonia nitrogen was determined colorimetrically by the Phenate Method as described in <u>Standard Methods</u>. To avoid interference from color, present in many of the water samples, sample blanks were run with each sample. The sample blanks consisted of the filtered water sample without the reagents. Nitrate nitrogen was determined colorimetrically by the Brucine Method, as described in <u>Standard Methods</u>.

TABLE 3-4

PARAMETERS MEASURED DURING INVESTIGATIONS AT THE HIDDEN LAKE WETLAND

PARAMETER	WETLAND (bi-weekly)	STORMWATER (each event)	RAINFALL (each event)	GROUNDWATER (monthly)	SAMPLE TYPE*
pH Conductivity	in field	X	X	in field	UF
Temperature	in field	X	X	in field	UF
Dies Oxygen	in field			in field	
ORP	in field			in field	
Alkalinity		v	v		
Turbidity	л v	A V	Λ	А	
Ammonia	× ×	A V	¥	¥	F
Nitrite	X X	X	X	X	F
Nitrate	x x	X	X	X	F
Organic-N	X X	л ¥	X	x	UF
Ortho-P	x A	x	X ·	x	Ŧ
Total P	X	x	X	X	UF
Phenol	x	X	A		F
TOC	x	X	X	X	F
Oil. Grease	x	X	-	-	UF
BOD	x	x		х	UF
Color	X	X		X	F
Total Residue	x	X	х		F
S.S.	x	x		_	UF
V.S.S .	X	X	,		UF
Total Metals	x	X	x	x	UF
Diss. Metals	X	x	x	x	F

Since many of the samples were colored, sample blanks were used for each sample. The sample blanks were prepared exactly the same as the samples except no brucine was added.

Nitrate nitrogen was also determined colorimetrically following the method described in <u>Standard Methods</u>. Sample blanks were used to eliminate the absorbance due to color in the samples. The sample blanks were prepared by adding 0.1 ml 6 N KCl to 10 ml of sample in order to compensate for the pH change produced by adding the reagents to the samples. Total Kjeldahl nitrogen was determined by the Macro-Digestion Technique described in <u>Standard Methods</u>. Sample volumes of 250 ml were used for digestion followed by subsequent distillation into boric acid. Nitrogen concentrations in the boric acid were determined by titrating with a standard acid. Two blanks were run with each set of samples. Organic nitrogen concentrations were determined by subtracting the ammonia nitrogen concentrations from the total Kjeldahl nitrogen concentration.

Heavy metal analysis in water samples was divided into determinations of dissolved and total concentrations. For a dissolved analysis, the sample was filtered through an acid-washed Whatman GF/C glass fiber filter. Each filter was soaked before use in 1:1 nitric acid for 24 hours. The filters were then rinsed by soaking in three changes of distilled water for 24 hours each. Immediately prior to use, the filter was rinsed an additional time by filtration of 300 ml distilled water followed by 100 ml of the sample to be filtered. These initial rinse waters were discarded, and a sample for metal analysis was then filtered. The filtration apparatus was constructed of polycarbonate to avoid metal contamination. For total metal analyses, no pretreatment was performed.
Both total and dissolved samples were then carried through an acid digestion procedure. One-hundred milliliters of sample were placed in an acid-washed 250 ml Erlenmeyer flask along with 2 ml of redistilled nitric acid. The sample was refluxed on a hot plate without boiling until the volume was reduced to between 5-10 ml. The sample was allowed to cool, diluted to a final volume of 20 ml, and stored in a disposable polyethylene beaker covered with parafilm until analysis.

All glassware used for sample digestion, as well as for preparation and storage of standards and reagents, was acid-washed prior to use. Glassware was first washed with a stiff brush in hot water using a phosphate-free detergent. After rinsing, the container was filled with hot 1:1 nitric acid for 30 seconds. This acid rinse was followed by five rinses with distilled water. All distilled water used for dilutions and blanks in metal analyses were first deionized then glass distilled, followed by a final deionization through a Barnstead Nanopure Cartridge system.

Analysis of heavy metals was performed on the acidified concentrated samples using a direct current argon plasma spectroscopic technique on a Spectrometrics Spectrospan III. The heavy metals analyzed during this research were Cd, Zn, Mn, Cu, Al, Fe, Pb, Ni, and Cr. The Spectrospan III performed three separate spectrum analyses for each metal on each sample and produced a printout listing each separate analysis, and average values, and a standard deviation for each metal. A standard solution and a distilled water blank were analyzed before and after each set of 6-8 samples. A computer program was written and used to correct the average values for each sample for drift in measurement of both the standard solution and blank solution.

Analysis of Heavy Metals and Nutrients in Sediments

Acid extractable analyses were conducted on the core samples collected on 3/12/85, 3/15/85, and 5/15/85 for phosphorus and each of the nine metals listed previously. Each core section was first dried at 103 °C to determine moisture content followed by ignition at 550 °C to determine organic content. The washed sample was ground with a mortar and pestle, and approximately 0.4 g of sediments (weighed to the nearest 0.1 mg) was placed in an acid-washed 250 ml Erlenmeyer flask. Five milliliters of redistilled nitric acid were added along with 100 ml of glass distilled and deionized water. the mixture was refluxed without boiling until a volume of approximately 10 ml was reached. The flask was allowed to cool and the supernatant was carefully decanted into a polyethylene disposable beaker. The remaining sediment was rinsed with two additions of 10 ml of distilled water which were added to the supernatant. The supernatant was diluted to a volume of 50.0 ml and covered with parafilm until analysis.

Determination of total organic nitrogen was also performed on wetland sediment samples. The samples were prepared by placing 1.0 g of wet sediment into a 800-liter Kjeldahl flask and adding 250 ml of deionized water. The total Kjeldahl nitrogen was then digested according to procedures outlined in <u>Standard Methods</u>. Moisture content was used to express nitrogen concentrations in terms of a dry weight basis.

Column Experiments

Two separate sets of column experiments were conducted from April 1985 to February 1986. In the first experiment, three soil columns of wetland sediments (0.66 m, 0.95 m and 0.90 m long) were obtained near well #2, well #3, and well #4, respectively, on April 13, 1985. Clear polycarbonate pipes (1.37 m long by 10 cm I.D. by 4.5 mm wall) were used to collect the columns. Columns were collected by driving the pipes into the soil with a sledgehammer. A metal rod inserted through pre-drilled holes in the pipe ends was used to remove the columns. The columns were sealed with rubber stoppers and taken to the laboratory.

A rubber stopper fitted with a tygon drainage tube was inserted in the bottom of each column. The columns were then mounted vertically to a large stand, and an overflow hole was drilled 15 cm above the soil surface in the top of each column. A synthetic stormwater solution was pumped into the top of each column from a 200-liter tank and the columns were allowed to drain naturally. The excess stormwater solution which overflowed was returned to the storage tank. The leachate from each column was collected in separate 1-liter nalgene sample bottles stored in an ice-filled cooler. The infiltration rate through the columns was monitored by measuring the volume collected in the sample bottles and the time to fill them. In order to obtain a sufficient sample volume for analysis, the samples from each column were stored at 4°C until 1700-2000 ml were collected. The samples were filtered through 0.45 micron glass fiber filters and stored at 4°C until analysis was completed.

A synthetic stormwater solution was prepared by adding nutrients and heavy metals to 170 liters of tap water in a 200-liter polycarbonate tank. The solution was prepared April 16, 1985 and used until the experiment was completed. Samples of the solution were collected every 2-3 days in 500 ml nalgene sample bottles and stored at 4°C until 2000 ml had been collected. The four samples were combined into a single composite sample, filtered through a 0.45 micron glass filter and stored at 4°C until analysis could be completed. Experimentation was conducted until August 1, 1985.

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After reviewing the results of the first set of column experiments, a second set was begun with all three soil columns obtained from the same area near well #3. Each column was approximately 1.0 m long. The columns were collected on September 11, 1985 in the same manner described previously.

In the laboratory, a rubber stopper fitted with a tygon drainage tube was inserted in the bottom of each column. The columns were mounted vertically to a support structure and wrapped with aluminum foil to prevent light from reaching the outside face of the soil columns. The overflow holes were drilled higher (15 cm above the soil surface) in an attempt to increase the flow rates through the columns.

The synthetic stormwater solution was prepared by adding small amounts of concentrated stock solutions to tap water which had been allowed to stand for 2-3 days to remove chlorine. The stormwater solution was prepared weekly and sampled every 2-3 days. Stormwater solution samples were combined into 2-liter composite samples and stored at 4°C until analysis could be completed.

The synthetic stormwater solution was delivered to the soil column by siphoning the solution from a 16-liter polycarbonate tank situated above the columns. The rate of stormwater solution discharging into the columns was regulated by valves at the ends of the tygon tubing delivering the solution to the columns. The flow into the columns was adjusted every 1-2 days to approximate the flow rate draining from the columns. The overflow from the columns was discarded.

Leachate from the columns was collected in 2.5-liter acid-washed glass bottles. The bottles were stored in a light-tight box and were emptied into 2-liter nalgene sample bottles whenever 1600-2000 ml had been collected. The flow rates for the columns were monitored by measuring the column collected and the time required to collect it. The samples were filtered through 0.45 micron glass fiber filters and stored at 4°C until analysis could be completed. Experimentation was conducted from September 19, 1985 to February 7, 1986.

Speciation of Heavy Metals in Sediments

Theoretically, it is chemically possible to partition solid material into specific metal fractions by using appropriate procedures. Recently, Tessler et al. (1979) reported an improved sequential extraction procedure for the speciation of particular trace metals and phosphorus. The new procedure eliminated many of the problems previously reported in single extraction procedures.

In this procedure, five fractions were extracted and are identified as follows:

- 1. <u>Soluble</u> ions contained in water which are trapped in interstitial pore spaces
- 2. <u>Exchangeable</u> ions which are associated with sediment carbonates as a precipitate or co-precipitate
- 3. <u>Bound to Carbonates</u> ions which are associated with sediment carbonates as a precipitate or co-precipitate
- 4. <u>Bound to Iron and Manganese Oxides</u> iron and manganese oxides may exist as nodule cement between particles
- 5. <u>Bound to Organic Matter</u> this incudes ions which are bound by adsorption or complexation to various forms of organic matter such as living organisms, detritus, and coatings on mineral particles

After a critical evaluation of the available literature, the following modification, as presented below, of the chemical extraction steps proposed by Tessler et al. (1979) were adopted. All sediment samples were initially air-dried and finely

ground by passage through a 600 micron plastic mesh to remove extraneous material. A minimum of three finely ground 2.0 g samples for each composite core sample collected on March 15, 1985 and on May 15, 1985 were taken through the following speciation steps. All extractions were conducted in 50 ml polypropylene centrifuge tubes to minimize losses of solid material.

Soluble

A 2.0 g sample of finely ground sediment was placed in a 50 ml polypropylene centrifuge tube with 16 ml of distilled/deionized water. The mixture was agitated continuously for 1 hour at room temperature (20°C). Following extraction, the mixture was centrifuged at 3000 rpm for 30 minutes. The supernatant was carefully decanted and prepared for analysis.

Exchangeable

The sediment residue from above was extracted at room temperature with 16 ml of 1.0 M MgCl₂ (pH 7.0) with continuous agitation for 1 hour. Following extraction, the mixture was centrifuged at 3000 rpm for 30 minutes. The supernatant was carefully decanted and prepared for analysis. The sediment residue was washed with 16 ml of distilled/deionized water by constant agitation for 5 minutes. After centrifugation for 30 minutes at 3000 rpm, this second supernatant was decanted off. The volume of rinse water was kept to a minimum to avoid excessive solubilization of solid material, particularly organic matter. The wash water for each of the three replicates was combined with the extract previously produced since ions present in the wash water

theoretically represent an amount which was released during extraction but not poured off with the extraction solution.

Bound to Carbonates

The sediment residue from above was extracted with 16 ml of 1.0 M NaOAc (pH 5.0) with continuous agitation at room temperature for 5 hours. Following extraction, the mixture was centrifuged at 3000 rpm for 30 minutes. The supernatant was removed for analysis and the residue washed with 16 ml of distilled/deionized water as before. Wash waters were combined with the initial extract and analyzed as described previously.

Bound to Fe/Mn Oxides

The residue from above was extracted with 40 ml of 0.04 M NH_2OH -HCl in 25% (V/V) acetic acid for 6 hours at 96°C with occasional agitation. After centrifugation at 3000 rpm for 30 minutes, the supernatant was removed for analysis and the residue was washed with 16 ml of distilled/deionized water as before, and the two samples combined.

Bound Organic Matter

To the residue from the above were added 6 ml of 0.02 M HNO_3 and 10 ml of 30% hydrogen peroxide adjusted to pH 2.0 with nitric acid. The mixture was heated to 85°C for 2 hours with occasional agitation. A second 6 ml aliquot of 30% hydrogen peroxide (adjusted to pH 2.0 with nitric acid) was then added and the sample was again heated to 85°C for 3 hours with intermittent agitation. After cooling, 10 ml of 3.2 M NH₄OAc in 20% nitric acid (V/V) were added, and the sample was diluted to 40 ml and

agitated continuously for 30 minutes. The addition of NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment. After centrifugation at 3000 rpm for 30 minutes, the supernatant was decanted for analysis.

Influence of pH and Redox Potential on the Chemistry of Phosphorus-Related Heavy Metals in Sediments

The effects of changes in pH and redox potential on release of phosphorus-related heavy metals in sediments were investigated in a series of experiments conducted using a system which allowed regulation of pH and automatic control of redox potential at a pre-selected value. A 2-liter, 4-neck flat bottom reaction vessel was used to contain sediment suspensions under selected conditions. The apparatus used for incubating sediment suspensions is shown in Figure 3-6. As indicated in this figure, each flask was fitted with a platinum electrode, a glass electrode for measurement of pH, a thermometer, two calomel half-cells, glass inlet tubes for air and nitrogen, an outlet tube for allowing gases to escape, and a sample port for adding acids or bases during pH adjustments or for sampling the sediments after completion of incubation. A water trap was used at the end of the outlet tube to prevent atmospheric oxygen diffusion into the sediments.

A composite sample of wetland sediment was formed by combining equal amounts of core samples collected at each of the surface water stations and was used in the incubation studies. The combined sediments were mixed thoroughly with a plastic rod prior to collection of a sub-sample. Moisture content, organic content, total phosphorus, and acid-extractable metal concentrations were determined on the mixed sample used in each of the incubation experiments.



Figure 3-6. pH and Redox Potential Control Apparatus for Incubating Sediment Suspensions.

To begin an experiment, 300 g of wet sediment, weighed to the nearest 0.1 g, was placed in the acid-washed reaction vessel along with 1800 ml of composite wetland surface water. A separate sample of surface water was collected for metal analysis. The reaction vessel was closed, and the suspension was circulated using a magnetic stirrer with a large teflon-coated magnetic stirring bar covered with tygon tubing to prevent excessive wear due to abrasion.

After stirring was begun, the redox potential was slowly adjusted by either bubbling in nitrogen gas or air until the desired level was reached. For highly reduced redox potentials, several days were often required to achieve the desired levels. Oxidized conditions were obtained more quickly. The suspension pH was adjusted at this time using ultra-pure HCl or NaOH to the proper level, and further refinement of pH and redox potential continued for 2-5 additional days. Sediment suspensions were then incubated for 5 days after the desired pH and redox potentials had been reached. Each experiment was conducted at a specified pH but included incubations at four redox potentials ranging from highly oxidized to highly reduced: +500 mV, +250 mV, 0 mV, and -250 mV. Values for pH which were tested included 5.0 and 6.5.

Redox potential was measured using a bright platinum electrode connected to a Corning Model 120 pH and millivolt meter. A separate saturated calomel reference electrode was used to complete the cell. A platinum wire was inserted into the side arm of the calomel electrode containing the mercury and connected to the reference side of the meter. The calomel electrode was connected to the suspension with a saturated potassium chloride-agar salt bridge. This reference electrode assembly and glass electrode were stated by Gambrell et al. (1977) in similar investigations to be more stable and require less frequent standardization than commercial combination pH electrodes, particularly in highly reduced suspensions. Adjustments to the calibration were less than 0.02 units in all experiments with several requiring no adjustments at all.

A meter relay was constructed and connected to the terminals used for measurement of redox potential. The purpose of the relay was to monitor redox potential and activate a small aquarium pump which would provide a controlled stream of air to the reaction vessel when the redox potential of the suspension dropped below the desired level. The level for activation of the pump could be set internally in the relay so that any desired redox potential could be maintained. The purpose of the air pump was to provide oxygen to offset the natural tendency for isolated sediments to become more reduced with time. The airflow from the pump was regulated with a flow meter at 5.0 ml/min to allow slow oxidation of the suspension during the aeration cycle. When the suspension was again oxidized to the proper level, the meter relay automatically switched off the aerator.

In studies requiring a highly reduced environment, nitrogen gas was added to the suspension to remove excess oxygen. For incubations conducted at less than 100 mV (Eh), a continuous stream of nitrogen gas was bubbled through the sediment suspension at a rate of 5.0 ml/min. Nitrogen gas was effective in purging excess oxygen from the system due to small leaks and prevented a buildup of gaseous decomposition products such as carbon dioxide. Removal of excess carbon dioxide was necessary to prevent undesirable changes in metal carbonate chemistry. Suspension pH was adjusted to the proper level initially and then readjusted when the pH changed by ± 0.1 unit.

During incubation of suspensions, the temperature was maintained at $28^{\circ}C \pm 1^{\circ}C$. The incubation temperature was an equilibrium between the heat generated by the stirring motor and the room temperature. If the suspension temperature increased above $28^{\circ}C$, the temperature was reduced by inserting thin sheets of polyethylene as required between the reaction vessel and the warm stirrer platform to maintain the desired temperature.

At the termination of an incubation period, a 100 ml sample of sediment suspension was withdrawn from the reaction vessel into a sealed 250 ml polycarbonate bottle using a siphon. The withdrawn volume was replaced by adding an equal volume of distilled water to the reaction vessel. In studies conducted under reducing conditions, the presence of free oxygen in the extracted sample could cause changes in redox potential that could result in immediate oxidation of metal ions to insoluble forms. To minimize possible oxidation of extracted sediments, all sample preparation procedures and filtration of reduced suspensions were conducted under a nitrogen purged atmosphere. Each of the sample collection bottles were modified by sealing a serum cap into a hole drilled in each bottle cap to permit transfer of extracted samples to and from the bottle without oxygen contamination. The sealed bottle was purged with nitrogen prior to adding an aliquot of reduced suspension.

The bottle containing the sediment suspension was then centrifuged for 30 minutes at 3000 rpm. The supernatant was removed using the apparatus shown in Figure 3-7. A syringe connected to a low pressure nitrogen source was inserted through the serum cap. A polyethylene pipette connected to a covered filtration funnel was inserted into the air space above the liquid. A vacuum was applied to the filtration flask which displaced



Figure 3-7. Apparatus for Filtering Supernatant Solutions Under a Nitrogen Atmosphere: (a) Pipette in N_2 Purge Position and (b) Pipette in Filtering Position.

the air in the flask by pulling nitrogen into the system. After purging for several minutes, the suction tube was pushed into the supernatant which was then drawn into the filter. The supernatant was filtered into a polycarbonate receiving flask containing 3 ml of redistilled nitric acid. After filtration, 75 ml of the acidified sample was digested as described previously and analyzed for heavy metals and phosphorus.

Algal Bioassay Procedures

Sample Collection and Preparation

After completion of laboratory analyses, the remaining volumes of collected surface water samples were combined by station to form a composite sample of surface water at each station during the course of the project. These samples were refrigerated in polyethylene containers until needed for bioassay experimentation. All sample bottles were completely filled to eliminate gas exchange and were refrigerated at 4°C to minimize biological and chemical changes in water quality.

In order to use a unialgal test species in the bioassay experiments, any indigenous algae in the sample had to be removed. The removal process involved autoclaving the sample at a pressure of 1.1 kg/cm² (15 psi) and a temperature of 121°C for 10 minutes per liter of sample, provided the total sterilization period was not less than 30 minutes. The autoclaving was then followed by filtration of the sample through a 47 mm diameter Millipore glass fiber filter with a 0.45 micron pore size. Treated samples were then stored in filled polyethylene bottles at 4°C until needed. In no case was the storage period greater than 24 hours. All samples for bioassay use were analyzed for the following parameters: (1) pH; (2) conductivity; (3) alkalinity; (4) ammonia-nitrogen;

(5) nitrate-nitrogen; (6) nitrite-nitrogen; (7) TKN; and (8) dissolved orthophosphorus.
Heavy metal analyses were also performed on the samples which included: (1) cadmium,
(2) zinc; (3) manganese; (4) copper; (5) aluminum; (6) iron; (7) lead; (8) nickel; and
(9) chromium.

Glassware Preparation

Glassware used as culture bottles or in the sample preparation was washed with a stiff bristle brush using Liqui-Nox non-phosphate detergent and rinsed thoroughly with tap water. All glassware was then rinsed in a 1:1 solution of hot hydrochloric acid followed by five rinses with ultra-pure distilled water. The glassware was then dried and covered until used.

Test Alga and Inoculum Preparation

Selenastrum capricornutum Printz, a unicellular test alga was used in all of the bioassay experiments as the test organism. A concentrated <u>Selenastrum</u> culture was obtained from Carolina Biological Supply. Approximately 2.0 ml of the culture was aseptically transferred to 200 ml of algal nutrient culture medium in a 1.0 liter pyrex erlenmeyer flask. The culture was incubated at $24^{\circ}C \pm 2^{\circ}C$ under continuous "cool white" fluorescent lighting (400 ft-candles \pm 10%) and shaken continuously at 100 oscillations per minute. At approximately 2-week intervals, a routine stock transfer of 2 ml of algal culture was transferred to a fresh culture medium to maintain a continuous supply of cells for experimental work.

Algal Bioassay Methods

All bioassays were conducted in 1000 ml narrow-neck erlenmeyer flasks containing 200 ml of sample. Flasks were incubated on an Eberbach table shaker with a modified plywood table top, 160 cm long and 80 cm wide, which was constructed to accommodate 66 erlenmeyer 1.0 liter flasks. During this bioassay period, the shaker table was adjusted to provide 100 oscillations per minute. All flasks were fitted with foam plugs to prevent contamination and allow for gas exchange. A constant temperature of $24^{\circ}C \pm 2^{\circ}C$ was maintained in the incubation room. Constant illumination was provided by four "cool white" fluorescent lights which were adjusted to provide an illumination of $400 \pm 10\%$ foot-candles as measured adjacent to the flask at the liquid level.

Algal bioassay experiments were designed to simulate a mixture of 25% wetland water from each of the fixed sample stations mixing into a receiving water accounting for the final 75% dilution. Hidden Lake (a eutrophic colored water, high in nutrients) and Lake Lee (a non-colored oligotrophic water, low in nutrients) were chosen as test waters. Triplicate replications of each combination of wetland stations and receiving waters were prepared in the culture flasks. All flasks were allowed to equilibrate under test conditions for 24 hours before inoculation with the algal species to allow for the test media used to come to a constant temperature and also to allow for equilibrium in gas exchange. Culture vessels were then inoculated with 2.0 ml of a 14-day old algal culture to produce an initial chlorophyll-a concentration of approximately 10 $\mu g/l$.

Standing Algal Crop Determinations

Measurements of growth responses were performed by determination of in-vivo fluorescence of chlorophyll-a using a Turner Model 111 Filter Fluorometer equipped with a Model 10-030 cuvette holder and special photomultiplier tube with enhanced red sensitivity. The Model 10-045 blue lamp was chosen as the light source in combination with a Model 5-60 primary excitation filter. The emission filter used was a Model 2-64 filter as recommended by Turner. Before measurements were taken, each incubation flask was swirled to assure a uniform mixing of the contents. A grab sample of approximately 4 ml from each flask was collected in a pyrex 13 x 100 mm test tube for measurement in the fluorometer. All test tubes were invented several times before measurement to assure uniform distribution of the algae. Only the 1x and 3x fluorometer ranges on the fluorometer were used, with all values recorded relative to the 3x scale. All sample sets were run in triplicate and results obtained in the three flasks were averaged (after removal of any outliers) for use in the data analysis. In order that the bioassay results could be expressed in terms of dry cell weight of cell mass per liter of solution, a previously prepared calibration curve was used to relate relative fluorescence to cell dry weight in mg/l.

Statistical Analysis of Data

A large number of statistical analyses were conducted during analysis of the experimental results from this research. All statistical procedures were performed with the SAS (Statistical Analysis System) computer package on the UCF IBM 4381 system and included PROC CORR for calculation of Pearson product moment correlation

coefficients; PROC PLOT to produce scatter diagrams of the values of one variable against the values of another variable for examination of relationships and functional forms; PROC MEANS to obtain simple univariate descriptive statistics such as means, standard deviation, minimum, and maximum values; PROC ANOVA for analysis of variance procedures involving balanced designs and data sets; PROC GLM for analysis of variance procedures for unbalanced data sets; and PROC REG and PROC STEPWISE for regression analysis to provide least-square estimates to various linear regression models.

CHAPTER 4

EXPERIMENTAL RESULTS

Introduction

To establish a record on the fate of nutrients and heavy metals in a southern hardwood wetland, a detailed sample collection program was conducted in the wetland site at Hidden Lake during 1984-1986. Samples of rainwater, stormwater, wetland surface water, groundwater, Hidden Lake water, and wetland sediments, along with hydrologic data, were collected from numerous sampling points and under various environmental conditions. The results of these investigations are presented in this chapter.

Hydrology of the Hidden Lake Wetland

Hydrologic inputs into the Hidden Lake wetland were monitored during 1984-1986 through the following methods: (1) continuous measurement of surface water inputs into the wetland through the input canal using an ISCO flow recorder; (2) measurements of daily evaporation at various locations within the wetland; (3) changes in wetland piezometric surface using a Stevens water level recorder; and (4) measurement of direct precipitation using a recording rain gauge. Each of these inputs is discussed in the following sections.

Rainfall Inputs

A hydrologic record of all rain events occurring at the Hidden Lake site from 12/1/84 to 6/6/86 is given in Appendix I. This record includes recorded measurements of total rainfall and calculated values for event duration, average rainfall intensity (in/hr), and antecedent dry period (days). Rain events ranged from 0.01 inch to 2.50 inches in total rainfall, with durations ranging from 0.08 to 11.83 hours, average intensities from 0.03 inches/hour to 8.62 inches/hour, and antecedent dry periods from 0.03 to 29.39 days. June (1985), July (1985), August (1985) and September (1985) were the wettest months, together contributing 34.21 inches of rainfall which comprised 71% of the total yearly rainfall of 48.07 inches. January (1985) and February (1985) were the driest months recorded during this study, with a combined total rainfall of only 1.49 inches.

Surface Water Inputs

A record of hydrologic surface inputs through the inflow canal to the Hidden Lake wetland is given in Appendix II. These tables contain the raw data recorded continuously by the ISCO flow recorder and represents the combined inputs from storm events as well as baseflow. At the end of each table, estimates of baseflow and runoff inputs are listed separately for each monthly period. Estimates of runoff inputs were obtained by examination of flow increases caused by rain events above the pre-event baseflow values. Measurements of flow through the weir were considered to be runoff related until approximately 2 hours following the end of a rain event. Visual observations during and following rain events indicated that portions of the watershed may continue to contribute runoff for as much as 2 hours following the cessation of a rain event. During the "wet" season, which extends from late June to early October, hydrologic inputs into the wetland flowpath through the canal were continuous, although large variations were measured in flow rate. Flow rates into the wetland ranged from as low as 0.10 m³/hour to as large as 350 m³/hour, although inputs of this larger magnitude were rare. Mean flow rate into the wetland during this period was approximately 22.4 m³/hour. This corresponds to a calculated mean residence time in the 1.0 ha flowpath, assuming a mean water depth of 15 cm and including the losses due to evaporation, transpiration and groundwater seepage, discussed in a later section, of 5.39 days with a range from 116 days at the lowest flow rate to 0.61 days at the greatest flow rate. Mean calculated flow velocity in the flowpath was 1.16 m/hour, with a range from 0.05 m/hour to 10.3 m/hour.

A comparison of hydrologic inputs to the Hidden Lake wetland, including baseflow, rainfall and runoff, is given in Table 4-1 and presented graphically in Figure 4-1. As would be expected, runoff inputs and rainfall volumes are closely related. Baseflow into the wetland also follows the same general pattern observed by rainfall and runoff. However, baseflow, which is primarily a groundwater supplied input, appears to lag approximately 30 days behind runoff and rainfall in terms of input volumes. For example, increased rainfall beginning in June was not observed as increases in baseflow until July. Also, when rainfall and runoff volumes dropped sharply in October, November and December, baseflow declined slowly over this period. Thus, it appears that stored groundwater which manifests itself in the form of baseflow is important in maintaining the wetland hydroperiod for portions of the year when rainfall is low.

An interesting relationship was observed between rainfall and the runoff coefficient "C" value at the Hidden Lake site. Using the monthly rainfall measured at

TABLE 4-1

SUMMARY OF HYDROLOGIC INPUTS TO THE HIDDEN LAKE WETLAND DURING 1985-86

MONTH	INPUTS TO WETLAND (m ³)				PERCENTAGE OF TOTAL		
	BASEFLOW	RUNOFF	DIRECT RAINFALL	TOTAL	BASEFLOW	RUNOFF	DIRECT RAINFALL
<u>1985</u>	307 7	62.6	170.0	621.2	63.0	10.1	26.0
Fahruary	550.2	127 1	170.0	051.5	61.5	10.1	20.9
Marah	330.2	137.1	208.0	1 226 5	01.5	13.5	23.2
April	705.6	440.3	975.0	2 564 9	30.3 27 5	34.5	38.0
May	/05.0	004.J 1/1 3	378.0	2,30 4 .9	27.5	53.0	46 1
Iune	744.0	2 834 0	1 453 0	5 031 9	14.8	56.3	28.9
July	8 887 5	2,034.9	2 004 0	13 680 0	65.0	20.4	14.6
Anoust	7 045 1	12 484 9	2,545.0	22 075 0	31.9	56.6	11.5
Sentember	6 555 1*	13 800 2*	2,545.0	23,000,3	28.5	60.0	11.5
October	6 849 0	1 874 2	635.0	9 358 2	73.2	20.0	6.8
November	4 507 9	900 4	465.0	5 873 3	76.8	15.3	79
December	3,701.4	2,077.4	660.0	6,438.8	57.5	32.3	10.3
TOTAL	40,315.5	38,735.3	12,551.0	91,594.8	44.0	42.3	13.7
<u>1986</u> January*							
February	1,794.1	900.4	335.0	3,029.5	59.2	29.7	11.1
March	1,164.4	1,082.2	871.0	3,117.6	37.3	34.7	28.0
April	175.7	20.4	122.0	318.1	55.2	6.4	38.4

* Estimated from rainfall records



Figure 4-1. Fluctuations in Hydrologic Inputs to the Hidden Lake Wetland During 1985.

the research trailer, it was possible to calculate the total volume of rain falling within the watershed boundaries each month. The total calculated inputs of runoff each month were divided by the total rain volume to obtain a runoff "C" value for each month. These values are plotted and compared with monthly rainfall in Figure 4-2. These calculated "C" values are actually weighted "C" values since they represent a mathematical average from all of the varied rain events each month. As seen in Figure 4-2, the weighted "C" value varies considerably over a yearly period and follows rainfall patterns fairly closely. Values of the runoff coefficient ranged from 0.017 in January to 0.219 in August. This pattern is presumably a result of fluctuations in available groundwater storage and infiltration rates over the year.

An important implication of the relationship given in Figure 4-2 is that measurements of runoff coefficients for a given land use must be conducted on a monthly basis over a minimum of a 1-year period to obtain an accurate representation of the actual watershed response. Values collected on only a few storm events could be biased substantially, either high or low, depending on the time of year when the study was performed. The most accurate weighted "C" value would be obtained by multiplying the monthly values presented in Figure 4-2 by the percentage of annual rainfall occurring during that month. The weighted runoff coefficient listed in Table 3-2 was calculated in this manner.

Evaporation in the Wetland

Measurements of evaporation were collected at various locations within the wetland using a Weather Measure Model 801 recording evaporimeter from March 27,



Figure 4-2. Variations in Weighted Runoff Coefficients at Hidden Lake During 1985.

4-7

1985 to January 25, 1986. Daily records were subdivided over 2-hour periods so that comparisons could be made with both time of day and time of year. A listing of the complete data set is given in Appendix III. The data set was divided into three distinct periods observed in the wetland during a given year: (1) the spring period from March to May when re-vegetation following the winter months is occurring, the wetland is actively growing, and rainfall as well as humidity is low; (2) the summer period of frequent rainfall and high humidity; and (3) the fall-winter season during November, December and January when growth slows, and leaf drop occurs.

A summary of the data in Appendix III is given in Figure 4-3. As would be expected, both hourly and seasonal variations in evaporation are apparent. In general, evaporation was lowest after midnight, with relatively constant values until approximately 10 a.m. After this time, evaporation increased rapidly, reaching a peak between 2-6 p.m., depending on the season. The rate would then decline somewhat slowly, reaching the minimum values again near midnight.

On a seasonal basis, evaporation was greatest in the spring, averaging 0.90 mm per day. During this period, the canopy is more open as re-vegetation is occurring, and the rainfall and humidity are typically low, all of which contribute to increases in evaporation. During summer, evaporation decreases somewhat, particularly in the morning to early afternoon periods when humidity beneath the canopy is generally near 100%. During the winter season, evaporation decreases to approximately 50% of that measured in the spring. Although the canopy is more open following leaf fall, the generally lower temperatures serve to reduce the evaporative losses.



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Figure 4-3. Mean Values of Evaporation Under the Wetland Canopy Per 2-Hour Interval by Season.

Fluctuation in Piezometric Surface in the Wetland

Fluctuations in piezometric surface within the Hidden Lake wetland were monitored continuously using a Stevens Water Level Recorder installed near groundwater well #2, about 25 m along the flowpath (Figure 3-3). An open 30 cm diameter standpipe was inserted to a depth of 1 m below the soil surface, and the recorder was housed in a plywood shelter above the standpipe with a 25 cm float suspended into the standpipe. Continuous measurements were collected from July 19, 1985 to June 26, 1986 and are listed in Appendix IV.

In the absence of rain events, the piezometric surface in the wetland was found to change slowly, with normal losses due to transpiration, evaporation or groundwater loss. However, during rain events, rapid increases in piezometric surface were observed with several increases in excess of 20 cm in a 2-hour period. Decreases following rain events were rapid at first, then occurring more slowly, with 90% of the increase lost in 24-48 hours by the combination of infiltration, evaporation, transpiration and dispersion of flow to lower areas of the wetland. A plot of piezometric surface during 1985-86 is given in Figure 4-4. The hydroperiod at this location was approximately 320 days.

The continuous measurements of the piezometric surface proved valuable in estimation of losses within the wetland due to transpiration and groundwater loss. To accomplish this, periods of the record were examined where rain events were not present to cause fluctuations in elevation. It was assumed that transpiration would occur primarily during the daylight hours. Therefore, decreases in piezometric surface during the night were assumed to be only a result of groundwater movement. Decreases in elevation from midnight to 6 a.m. were assumed to represent groundwater losses and it



Figure 4.4 Fluctuations in Piezometric Surface During 1985 in the Hidden Lake Wetland.

was also assumed that this loss would be constant over a given 24-hour period. The additional decrease in piezometric surface was attributed to losses by transpiration and evaporation, with measured evaporation subtracted to yield transpiration. Decreases in piezometric surface during the period from March to May, the summer months, and the fall-winter season are given in Appendix V.

The results of the calculated losses due to transpiration, evaporation and groundwater flow for the March to May period is presented in Figure 4-5. During this period, evaporative losses were the least significant component, representing only 5% of the total loss on a daily basis. Groundwater losses, assumed to be constant, represented approximately 33% of total losses. Transpiration loss was quite significant during this period of re-vegetation. Transpiration losses peaked rapidly during the daylight hours and declined rapidly at night. Total water loss from the wetland during this period averaged 17.73 mm per day.

A hydrologic balance for the wetland during the summer months is presented in Figure 4-6. Losses due to evaporation and groundwater flow appear to be similar during this period to that observed for the spring months. However, losses due to transpiration have increased substantially to 18.25 mm per day, comprising 71% of total water loss. Total water loss during this period averaged 25.83 mm/day.

During the late fall and winter months, the hydrologic regime of the wetland appears to change dramatically, as seen in Figure 4-7. Losses due to transpiration and evaporation have declined to their lowest yearly values, representing only 16% of the values measured in the summer. Groundwater losses are a more important component during this period, representing 39% of the total losses. Hydrologic losses during the late fall-winter period averaged 5.00 mm per day.



Figure 4.5 Comparisons of Hydrologic Losses from the Hidden Lake Wetland During Spring Re-vegetation.



Figure 4.6. Comparisons of Hydrologic Losses from the Hidden Lake Wetland During the Summer Months.



Figure 4-7. Comparisons of Hydrologic Losses from the Hidden Lake Wetland During Fall/Winter.

In addition to the continuous record of piezometric surface near the 25 m sample site, records of piezometric surface were also collected at each of the four groundwater monitoring wells at least once each month during 1985. The measured piezometric elevations are listed in Table 4-2, and seasonal averages are given below the table. During January-March and October-December, a slight positive gradient appears to exist along the flowpath toward Hidden Lake. The wetland appears to be discharging groundwaters to Hidden Lake during this period. However, during the period from April-September, piezometric surfaces within the wetland are lower in elevation than either the upland area, represented by well #1, or Hidden Lake. As a result, groundwater movement appears to be into the wetland from both the upland areas and from Hidden Lake. Apparently, the large losses due to evapotranspiration in the wetland during the spring and summer create a decrease in piezometric surface beneath the wetland and affect the direction of groundwater flow.

<u>Characteristics of Rainwater</u> <u>Collected at the Hidden Lake Wetland</u>

To establish a record of the characteristics of direct rainfall, a wet/dry fallout collector was used to obtain samples of bulk wet precipitation at the research trailer from March 21, 1985 to December 5, 1985, over a wide range of rainfall intensities, durations and antecedent dry periods. Composite rainfall samples were collected from a total of 22 separate storm events and analyzed over this period for nutrients and heavy metals. Total rainfall amounts for sampled storm events ranged from 0.15 to 2.36 inches, with antecedent dry periods of 0.1 to 20.2 days.

TABLE 4-2

MEASUREMENTS OF PIEZOMETRIC SURFACE AT EACH OF THE GROUNDWATER MONITORING WELLS AT HIDDEN LAKE DURING 1985

	PIEZOMETRIC ELEVATION (m, MSL)							
	WELL #1 (Ref. 12.601)	WELL #2 (Ref. 12.506)	WELL #3 (Ref. 12.329)	WELL #4 (Ref. 12.116)	HIDDEN LAKE			
1/23/85 2/20/85 3/20/85 4/10/85 4/17/85 5/10/85 5/16/85 5/16/85 5/30/85 6/06/85 6/13/85 6/19/85 7/11/85	11.290 11.585 11.415 11.186 11.674 11.189 11.119 11.052 10.994 11.149 11.515 11.476	11.155 11.448 11.363 11.128 11.463 11.128 11.024 10.918 10.896 11.534 11.509 11.549	11.399 11.378 11.186 10.924 11.256 10.942 10.875 10.817 10.808 10.945 11.235 11.241	11.201 11.470 11.290 11.104 11.372 11.104 11.046 10.954 10.878 10.817 11.387 11.366	11.378 11.474 11.298 11.156 11.404 11.112 11.096 11.085 11.006 11.021 11.165 11.241			
7/18/85 8/02/85 8/30/85 9/13/85 10/11/85 11/12/85	11.707 11.671 11.841 11.744 11.774 11.802	11.741 11.677 11.686 11.692 11.720 11.713	11.552 11.415 11.530 11.521 11.552 11.537	11.396 11.479 11.518 11.506 11.518 11.512	11.521 11.662 11.668 11.476 11.488 11.494			
<u>Mean</u> Values								
JanMar.	11.430	11.322	11.321	11.320	11.313			
AprJune	11.235	11.200	10.978	11.083	11.131			
July-Sept.	11.688	11.669	11.452	11.453	11.514			
OctDec.	11.788	11.712	11.545	11.515	11.491			

Measured concentrations of water quality parameters for each of the individual storm events are presented in Appendix VI. A summary of the mean chemical characteristics of rainwater collected at Hidden Lake is given in Table 4-3. In general, rainwater was characterized as somewhat acidic with little or no alkalinity, low in color, and generally low in dissolved solids, as evidenced by the low values for conductivity and residue. Mean concentrations of dissolved orthophosphorus and total phosphorus were also low, with the dissolved form comprising approximately 90% of the total amount. Concentrations of nitrogen species were generally low, with the nitrate ion measured as the most abundant form.

Large variabilities were noted for most measured parameters between storm events. As seen in Table 4-3, measured values of pH ranged in excess of 2 units, with wide ranges also evident for color, residue and TOC. Of the nutrient forms measured, nitrogen appears to be more variable than phosphorus, particularly for ammonia and nitrate.

A summary of mean concentrations of dissolved heavy metals in rainfall samples is given in Table 4-4. In general, concentrations of most metals were relatively low in rainwater with the exception of cadmium, which had a calculated mean rainfall value in excess of the Florida Administrative Code (F.A.C.) Chapter 17-3 criterion of 0.8 μ g/l for Class III waters. As seen in the raw data presented in Appendix VI, as well as in the summary data listed in Table 4-4, a considerable variability was found for most heavy metal concentrations between storm events. This variability was especially apparent for copper, aluminum, zinc and iron. Of the heavy metals which were measured in rainfall, the following order was observed in terms of dissolved concentrations:
SUMMARY OF MEAN CHEMICAL CHARACTERISTICS OF RAINWATER COLLECTED AT HIDDEN LAKE

DADAMETER	TINITO	MEAN	RANGE O	F VALUES	COEFFICIENT
	C1112	VALUE ¹	MINIMUM	MAXIMUM	VARIATION
pH	s.u.	4.76	4.01	6.21	9.9
Conductivity	µmho/cm	10.5	4	26	54.2
Alkalinity	mg/l	0.45	0	0.5	32.4
Turbidity	NTU	0.6	0.1	2.0	85.1
NH₃-N	μg/l	64	5	317	152
NO3-N	μg/1	136	21	365	74.3
Organic N	μg/1	48	5	153	93.3
Ortho-P	μg/l	8	2	14	31.8
Total P	μg/1	9	2	21	44.3
BOD	mg/l	1.1	0.2	2.4	43.5
Color	Pt-Co Units	11	3	27	63.9
Residue	mg/l	32	3.2	124	106
S.S.	mg/l	1.1	0.3	2.5	50.4
TOC	mg/l	2.0	0.6 5.7		66.6

1. n = 22 samples

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS OF RAINWATER COLLECTED AT HIDDEN LAKE

DISSOLVED	MEAN	RANGE O	RANGE OF VALUES				
HEAVY METAL	HEAVY VALUE ¹ METAL (µg/l)		MAXIMUM (µg/l)	OF VARIATION			
Cd	2.8	0.05	9.0	83.0			
Zn	13.7	3.0	33.0	64.9			
Mn	3.9	0.5	13.0	86.7			
Cu	27.0	1.0	140	109			
Al	24.3	0.5	1 07	132			
Fe	11.7	0.5	42.0	104			
Pb	3.6	0.5	10.0	81.7			
Ni	1.2	0.5	4.0	98.8			
Cr	0.7	0.05	2.1	110			

1. n = 22 samples

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Cu > Al > Zn > Fe > Mn > Pb > Cd > Ni > Cr

A summary of analysis of variance comparisons for rainwater characteristics between "wet" and "dry" seasons is given in Table 4-5. For this analysis, the rainfall data set was divided into samples collected in the "wet" period from June to early October and those collected in the remaining "dry" months. Of the parameters listed in Table 4-5, only copper and nickel were found to have significant differences at the 0.05 level in concentrations between the two periods. Copper was significantly higher during the "wet" season, while nickel was significantly higher in the "dry" season. However, even though significant differences were not observed for most parameters, all measured parameters (except phosphorus, cadmium, zinc, and copper) were greater in value in the "dry" period than in the "wet" period.

Correlations between all measured rainfall parameters listed in Tables 4-3 and 4-4 and rainfall characteristics, such as total rain amount, mean rainfall intensity, rain duration and antecedent dry period, were performed using the PROC CORR package of SAS to examine whether or not rainfall characteristics were influenced by any of these parameters. No significant correlations were found at the 0.05 level between any of the general measured parameters in Table 4-3 or the heavy metals listed in Table 4-4 and any of the measured rainfall characteristics suggesting that the chemical characteristics of rainfall are not affected to a significant degree by characteristics of the rain event. In other words, general composite chemical characteristics of rainfall appear to be independent of rainfall parameters such as total rain amount, rain duration, rainfall intensity and antecedent dry period.

SUMMARY OF ANOVA COMPARISONS FOR RAINWATER BETWEEN "WET" AND "DRY" SEASONS

		MEAN CONC	PROBABILITY	
PARAMETER	UNITS	"WET" SEASON	"DRY" SEASON	UNEQUAL MEANS
pH	s.u.	5.06	5.01	17.5
Conductivity	μ mho/cm	8.6	12.2	85.1
Alkalinity	mg/l	0.5	0.4	80.7
NH ₃ -N	μg/1	27	94	89.2
NO₃-N	μg/l	109	158	73.7
Organic N	μg/l	54	42	46.0
Diss. OP	μg/l	9.1	7.1	93.7
Total P	μg/l	10.2	8.3	76.9
TOC	mg/l	1.8	2.1	46.5
Diss. Cd	μg/l	3.5	2.3	76.0
Diss. Mn	μg/l	3.9	4.0	3.1
Diss. Zn	μg/l	14.6	13.0	31.5
Diss. Cu	μg/l	41	15	96.6
Diss. Al	μg/l	14	33	84.7
Diss. Fe	μg/l	10.7	12.6	28.4
Diss. Pb	μg/l	3.3	3.9	39.0
Diss. Ni	μg/l	0.6	1.7	97.0
Diss. Cr	μg/l	0.38	0.93	91.7

<u>Characteristics of Stormwater</u> Inputs to the Hidden Lake Wetland

Flow-weighted composite runoff samples were collected from the inflow canal during rain events using a refrigerated ISCO automatic sampler. A flow recorder was used to monitor the quantity of runoff into the wetland. Runoff samples were collected from January 18, 1985 to November 11, 1985, over a wide range of rainfall intensities, durations and antecedent dry periods. A total of 24 storm events, including a total of 96 separate runoff samples, were collected and analyzed over this period for water quality parameters and heavy metals. Total rainfall amounts for the sampled storm events ranged from 0.38 to 6.00 cm, with antecedent dry periods of 0.1 to 20.2 days.

Measured concentrations of all water quality parameters and heavy metals collected during each of the individual storm events are presented in Appendix VII. A summary table of the mean general chemical characteristics of the residential stormwater runoff is presented in Table 4-6. Stormwater runoff collected at Hidden Lake can be characterized as slightly acidic in nature, with a moderate alkalinity, relatively low in forms of inorganic nitrogen and dissolved phosphorus, and low in solids content, as evidenced by the low values for turbidity and suspended solids. Approximately 62% of the phosphorus load was particulate in nature and 58% of the suspended solids were inorganic materials. Measurable concentrations of phenol, not listed in Table 4-6, were found on only two of the 22 sample dates (Appendix VII). Concentrations of organics, TOC, and oil and grease were also relatively low in value. Oil and grease were found in measurable quantities at the start of the project, but concentrations decreased to levels below detection limits after a few months. The reason for this decline is not known. At

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS OF RUNOFF COLLECTED AT HIDDEN LAKE

		MEAN	RANGE O	F VALUES	COEFFICIENT
PARAMETER	UNITS	VALUE ¹	MINIMUM	MAXIMUM	VARIATION
pН	s.u.	5.91	5.12	7.64	9.12
Conductivity	µmho/cm	143	53	247	31.1
Alkalinity	mg/l	65.6	25.8	103	30.7
Turbidity	NTU	6.4	0.6	57.6	152
NH₃-N	μg/1	56	< 10	209	80.2
NO ₂ -N	μg/1	1.0	< 0.1	8.2	136
NO3-N	μg/l	68	15	276	80
Organic N	μg/l	487	29	1220	42.7
Ortho-P	μg/l	27	0.5	110	94.3
Total P	μg/l	72	4	598	116
TOC	mg/l	12.6	3.9	18.2	19.6
BOD	mg/l	2.6	0.2	7.4	53.8
Color	Pt-Co Units	85	21	299	58.5
Residue	mg/l	135	59	277	24.3
S.S.	mg/l	6.2	0.7	117	237
V.S.S.	mg/l	2.6	0.07	32.5	165
Oil, Grease	mg/l	3.6	< 2	19.3	143

1. n = 96 samples

no time were concentrations of oil and grease of sufficient quantity to cause a shine on the water surface in the inflow canal.

Measured concentrations of heavy metals in runoff samples collected at Hidden Lake are summarized in Table 4-7. In general, runoff inputs were very low in concentrations of all heavy metals measured, with the possible exceptions of aluminum and iron. Dissolved metal concentrations in the residential runoff exhibited the following order:

$$Mn < Cr < Ni < Cd = Zn < Cu < Pb < Fe < Al$$

As seen in Table 4-7, the majority of metal inputs, with the exception of aluminum, were soluble in form, with soluble fractions in excess of 80% for five of the nine measured metals. Even lead, which is routinely associated with large particulate fractions, was found, primarily in a soluble form, at this site. The extremely low metal concentrations found in this runoff, as well as the particulate loadings, are very likely a result of the apparent excellent pretreatment for runoff provided by the swale systems used as part of the stormwater conveyance systems.

As seen in Appendix VII, a considerable variability was observed both between storm events, as well as heavy metals. This variability was especially apparent for copper, aluminum, iron and lead. In order to investigate causative factors for this variability, a series of correlations were performed using the PROC CORR package of SAS to examine relationships between the chemical characteristics of runoff events and the characteristics of the rain event, such as total rainfall, storm duration, rainfall

SUMMARY OF MEAN CONCENTRATIONS OF HEAVY METALS IN RUNOFF COLLECTED AT HIDDEN LAKE DURING 1985

	M	EAN	RANGE C	OF VALUES	COEFFICIENT
METAL	VALUE ¹ $(\mu g/l)$		MINIMUM (µg/l)	MAXIMUM (µg/l)	OF VARIATION
Dissolved					
Cd	4.6	(88.5) ²	< 0.1	13	64.8
Zn	4.6	(85.2)	< 1	21	81.9
Mn	2.5	(62.5)	< 1	7.0	47.1
Cu	19.6	(74.5)	< 1	62	75.7
Al	20.6	(36.8)	16	1,273	105
Fe	67.3	(59.0)	4	128	38.2
Pb	29.5	(91.9)	5	56	39.1
Ni	3.2	(86.5)	0.4	8.6	55.3
Cr	3.1	(83.8)	< 0.1	7.0	35.2
Total	-				
Cd	5	5.2	< 0.1	14	55.7
Zn	5	i.4	< 1	23	90. 1
Mn	4	.0	< 1	16	68.4
Cu	2	6.3	< 1	155	79.6
Al	5	60	98	10,300	237
Fe	1	14	49	578	77.4
Pb	3	2.1	11	60	36.0
Ni	3.7		0.4	14	58.3
Cr	3	.7	0.2	10	41.0

n = 92 samples
Percentage of dissolved form out of total

intensity and antecedent dry period. A summary of the general water quality characteristics which produced significant correlations at the 0.05 level or better is given in Table 4-8.

Significant correlations were found at the 0.05 level between total rainfall and all of the listed parameters. Increasing amounts of total rainfall were found to decrease pH, conductivity and alkalinity, while increasing concentrations of the other parameters. Increasing rainfall duration was found to be positively correlated with pH, conductivity and alkalinity. Correlations between antecedent dry period and the listed parameters were generally much weaker than the other rainfall characteristics. Significant positive correlations were found with pH and alkalinity, while significant negative correlations were found for ammonia and BOD. Rainfall intensity was found to have a significant negative correlation with conductivity, alkalinity and orthophosphorus.

A summary of significant correlations between measured concentrations of heavy metals and rainfall characteristics is given in Table 4-9. To simplify presentation of the data, only metal species exhibiting significant correlations are presented in the table. As seen with the general runoff characteristics, each of the heavy metals listed exhibited strong correlations with total rainfall, although some of the correlations were positive while others were negative. Correlations between runoff concentrations of heavy metals and rainfall duration and intensity were generally weak, although a few of the metals listed exhibited significant correlations. A similar situation was observed for correlations with antecedent dry periods, with only dissolved and total lead exhibiting significant relationships.

CORRELATIONS BETWEEN TOTAL RAINFALL, STORM DURATION, ANTECEDENT DRY PERIOD, STORM INTENSITY AND RUNOFF QUALITY CHARACTERISTICS AT HIDDEN LAKE

PARAMETER CORRELATION COEFFICIENT		RAIN ¹	RAINFALL DURATION ¹		ANTECEDENT DRY PERIOD ²		RAIN INTENSITY ¹	
		PROB. OF CORRELATION	CORRELATION COEFFICIENT	PROB. OF CORRELATION	CORRELATION COEFFICIENT	PROB. OF CORRELATION	CORRELATION COEFFICIENT	PROB. OF CORRELATION
pН	- 0.306	99.4	0.322	99.6	0.241	96.3	- 0.208	93.4
Conductivity	- 0.545	99.9	0.390	99.9	0.195	90.7	- 0.397	99.9
Alkalinity	- 0.585	99.9	0.345	99.8	0.239	96.1	- 0.530	99.9
Turbidity	0.576	99.9	0.166	85.5	- 0.112	65.9	- 0.007	4.6
Ammonia N	0.458	99.9	0.206	93.2	- 0.248	96.8	- 0.036	24.5
Nitrate N	0.524	99.9	0.062	41.1	- 0.113	66.5	0.089	56.4
Organic N	0.299	99.3	- 0.213	94.0	- 0.159	82.7	0.200	92.3
BOD	0.234	96.2	- 0.215	94.3	- 0.258	97.5	- 0.013	9.2
Ortho-P	0.553	99.9	0.013	9.9	- 0.202	91.7	0.305	99.4
Total P	0.610	99.9	0.069	45.5	- 0.096	58.5	0.150	81.4
SS	0.467	99.9	0.100	61.7	0.014	9.3	0.003	2.4
VSS	0.508	99.9	0.038	26.0	- 0.007	4.6	0.038	26. 1

1. Number of observations = 79

2. Number of observations = 75

CORRELATIONS BETWEEN CONCENTRATIONS OF HEAVY METALS AND RAIN EVENT CHARACTERISTICS AT HIDDEN LAKE

TOTAL RAIN		RAIN ¹	RAINFALL DURATION ¹		ANTECEDENT DRY PERIOD		RAIN INTENSITY ¹	
	CORRELATION	PROB. OF	CORRELATION	PROB. OF	CORRELATION	PROB. OF	CORRELATION	PROB. OF
	COEFFICIENT	CORRELATION	COEFFICIENT	CORRELATION	COEFFICIENT	CORRELATION	COEFFICIENT	CORRELATION
Dissolved								
Cu	0.301	99.6	- 0.120	94.2	- 0.120	94.3	0.307	99.7
Al	0.511	99.9	0.247	98.2	- 0.097	64.1	0.006	4.3
Pb	- 0.346	99.9	0.148	83.9	0.422	99.9	- 0.081	55.4
Ni	- 0.220	96.4	0.088	59.3	0.189	92.7	0.052	37.2
Cr	- 0.266	98.9	- 0.018	13.8	0.080	55.1	0.022	16.1
Total								
Zn	0.290	99.5	- 0.095	63.1	- 0.145	82.9	0.320	99.8
Mn	0.375	99.9	- 0.019	14.0	- 0.003	2.3	0.082	55.9
Cu	0.303	99.6	- 0.168	88.8	- 0.103	70.0	0.200	94.3
Al	0.393	99.9	0.102	66.5	0.061	43.3	- 0.008	6.1
Fe	0.418	99.9	0.111	70.5	0.072	50.3	0.076	52.5
Pb	- 0.218	96.3	0.143	82.4	0.395	99.9	- 0.061	43.4

1. Number of observations = 91

4-29

A summary of analysis of variance comparisons for stormwater characteristics between "wet" and "dry" seasons is given in Table 4-10. Significant differences were found at the 0.05 level between the two periods for pH, conductivity, alkalinity, and all of the heavy metals measured except aluminum and iron. For each of the significant differences which were found, all measured parameters were greater in value in the "dry" season than in the "wet" season, with the exceptions of zinc and copper, which were greater in value in the "wet" season. As seen in Table 4-5, zinc and copper were also found in greater concentrations in rainwater during "wet" periods than "dry" periods. Although significant differences were not observed for the remaining parameters listed in Table 4-10, many mean values were greater in the "dry" season, such as TOC, BOD, SS, and VSS. Concentrations of nitrogen and phosphorus were very similar between the two seasons.

Calculated mass loading rates for selected pollutants from the residential watershed are given in Table 4-11 and compared with loading rates from a residential area with curb and gutter drainage near Lake Eola in Orlando, as reported by Wanielista (1978). Loading rates from the residential watershed at Hidden Lake are apparently much lower than values reported by Wanielista. These lower loading rates are presumably another indication of the pretreatment effectiveness of the swale system used at Hidden Lake.

<u>Characteristics of Surface</u> Water in the Hidden Lake Wetland

Surface water samples were collected at nine fixed stations on a bi-weekly basis from December 1984 to December 1985 to characterize average concentrations of

SUMMARY OF ANOVA COMPARISONS OF STORMWATER CHARACTERISTICS IN "WET" AND "DRY" SEASONS

		MEAN CON	CENTRATION	PROBABILITY
PARAMETER	UNITS	"WET" SEASON	"DRY" SEASON	UNEQUAL MEANS
pH	s.u.	5.89	6.36	99.9
Conductivity	μ mho/cm	109	160	99.9
Turbidity	NTU	4.4	7.5	84.6
Alkalinity	mg/l	49.7	73.6	99.9
NH₄-N	$\mu g/l$	60	54	48.9
NO ₃ -N	$\mu g/l$	73	65	45.8
Organic N	μg/l	473	495	37.2
Diss. OP	$\mu g/l$	31	26	64.9
Total P	μg/l	72	72	3.3
TOC	mg/l	12.1	12.9	85.4
BOD	mg/l	2.5	2.6	29.7
S.S .	mg/l	4.2	7.2	67.1
V.S.S .	mg/l	2.0	2.9	63.6
Heavy Metals				
Diss. Cd	μg/l	3.4	5.1	99.1
Diss. Mn	μg/l	1.8	2.7	99.9
Diss. Zn	μg/l	6.6	3.7	99.9
Diss. Cu	μg/l	28.0	15.8	99.9
Diss. Al	μg/l	179	217	57.4
Diss. Fe	μg/l	70	66	51.7
Diss. Pb	μg/l	23.0	32.3	99.9
Diss. Ni	μg/l	2.4	3.6	99.8
Diss. Cr.	μg/l	2.7	3.3	94.8
Total Cd	μg/l	4.1	5.7	99.0
Total Mn	μg/l	3.1	4.4	96.4
Total Zn	μg/l	7.1	4.7	97.4
Total Cu	μg/l	36	22	99.5
Total Al	μg/1	305	672	76.5
Total Fe	μg/l	94	123	88.7
Total Pb	μg/l	25.3	35.0	99.9
Total Ni	μg/l	2.5	4.2	99.9
Total Cr	μg/l	3.0	3.9	98.6

SUMMARY OF MASS LOADING RATES FROM STORMWATER RUNOFF GENERATED WITHIN THE RESIDENTIAL WATERSHED AT HIDDEN LAKE

PARAMETER	MASS LOADINGS (kg/ha/year)						
	HIDDEN LAKE	LAKE EOLA ¹					
NH3-N	0.062						
NO ₃ -N	0.076	2.20					
Organic N	0.543	1.80					
Ortho-P	0.031	0.80					
Total P	0.080	2.20					
TOC	14.1	139					
BOD	2.90	74.6					
Suspended Solids	6.91	195					
Total Cd	0.006	'					
Total Zn	0.006						
Total Mn	0.004						
Total Cu	0.029						
Total A1	0.624						
Total Fe	0.127						
Total Pb	0.036						
Total Ni	0.004						
Total Cr	0.004						

1. Wanielista (1978) for a 6.52 ha residential area near Lake Eola.

nutrients, heavy metals and other water quality parameters in the Hidden Lake wetland. The sample collection program consisted of 22 sample dates during the study period with a total of 88 separate samples collected. On twelve of the collection dates during the period from January 13, 1985 to July 3, 1985, no surface water was present for at least seven of the nine fixed sampling stations. In general, surface water inputs to the wetland during this period infiltrated into groundwaters rapidly, and surface water extended only to the 25 m or 50 m sample station. However, from mid-July to the end of the project in December, surface water was present at each of the fixed sample stations. Water quality parameters measured at each of the sample stations on each sample collection date are listed in Appendix VIII.

A summary of mean general chemical characteristics of surface waters along the wetland flowpath and in the control area during the sampling period is presented in Table 4-12. Upon entering the wetland flowpath, significant changes begin to occur for most of the parameters listed in Table 4-12. As seen in Figure 4-8, pH, alkalinity, and dissolved oxygen all begin gradual declines with increasing distance along the flowpath. Mean pH values (based on hydrogen ion concentration) were found to decrease from 6.54 at the inlet canal weir to 5.69 at the 150 m location, an overall decrease of 13% in pH value during travel through the wetland flowpath. The control area was observed to have depressed pH values in comparison to the wetland flowpath with a mean pH value of 4.88. This value was almost two full pH units less than mean values measured in the inflow canal and in stormwater and one pH unit less than the minimum mean value measured along the wetland flowpath area.

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS OF SURFACE WATERS ALONG THE FLOWPATH AND CONTROL AREAS IN THE HIDDEN LAKE WETLAND

					CONTROL	HIDDEN					
	UNIIS	WEIR	10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA	LAKE
pH	s.u.	6.54	6.43	6.25	6.19	6.02	5.92	5.87	5.65	4.88	5.57
Conductivity	µmho/cm	194	183	177	163	150	138	136	1 12	92	109
Diss. Oxygen	mg/l	7.4	6.7	4.0	2.8	2.0	1.6	1.3	1.7	0.9	
ORP	mV	411	380	271	222	168	182	176	173	79	
Alkalinity	mg/l	79	72	67	61	57	50	50	39	14	25
NH ₃ -N	μg/l	44	41	54	90	95	80	61	56	48	55
NO3-N	μg/l	39	43	40	42	36	38	42	35	31	20
Organic N	μg/1	398	364	484	353	360	471	545	713	1163	1696
Ortho-P	μg/l	28	20	29	32	49	61	54	76	130	67
Total P	μg/l	59	48	67	62	85	103	110	148	177	166
BOD	mg/l	1.7	1.5	1.8	1.4	1.5	1.3	1.1	1.4	0.9	2.0
Color	Pt-Co Units	73	94	101	109	126	150	172	226	505	515
Residue	mg/l	146	162	149	145	152	156	149	146	178	181
SS	mg/l	2.7	4.0	4.8	4.0	4.7	3.7	3.4	4.6	1.8	4.8
Turbidity	NTU	4.6	4.3	5.2	5.7	6.4	5.2	5.2	5.1	2.9	1.2
No. of S	amples	20	10	11	8	8	8	7	7	8	9



Figure 4-8. Changes in pH, Alkalinity, and Dissolved Oxygen During Flow of Surface Waters Through the Hidden Lake Wetland.

Measurements of dissolved oxygen indicated an aerobic water column at the weir with a mean value of 7.4 mg/l. Upon entering the wetland flowpath, dissolved oxygen values declined rapidly, beginning at the 25 m sampling station and decreasing steadily to the final sample location at 150 m, for a total decrease of 77%. Mean oxygen saturation values along the wetland flowpath decreased from 87% at the weir to 33.5% at 50 m, 18.9% at 100 m, and 20.2% at 150 m. The control area was characterized by chronic low levels of dissolved oxygen, with as many as 50% of the measured values being below 0.5 mg/l. Measurements of ORP indicated a "moderately reduced" environment throughout the wetland flowpath, becoming increasingly reduced with flowpath distance. Mean values of ORP decreased from 411 mV (Eh) at the weir to 173 mV (Eh) at a distance of 150 m along the flowpath area. The control area, however, was characterized as a "reduced" environment, based on a mean ORP value of 79 mV (Eh), with 75% of collected samples having values below 60 mV (Eh). In general, surface waters in the first 50 m of the flowpath were characterized as oxidized (> 200mV), while surface waters after this distance were slightly reduced (< 200 mV).

As seen in Figure 4-9, forms of nitrogen were affected to varying degrees during flow through the wetland flowpath. In general, concentrations of inorganic nitrogen were very low at all sample stations, with organic nitrogen present as the dominant species. Concentrations of ammonia increased over the first 75 m from 44 μ g/l to 95 μ g/l, with a decline over the next 75 m to 56 μ g/l. Concentrations of ammonia in the control area were similar to input concentrations. Little change was observed in concentrations of nitrate during flow through the wetland, with concentrations in the control area similar to input concentrations. Organic nitrogen was found to generally increase in the wetland



Figure 4-9. Changes in Nitrogen Species During Flow Through the Hidden Lake Wetland.

from 398 μ g/l at the input weir to 713 μ g/l at a distance of 150 m. Concentrations in the control area jumped to 1163 μ g/l.

Changes in phosphorus concentrations during flow through the wetland are shown in Figure 4-10. In general, mean dissolved orthophosphorus concentrations were found to increase with distance along the wetland flowpath. Mean orthophosphorus concentrations increased from 28 μ g/l at the inlet canal weir to 76 μ g/l at the 150 m sample station, for a relative increase of 171% during travel through the flowpath area. Mean orthophosphorus concentrations in the control area were, in general, much greater than those found in the flowpath. Elevated concentrations of dissolved orthophosphorus in the control area were determined to be 364% greater than average inputs into the wetland and 71% greater than the maximum flowpath value at 150 m. Increases in concentrations of orthophosphorus appear to follow closely the decreases in pH and dissolved oxygen shown in Figure 4-8.

Total phosphorus concentrations followed the same patterns evident for dissolved orthophosphorus. Total phosphorus concentrations increased with flow distance throughout the wetland area from 59 μ g/l at the inlet canal weir to 148 μ g/l at the 150 m sample station, for a net increase of 151% as the surface water traversed the wetland flowpath. The mean concentration of total phosphorus in the control area, 177 μ g/l, was 200% greater than average inputs of total phosphorus into the wetland and 20% greater than the maximum flowpath value.

Of the remaining parameters listed in Table 4-12, only color was found to be significantly affected by flow through the wetland system. Color appears to increase rapidly with increasing flow distance from a mean of 73 at the input canal to 226 at a



Figure 4-10. Changes in Mean Phosphorus Concentrations During Flow Through the Hidden Lake Wetland.

distance of 150 m, an increase of 210%. However, measurements of color in the isolated control area were substantially elevated with a mean value of 505, representing an increase of 592% over the mean input value. Concentrations of BOD, residue, suspended solids and turbidity did not appear to be changed during flow through the wetland. However, it should be noted that the input concentrations of these parameters, especially BOD, SS, and turbidity, were extremely low. Concentrations of each of these parameters were found to be approximately 50% less in the isolated control area than at the 150 m sample station. A summary of percent change in measured parameters during flow in the wetland is given in Table 4-13.

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Mean chemical characteristics of Hidden Lake are also listed in Table 4-12, with a complete listing of all collected data given in Appendix IX. In general, the chemistry of Hidden Lake appears to be a mixture of characteristics of the flowpath area as well as the control area. Hidden Lake was found to be similar to flowpath areas in terms of pH, conductivity, inorganic nitrogen, orthophosphorus, BOD, and suspended solids. However, the elevated measured values of organic nitrogen, total phosphorus, color, and residue were characteristic of the isolated control area.

An analysis of variance comparison of general surface water characteristics between flowpath and control areas is given in Table 4-14. For this analysis, only the first five sample stations were included since the 125 m and 150 m locations were affected by runoff inputs on an irregular basis and generally only as a result of large rain events. Significant differences were found at the 0.05 level for all general parameters measured except temperature, turbidity, ammonia, nitrate, BOD, and solids. Conductivity, pH, dissolved oxygen, ORP, and alkalinity were all significantly greater

PERCENT CHANGE IN MEASURED PARAMETERS FROM INPUT VALUES DURING FLOW IN THE WETLAND

			_		CONTROL	HIDDEN				
		10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA	LAKE
pH	s.u.	- 1.7	- 4.4	- 5.4	- 8.0	- 9.5	-10.2	-13.6	-25.4	-14.8
Conductivity	μ mho/cm	- 5.7	- 8.8	-16.0	-22.7	-28.9	-29.9	-42.3	-52.6	-43.8
Diss. Oxygen	mg/l	- 9.5	-45.9	-62.2	-73.0	-78.4	-82.4	-77.0	-87.8	
ORP	mV	- 7.5	-34.1	-46.0	-59.1	-55.7	-57.2	-57.9	-80.8	
Alkalinity	mg/l	- 8.9	-15.2	-22.8	-27.8	-36.7	-36.7	-50.6	-82.3	-68.4
NH3-N	μg/l	- 6.8	+22.7	+ 105	+ 116	+81.8	+38.6	+27.3	+ 9.1	+25.0
NO3-N	μg/l	+ 10.3	+ 2.6	+ 7.7	- 7.7	- 2.6	+ 7.7	-10.3	-20.5	-48.7
Organic N	μg/l	- 8.5	+21.6	-11.3	- 9.5	+18.3	+36.9	+79.1	+ 192	+ 326
Ortho-P	μg/l	-28.6	+ 3.6	+14.3	+75.0	+ 118	+92.9	+ 171	+ 364	+ 139
Total P	μg/1	-18.6	+13.6	+ 5.1	+44.1	+74.6	+86.4	+ 151	+ 200	+ 181
BOD	mg/l	-11.8	+ 5.9	-17.6	-11.8	-23.5	-35.3	-17.6	-47.1	+17.6
Color	Pt-Co Units	+28.8	+38.4	+49.3	+72.6	+ 106	+ 136	+ 210	+ 592	+ 606
Residue	mg/l	+11.0	+ 2.1	- 0.7	+ 4.1	+ 6.8	+ 2.1	0.0	+21.9	+ 24.0
SS	mg/l	+48.1	+77.8	+48.1	+74.1	+37.0	+25.9	+70.4	-33.3	+77.8
Turbidity	NTU	- 6.5	+13.0	+23.9	+39.1	+13.0	+13.0	+10.9	-37.0	-73.9

COMPARISON OF SURFACE WATER CHARACTERISTICS IN FLOWPATH AND CONTROL AREAS

		CONCEN	TRATION	PROBABILITY
PARAMETER	UNITS	FLOWPATH ¹	CONTROL AREA	UNEQUAL MEANS
pH	s.u.	6.22	4.94	99.9
Conductivity	μ mho/cm	165	92	99.9
Temperature	°C	24.5	23.5	52.0
Diss. Oxygen	mg/l	3.6	0.9	99.0
ORP	mV	256	79	99.2
Alkalinity	mg/l	62.9	14.2	99.9
Turbidity	NTU	5.4	2.9	58.2
NH₃-N	μg/l	70.8	47.9	52.3
NO3-N	μg/l	39.6	31.3	50.5
Organic N	μg/l	406	1163	99.9
Diss. OP	μg/l	36	130	99.9
Total P	μg/l	71	177	99.9
тос	mg/l	15.6	42.5	99.9
BOD	mg/l	1.5	0.9	79.0
S.S.	mg/l	4.3	1.8	68.7
V.S.S.	mg/l	1.6	1.3	32.8

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1. Comprised of the following sample stations: 10 m, 25 m, 50 m, 75 m and 100 m.

in value in the flowpath area, while organic nitrogen, dissolved orthophosphorus, total phosphorus, and TOC were significantly lower in the flowpath area than in the control area.

A summary of mean heavy metal concentrations in the wetland surface waters is given in Table 4-15. In general, baseflow inputs of heavy metals to the wetland through the inlet canal were extremely low in value with the possible exceptions of lead, iron and aluminum. In excess of 80% of inputs for all metals, except aluminum and iron, were in a dissolved form as they entered the wetland. Dissolved fractions of metal species generally increased for all metals during travel through the wetland as particulate forms settled out, and most metals, except aluminum and iron, exhibited soluble fractions near 100% at the 150 m sample station. As seen in Table 4-15, soluble fractions of iron and aluminum increased in the isolated control area and in Hidden Lake, while soluble fractions of all other metal species decreased.

A summary of removal efficiencies for heavy metals in the wetland treatment system is given in Table 4-16. Dissolved forms of all metals measured were removed to varying degrees with the exceptions of manganese, copper, iron and aluminum. However, reductions for dissolved metal species which exhibited removal were generally small with all calculated values less than 36%. On the other hand, dissolved forms of manganese were found to increase by 43%, aluminum by 93% and iron by 223% during travel to the 150 m sample site. Dissolved concentrations of zinc, manganese, copper, iron and aluminum were lower in the flowpath area than in the control region, while cadmium, lead, nickel and chromium were found in lower concentrations of most

SUMMARY OF MEAN HEAVY METAL CONCENTRATIONS IN WETLAND SURFACE WATERS AT HIDDEN LAKE DURING 1985 (All values given as $\mu g/l$)

HEAVY	MEAN		ISOLATED	HIDDEN						
METAL	CONCENTRATION	10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA	LAKE
Diss.	_									
Cd	4.6 (92)*	3.8 (79)	3.9 (93)	4.7 (98)	5.3 (93)	4.6 (92)	3.7 (95)	3.9 (93)	2.3 (66)	3.8 (76)
Zn	4.6 (96)	5.0 (85)	3.9 (85)	3.4 (100)	3.9 (100)	4.5 (94)	5.7 (100)	4.0 (100)	6.6 (70)	17.2 (97)
Mn	3.0 (86)	2.6 (87)	3.1 (91)	3.4 (97)	4.9 (100)	5.0 (98)	4.6 (92)	4.3 (93)	7.6 (88)	8.0 (45)
Cu	10.7 (80)	13.8 (86)	19.9 (98)	17.4 (98)	15.5 (96)	17.4 (97)	25.6 (100)	14.3(100)	28.7 (86)	19.1 (73)
Al	143 (62)	149 (59)	176 (59)	148 (60)	158 (60)	194 (65)	193 (70)	276 (72)	296 (92)	252 (86)
Fe	70.1 (76)	80.7 (76)	105 (85)	131 (85)	182 (87)	177 (82)	176 (71)	226 (79)	389 (92)	347 (83)
Pb	32.4 (97)	28.3 (95)	24.7 (92)	27.4 (99)	24.3 (95)	23.5 (96)	25.3 (98)	20.6 (95)	15.9 (90)	29.6 (93)
Ni	3.6 (92)	3.1 (91)	2.7 (90)	3.0 (100)	2.8 (93)	3.1 (97)	2.9 (97)	2.4 (96)	1.9 (83)	2.3 (92)
Cr	3.8 (100)	3.1 (84)	2.8 (97)	3.0 (94)	2.7 (90)	2.5 (89)	2.8 (97)	2.3 (82)	1.9 (90)	2.0 (87)
Total										
Cd	5.0	4.8	4.2	4.8	5.7	5.0	3.9	4.2	3.5	5.0
Zn	4.8	5.9	4.6	3.4	3.9	4.8	5.7	4.0	9.4	17.8
Mn	3.5	3.0	3.4	3.5	4.9	5.1	5.0	4.6	8.6	17.8
Cu	13.4	16.1	20.4	17.8	16.1	17.9	25.6	14.3	33.4	26.1
Al	230	253	297	247	262	300	275	386	323	292
Fe	92.4	106	123	154	210	216	249	286	421	416
Pb	33.5	29.7	26.8	27.6	25.5	24.5	25.9	21.6	17.6	32.0
Ni	3.9	3.4	3.0	3.0	3.0	3.2	3.0	2.5	2.3	2.5
Cr	3.8	3.7	2.9	3.2	3.0	2.8	2.9	2.8	2.1	2.3
# Obs.	19	9	10	8	8	8	7	7	7	9

1. Percentage of dissolved species given in parentheses.

SUMMARY OF REMOVAL EFFICIENCIES FOR HEAVY METALS IN THE WETLAND AT HIDDEN LAKE

HEAVY METAL	TYPE OF SPECIES	INPUT CONC. (μg/l)	AVERAGE CONC. AT 150 m (µg/l)	PERCENT CHANGE FROM INPUT	CONTROL AREA (µg/l)
Cd	Dissolved	4.6	3.9	- 15	2.3
	Particulate	0.4	0.3	- 25	1.2
Zn	Dissolved	4.6	4.0	-13	6.6
	Particulate	0.2	0.0	- 100	2.8
Mn	Dissolved	3.0	4.3	+ 43	7.6
	Particulate	0.5	0.3	- 40	1.0
Cu	Dissolved	10.7	14.3	+ 34	28.7
	Particulate	2.7	0.0	- 100	4.7
Al	Dissolved	143	276	+ 93	296
	Particulate	87	110	+ 26	27
Fe	Dissolved	70	226	+ 223	389
	Particulate	22	60	+ 173	32
Рb	Dissolved	32.4	20.6	- 36	15.9
	Particulate	1.5	1.0	- 33	1.7
Ni	Dissolved	3.6	2.4	- 33	1.9
	Particulate	0.3	0.1	- 67	0.4
Cr	Dissolved Particulate	3.8 0.0	2.3 0.5	- 39	1.9 0.2

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heavy metals into the wetland were extremely low with many near the limits of detection. As a result, even small measurement errors could result in significant changes in the removal efficiencies listed in Table 4-16.

Particulate forms of all metals, except iron and aluminum, were removed to varying degrees, ranging from 25% for cadmium to 100% for zinc and copper. In general, the flowpath area exhibited lower concentrations of particulate species than the control area, with the exceptions of iron and aluminum.

An analysis of variance comparison of heavy metal concentrations between flowpath and control areas is given in Table 4-17. Significant differences were found at the 0.05 level for all dissolved metal species except copper. Cadmium, lead, nickel, and chromium were higher in concentration along the flowpath, while the remaining metals were lower in concentration along the flowpath. Similar patterns were found for total metal concentrations except that cadmium, aluminum, and nickel were no longer significantly different between the two areas.

Comparisons of Surface Waters During "Wet" and "Dry" Seasons

The surface water data was divided into two data sets, one of which contained data collected from July to early October when the wetland contained continuous standing water and the majority of rainfall events occurred, and one containing data from November to June when rainfall events were sporadic. The month of June, which was included in the comparisons of "wet" and "dry" periods for rainfall and runoff, was not included in the "wet" season for comparisons of surface waters. The heavy rains which

COMPARISON OF HEAVY METAL CONCENTRATIONS IN SURFACE WATERS IN FLOWPATH AND CONTROL AREAS

	CONCENTRA	ATION (µg/l)	PROBABILITY OF UNEQUAL MEANS	
METAL	FLOWPATH ¹	CONTROL AREA		
Dissolved				
Cd Zn Mn Cu Al Fe Pb Ni Cr	4.4 4.2 3.7 16.9 165 132 25.7 2.9 2.8	2.3 6.6 7.6 28.7 296 389 15.9 1.9 1.9	98.5 97.5 99.8 90.4 99.7 99.9 99.8 95.5 99.5	
Total				
Cd Zn Mn Cu Al Fe Pb Ni Cr	4.9 4.5 3.9 17.7 273 159 26.9 3.1 3.1	3.5 9.4 8.6 33.4 323 421 17.6 2.3 2.1	83.0 99.7 99.9 95.5 37.6 99.9 99.9 90.2 99.6	

1. Comprised of the following sample stations: 10 m, 25 m, 50 m, 75 m and 100 m.

began in late June were preceded by a long period of deficient rainfall and, as a result, the wetland did not have standing water at many sample locations during June. Much of the runoff inputs during June were infiltrated into the soil to fill up the lost soil moisture. Standing water did not become uniform throughout the wetland until early July. Therefore, the effects of runoff inputs on surface waters could only be measured after this time, and the "wet" season was chosen to start at that time.

A comparison of general surface water characteristics between flowpath and control areas in "wet" and "dry" seasons is given in Table 4-18. During the "dry" season, significant differences were observed between the flowpath and control areas for pH, alkalinity, dissolved and total phosphorus, organic nitrogen, and TOC. Mean values of pH and alkalinity were greater in the flowpath area during this time, while organic nitrogen, dissolved and total phosphorus, and TOC were greater in the isolated control area. It should be noted that although significant differences were not found, the flowpath area also exhibited greater mean values of temperature, dissolved oxygen, ORP, turbidity, ammonia nitrate, BOD, SS, and VSS than the control area.

During the "wet" season, when inputs into the flowpath occurred more regularly, the number of significant differences between the two areas increased substantially. Significant differences between the two areas were observed for pH, conductivity, temperature, dissolved oxygen, alkalinity, organic nitrogen, dissolved and total phosphorus, and TOC. In general, the differences in mean values between the two areas was greater in the "wet" season than the "dry" season. These differences are particularly apparent for pH, conductivity, temperature, alkalinity and TOC. As observed during the "dry" season, mean values of pH, conductivity, temperature, dissolved oxygen, and

COMPARISON OF SURFACE WATER CHARACTERISTICS BETWEEN "WET" AND "DRY" SEASONS

		"DRY" SE No	ASON CONCEN OVEMBER - JUN	ITRATION IE	"WET" SEASON CONCENTRATION JULY - OCTOBER			
PARAMETER	UNITS	FLOWPATH ¹	CONTROL AREA	PROB. OF UNEQUAL MEANS	FLOWPATH	CONTROL AREA	PROB. OF UNEQUAL MEANS	
pH	s.u.	6.24	5.17	99.9	6.20	4.85	99.9	
Conductivity	µmho/cm	147	91	85.8	181	93	99.9	
Temperature	°C	21.9	20.7	36.6	26.8	24.6	99.2	
Diss. Oxygen	mg/l	3.3	0.7	89.2	3.38	1.0	95.5	
ORP	mV	315	77	94.6	206	80	90.6	
Alkalinity	mg/l	55.5	14.1	98.7	69.4	14.2	99.9	
Turbidity	NTU	10.1	1.9	75.7	3.3	1.2	91.2	
NH ₃ -N	μg/l	99.1	84.0	14.6	46.0	33.4	59.0	
NO ₃ -N	$\mu g/l$	38.2	10.0	62.7	40.8	39.8	10.9	
Organic N	μg/l	329	1080	99.9	473	1197	99.9	
Diss. OP	μg/l	42	177	99.9	31	112	99.9	
Total P	μg/l	95	243	99.6	51	151	99.9	
TOC	mg/l	13.8	31.4	99.9	16.8	46.9	99.9	
BOD	mg/l	2.4	1.2	83.2	0.8	0.8	11.1	
SS	mg/l	7.8	2.7	60.9	1.2	1.4	24.0	
VSS	mg/l	2.7	1.7	48.3	0.7	1.2	50.5	

1. Comprised of the following sample stations: 10 m, 25 m, 50 m, 75 m and 100 m.

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alkalinity were greater along the flowpath, while organic nitrogen, phosphorus, and TOC were greater in the control areas.

A comparison of heavy metal concentrations in surface waters between "wet" and "dry" periods is given in Table 4-19. During the dry season, no significant differences were observed between the two areas for any of the dissolved or total metals measured. However, even though significant differences were not found, concentrations of zinc, manganese, aluminum, and iron were greater in the control area, while cadmium, copper, lead, nickel, and chromium were greater in the flowpath area.

During the "wet" season, the number of significant differences between the two areas increases. Significant differences are now observed for dissolved cadmium, manganese, aluminum, iron, and lead and for total zinc, manganese, copper, iron, lead, and chromium. As observed during the "dry" season, concentrations of zinc, manganese, copper, aluminum, and iron were greater in the control area, while cadmium, nickel, and chromium were greater in the flowpath.

<u>Characteristics of Groundwater</u> <u>in the Hidden Lake Wetland</u>

Multi-port groundwater sampling devices were constructed and installed with sample ports 0.1 m, 0.5 m, and 1.0 m beneath the wetland soil surface. A total of four monitoring wells were installed, with one in an area upstream of the wetland, two in the major flowpath, and one in the control area. Groundwater samples and simultaneous measurements of piezometric surface were collected on a monthly basis from November 1984 to November 1985. The sample collection program consisted of 13 sample dates

COMPARISON OF HEAVY METAL CONCENTRATIONS IN SURFACE WATERS BETWEEN "WET" AND "DRY" SEASONS

	"DRY" S	EASON CONCENT NOVEMBER - JUNE	TRATION	"WET" SEASON CONCENTRATION JULY - OCTOBER				
PARAMETER	FLOWPATH ¹ (µg/l)	CONTROL AREA (µg/l)	PROB. OF UNEQUAL MEANS	FLOWPATH ¹ (µg/l)	CONTROL AREA (µg/l)	PROB. OF UNEQUAL MEANS		
Dissolved								
Cd	4.4	3.2	58.2	4.4	2.0	97.6		
Zn	4.6	7.0	92.7	3.9	6.4	90.8		
Mn	3.3	5.5	85.5	4.0	8.4	99.0		
Cu	5.8	5.0	17.2	23.4	38.2	91.1		
Al	148	221	90.0	176	327	98.5		
Fe	162	268	89.0	115	437	99.9		
Pb	24.9	13.5	89.4	26.1	16.8	99.4		
Ni	3.0	2.4	57.1	2.9	1.7	91.8		
Total								
Cd	4.6	3.2	63.0	5.0	3.7	71.2		
Zn	5.1	7.0	80.3	4.2	10.4	99 .1		
Mn	3.4	5.5	85.7	4.3	9.8	99.7		
Cu	5.9	5.0	19.6	24.7	44.8	96.4		
Al	216	221	4.4	306	364	30.4		
Fe	183	294	90.4	145	472	99.9		
Pb	25.5	16.0	· 83.6	27.7	18.2	99.9		
Ni	3.1	2.4	64.8	3.1	2.2	80.9		
Cr	2.9	1.8	94.9	3.3	2.2	97.5		

1. Comprised of the following sample stations: 10 m, 25 m, 50 m, 75 m and 100 m.

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during the study period, with a total of 133 samples being collected. A complete listing of all measured parameters at each well on each sample date is given in Appendix X.

A summary of mean general characteristics of groundwaters in the wetland is given in Table 4-20. As seen in Appendix X, considerable variations were observed for most parameters, both horizontally throughout the wetland and vertically within each well. In general, groundwaters at each of the four sites is characterized as slightly acidic with pH values between 4.84 and 5.96, low in dissolved oxygen and reduced in terms of ORP. In groundwaters upstream of the wetland (well #1), pH values below 5.0 were found 45% of the time during the study period. The upland waters were characterized as being in a reduced state with mean values less than 80 mV at all sample depths and values below 0 mV in 17% of all samples collected. During the study period, dissolved oxygen concentrations were measured as 0 mg/l in 67% of all samples collected.

In well #2, located at a distance of 25 m along the flowpath, mean values of pH were higher than those measured in the upland region, with values ranging from 5.96 at 0.1 m to 5.37 at 1.0 m. Measured values of ORP, although still in a reduced state, were greater at all depths in well #2 than in the upland area, with values ranging from 139 to 52 mV, with 27% of all samples measured at less than 0 mV. Measurements of pH and ORP in well #3, located at 150 m along the flowpath, were similar to those measured in well #2.

Measurements of pH in the control area well (well #4) were the lowest of all groundwaters, with mean values ranging from 4.84 at 0.1 m to 5.18 at 1.0 m. The mean ORP of groundwaters in the control area declined to 27 mV at 1.0 m, with 25% of all measured values less than 0 mV.

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS IN GROUNDWATERS AT THE HIDDEN LAKE WETLAND

PARAMETER	UNITS	UPSTREAM OF WETLAND		F	FLOWPATH AT 25 m		FLOWPATH AT 150 m			CONTROL AREA			
		0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m
pН	s.u.	5.05	5.17	5.15	5.96	5.61	5.37	5.42	5.38	5.76	4.84	4.98	5.18
Conductivity	μ mho/cm	137	118	115	229	153	128	139	158	290	100	111	135
Diss. Oxygen	mg/l	0.4	0.1	0.1	3.5	0.1	0.0	0.4	0.5	0.1	0.0	0.2	0.1
ORP	mV	78	76	68	139	83	52	77	107	83	57	72	27
Alkalinity	mg/l	29	38	42	100	54	42	50	48	122	16	18	32
NH3-N	μg/l	107	100	113	386	227	358	159	320	1131	445	982	1238
NO3-N	μg/l	76	40	46	60	. 43	83	41	61	68	14	42	19
Organic N	μg/l	572	122	210	300	311	432	567	575	378	1627	1456	1421
Ortho-P	μg/l	23	40	49	24	25	42	55	31	29	309	332	429
BOD	mg/l	2.6	1.8	1.8	3.0	2.0	2.8	2.4	1.7	3.3	3.5	4.7	5.1
Color	Pt-Co Units	390	205	368	188	173	177	268	268	132	664	713	569
Residue	mg/l	187	142	172	211	156	126	141	163	238	169	182	201
Number of	Number of Samples		12	12	10	11	12	10	11	11	11	12	12

A comparison of mean values of pH and redox potential in surface waters and groundwaters in the flowpath and control areas is given in Figure 4-11. Flowpath areas were greater in both pH and redox potential than the isolated control area. For pH, the differences were most pronounced in the top 0.5 m, with values becoming similar at the 1.0 m depth. Measurements of ORP were substantially elevated along the flowpath in the top 0.1 m, with similar values at depths of 0.5 m or more.

Concentrations of nitrate nitrogen were relatively low in all of the groundwater tested, with mean values at all wells less than 0.1 mg/l. Ammonia nitrogen was lowest in the upland area, with mean values near 100 μ g/l. Measured concentrations of ammonia were greater along the flowpath area, with mean values near 300 μ g/l at the 25 m well and near 500 μ g/l at the 150 m well. Mean concentrations in the control area were substantially greater than along the flowpath, with an overall mean near 900 μ g/l. Increases in ammonia concentrations with increasing depth were observed in both well #3 and well #4. In general, concentrations of organic nitrogen observed the same patterns stated previously for ammonia, with a mean of 301 μ g/l in the upland area, 348 μ g/l at the 25 m well, 497 μ g/l at the 150 m well, and 1501 μ g/l in the control area.

Concentrations of orthophosphorus in groundwaters in the wetland area are shown in Figure 4-12. Measured concentrations of orthophosphorus were similar in groundwaters in the upland and flowpath areas, with a mean of 37 μ g/l in the upland area, 30 μ g/l at 25 m, and 38 μ g/l at 125 m. Concentrations in the control area were substantially greater than either the upland or flowpath with a mean near 357 μ g/l.

A summary of mean heavy metal concentrations in groundwaters is given in Table 4-21. In general, concentrations of cadmium, manganese, nickel, and chromium were

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Figure 4-11. Comparison of Mean Values for pH and Redox Potential in the Flowpath and Control Areas in the Hidden Lake Wetland.



Figure 4-12. Comparison of Dissolved Orthophosphorus Concentrations in the Surface and Groundwaters in the Hidden Lake Wetland.

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SUMMARY OF MEAN HEAVY METAL CONCENTRATIONS IN GROUNDWATER MONITORING WELLS AT THE HIDDEN LAKE WETLAND

HEAVY METAL (Dissolved)	UPSTREAM OF WETLAND (µg/l)			FLOWPATH AT 25 m (µg/l)			FLOWPATH AT 150 m (µg/l)			CONTROL AREA (µg/l)		
(Dissolved)	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m
Cd	2.8	3.3	3.8	5.9	5.2	4.9	5.2	5.7	7.0	3.9	4.5	5.8
Zn	32.5	49.5	51.2	20.9	16.3	21.0	21.1	24.0	23.6	37.3	42.6	26.4
Mn	6.9	5.5	6.0	18.0	8.1	7.9	7.6	13.0	19.7	9.8	12.5	28.7
Cu	32.9	30.6	36.9	30.3	42.2	29.7	28.4	35.5	40.5	28.0	54.8	28.7
Al	1211	1045	1701	290	262	310	464	609	247	710	976	744
Fe	977	1197	1030	868	724	1102	1911	1815	2586	1172	1586	2285
РЬ	21.6	17.9	23.0	35.8	27.2	21.2	25.3	26.9	47.5	21.6	26.4	31.3
Ni	3.9	3.2	3.0	5.8	3.1	2.7	3.6	3.8	5.0	3.2	4.3	5.0
Cr	2.8	2.8	4.3	3.7	3.3	2.7	2.9	2.9	3.5	2.8	3.0	3.4
# of Samples	11	12	12	10	11	12	9	11	11	10	12	12

extremely low in all measured groundwaters. Concentrations of both aluminum and iron were found to generally increase with increasing depth in all wells. In general, concentrations of aluminum and iron were lower along the flowpath at 25 m and greater at the 150 m site and in the control area.

A comparison of general groundwater characteristics between the four well locations using analysis of variance procedures is given in Table 4-22. For these analyses, all sample ports for a given well were combined to form a single data set for each well so that the wells could be compared independently of depth.

Significant differences were found at the 0.05 level between the four groundwater locations for all measured general parameters except temperature, ORP, nitrate, and BOD. In general, two distinct patterns were observed for parameters which exhibited a significant difference. The first pattern observed was that measured values of many parameters were greatest along the flowpath, lower in the upland area and lowest in the control area. This pattern was found for pH, conductivity, dissolved oxygen, and alkalinity. Although significant differences were not found, measured values of ORP and nitrate also fit the pattern. The second observed pattern was the reverse of the previous pattern, with the greatest values of a parameter found in the control and lowest along the flowpath and upland areas. This pattern was found for ammonia, organic nitrogen, dissolved oxygen, alkalinity, ORP, and nitrate, while groundwaters in the stagnant control area were greater in ammonia, organic nitrogen, dissolved phosphorus, and TOC.

A comparison of heavy metal concentrations in groundwaters in the wetland is given in Table 4-23. Significant differences were found between the four well sites for

COMPARISON OF GENERAL CHARACTERISTICS IN GROUNDWATERS IN THE HIDDEN LAKE WETLAND

PARAMETER	WELL LOCATION	MEAN VALUE	UNITS OF MEASUREMENT	PROB. OF UNEQUAL MEANS	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
рН	Flowpath - 25 m Flowpath - 150 m Upland Control	5.68 5.56 5.15 5.09	units	99.9	A A B B
Conductivity	Flowpath - 150 m Flowpath - 25 m Upland Control	199 167 123 116	µmho/cm	99.9	A A B B
Temperature	Flowpath - 25 m Upland Flowpath - 150 m Control	21.5 21.3 20.4 20.0	°C	80.9	A A A A
Diss. Oxygen	Flowpath - 25 m Flowpath - 150 m Upland Control	1.14 0.33 0.20 0.13	mg/l	98.9	A A B B
ORP	Flowpath - 150 m Flowpath - 25 m Upland Control	90 88 74 52	mV	48.7	A A A A
Alkalinity	Flowpath - 150 m Flowpath - 25 m Upland Control	74.6 63.4 36.6 22.4	mg/l	99.9	A A B B
NH₃-N	Control Flowpath - 150 m Flowpath - 25 m Upland	914 561 323 107	μg/l	99.9	A B C C
NO₃-N	Flowpath - 25 m Flowpath - 150 m Upland Control	63 57 53 26	μg/l	93.4	A A A A

PARAMETER	WELL LOCATION	MEAN VALUE	UNITS OF MEASUREMENT	PROB. OF UNEQUAL MEANS	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Organic N	Control Flowpath - 150 m Flowpath - 25 m Upland	1493 503 352 293	μg/l	99.9	A B B C C
Diss. P	Control Upland Flowpath - 150 m Flowpath - 25 m	359 38 37 31	μg/l	99.9	A B B B
тос	Control Flowpath - 150 m Upland Flowpath - 25 m	46.5 20.4 16.6 15.9	mg/l	99.9	A B B B
BOD	Control Flowpath - 150 m Upland Flowpath - 25 m	3.0 2.5 2.0 2.0	mg/l	84.9	A A A A

TABLE 4-22 -- CONTINUED

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COMPARISON OF HEAVY METAL CONCENTRATIONS IN GROUNDWATERS IN THE HIDDEN LAKE WETLANDS

HEAVY METAL	WELL LOCATION	MEAN CONCENTRATION (µg/l)	PROB. OF UNEQUAL MEANS	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Cd	Flowpath - 150 m Flowpath - 25 m Control Upland	6.0 5.3 4.8 3.3	99.9	A A A B B
Zn	Flowpath - 150 m Flowpath - 25 m Control Upland	23.0 19.4 35.3 44.7	96.2	A A A A
Mn	Flowpath - 150 m Flowpath - 25 m Control Upland	13.8 11.0 17.4 6.1	99.6	A B A B A B
Cu	Flowpath - 150 m Flowpath - 25 m Control Upland	35.2 34.0 37.7 33.5	3.8	A A A A
Al	Flowpath - 150 m Flowpath - 25 m Control Upland	439 288 816 2351	99.9	B B B A
Fe	Flowpath - 150 m Flowpath - 25 m Control Upland	2116 905 1711 2956	99.6	A B B A B A
Рb	Flowpath - 150 m Flowpath - 25 m Control Upland	33.7 27.6 26.7 20.8	99.9	A A B A B B
Ni	Flowpath - 150 m Flowpath - 25 m Control Upland	4.2 3.8 4.3 3.4	68.3	A A A A
Cr	Flowpath - 150 m Flowpath - 25 m Control Upland	3.1 3.2 3.1 3.3	6.9	A A A A

all metals except copper, nickel, and chromium. For those metals exhibiting significant differences, several patterns were observed. First, metals, such as cadmium and lead, were greater in concentration along the flowpath than in the upland or control areas, with flowpath concentrations of both metals approximately 50% greater than in the control or upland areas. Other metals, such as zinc and aluminum, were lower in concentrations along the flowpath than in the upland or control areas. For zinc, flowpath concentrations were approximately 50% less than in the control or upland area. Manganese was significantly lower in the upland area than in the remaining areas, while concentrations of iron were significantly lower at the 25 m well than at any of the remaining wells.

<u>Characteristics of Sediments</u> in the Hidden Lake Wetland

Sediment analyses were conducted on core samples collected near the sample stations in the flowpath and control areas (Figure 3-3) to characterize the deposition and attenuation of heavy metals and nutrients. Each core sample was divided into the following layers: 0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm, and 15-20 cm. Three 5-cm diameter samples were collected at each fixed station and combined to form a single sample at each location. Each layer was analyzed for extractable heavy metals, moisture content, organic content, total phosphorus, and total nitrogen. A complete listing of measured parameters in sediment core samples is given in Appendix XI.

Horizontal Variations in Sediment Characteristics

Horizontal variations in sediment characteristics were investigated using mean measured values for various parameters in the top 1 cm in the wetland flowpath and control areas. Accumulation patterns of heavy metals in the top 1 cm are shown in Figure 4-13. The majority of the metals appear to reach peak sediment concentrations at a distance of 25-50 m from the inflow canal, followed by constant or slightly fluctuating concentrations with increasing distance into the wetland. Zinc appears to be the only metal which exhibited a pronounced peak in sediment concentration followed by a significant decline. All of the heavy metals, except copper, appear to be accumulating in the surface sediments of the flowpath area since surface sediment concentrations in the control area were lower than along the flowpath. Concentrations of copper, however, appear to be approximately twice as high in the control area than along the flowpath.

Horizontal variations of phosphorus, nitrogen, organic content, and moisture content are shown in Figure 4-14. Both organic and moisture content peaked quickly in the wetland, reaching near peak values at a distance of 25 m. Very slight increases in both of these parameters were found over the remaining flowpath. Concentrations of both parameters were greater in the control area than along the flowpath. This increase was most pronounced for organic content, which increased from 52% at 150 m to 83% in the control area. Sediment concentrations of nitrogen and phosphorus also peaked quickly, reaching near constant values at 25 m. Total nitrogen increased slightly over the remaining flowpath area, while phosphorus remained relatively constant. Sediment concentrations of nitrogen were greater than in the flowpath area. Concentrations of nitrogen increased approximately 40%, while phosphorus decreased 40%.



Figure 4-13. Accumulation Patterns of Heavy Metals in the Top 1 cm of the Wetland Treatment System.



Figure 4-14. Accumulation Patterns of Phosphorus, Nitrogen, Organic Content and Moisture Content in the Top 1 cm of the Wetland Treatment System.

Vertical Variations in Sediment Characteristics

Mean vertical concentrations of nitrogen, phosphorus, organic content, and moisture content in the top 20 cm of the flowpath and control areas are shown in Figure 4-15. Sediment concentrations of phosphorus were greatest near the surface and decreased in a linear fashion with increasing sediment depth. Concentrations in flowpath and control areas appear to be very similar. However, contrary to the patterns observed for phosphorus, surface concentrations of nitrogen were the minimum soil values measured. Nitrogen concentrations appear to increase with increasing sediment depth, reaching a maximum value approximately 10 cm below the surface, followed by rapid decline. Sediment nitrogen appears to be more abundant in the control area than along the flowpath at all of the measured depths.

As seen in Figure 4-15, both organic content and moisture content increase with increasing sediment depth, reaching constant values after approximately 10 cm. Both parameters were greater in value in the control area than in the flowpath, although the differences were more pronounced for organic content than moisture content.

Vertical accumulations of nickel, chromium, aluminum, and iron in the wetland sediments are shown in Figure 4-16. Concentrations of each of the four metals are greatest near the surface and decrease with increasing sediment depth. This rapid attenuation is most pronounced for chromium, aluminum, and iron, and less pronounced for nickel. Each of the metals also appear to be in greater concentrations in the flowpath areas than in the control area. These differences in concentrations appear to be most pronounced near the surface with sediment concentrations becoming similar in flowpath and control areas at depths of 10 cm or greater.



Figure 4-15. Sediment Concentrations of Phosphorus, Nitrogen, Organic Content, and Moisture Content in the Top 20 cm of the Hidden Lake Wetland.



Figure 4-16. Sediment Concentrations of Heavy Metals in Flowpath and Control Areas in the Hidden Lake Wetland.

Vertical accumulations of zinc, lead, cadmium, and copper are shown in Figure 4-17. Zinc was found in substantially greater concentrations in flowpath soils than in control area soils at depths of 10 cm or less. Below this depth, concentrations in each of the areas were similar even though the flowpath was still slightly higher in value. However, contrary to the pattern observed for zinc and the previous metals shown in Figure 4-16, both copper and lead were greatest in sediment concentration in the control area soils. The differences were most pronounced in the top 10 cm, with relatively similar values below this depth for the two areas. Sediment concentrations of cadmium were the lowest of the measured metals, and no distinct differences were observed in sediment concentrations between the two test areas.

Comparisons Between Flowpath and Control Areas

A comparison of mean sediment parameters in the flowpath and control areas by core layer is given in Table 4-24. An analysis of variance procedure was used to test for significant differences between the two areas for each of the parameters listed in Table 4-24. In performing the analyses, measurements at each of the depths were combined together so that the top 20 cm of the flowpath could be compared with the top 20 cm of the control area. A summary of these ANOVA procedures is given in Table 4-25. Significant differences were found between the two areas at the 0.05 level for copper, iron, organic content, and organic nitrogen. Copper, organic content, and nitrogen were significantly higher in the control area, while iron was found to be significantly higher in the flowpath area. However, even through significant differences were not observed for the other measured parameters, zinc, aluminum, iron, nickel, and chromium appear



Figure 4-17. Sediment Concentrations of Heavy Metals in Flowpath and Control Areas in the Hidden Lake Wetland.

COMPARISON OF MEAN SEDIMENT PARAMETERS IN LAYERS WITHIN WETLAND AND CONTROL AREAS AT HIDDEN LAKE

SAMPLE		SEDIMENT CONCENTRATION (µg/g dry weight)											MOISTURE CONTENT
	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	Mn	Р	N	(%)	(%)
Wetland Area ¹													
0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	2.36 2.25 1.62 1.19 1.22	49.4 45.7 25.0 10.9 8.72	6.89 6.44 6.78 5.52 4.32	55,895 42,658 19,982 5,984 5,845	7,207 5,670 4,213 2,787 3,252	41.9 37.9 40.3 28.6 23.7	14.5 12.0 80.8 5.72 5.39	40.1 32.4 17.1 8.43 9.99	19.8 15.5 13.1 9.69 7.94	1,683 1,404 1,185 603 478	9,209 10,570 17,309 18,486 14,828	44.3 50.3 74.7 81.6 83.2	71.1 72.9 79.0 79.6 78.0
Control Area ¹													
0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	2.89 2.14 1.32 1.51 1.56	38.1 26.2 10.8 8.30 5.21	11.0 8.14 6.75 6.47 5.82	49,084 35,048 10,596 7,477 5,859	4,390 3,367 2,308 2,242 1,924	56.9 49.5 38.0 28.3 23.5	12.6 9.93 5.84 4.98 4.42	30.5 22.6 8.07 7.15 8.55	15.7 14.8 7.17 13.2 12.9	1,676 1,385 1,130 815 434	10,716 14,716 22,806 20,181 16,602	53.6 67.0 85.2 87.2 85.7	71.4 78.1 81.2 81.4 81.5

1. n = 21 samples

2. n = 18 samples

SUMMARY OF ANOVA PROCEDURES FOR SEDIMENT PARAMETERS IN THE FLOWPATH AND CONTROL AREAS

HEAVY	PROBABILITY OF UNEOUAL	MEAN CONCENTRATION (μg/g)				
METAL	MEANS	FLOWPATH	CONTROL			
Cd	46.6	1.74	1.88			
Zn	94.7	27.2	17.7			
Cu	98.5	6.51	7.63			
Al	45.9	24,522	21,613			
Fe	99.9	4,186	2,846			
Pb	60.5	36.5	39.3			
Ni	90.4	9.40	7.55			
Cr	87.3	20.2	15.4			
Organic Content	97.9	66.4	75.7			
Moisture Content	76.7	76.1	78.7			
Р	42.8	1,071	1,088			
Ν	97.8	14,080	17,002			

to be present in greater concentrations along the flowpath, while cadmium and lead appear to be greater in sediment concentrations in the control area.

An additional analysis of variance procedure was conducted between the two areas for the measured parameters with each of the core layers analyzed separately. Significant differences were found only for iron, organic content, copper, lead, and chromium at any of the five core layers. A summary of these significant differences is given in Table 4-26. The extent of significant differences in sediment concentrations of iron extended, with the exception of the 10-15 cm layer, to depths of 20 cm or greater, with flowpath concentrations much greater than those in the control area. Differences in organic content also extended to approximately 10 cm, after which the concentrations became similar. Both copper and lead exhibited significantly higher concentrations in the top 5 cm of the control area, while chromium was significantly greater in the flowpath in the 0-1 cm layer and the 5-10 cm layer.

The attenuation of heavy metals in the wetland sediments was modeled using the PROC GLM package of SAS for a variety of linear and logarithmic models. Metal concentrations in both the flowpath and control areas were found to best fist a semi-log model of the form: $\ln (C/C_0) = (K) \times depth$. A summary of the regression statistics for the semi-log model is given in Table 4-27 where the tested metals are listed in order of decreasing attenuation coefficient (K). This procedure allows the metals to be ranked in order of stability in the sediments since a large attenuation coefficient indicates that the majority of a particular species has not been retained near the surface and has not migrated to lower depths. A small value of K suggests that the sediments have less affinity for a particular metal and it is migrating downward through the sediments more rapidly.

SUMMARY OF SIGNIFICANT DIFFERENCES BETWEEN SEDIMENT CHARACTERISTICS IN FLOWPATH AND CONTROL AREAS BY CORE LAYER

	CODE	PROB. OF	MEAN	VALUE ¹
PARAMETER	LAYER	UNEQUAL MEANS	FLOWPATH	CONTROL AREA
Fe	0-1 cm	99.9	7207	4391
	1-5 cm	97.5	5670	3367
	5-10 cm	99.8	4213	2308
	10-15 cm	67.0	2788	2242
	15-20 cm	99.9	3252	1924
Organic	0-1 cm	95.8	44.3	53.6
Content	1-5 cm	94.2	50.3	67.0
	5-10 cm	94.0	74.7	85.2
	10-15 cm	92.0	81.6	87.2
	15-20 cm	53.1	83.1	85.7
Cu	0-1 cm	99.9	6.9	11.0
	1-5 cm	94.3	6.4	8.1
	5-10 cm	4.3	6.8	6.7
	10-15 cm	77.5	5.5	6.5
	15-20 cm	73.6	4.3	5.8
Pb	0-1 cm	99.7	41.9	56.9
	1-5 cm	98.0	37.9	49.5
	5-10 cm	43.2	40.3	38.0
	10-15 cm	6.8	28.6	28.3
	15-20 cm	3.3	23.7	23.5
Cr	0-1 cm	99.5	40.1	30.5
	1-5 cm	85.8	32.4	22.6
	5-10 cm	97.6	17.1	8.1
	10-15 cm	50.1	8.4	7.2
	15-20 cm	56.0	10.0	8.6

1. All mean values given as $\mu g/g$ dry sediment except organic content which is listed as percent.

SUMMARY OF HEAVY METAL ATTENUATION IN THE TOP 20 cm OF THE WETLAND SEDIMENTS FOR THE MODEL: ln (C/Co) = (K) x DEPTH

	FLOW	PATH	CONTRO	CONTROL AREA			
HEAVY METAL	ATTENUATION COEFFICIENT (K)	VALUE OF R ²	ATTENUATION COEFFICIENT (K)	VALUE OF R ²			
Al	- 0.140	0.912	- 0.141	0.946			
Zn	- 0.128	0.941	- 0.130	0.973			
Cr	- 0.107	0.878	- 0.099	0.859			
Ni	- 0.077	0.890	- 0.068	0.937			
Mn	-0.056	0.931	- 0.061	0.951			
Cd	- 0.055	0.620	- 0.033	0.150			
Pb	- 0.051	0.869	- 0.055	0.885			
Fe	- 0.048	0.706	- 0.053	0.900			
Cu	- 0.018	0.435	- 0.042	0.875			
Organic Content	0.042	0.859	0.034	0.851			
Р	- 0.070	0.846	- 0.067	0.880			

As seen in Table 4-27, aluminum, zinc, and chromium appear to be attenuated rapidly in the wetland sediments in both the flowpath and control areas. The attenuation rates of aluminum and zinc are virtually identical in the two areas; however, chromium appears to be better retained in the flowpath than in the control area. The remaining metals listed in Table 4-27 appear to be attenuated to a lesser degree than aluminum, zinc, or chromium. In the flowpath area, nickel is attenuated at the next most rapid rate, followed by manganese, cadmium, lead, and iron. Copper has the lowest rate of attenuation in the flowpath, with a value approximately one order of magnitude less than that of aluminum or zinc. The much greater value of K for copper in the control area indicates a greater affinity for copper in the control area sediments than in the flowpath.

Effects of Sediment Desiccation on Nutrient and Metal Concentrations

As described in Chapter 3, complete sets of core samples were collected along the flowpath area on two separate dates. The first collection date was March 15, 1985. On this date, standing water was present in most areas of the wetland and the soils were saturated at each of the core sample locations. The second sample collection date, May 15, 1985, was preceded by a long period of deficient rainfall. The piezometric surface in the wetland had dropped to a depth of 1 m below the soil surface. Wetland soils on this date were moist, but not inundated with water. A comparison of sediment characteristics between these two dates was conducted to determine if periods of drying affected the ability of the soils to retain heavy metals and nutrients. Analysis of variance procedures were used for comparison of these two dates, and the parameters exhibiting significant differences are summarized by layer in Table 4-28.

SUMMARY OF SIGNIFICANT DIFFERENCES BETWEEN SEDIMENT CHARACTERISTICS IN THE FLOWPATH IN "WET" AND "DRY" PERIODS

	CODE	PROB. OF	MEAN	VALUE ¹
PARAMETER	LAYER	UNEQUAL MEANS	3/15/85 "WET"	5/15/85 "DRY"
Moisture	0-1 cm	96.7	71.1	62.8
Content	1-5 cm	88.5	72.9	66.1
	5-10 cm	93.4	79.0	73.4
	10-15 cm	93.4	79.6	73.3
	15-20 cm	45.9	78.0	76.4
Fe	0-1 cm	98.3	7207	5294
	1-5 cm	83.5	5670	4367
	5-10 cm	96.3	4213	3107
	10-15 cm	25.5	2788	2989
	15-20 cm	45.0	3252	2973
Pb	0-1 cm	99.5	41.9	56.6
	1-5 cm	99.6	37.9	52.8
	5-10 cm	71.4	40.3	35.7
	10-15 cm	27.8	28.6	27.2
	15-20 cm	61.6	23.7	20.4
Р	0-1 cm	4.6	1683	1673
	1-5 cm	12.1	1404	1435
	5-10 cm	99.2	1185	812
	10-15 cm	27.6	603	555
	15-20 cm	86.8	478	344

1. All mean values given as $\mu g/g$ dry sediment except moisture content which is listed as percent.

Significant differences in sediment moisture content were observed at the 0.05 level in the top 1 cm and at the 0.1 level down to a depth of 15 cm, although the measured values during the "dry" period were not greatly different than those found in the period of saturated soils. Significant differences in iron content were also observed in the top 10 cm. Concentrations were less in the dry condition than in the moist condition. Lead was observed to be significantly higher in the top 5 cm during moist periods than during dry periods. Significant differences in sediment phosphorus were observed at only the 5-10 cm layer, with lower values at this depth during dry conditions.

<u>Chemical Speciation of Phosphorus and</u> <u>Heavy Metals in the Wetland Soils</u>

Each sediment core was also carried through a series of sequential extraction procedures to examine the type of chemical associations and stability of phosphorus and metal species in the sediments. This procedure allowed sediment associations to be divided into fractions of soluble, exchangeable, bound to carbonates, bound to Fe/Mn oxides, and bound to organic matter. It is generally believed that the stability of sediment associations increases in the same order.

A summary of chemical speciation for cadmium, zinc, manganese, copper, and aluminum in the top 20 cm of the flowpath and control areas is given in Table 4-29. Each of the metals listed exhibited relatively small soluble fractions in both flowpath and control areas. However, of the soluble fractions measured, cadmium, zinc, and manganese were greater in the control area, while copper and aluminum were greater along the flowpath. In the control area, smaller fractions of exchange and carbonate

SUMMARY OF MEAN METAL SPECIATION OF Cd, Zn, Mn, Cu, AND A1 IN THE TOP 20 cm OF THE WETLAND AT HIDDEN LAKE

	Cd		Zn		Mn		Cu		Al	
METAL SPECIATION	FLOWPATH	CONTROL AREA								
Soluble	3.0*	5.6	1.5	5.3	0.1	0.2	4.2	2.5	0.5	0.3
Exchange	71.1	58.7	21.9	16.8	56.7	53.2	5.4	5.9	0.4	0.7
Bound to Carbonates	11.1	. 8.8	11.8	17.1	15.8	19.0	2.5	4.8	2.4	1.5
Fe/Mn Oxides	8.9	14.5	34.6	25.8	17.2	17.2	12.7	24.7	14.3	9.5
Organic Bound	5.9	12.4	30.1	35.0	10.2	10.4	75.2	62.1	82.4	88.0
Total Metal Released	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* All values given as percent.

bonds were found and larger fractions of Fe/Mn and organic bonds indicating a better affinity for retention of cadmium in the control area than in the flowpath. Speciation of zinc and manganese appear to be very similar between the two areas, although the bonding mechanisms for zinc in the control area appear to be slightly weaker than the bonds present in the flowpath. Speciations of copper and aluminum also appear to be similar between the two areas with the primary bonding mechanisms composed of Fe/Mn oxides and relatively stable organic associations. However, copper was observed to have a larger Fe/Mn association in the control area indicating that changes in ORP or pH may affect copper retention in this area.

Chemical speciations of iron, lead, nickel, chromium, and phosphorus in the top 20 cm of flowpath and control areas are given in Table 4-30. Iron was found to be associated primarily with organic fractions in both areas with smaller percentages of Fe/Mn bonding. Lead appears to be bound to flowpath sediments by weak exchange associations. However, bonding of lead in the control area appears to be more stable since the weak exchange association is smaller, and more stable carbonate, Fe/Mn, and organic bonds increase. Speciation of nickel in the wetland sediments appears to be divided approximately equally between a weak exchange fraction and a stable organic fraction with very little bonding to carbonates or Fe/Mn oxides. Chromium was found to be relatively stable in both areas with organic fractions of 80% or more and exchange fractions of approximately 10%. Speciation of phosphorus is very similar in both flowpath and control areas with approximately 85% of all sediment phosphorus found in stable organic associations.

SUMMARY OF MEAN METAL SPECIATION OF P, Fe, Pb, Ni, AND Cr IN THE TOP 20 cm OF THE WETLAND AT HIDDEN LAKE

	Р		Fe		Рь		Ni		Cr	
METAL SPECIATION	FLOWPATH	CONTROL AREA								
Soluble	1.0*	1.5	0.2	0.2	0.9	1.6	2.1	5.6	1.3	1.9
Exchange	1.3	2.0	1.1	0.9	73.0	45.5	45.5	36.4	13.2	9.5
Bound to Carbonates	3.8	2.5	0.6	0.5	12.6	21.5	2.1	0.1	0.9	0.01
Fe/Mn Oxides	7.9	10.3	39.6	31.5	5.7	11.0	8.5	8.3	4.1	3.0
Organic Bound	86.0	83.7	58.5	66.9	7.8	20.4	41.8	49.6	80.5	85.5
Total Metal Released	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* All values given as percent.

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A summary of chemical speciation along the flowpath by sediment layer is given in Table 4-31. Several patterns appear evident in this data. First, soluble fractions of most metals appear to increase with increasing depth, except aluminum and iron, which decrease with increasing depth. Second, exchange fractions of most metals increase with increasing depth. Third, carbonate associations of zinc, copper, aluminum, iron, and manganese appear to decrease with increasing depth while associations with the remaining metals increase. Sediment associations with Fe/Mn oxides were found to decline rapidly with increasing depth for all metals. This is presumably a result of lower values of pH and ORP at these lower sediment depths. Finally, two distinct patterns appear to be present for organic associations in the flowpath area. Metals such as cadmium, copper, iron, lead, and manganese increase in organic associations with The remaining metals, zinc, aluminum, phosphorus, nickel, and increasing depth. chromium, appear to increase in organic bonding with increasing depth, reaching a peak value at approximately 10 cm, followed by a rapid decline in organic associations below 10 cm.

Effects of pH and Redox Potential on Metal-Sediment Stability

Sediment core samples were incubated under various conditions of redox potential and pH, as described previously, to investigate the effects of changes in sediment conditions on the stability of metal-sediment associations. Redox potentials of +500 mV, +250 mV, 0 mV, and -250 mV, ranging from oxidized to highly reduced, and pH values of 5.0 and 6.5, characteristics of control and flowpath areas were investigated. The results of these incubations for cadmium, zinc, and manganese are

SUMMARY OF METAL SPECIATION IN THE TOP 20 cm OF THE FLOWPATH IN THE WETLAND AT HIDDEN LAKE

METAL	SEDIMENT	METAL ASSOCIATION (µg/g)							
SPECIATION		Cd	Zn	Cu	Al	P			
Soluble	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	0.05 0.07 0.10 0.10 0.09	0.09 0.09 0.12 0.09 0.14	0.21 0.14 0.15 0.23 0.47	21 42 13 7 4	1.97 2.46 3.12 6.87 7.95			
Exchange	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	0.46 0.54 0.59 0.53 0.55	3.68 7.56 6.18 5.96 4.79	< 0.01 0.04 < 0.01 < 0.01 < 0.01	25 32 38 35 40	2.49 3.21 5.37 9.12 9.34			
Bound to Carbonates	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	0.03 0.12 0.29 0.28 0.40	5.78 6.39 5.81 4.05 3.20	0.70 < 0.01 < 0.01 < 0.01 < 0.01	280 311 173 47 40	17.0 12.2 17.5 21.9 18.6			
Bound to Fe/Mn Oxides	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	0.15 0.06 0.10 0.11 0.15	21.6 17.0 11.4 6.50 4.15	0.80 0.45 0.21 0.70 0.35	1933 1544 621 596 179	66.0 22.8 26.8 35.2 31.8			
Organic Bound	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	0.04 0.03 0.08 0.04 0.16	9.60 10.7 14.4 8.83 8.88	3.55 3.20 5.07 5.18 5.64	5830 9016 9144 3994 3680	400 499 580 303 208			

METAL SPECIATION	SEDIMENT LAYER	METAL ASSOCIATION (μg/g)				
		Fe	Pb	Ni	Cr	Mn
Soluble	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	2 3 1 1 1	0.23 0.30 0.50 0.42 0.42	0.05 0.06 0.11 0.10 0.08	0.06 0.07 0.10 0.09 0.10	0.03 0.02 0.06 0.03 0.03
Exchange	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	3 6 6 4 8	< 0.01 6.67 8.00 6.00 5.33	0.44 0.60 0.73 0.60 0.72	0.13 0.25 0.51 0.45 0.62	4.78 5.42 6.39 4.84 4.94
Bound to Carbonates	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	13 13 9 4 5	4.30 4.21 7.81 6.83 9.00	< 0.01 0.02 0.18 0.21 0.35	0.10 0.16 0.21 0.05 0.10	2.69 1.66 1.89 0.81 0.85
Bound to Fe/Mn Oxides	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	993 1634 341 314 154	3.03 2.50 2.74 2.44 3.10	0.65 1.64 0.31 0.21 0.22	0.85 0.52 0.30 0.23 0.11	2.78 1.94 2.94 2.22 2.20
Organic Bound	0-1 cm 1-5 cm 5-10 cm 10-15 cm 15-20 cm	386 489 942 908 1398	1.08 1.55 4.97 7.78 7.85	1.26 2.05 2.46 1.71 2.27	5.87 7.95 7.62 3.26 4.13	0.97 1.11 1.92 1.66 2.34

TABLE 4-31 -- CONTINUED

presented in Figure 4-18. Each of these metals were more soluble at the lower pH of 5.0 than at 6.5. Both cadmium and manganese appear to be more soluble under oxidized conditions, while zinc is more soluble, particularly at the lower pH, under reduced conditions. At a pH of 6.5, approximately 40% of the total cadmium content in the sediments was released into solution. However, at a pH level of 5.0, the release of cadmium into the sediments was near 100%, suggesting that cadmium has little affinity for the sediment phase under these conditions. Zinc was released from the sediments at pH 6.5 in a manner similar to that of cadmium at the same pH. Manganese was released to a lesser degree than either zinc or cadmium, with approximately 10-20% release at pH 6.5 and 20-40% at pH 5.0.

The effects of pH and redox potential on the release of lead, nickel, and chromium are shown in Figure 4-19. The general patterns of release of lead and nickel from the wetland sediments appear to be very similar, although in general, lead was found to have less affinity for the sediments than nickel. Both metals were found to be more soluble under oxidized conditions than under reduced conditions. Chromium was more soluble at all redox potentials at pH 6.5 than at pH 5.0 and slightly more soluble under oxidized conditions than under reduced. This behavior suggests that control area sediments may be better suited to retain chromium than flowpath sediments.

The release of copper, aluminum, and iron from wetland sediments under various combinations of redox potential and pH is shown in Figure 4-20. Both aluminum and iron were more soluble under conditions of low pH. However, the solubility of iron increased under reduced conditions, while aluminum solubility increased under oxidized conditions. In general, the release of aluminum and iron was only a small fraction of



Figure 4-18. Release of Cadmium, Zinc, and Manganese from Wetland Sediments Under Various Combinations of Redox Potential and pH.



Figure 4-19. Release of Lead, Nickel, and Chromium from Wetland Sediments Under Various Combinations of Redox Potential and pH.



Figure 4-20. Release of Copper, Aluminum, and Iron from Wetland Sediments Under Various Combinations of Redox Potential and pH.

the total sediment content, with all measured release rates equal to 8% or less. As observed in most of the previous discussions, patterns involving copper were somewhat different than those observed for other metals. Under oxidized conditions at the higher pH value, copper was released almost completely from the wetland sediments. However, at a lower pH of 5.0, the release was less than 20% under the same redox conditions.

The release of phosphorus from wetland sediments is shown in Figure 4-21. Phosphorus was released in amounts ranging from 10-20%, indicating a substantial affinity of the sediments to retain phosphorus even under conditions of low pH and redox potential. The release of phosphorus was affected more by pH value than redox potential, with lower values of pH generally producing more release than higher values of pH. This trend is particularly evident under oxidized conditions, becoming less significant under reduced conditions.

<u>Rates of Nutrient and Heavy Metal</u> <u>Exchange in the Hidden Lake Wetland</u>

Five isolation experiments were conducted to provide information on the rates of nutrient and heavy metal uptake in circulated and stagnant systems, with and without sediment contact. A simulated stormwater solution was prepared with nutrient and heavy metal concentrations similar to those measured in residential stormwater runoff. Two sample collection ports, similar to those described previously for collection of surface water samples, were permanently installed inside each chamber. A thin polyethylene sheet was placed over the sediments in one of the chambers so that test waters could be isolated from the sediments. The other two chambers allowed free contact with the wetland sediments. Simulated stormwater solutions were then placed




inside each chamber, and changes in concentrations were monitored under various conditions.

In the first experiment, one chamber was established to simulate slow circulation and movement of water through the wetland with sediment contact at a residence time of 4.60 days. Another chamber was used to simulate sediment contact in a stagnant water system. The remaining chamber was used as a control system with circulation but no sediment contact. Samples were collected from each isolation chamber one hour after additions of the simulated stormwater mixture and then seven additional times during the 18-day experimental duration from 10/17/85 to 11/04/85, generally at one- to two-day intervals. The second rate experiment was set-up in the same manner as the first (residence time of 4.60 days) with the exception that the previous stagnant chamber was converted to the circulation system and the previous circulated chamber became the stagnant system. In the third rate experiment, the same experimental set-up as the second experiment was used, with the residence time being decreased by 50% to 2.3 days.

A complete listing of all experimental data collected during the three rate experiments is given in Appendix XII. In general, the patterns of chemical exchange within the three test chambers were very similar for each of the three long-term experiments. As an example, a summary of chemical characteristics for the first isolation experiment, conducted from 10/12/85 to 11/04/85, is given in Table 4-32. Each of the three chambers was found to exhibit a general slight decline in pH value of approximately 0.3 units over the 18-day period. This decrease in pH was accompanied by a corresponding overall decline in alkalinity, although each of the chambers increased somewhat in both pH and alkalinity during the period from 2-4 days. Dissolved oxygen

SUMMARY OF CHEMICAL CHARACTERISTICS IN LONG-TERM ISOLATION EXPERIMENTS CONDUCTED 10/17/85 TO 11/04/85

CHAMBER	INCUBATION PERIOD (days)	pН	COND. (µmho/cm)	D.O. (mg/l)	ALK. (mg/l)	NH₃-N (μg/l)	NO3-N (μg/l)	ORGANIC N (µg/l)	TOTAL N (μg/l)	ORTHO-P (µg/l)
Sediment	Initial	6.51	176	6.4	68.4	239	282	1397	1918	274
Contact	0.04	6.42	173	4.8	59.0	377	239	1017	1633	191
(Circulated)	1.00	6.48	174	1.5	65.3	482	48	730	1260	77
` ´	1.80	6.55	166	1.5	71.1	269	70	822	1161	80
	3.85	6.41	176	0.8	74.8	137	40	832	1009	68
	5.94	6.23	202	1.1	63.3	38	38	1174	1250	96
	8.94	6.38	209	1.7	62.7	51	44	888	983	113
	10.9	6.26	199	1.0	58.7	28	38	941	1007	59
	17.9	6.21	208	1.1	58.0	5	41	1150	1196	33
Sediment	Initial	6.51	176	6.4	68,4	239	282	1397	1918	274
Contact	0.04	6.32	172	3.0	70.0	441	201	710	1352	159
(Stagnant)	1.00	6.34	183	1.4	70.0	775	56	800	1631	80
,	1.80	6.42	182	1.9	69.5	829	43	746	1618	80
	3.85	6.36	201	1.4	74.2	876	51	881	1808	80
	5.94	6.22	212	0.7	69.5	596	55	616	1267	96
	8.94	6.28	192	1.4	57.4	317	43	986	1346	47
	10.9	6.21	170	1.5	60.5	191	35	1203	1429	44
	17.9	6.27	168	1.8	51.1	278	27	1479	1784	35
No	Initial	6.51	176	6.4	68.4	239	282	1397	1918	274
Sediment	1.00	6.74	175	5.6	72.7	100	264	1112	1476	261
Contact	1.80	6.64	166	4.2	78.4	11	241	958	1210	233
	3.85	6.42	173	1.6	73.2	< 10	38	785	828	170
	5.94	6.30	193	1.6	63.2	· < 10	37	787	829	169
	8.94	6.34	192	1.0	58.5	< 10	26	843	874	125
	10.9	6.26	185	0.7	55.3	< 10	24	783	812	69
	17.9	6.22	186	1.2	44.8	< 10	21	786	812	64

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concentrations also declined in each chamber, although much more rapidly with sediment contact than without sediment contact. The circulated chamber with sediment contact became anaerobic (< 1 mg/l) after 2-3 days, while the stagnant chamber with sediment contact became anaerobic after approximately 4 days. The control chamber with no sediment contact required 9 days for dissolved oxygen levels to go below 1 mg/l.

Concentrations of nitrogen species were affected to varying degrees during the 18day incubation. In the chamber which was circulated with sediment contact, ammonia increased for approximately 2 days, then decreased rapidly to extremely low levels. Removal of nitrate by the sediments was even more rapid, with a removal of approximately 85% after 2 days. Concentrations of soluble organic nitrogen declined only slightly over the test period although fluctuations were apparent. Total nitrogen declined by approximately 40% after 1-2 days, largely as a result of decreases in ammonia and nitrate. The behavior of nitrogen removal in the stagnant chamber without circulation was substantially different than the circulated chamber. In the absence of circulation, ammonia was not removed and actually increased after 4 days to values 260% greater than initial values. Nitrate, however, was removed in a manner similar to that observed in the circulated chamber with the majority of the observed removal occurring in the first 1-2 days. Organic nitrogen exhibited an initial decrease of near 40% in the first few days, but had increased to initial levels at the end of the experiment. Removal of total nitrogen in the stagnant chamber was much less than that of the circulated chamber due largely to the lack of ammonia removal. The chamber with no sediment contact was found to have rapid and virtually complete removal of both ammonia and nitrate after 2 days, suggesting that sediments are not an important

component in this removal process. Reductions in organic nitrogen of approximately 40% and in total nitrogen of 60% were observed with no sediment contact.

Removal of orthophosphorus in chambers with sediment contact was observed to be rapid, with the majority of removal occurring in the first 24 hours. Final equilibrium concentrations in the chambers with sediment contact appear similar either with or without mixing action. Removal of phosphorus in the control chamber with no sediment contact was both much slower than was observed with sediment contact and also reached a final equilibrium value approximately twice that found with sediment contact. Therefore, unlike the trends observed for nitrogen, the sediments appear to be very important in regulating both the rate and extent of phosphorus removal in the wetland. Removal of orthophosphorus in each of the three isolation chambers for this experiment is summarized in Figure 4-22.

A summary of heavy metal concentrations in the same initial isolation experiment is given in Table 4-33, along with field measurements of ORP in each of the chambers. Several important trends are apparent in this data. First, the sediments are extremely important in regulating the removal of heavy metals from the water column. In the presence of sediment contact in the circulated system, maximum removal of most metals occurred in the first 3-4 days, although substantial removals were apparent for all species, except aluminum and iron, after only 24 hours. The chamber without sediment contact reacted much more slowly with maximum removals for most metals observed after 6 days, and at equilibrium concentrations in most cases which were greater than the sediment chambers.



Figure 4-22. Removal of Dissolved Orthophosphorus in Long-Term Isolation Experiments at Hidden Lake With and Without Sediment Contact.

SUMMARY OF HEAVY METAL CONCENTRATIONS IN LONG-TERM ISOLATION EXPERIMENTS CONDUCTED FROM 10/17/85 TO 11/04/85

CUAMPER	INCUBATION			DISS	OLVED MI	ETAL CON	CENTRATI	ON (µg/l)			ORP
	(days)	Cd	Zn	Mn	Cu	Al	Fe	Рb	Ni	Cr	(mV)
Sediment	Initial	19	80	22	106	181	258	110	24	22	247
Contact	0.04	11	47	17	155	241	323	53	15	15	279
(Circulated)	1.00	13	46	6	119	256	303	57	9.8	12	268
	1.80	14	32	7	90	324	348	51	8.4	11	264
	3.85	12	20	11	39	153	255	32	4.4	5.0	284
	5.94	3.3	13	8	50	98	224	34	7.7	3.2	263
	8.94	2.9	13	2	19	39	191	33	5.5	3.6	267
	10.9	4.6	29	28	31	133	271	53	8.1	8.1	237
	17.9	4.2	22	17	22	145	206	46	5.2	4.6	246
Sediment	Initial	19	80	22	106	181	258	110	24	22	247
Contact	0.04	16	48	8	37	154	164	27	8.6	7.4	236
(Stagnant)	1.00	13	34	15	59	232	216	49	8.0	11	220
	1.80	16	85	12	84	200	266	52	13	10	198
	3.85	17	27	3	42	225	725	45	7.5	7.6	169
	5.94	3.8	42	16	57	184	344	37	5.2	2.4	177
	8.94	4.3	18	8	48	165	478	45	7.3	7.1	192
	10.9	3.9	23	4	27	182	382	43	7.7	8.1	187
	17.9	3.8	25	5	23	161	391	46	6.6	6.9	241
No	Initial	19	80	22	106	181	258	110	24	22	247
Sediment	1.00	18	71	18	101	204	258	107	24	22	243
Contact	1.80	12	26	13	53	231	282	40	15	17	234
	3.85	16	46	4	63	209	274	77	19	18	217
	5.94	4.3	34	8	38	185	134	60	13	9.3	229
	8.94	4.6	46	24	32	128	197	65	19	16	224
	10.9	2.9	38	28	34	137	201	90	17	17	214
	17.9	2.4	37	39	31	142	153	53	16	16	210

Another important factor in the removal of heavy metals from the water phase is the ORP value. For example, the circulated chamber with sediment contact exhibited excellent metal removal until approximately day 10 when the ORP dropped below 240 mV. At that point, concentrations of metal species increased substantially. The stagnant chamber with sediment contact was found to have values of ORP less than 240 mV during the first day. Removal of metal species was still observed to occur in this chamber but at a much slower rate with final equilibrium values similar to those measured in the circulated chamber at values less than 240 mV.

Although all of the measured metal species appear to be affected by sediments and by changes in redox potential, iron is approximately affected to the greatest degree. A summary of the behavior of both iron and aluminum from the experiments conducted from 11/8/85 to 11/22/85 is given in Figure 4-23. Under oxidized conditions and in the absence of sediment contact, both aluminum and iron can be removed from the water phase to a small degree. However, in the presence of sediment contact under oxidized conditions, both metals appear to reach equilibrium concentrations near 250 μ g/l. As the water phase becomes reduced, concentrations of aluminum increased slightly while concentrations of iron increased two-fold and appeared to be increasing even further.

The final two isolation chamber experiments were designed to examine the shortterm removal kinetics of pollutant concentrations over a 24-hour incubation period. Only two isolation chambers were used in the simulations, one with sediment contact and one without. Two refrigerated ISCO automatic sequential samplers were used in the sampling process so that samples could be collected on a regular basis over the 24-hour period. Experiments were conducted on two separate dates and a summary of mean



Figure 4-23. Fate of Aluminum and Iron in Long-Term Isolation Experiments at Hidden Lake.

chemical characteristics for the two experiments is given in Table 4-34. In the chamber with no sediment contact, measured values of pH, conductivity, alkalinity, nitrate, organic nitrogen, and total nitrogen were relatively unchanged. Small reductions in concentrations were observed for ammonia and orthophosphorus over the 24-hour period. However, in the presence of sediment contact, pH, conductivity, alkalinity, nitrate, organic nitrogen, total nitrogen, and orthophosphorus declined in measured values substantially. The only measured parameter which was not reduced in value was ammonia which actually appeared to increase in concentration over the 24-hour period. Measurements of ORP indicated an aerobic water column in both chambers at the end of the 24-hour experiment.

A summary of the removal characteristics of phosphorus for the two experiments is given in Figure 4-24. The removal potential for dissolved orthophosphorus was found to be greatest in the experiments involving direct sediment contact. In both experiments, the removal potential of the system with sediment contact averaged 75%, whereas the removal potential of the system without sediment contact averaged only 15% during the 24-hour experimental incubation period. As seen in Figure 4-24, both experiments behaved similarly with respect to the short-term removal kinetics of dissolved orthophosphorus. The removal of phosphorus in both experiments was found to reach an "equilibrium concentration" of approximately 50 μ g/l within the wetland system after an incubation period of 24 hours.

Characteristics of nitrogen removal for the short-term experiments are shown in Figure 4-25. The sediments appear to be a source of ammonia to the water column since concentrations of ammonia decrease without sediment contact and increase in the

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS IN 24-HOUR RATE EXPERIMENTS CONDUCTED ON 1/21/86 AND 1/23/86

CHAMBER	INCUBATION PERIOD (hours)	рН	COND. (mg/l)	ALK. (mg/l)	NH3-N (μg/l)	NO3-N (μg/l)	ORGANIC N (µg/l)	TOTAL N (µg/l)	ORTHO-P (µg/l)
With	Initial	6.47	175	71.0	285	278	674	1227	216
Sediment	0.25	6.97	164	68.6	205	225	671	1257	165
Contact	1.00	6.53	157	68.1	250	218	557	1036	149
	3.00	6.43	161	67 .1	278	206	510	994	135
	5.00	6.32	160	65.5	297	190	445	932	118
	7.00	6.27	153	63.3	310	180	463	953	106
	9.00	6.30	152	62.4	306	165	422	893	95
	11.00	6.28	152	60.7	315	156	503	974	86
	13.00	6.23	1 48	58.0	319	155	409	883	82
	15.00	6.33	145	58.0	331	141	367	839	76
	17.00	6.37	1 43	57.1	339	127	434	900	69
	19.00	6.45	142	56.1	337	123	39 1	851	61
	21.00	6.38	149	53.5	341	138	463	942	56
	23.00	6.29	142	53.6	305	115	468	888	54
	25.00	6.18	148	53.7	332	1 06	458	896	57
Control	Initial	6.47	175	71.0	265	278	674	1217	221
(No Sediment	1.00	6.41	183	71.0	258	273	658	1189	214
Contact)	3.00	6.46	186	72.3	230	275	651	1156	210
ŗ	5.00	6.50	183	70.9	244	279	665	1188	207
•	7.00	6.58	186	71.5	251	275	659	1185	206
	9.00	6.53	183	70.6	251	277	659	1187	202
	11.00	6.54	182	70.8	235	282	659	1176	200
	13.00	6.54	185	72.3	225	274	609	1108	196
	15.00	6.53	185	72.5	200	272	648	1120	193
	17.00	6.63	182	70.8	190	249	674	1113	188
	19.00	6.60	183	70.9	192	246	566	1004	182
	21.00	6.52	188	70.9	174	269	644	1087	189
	23.00	6.48	190	70.3	156	257	60 1	1014	187



Figure 4-24. Changes in Concentrations of Dissolved Orthophosphorus in Isolation Chambers With and Without Sediment Contact Over a 24-Hour Period.



Figure 4-25. Mean Changes in Concentrations of Nitrogen Species in Isolation Chambers With and Without Sediment Contact for Experiments Conducted 1/21/86 and 1/23/86.

presence of sediments. However, the sediments do not appear to be a source of nitrate since nitrate concentrations remained constant in the absence of sediments and decreased in the presence of sediments.

A summary of mean heavy metal removal for the two short-term experiments in given in Table 4-35. In the absence of sediment contact, virtually no removal of any heavy metals were observed. However, in the chamber with sediment contact, removal of all measured metals was observed to some degree over the 24-hour period, except aluminum and iron. Removals from the water phase appeared to be greatest for zinc, lead, and nickel, while cadmium, manganese, copper, and chromium were reduced only slightly.

A summary of the removal characteristics for zinc and lead is given in Figure 4-26. In the absence of sediment contact, lead does not appear to be removed to any degree, while zinc is removed slightly. However, in the presence of sediments, both lead and zinc exhibit substantial initial uptake, followed by a gradual further decline for lead and a more rapid decline for zinc. A summary of the removal characteristics of copper and nickel is given in Figure 4-27. Both copper and nickel do not appear to be removed in the absence of sediment contact. However, in the chamber with sediment contact, a small removal of copper was observed, while a much larger removal of nickel was found.

Channel Experiments

As described in Chapter 3, a 30 m long channel was constructed and filled with wetland soil to examine the effects of flow rate and retention time on the removal of

SUMMARY OF MEAN HEAVY METAL CONCENTRATIONS IN 24-HOUR RATE EXPERIMENTS CONDUCTED ON 1/21/86 AND 1/23/86

	INCUBATION			DI:	SSOLVED N	IETAL CONC	CENTRATION	(μg/l)		
CHAMBER	(hours)	Cđ	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr
With	Initial	6.2	37	7	57	103	56	43	19	9.6
Sediment	0.25	5.2	28	5	45	119	78	51	11	10.1
Contact	1.00	5.1	26	4	57	128	84	46	10	10.8
	3.00	5.1	29	5	51	201	94	61	8.9	10.2
	5.00	5.0	22	5	42	209	112	48	8.3	7.5
	7.00	5.3	20	4	44	218	84	43	7.6	10.0
	9.00	4.7	20	5	38	182	100	41	6.8	10.2
	11.00	4.8	19	5	40	198	121	44	6.6	9.9
	13.00	3.8	17	5	39	163	102	36	4.5	7.1
	15.00	4.0	14	4	41	149	97	35	3.9	6.8
	17.00	4.6	14	3	34	164	98	37	4.2	7.7
	19.00	5.4	14	6	27	164	102	39	4.3	9.4
	21.00	5.4	13	3	30	171	108	38	4.2	8.8
	23.00	5.6	11	6	35	170	108	38	4.4	8.2
	25.00	4.1	10	2	34	181	118	30	3.9	7.1
Control	Initial	6.2	37	7	57	103	56	44	19	9.6
(No	1.00	6.7	35	6	55	107	63	51	19	10.0
Sediment	3.00	7.2	42	5	43	140	73	64	16	10.3
Contact)	5.00	7.5	42	5	57	136	71	58	16	9.2
	7.00	7.1	31	5	52	107	- 78	46	19 ·	11.2
	9.00	7.9	30	8	56	137	89	58	15	14
	11.00	5.8	33	8	64	120	79	63	17	14
	13.00	7.1	28	6	45	124	81	59	17	13
	15.00	6.2	22	4	46	89	73	56	17	14
	17.00	8.1	23	7	39	103	96	63	15	14
	19.00	9.6	27	8	50	123	94	82	16	13



Figure 4-26. Removal of Dissolved Lead and Zinc in Short-Term Isolation Experiments at Hidden Lake.



Figure 4-27. Removal of Dissolved Copper and Nickel in Short-Term Isolation Experiments at Hidden Lake.

pollutants in a simulated stormwater mixture. A total of six experiments were conducted with flow velocities ranging from 0.36 to 0.02 m/min and residence times between 1.39 and 25.0 hours. Longer retention times were difficult to maintain since losses due to evaporation and transpiration over periods in excess of 25 hours reduced the water volume in the channel to levels where a continuous flow no longer occurred. A complete listing of the chemical characteristics of the six channel experiments is given in Appendix XIII, and a summary of the six experiments is given in Table 4-36.

Measured values of pH, initially in a relatively neutral state, did not appear to be affected to a large degree by either retention time or distance along the flow channel. Both conductivity and alkalinity were found to decrease with increasing flow distance at the shortest retention time of 1.39 hours, but appeared to increase slightly over the same flow distance at longer retention times. A similar pattern was observed for ammonia with retention times of 1.39 hours producing a decrease in concentration, while longer retention times increased concentrations. At longer retention times, ammonia concentrations increased substantially over the 30 m flow distance. An opposite pattern was observed for organic nitrogen. Organic nitrogen was found to increase with increasing flow distance at the lower residence times and decreased with increasing flow distance at the longest residence time of 24 hours. Concentrations of nitrate were removed almost completely over the 30 m distance at residence times up to 4 hours. Above a residence time of 4 hours, removal of nitrate was still observed although the maximum removal dropped to 50% at a residence time of 25 hours. Removal of orthophosphorus appeared to be closely correlated with residence time, with net removals observed at residence times of 4 hours or more and net increases at shorter residence times.

SUMMARY OF CHEMICAL CHARACTERISTICS OF CHANNEL EXPERIMENTS USING HIDDEN LAKE WETLAND SOILS

	UNITS OF	EXPERI CHARAC	MENTAL TERISTICS	MEAN	RATIO OF MEASURED CONCENTRATION TO INPUT CONCENTRATION			
PARAMETER	UNITS OF MEASUREMENT	MEAN FLOW VELOCITY (m/min)	RETENTION TIME (hr)	INPUT CONCENTRATION	10 m	20 m	30 m	
рН	units	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	7.41 6.48 6.74 6.52 6.19 6.61	1.01 0.99 1.02 1.01 0.99 1.01	1.05 0.98 1.02 0.99 0.95 1.00	0.93 0.97 1.17 0.98 0.94 1.00	
Conductivity	µmho/cm	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	247 259 273 261 245 234	1.08 1.02 1.02 1.01 1.02 0.97	0.81 1.05 1.07 1.03 1.05 1.03	0.74 1.06 1.05 1.04 1.07 1.05	
Alkalinity	mg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	134 127 119 131 115 106	0.89 0.98 1.03 0.92 1.03 1.17	0.60 0.91 1.04 0.95 1.10 1.11	0.50 0.99 1.07 0.96 1.04 1.18	
NH₃-N	μg/1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	54 46 49 44 45 21	1.19 1.04 0.44 1.00 1.00 2.19	0.72 1.37 1.33 0.75 1.02 2.52	0.54 1.78 0.67 1.30 2.40 3.86	

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TABLE 4-36 -- CONTINUED

	UNITS OF	EXPERI CHARAC	MENTAL TERISTICS	MEAN	RATIO OF MEASURED CONCENTRATION TO INPUT CONCENTRATION			
PARAMETER	MEASUREMENT	MEAN FLOW VELOCITY (m/min)	RETENTION TIME (hr)	INPUT CONCENTRATION	10 m	20 m	30 m	
NO3-N	μ <u>g</u> /l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	133 196 226 180 179 102	0.04 0.10 0.23 0.23 0.47 0.64	0.04 0.03 0.25 0.12 0.35 0.76	0.04 0.03 0.04 0.03 0.31 0.53	
Organic N	μg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	98 106 72 123 238 343	2.59 1.55 2.22 1.00 0.87 1.01	6.87 2.12 2.25 0.97 0.80 0.99	10.4 2.51 2.69 1.02 0.67 0.83	
Ortho-P	μg/1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	58 64 64 81 84 250	1.52 0.86 0.92 0.59 0.73 0.87	2.03 1.30 1.06 0.57 0.75 0.62	2.21 1.38 1.02 0.75 0.79 0.62	
тос	mg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	22.5 7.4 1.9 1.7 1.6 2.2	1.06 1.30 1.21 1.12 1.69 1.55	0.56 1.46 1.89 1.06 1.56 1.50	0.62 1.68 1.58 1.29 1.13 1.64	

TABLE4-36 -- CONTINUED

	UNITS OF -	EXPERI CHARAC	MENTAL TERISTICS	MEAN	RATIO OF MEASURED CONCENTRATION TO INPUT CONCENTRATION			
PARAMETER	MEASUREMENT	MEAN FLOW VELOCITY (m/min)	RETENTION TIME (hr)	INPUT CONCENTRATION	10 m	20 m	30 m	
Dissolved Cd	μg/ 1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	7.1 6.6 3.8 3.7 9.6 6.1	0.89 0.91 1.00 1.00 1.15 1.13	0.96 0.89 1.47 1.14 1.35 1.28	1.10 1.05 1.66 1.05 1.67 1.26	
Dissolved Zn	μg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	187 179 68 51 48 41	0.17 0.53 0.65 0.61 0.46 0.66	0.06 0.23 0.59 0.61 0.44 0.66	0.05 0.09 0.16 0.39 0.40 0.51	
Dissolved Cu	μg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	43 83 22 79 40 24	0.49 0.71 0.64 0.13 0.23 0.92	0.60 0.58 0.77 0.10 0.20 0.46	0.56 0.17 0.73 0.10 0.15 0.33	
Dissolved Al	μg/1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	93 69 59 72 69 64	1.15 1.33 1.08 1.07 1.07 1.61	2.16 1.94 1.41 1.54 0.68 1.05	1.70 1.70 1.31 1.03 0.65 0.94	

TABLE4-36 -- CONTINUED

	UNITS OF	EXPERI CHARAC	MENTAL TERISTICS	MEAN	RATIO OF MEASURED CONCENTRATION TO INPUT CONCENTRATION			
PARAMETER	MEASUREMENT	MEAN FLOW VELOCITY (m/min)	RETENTION TIME (hr)	INPUT CONCENTRATION	10 m	20 m	30 m	
Dissolved Fe	μ <u>g</u> /l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	28 20 27 42 35 44	2.21 3.90 0.67 0.98 1.23 0.71	2.36 2.25 0.67 0.93 1.34 0.66	3.82 3.40 1.04 0.57 1.23 0.61	
Dissolved Pb	μg/l	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	53 50 53 51 61 48	0.92 1.06 0.87 0.81 1.13 1.00	0.68 0.88 0.92 0.86 1.30 1.19	0.72 0.88 1.08 0.96 1.77 1.21	
Dissolved Ni	μg/1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	5.8 4.5 6.6 5.2 10.0 5.5	0.97 1.29 0.56 0.92 1.30 0.82	0.97 0.91 0.73 0.92 1.50 1.71	0.88 1.11 1.18 1.23 2.40 1.60	
Dissolved Cr	μg/1	0.36 0.26 0.16 0.12 0.07 0.02	1.39 1.92 3.13 4.17 7.14 25.0	0.6 0.7 1.9 5.0 11.0 6.1	0.83 1.14 0.53 1.14 1.36 0.90	0.33 0.43 0.58 1.28 1.63 1.80	0.83 0.57 0.79 1.30 2.30 1.80	

Of the heavy metals measured, the best removal efficiencies were observed for zinc. Removal of zinc averaged 90-95% at residence times of 2 hours or more, but declined to only 50% at 25 hours. Cadmium, lead, nickel, and chromium appeared to exhibit similar removal characteristics. For each of these metals, a small removal was observed at short retention times, generally less than 2 hours. However, at longer retention times, the sediments appear to act as a source of these metals into the water column. Similar patterns were also observed for aluminum and iron. Removal of these metals appears to be improved by longer retention times since both metals were added to the water column at short residence times and removed when the residence times exceeded approximately 10 hours.

Core Column Studies

As described previously, two separate sets of column studies were conducted on 1 m core samples collected within the wetland. The first set of core columns were collected on April 13, 1985 at locations near three of the groundwater monitoring sites. After returning to the laboratory, a synthetic stormwater solution was passed through the columns at varying flow rates for 110 days. Approximately 200 liters of a synthetic stormwater mixture was prepared in a large plastic tank. A small pump was used to pump the mixture from the tank into the columns and an overflow tube, which returned excess water to the tank, was used to maintain a constant head on each column.

For these experiments, the same stormwater solution was used for the entire experiment. However, analyses indicated wide fluctuations in many measured parameters in the mixture, presumably as a result of biological activity within the tank over time. Some parameters such as orthophosphorus declined significantly over this period. These widely fluctuating concentrations made comparisons to the effluent difficult, and the validity of these experiments were questioned. In addition, green algae had begun to reproduce inside the clear polycarbonate tubes leading to further questions of the results. As a result, it was decided to conduct another set of core experiments which corrected the problems evident in the first set.

The second set of three 1 m long core columns was collected on September 11, 1985 with each collected from areas near the 150 m flowpath well. During this set of experiments, the columns were tightly wrapped with aluminum foil to prevent light penetration and the stormwater solution was prepared weekly. Chemical characteristics of the simulated mixture remained relatively stable using this technique. A complete listing of the data collected during this experiment is given in Appendix XIV.

A summary of mean influent and effluent characteristics during the second column study is given in Table 4-37. Each of the columns was allowed to flow by gravity. Even though all columns were collected within the same area, three distinct flow rates were obtained in the columns with each one approximately one-half of the rate of the previous column. Flow rates were 0.21 m/day, 0.13 m/day, and 0.08 m/day, corresponding to retention times of 4.76, 7.69, and 12.5 days, respectively. Input concentrations were intended to simulate concentrations commonly found in stormwater runoff.

As seen in Table 4-37, input concentrations of all parameters were reduced during travel through the columns except ammonia, color, and iron. Measured values of pH dropped approximately 0.5 unit during flow through the 1 m columns. Corresponding

SUMMARY OF MEAN INFLUENT AND EFFLUENT CHARACTERISTICS IN CORE COLUMN INVESTIGATIONS

	LINUTO	INPUT	FLOW = 0 R.T. = 4	0.21 m/day .76 days*	FLOW = (R.T. = 7	0.13 m/day 7.69 days	FLOW = 0.08 m/day R.T. = 12.5 days		
PARAMETER	UNITS	VALUE	MEAN VALUE	PERCENT CHANGE	MEAN VALUE	PERCENT CHANGE	MEAN VALUE	PERCENT CHANGE	
pH Conductivity Alkalinity NH ₃ -N NO ₃ -N Organic N Ortho-P Color	s.u. µmho/cm mg/l µg/l µg/l µg/l µg/l Co-Pt Units	6.23 199 107 111 335 422 252 44	5.64 139 47.8 616 128 221 58 115	- 9.5 - 30 - 55 + 455 - 62 - 48 - 77 + 161	5.73 140 56.3 1000 38 246 89 159	- 8.0 - 30 - 47 + 801 - 89 - 42 - 65 + 261	5.71 157 61.5 780 31 374 71 178	- 8.3 - 21 - 43 + 603 - 91 - 11 - 72 + 305	
<u>Dissolved</u> <u>Metals</u>	· · · · ·								
Cd Zn Mn Cu Fe Pb Ni Cr	μg/l μg/l μg/l μg/l μg/l μg/l μg/l	17.4 53 8.2 157 39 65 34 6.7	4.5 11 6.0 26 126 38 5.5 3.6	- 74 - 79 - 27 - 83 + 223 - 42 - 84 - 46	5.1 9.6 6.9 30 172 35 4.4 2.6	- 71 - 82 - 16 - 81 + 341 - 46 - 87 - 61	5.1 35 7.6 27 121 49 6.3 4.7	- 71 - 34 - 7.3 - 83 + 210 - 25 - 82 - 30	

decreases in alkalinity were also observed. Concentrations of ammonia increased substantially during travel in the columns, with larger increases at slower flow rates. Both nitrate and organic nitrogen were decreased during travel, with nitrate removal increasing with decreasing flow rates and organic nitrogen removal decreasing with decreasing flow rates. Orthophosphorus removal averaged 71% for the three columns and appeared to decrease slightly at longer retention times.

Of the heavy metals measured, zinc, cadmium, copper, and nickel were removed very effectively by the wetland soils with removal efficiencies ranging from 74-87%. Although the removal of zinc decreased substantially at the longest retention time of 12.5 days, other metals, such as manganese, lead, and chromium, were removed to lesser degrees. Similar to the pattern noted for zinc, the removal of manganese, lead, and chromium decreased substantially at the longest retention times.

Correlations between pH, alkalinity, and flow rate and the remaining measured parameters are listed in Table 4-38. Significant positive correlations were found between pH and nitrate, orthophosphorus, color, and all of the heavy metals except manganese. The correlation between pH and iron was negative, indicating that decreases in pH result in increases in concentrations of iron. Significant correlations were found between alkalinity and each of the measured parameters. All correlations with alkalinity were positive, suggesting that increases in alkalinity produce increases in other measured parameters, except for ammonia, BOD, color, and iron, which exhibited negative correlations. Some of the calculated correlation coefficients were particularly large, especially for orthophosphorus (r = 0.633), cadmium (r = 0.692), zinc (r = 0.628), copper (r = 0.801), and nickel (r = 0.724). Correlations with flow rate or retention

CORRELATIONS BETWEEN pH, ALKALINITY, AND FLOW RATE WITH OTHER PARAMETERS IN THE CORE COLUMN INVESTIGATIONS

	р	H	ALKA		FLOW	RATE
PARAMETER	PROB. OF CORR.	VALUE OF r	PROB. OF CORR.	VALUE OF r	PROB. OF CORR.	VALUE OF r
NH ₃ -N	82.1	- 0.135	99.9	- 0.492	99.9	- 0.373
NO3-N	99.8	0.302	99.9	0.356	27.6	- 0.039
Organic N	21.2	0.027	99.9	0.469	55.7	0.085
Ortho-P	99.9	0.495	99.9	0.633	99.9	- 0.377
BOD	27.1	0.035	99.0	- 0.256	99.8	- 0.327
Color	99.9	- 0.333	99.9	- 0.518	99.9	- 0.560
Dissolved Metals						
Cd	99.9	0.485	99.9	0.692	22.3	- 0.031
Zn	97.3	0.219	99.9	0.628	68.3	- 0.110
Mn	67.3	0.098	99.2	0.262	97.3	0.241
Cu	99.9	0.450	99.9	0.801	92.7	0.197
Fe	99.6	- 0.288	99.9	- 0.459	3.6	0.006
Рb	99.9	0.427	99.9	0.558	99.9	- 0.445
Ni	99.9	0.495	99.9	0.724	48.6	- 0.072
Cr	99.9	0.444	99.8	0.311	98.2	- 0.258

time were the weakest correlations measured for most parameters. Significant positive correlations were found between flow rate and ammonia and manganese, while negative correlations were observed between flow rate and orthophosphorus, BOD, color, lead, and chromium. Increasing retention time apparently increases measured concentrations of these parameters.

<u>Changes in Algal Productivity of Stormwater</u> <u>Runoff During Flow Through the Hidden Lake Wetland</u>

Two algal bioassay experiments were conducted to evaluate changes in algal productivity of runoff inputs during surface flow through the wetland at Hidden Lake. <u>Selenastrum capricornutum</u> Printz, a unicellular test alga, was selected as the test organism in all of the bioassay experiments. In order that a unialgal test species could be used, any indigenous algae in the composite surface water samples were removed through autoclaving of the samples.

Algal bioassay experiments were designed to simulate a mixture of 25% wetland surface water from each of the fixed sample stations mixing into a receiving water accounting for the final 75% dilution. Hidden Lake, a highly colored water which is high in nutrients, and Lake Lee, a non-colored water which is low in nutrients, were chosen as the receiving waters for the tests. Water quality characteristics for the composite wetland and receiving water samples used in the algal bioassay experiments are presented in Table 4-39. Concentrations of dissolved orthophosphorus, TOC, and color in the composite samples were found to increase with flow distance within the wetland, whereas pH values remained within the neutral range.

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WATER QUALITY CHARACTERISTICS FOR COMPOSITE WETLAND AND RECEIVING WATER SAMPLES USED IN THE ALGAL BIOASSAY EXPERIMENTS DURING FEBRUARY 1986

	LINITS	STORM-			FL	OWPATH				CONTROL	HIDDEN	LAKE
FARAMETER	UNII 5	WATER	10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA	LAKE	LEE
pH Conductivity Alkalinity Organic-N Inorganic-N Ortho-P TOC	s.u. μmho/cm mg/l μg/l μg/l μg/l mg/l	6.75 136 33.7 299 72 25 10.2	6.92 143 49.5 296 54 18 7.4	6.95 132 51.6 281 50 24 11.0	6.67 133 42.3 352 65 25 12.4	6.65 118 49.5 377 56 40 14.0	6.78 113 54.8 367 80 54 13.9	6.77 124 46.3 337 119 61 14.4	6.79 115 51.6 498 122 77 16.4	6.81 123 49.5 1220 101 122 36.7	7.89 142 55.8 1322 233 54 39.1	8.13 126 61.1 187 117 15 12.6
Color	Pt-Co Units	69	85	80	85		127	109	214	583	489	
<u>Metals</u>												
Cd	μg/l	4.9	6.7	4.2	5.3	5.3	14.1	4.9	5.0	4.4	3.1	3.8
Zn	μg/l	13	15	13	16	22	26	22	21	38	31	14
Mn	μg/l	2	2	9	3	4	2	2	2	9	4	4
Cu	μg/l	57	46	77	56	42	45	56	76	131	32	68
Al	μg/l	170	140	108	167	155	156	125	164	299	273	69
Fe	μg/l	93	92	97	135	171	160	128	201	513	291	118
Pb	μg/l	26	31	29	33	36	28	24	23	19	12	0.9
Ni	μg/l	4.0	4.8	7.3	5.8	5.0	6.0	3.1	7.1	2.1	2.9	0.6
Cr	μg/l	2.0	3.9	3.1	5.4	5.2	4.7	4.1	3.7	2.8	2.8	2.1

The growth responses of <u>Selenastrum</u> in the composite surface water samples with Hidden Lake as the receiving water is graphically presented in Figure 4-28. The results indicate that the growth response of <u>Selenastrum</u> is relatively low in the wetland waters. In general, the cell yield decreased as the distance along the flowpath increased. The growth responses of the composite wetland samples along the flowpath observed the following order with respect to maximum yield:

$$10 \text{ m} > \text{Weir} > 50 \text{ m} > 75 \text{ m} > 125 \text{ m} > 25 \text{ m} > 150 \text{ m} > 100 \text{ m}$$

with the control area producing a maximum yield equivalent to that of the sampling station at 150 m.

The second algal bioassay experiment used Lake Lee, an oligotrophic water body, as the receiving water used in the composite water mixtures. Results of the experimental assay using <u>Selenastrum</u> are graphically depicted in Figure 4-29. The algal productivity based on maximum yield was found to be very low, with the greatest yield, 2.06 mg/l dry cell weight, occurring in the 125 m sample culture. Contrary to the trend observed using Hidden Lake as the test water, algal productivity in the Lake Lee water increased with increasing travel distance through the wetland. Maximum growth responses observed the following order:

$$125 \text{ m} > 150 \text{ m} = 100 \text{ m} > 75 \text{ m} > 50 \text{ m} > 10 \text{ m} > \text{Weir} > 25 \text{ m}$$

The experimentation indicates that the productivity of an oligotrophic receiving water body is influenced to a greater degree by inputs of wetland surface water than a colored, eutrophic receiving water.



Figure 4-28. Changes in Maximum Algal Production in Bioassay Experiments Conducted Using Composite Water Samples Collected Along the Flowpath in the Hidden Lake Wetland.



Figure 4-29. Changes in Maximum Algal Production in Bioassay Experiments Conducted Using Composite Water Samples Collected Along the Flowpath in the Wetland at Lake Lee.

CHAPTER 5

DISCUSSION

Introduction

The discussion of experimental results contained in this chapter is intended to present a logical progression of the fate of nutrients and heavy metals in the Hidden Lake wetland with special emphasis on the suitability of this treatment system for management of runoff inputs. It will begin with a discussion of the hydrology of the wetland following its modification for use as a stormwater management system. A comparison of rainfall and runoff characteristics will be given along with estimates of loading rates from the various inputs to the Hidden Lake wetland. Next, the fate of nutrients and heavy metals will be discussed along with factors which tend to increase or decrease the ability of the wetland to initially remove and retain these pollutants. Finally, recommendations will be made concerning specific design parameters which may improve or enhance the efficiency of wetland treatment systems.

Hydrology of the Hidden Lake Wetland

As indicated in Chapters 3 and 4, hydrologic inputs into the Hidden Lake wetland were monitored during 1984-86 through the following methods: (1) continuous measurement of surface water inputs into the wetland through the input canal; (2) measurements of daily evaporation at various locations within the wetland; (3) changes in piezometric surface within the wetland using a Stevens water level recorder; and (4) measurement of direct precipitation using a recording rain gauge.

A summary of hydrologic inputs and losses from the Hidden Lake wetland is given in Table 5-1. In this table, the fate of direct hydrologic inputs, calculated as the sum of baseflow plus runoff plus direct rainfall, are allocated into losses from the wetland itself and direct surface discharges to Hidden Lake. Direct losses from the wetland were calculated as the sum of evapotranspiration plus groundwater seepage using the measured seasonal values for these parameters given in Figures 4-5 to 4-7. In general, discharges to Hidden Lake were calculated as the difference between direct inputs and direct losses from the wetland. However, the following conditions must also be satisfied before a surface discharge to Hidden Lake was possible: (1) the piezometric surface in the wetland adjacent to Hidden Lake, as monitored at the control well (see Table 4-2) near Hidden Lake, must exceed the soil surface elevation of the wetland near Hidden Lake which is approximately 11.35 m; and (2) the surface elevation of Hidden Lake must be less than the piezometric surface in the wetland. Using these conditions, the surface discharges to Hidden Lake listed in Table 5-1 were calculated.

As seen in Table 5-1, approximately 70% of the total direct inputs into the wetland were retained there and lost by a combination of evapotranspiration and groundwater seepage. During six months of the study period, 100% of the direct inputs were totally retained with no surface discharge to Hidden Lake, and in 9 of the 12 months, retention within the wetland was in excess of 80% of direct inputs. However, during September, November, and December, a continuous direct hydrologic connection was established between the wetland and Hidden Lake, and retention of inputs within the

TABLE 5-1

SUMMARY OF HYDROLOGIC INPUTS AND LOSSES FROM THE HIDDEN LAKE WETLAND DURING 1985

•	DIRECT INPUTS	FATE OF	F INPUTS 1 ³)	FATE OF INPUTS (m ³)			
MONTH	(BASEFLOW + RUNOFF + RAINFALL) (m ³)	LOSS TO E.T. + G.W.* + CHANGE IN STORAGE	DISCHARGE TO HIDDEN LAKE	LOSS TO E.T. + G.W.*	DISCHARGE TO HIDDEN LAKE		
January	631.3	631.3	0.0	100.0	0.0		
February	895.3	895.3	0.0	100.0	0.0		
March	1,226.5	1,226.5	0.0	100.0	0.0		
April	2,564.9	2,564.9	0.0	100.0	0.0		
May	819.3	819.3	0.0	100.0	0.0		
June	5,031.9	4,440.8	591.1	88.3	11.7		
July	13,680.0	12,664.1	1,015.9	92.6	7.4		
August	22,075.0	22,075.0	0.0	100.0	0.0		
September	23,000.3	7,749.0	15,251.3	33.7	66.3		
October	9,358.2	7,749.0	1,609.2	82.8	17.2		
November	5,873.3	1,500.0	4,373.3	25.5	74.5		
December	6,438.8	1,500.0	4,938.8	23.3	76.7		
TOTAL	91,594.8	63,815.2	27,779.6	69.7	30.3		

* Sum of evapotranspiration plus groundwater seepage.

wetland was reduced to 25-35%. Approximately 88% of all discharges to Hidden Lake occurred during the three months listed above.

A summary of mean daily values of transpiration and evaporation in the Hidden Lake wetland by season is given in Table 5-2. Losses due to transpiration from plant surfaces far exceed losses from evaporation at the water surface. During the spring months when revegetation is occurring, transpiration accounts for 92% of all losses from the wetland with a total loss of approximately 11.89 mm/day. However, during the hot and humic summer months, transpiration rates were found to increase 66% over the spring period, while evaporation decreased by 22%. Total losses increased to a value of 18.95 mm/day. The fall and winter period produced the lowest rates of transpiration and evaporation measured during the year. Although transpiration was still the largest loss term, the mean value decreased by 75-85% from values measured during other times of the year. Total losses from the two terms combined averaged only 3.05 mm/day. A substantial reduction in leaf area as a result of leaf fall along with decreasing surface water temperatures contributed to these lower values.

A comparison of transpiration and evaporation rates in a cypress canopy from work by Brown et al. (1979) is also given in Table 5-2. In general, rates of transpiration in the cypress dome were found to be approximately one order of magnitude less than those measured in the hardwood wetland at Hidden Lake, while rates of evaporation were several times greater. Presumably, the more open character of a cypress dome contributed to an increase in evaporation, and the substantially smaller and evergreen type leaf of the cypress trees reduced transpiration losses. These significant hydrological differences between hardwood wetlands and cypress domes allow hardwood wetlands to

TABLE 5-2

COMPARISON OF RATES OF TRANSPIRATION AND EVAPORATION IN THE HIDDEN LAKE HARDWOOD WETLAND AND A CYPRESS CANOPY

PERIOD	HIDDEN LAKE WETLAND (mm/day)		CYPRESS CANOPY* (mm/day)	
	TRANSPIRATION	EVAPORATION	TRANSPIRATION	EVAPORATION
March-May June-October November-February	10.99 18.25 2.58	0.90 0.70 0.47	1.79 1.86 0.48	2.26 1.40 1.49

* SOURCE: Brown, Sandra L.; Flohrschutz, Eric W.; and Odum, Howard T. "Metabolism and Transpiration of Cypress Domes in North-Central Florida," Center for Wetlands, University of Florida, 1979.
act largely as retention areas during much of the year, while cypress domes are generally observed to be flow-through systems. This difference greatly enhances the attractiveness of hardwood areas as stormwater management systems since large portions of input volumes can be totally retained during many months of the year.

As discussed in a later section, maximizing retention of hydrologic runoff inputs within the wetland is necessary to achieve a net annual mass removal of runoff constituents such as ammonia, organic nitrogen, soluble phosphorus, and iron which often increase in concentration during flow through a peat wetland, particularly if the input concentrations are relatively low. By simply increasing the wetland treatment area or decreasing the contributing watershed area, it is possible to retain larger portions of direct inputs, relying on losses by evapotranspiration to reduce stored volumes. For example, the hardwood wetland area required to provide full retention of runoff inputs during the summer period for a typical month with 10 inches of rainfall on an average residential watershed with a runoff coefficient of 0.25 is 1.0 hectare of wetland for each 8.95 hectare of contributing watershed.

As seen in Table 4-1, the continuous seepage of baseflow into the wetland through the inflow canal constituted the largest single input to the wetland during the study period, accounting for an average of 44% of all direct inputs. In general, the percentage of direct inputs contributed by baseflow was greatest during the fall and winter seasons when rainfall is lowest, with baseflow accounting for as much as 60-77% of total inputs during this period. However, during the spring and summer months when rainfall was more abundant, runoff inputs became the largest input source and baseflow was reduced to only 15-30% of total inputs. The continual input of baseflow into the wetland through the inflow canal appears to be a dominant factor regulating the composition of the wetland community following modification of a wetland to serve as a stormwater management system. Although runoff inputs occur only during rain events, baseflow, derived largely from groundwater seepage into the input canal, is a continual input over much of the year, even during typically dry months when runoff inputs are infrequent or non-existent. This continual source has the effect of increasing the hydroperiod of the wetland to extend over much of the year.

In wetland systems such as hydric hammocks with an ordinary hydroperiod of 100-150 days, modification to serve as a stormwater treatment system would likely bring about a change in community structure by conversion to a wetland with a longer hydroperiod. This change in structure would occur relatively slowly with unpredictable effects on the ability of the system to absorb pollutants. It is likely that the hydroperiod of the Hidden Lake wetland has been increased as a result of its use as a stormwater treatment facility since the normal hydroperiod for a bayhead is 200-250 days, while a period of 320 days was measured in this research.

Visual observations indicated that changes in hydroperiod in the Hidden Lake wetland may be slowly altering the balance of the canopy species which is currently divided approximately equally between red maple, sweet bay and sweetgum. Germination of red maple seedlings is inhibited under inundated conditions and few young maples were observed in the wetland. Species of sweet bay and sweetgum, however, which are more tolerant of saturated soils, appear to be reproducing well. This trend, if it continues, may slowly bring about a change in canopy dominance from a

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mixture to a predominantly bay and sweetgum community. However, this community change appears gradual and is not likely to affect either ecosystem function or treatment ability to a significant degree. On the other hand, conversion of a community characterized by a short hydroperiod to one with a virtually continuous hydroperiod would likely result in a rapid and initially destructive alteration. As a result, wetland systems which appear best suited for modification as stormwater treatment facilities are those characterized by longer hydroperiods, such as cypress domes, bayheads, or marshes (see Table 2-2). Change in community structure in these systems appears less likely as a result of modification to serve as a stormwater treatment facility than systems with shorter hydroperiods.

As discussed in Chapter 4, estimates of loss in piezometric surface as a result of groundwater seepage were performed by measurement of decreases in piezometric surface during night time hours when transpiration was minimal. Using this method, losses due to groundwater seepage were found to be 5.84 mm/day in the spring (33% of total losses), 6.86 mm/day during the summer (27% of total losses), and 1.95 mm/day in the fall and winter (39% of total losses). While it is felt certain that losses were actually occurring at the point near well #2 where piezometric measurements were conducted, the fate of these losses is poorly understood and appears complex. Although it would initially seem likely to assume that the movement of groundwaters was in a general direction from the wetland to Hidden Lake, examination of the measurements of piezometric surface contained in Table 4-2 indicate that this is rarely the case. In fact, on all but three measurement dates, during the period from September to November, the piezometric surface in Hidden Lake was actually higher than the control area near the lake, and groundwater movement appears to be from Hidden Lake into the wetland.

As seen in Table 4-2, the lowest piezometric elevation in the study area was found near well #3 which was located near the 150 m flowpath station. During these times, the general pattern of groundwater movement appears to be from the inflow area of the wetland toward well #3 as well as from Hidden Lake toward well #3, creating somewhat opposing flow regimes, both of which terminated in this area. There are two apparent possible explanations for these unusual flow patterns. First, transpiration losses in this area could be much larger than those measured near well #2, resulting in a more rapid lowering of the piezometric surface in this area than in other areas. This possibility is supported by the observation that the area of the wetland near well #3 clearly contained the largest and most mature canopy species, dominated by extremely large red maple and bay species. Second, a fault or underground fracture of the underlying clay aquatard may have occurred in this area, allowing a rapid loss to deeper groundwaters. However, regardless of the actual reason for the somewhat unexpected flow pattern, general groundwater movement is apparently toward well site #3 from both Hidden Lake and the inflow region.

Rainfall/Runoff Characteristics

A comparison of mean chemical characteristics of rainwater and stormwater runoff collected at the Hidden Lake site is given in Table 5-3. Rainwater was found to be relatively dilute and low in concentration for all general parameters with the possible exception of nitrate and for all heavy metals with the exception of copper, which was the most concentrated heavy metal measured. Although the presence of elevated nitrate concentrations in rainwater is not surprising, elevated concentrations of copper are less

SUMMARY OF MEAN CHEMICAL CHARACTERISTICS OF RAINWATER AND STORMWATER COLLECTED AT HIDDEN LAKE

PAR	AMETER	UNITS	RAINWATER	STORMWATER
	pH	s.u.	4.76	5.91
Con	ductivity	µmho/cm		143
		mg/l	0.5	00
	urbiaity		0.0	0
	NFI3-IN	$\mu g/1$	04 126	50
	NO_3-N	$\mu g/I$	130	08
Ur	ganic N	$\mu g/1$	48	487
	rtno-P	$\mu g/1$	8	28
	otal P	μg/1	9	12
	BOD	mg/l	1.1	2.6
	Color	Pt-Co Units	11	85
R	lesidue	mg/l	32	135
	SS	mg/l	1.1	6.2
	TOC	mg/l	2.0	12.6
Oil	l/Grease	mg/l	0.0	3.6
Heav	vy Metals			
Cd	Diss.	μg/1	2.8	4.6
	Total	μg/1		5.2
		,		
Zn	Diss.	μg/1	13.7	4.6
	Total	$\mu g/l$		5.2
		,		
Mn	Diss.	μg/1	3.9	2.5
	Total	не/1		4.0
1		, PD , -		
Cu	Diss.	ug/1	27	19.6
	Total	μg/1		26.3
		r.o		
Al	Diss.	ug/1	24.3	20.6
	Total	μg/1		560
		1.0		
Fe	Diss.	μg/1	11.7	67.3
	Total	ug/1		114
		M9		
Ph	Diss.	<i>µ</i> ø/1	3.6	29.5
1.	Total	μσ/1		32.1
	1.0441	۳6 ^{, 1}		52.1
Ni	Diss	ug/1	12	32
***	Total	μα/1	-	37
	10441	μ ^β (1		5.1
Cr	Diss	uc/1	07	3 1
	Totel	μg/1	0.7	27
		με/1		5.1

understood. However, Nriagu (1979) indicates that copper can enter the atmosphere from a variety of natural and anthropogenic sources such as windblown dusts, forest fires, seasalt sprays, waste incineration, and coal combustion, all of which can contribute to elevated concentrations in rainwaters.

Since stormwater runoff originates as rainfall, differences in chemical characteristics between rainfall and runoff reflect the contribution and influence of the watershed over which the rainfall is deposited. Flow over the watershed area generally resulted in increases in concentrations of virtually all of the general parameters measured. The watershed was found to contribute substantial amounts of alkalinity, turbidity, organic nitrogen, phosphorus, residue, suspended solids, and TOC. However, contrary to the trends observed for other general parameters, mean concentrations of ammonia and nitrate were lower in runoff water than in rainwater, suggesting that the watershed has absorbed some of the original mass in the rainfall rather than contributing to it. Movement through the watershed was found to increase concentrations of cadmium, aluminum, iron, lead, nickel, and chromium while decreasing the concentration of zinc.

Of the heavy metals measured in rainfall, the following order was observed in terms of dissolved concentrations:

Cu > Al > Zn > Fe > Mn > Pb > Cd > Ni > Cr

while runoff waters were found to have the following order:

$$Al > Fe > Pb > Cu > Zn = Cd > Ni > Cr > Mn$$

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Contributions of aluminum, iron, and lead by the watershed to the runoff flow are clearly evident since each of these metals increases substantially in significance in runoff water over that found in rainfall. Excluding aluminum and iron, which are common constituents of soils, lead, copper, and zinc were the most abundant heavy metals in the runoff water, together accounting for 80% of dissolved heavy metals present and 79% of the total metals found.

This somewhat unusual trend for certain pollutants to actually decrease during travel through a watershed can be explained largely by the type of drainage system used at Hidden Lake. As discussed in Chapter 3, the drainage system consists primarily of a system of grassed swales which discharge into inlets near the inflow canal. In some areas of the development, this swale flow continues for several blocks before discharge into inlets. Harper (1985) reported that grassed swales can rapidly adsorb many runoff pollutants during flow over only a few hundred feet. Inorganic forms of nitrogen, soluble phosphorus, and zinc were found by Harper (1985) to be removed and retained by adsorption mechanisms particularly well. The swale system, therefore, appears to be functioning as a pre-treatment system which for some pollutants reduces concentrations to less than those found in the original rainwater.

A comparison of mean chemical characteristics of runoff waters collected at Hidden Lake with two other residential areas in central and southern Florida is given in Table 5-4. With the exceptions of conductivity and alkalinity, measured concentrations of every parameter tested are substantially lower at Hidden Lake than at the other residential sites. In general, most constituents at the other sites appear to be present in concentrations 5-10 times greater than those measured at Hidden Lake. Many of these

COMPARISON OF MEAN CHEMICAL CHARACTERISTICS OF RUNOFF WATERS COLLECTED AT THE HIDDEN LAKE WITH OTHER RESIDENTIAL SITES IN FLORIDA

			MEAN F	UNOFF CONCENT	RATION
PAR	RAMETER	UNITS	HIDDEN LAKE (22.36 ha)	LAKE EOLA ¹ (6.52 ha)	BROWARD COUNTY ² (18.5 ha)
	 pН	s.u.	5.91	7.72	
Co	nductivity	μ mho/cm	143	128	96
A	lkalinity	mg/l	66	67.3	
	urbidity	NTU	6	24	13
	NH ₃ -N	μg/I	56	250	. 330
	$NO_3 - N$	$\mu g/I$	08	2500	400
	rganic N	$\mu g/1$	48/	2270	210
	JIMO-P Datal D	$\mu g/1$	20	230 590	310
		$\mu g/1$	26	94	41
	Color	Pt-Co Units	85		31
l I	Color Residue	mg/l	135		113
· ·	SS	mg/l	6.2	80	26
	TOC	mg/l	12.6	72	14
Hea	vy Metals				
Cd	Diss.	μg/1	4.6		
	Total	μg/1	5.2		0.8
Zn	Diss.	μg/l	4.6		
	Total	μg/l	5.4		86
Mn	Diss.	μg/l	2.5		
	Total	μg/1	4.0		
Cu	Diss.	μg/1	19.6		
	Total	μg/l	26.3		8.0
Al	Diss.	μg/l	20.6		
	Total	μg/l	560		
Fe	Diss.	μg/l	67.3		
	Total	μg/1	114		298
Ph	Diss.	μø/l	29.5		
	Total	μα/1	32.1		167
		r.o.			
Ni	Diss.	μg/l	3.2		
	Total	μg/l	3.7		
Cr	Diss.	μg/l	3.1		
	Total	μg/l	3.7		

1. Wanielista, et al. (1982)

2. Mattraw and Miller (1981)

differences may be due to the pre-treatment effect of the swale drainage system, as discussed previously, but differences in activity levels and community design may also be important.

Mass loading rates from the Hidden Lake watershed were calculated using mean runoff concentrations and measured runoff volumes discharging through the input canal. These values are presented in Table 5-5 along with loading rates from a residential area near Lake Eola, near Orlando, Florida, for comparison. As observed for the measured concentrations of constituents in runoff waters at Hidden Lake, mass loading rates from the watershed are also extremely low. Loading rates for each parameter presented in Table 5-5 are substantially lower than values measured near Lake Eola with differences in some loading rates as much as a factor of 10 or more.

The extremely low loading rates of pollutants generated within the Hidden Lake watershed are presumably a result of two factors. First, concentrations of stormwater constituents in the Hidden Lake watershed are initially low as a result of pre-treatment by swale systems. Second, the swale drainage system allows a large part of the runoff volume to infiltrate into the ground and not reach the inflow canal where flow measurements were taken. As indicated in Table 3-2, the weighted runoff coefficient for the entire watershed was only 0.11 which is much lower than most published values for residential watersheds. The swale drainage system not only provided pre-treatment by reducing concentrations of runoff constituents, it also served to eliminate much of the total runoff volume. Therefore, the swale system was responsible for substantial reductions in mass loading rates from the watershed by improving runoff quality and reducing runoff quantity. As a result, the quality of runoff waters entering the treatment

COMPARISON OF MEAN MASS LOADING RATES FOR RUNOFF CONSTITUENTS FROM THE 22.36 HECTARE RESIDENTIAL WATERSHED AT HIDDEN LAKE AND A 6.52 HECTARE RESIDENTIAL WATERSHED AT LAKE EOLA, FLORIDA

PARAM	ETER	MASS LOAD FROM WA (kg/ha-	DING RATE TERSHED -year)
		HIDDEN LAKE (22.38 ha)	LAKE EOLA* (6.52 ha)
NHa	-N	0.062	
NO ₃	-N	0.076	2.20
Organ	ic N	0.543	1.80
Ortho	o-P	0.031	0.80
Tota	l P	0.080	2.20
BO	D	2.90	74.6
SS		6.91	195
TO	С	14.1	139
Heavy N	<u>Aetals</u>		
Cd	Diss.	0.005	
	Total	0.006	
Zn	Diss.	0.005	
	Total	0.006	
Mn	Diss.	0.003	
	Total	0.004	
Gu	Disa	0.022	
Cu	Diss.	0.022	
	1 otal	0.029	
A1	Diss	0.023	
	Total	0.624	
Fe	Diss.	0.075	
	Total	0.127	
Pb	Diss.	0.033	
	Total	0.036	
			·
Ni	Diss.	0.004	
	Total	0.004	
_			
Cr	Diss.	0.004	
	Total	0.004	

* Wanielista, et al. (1982)

system at Hidden Lake was found in this research to be better than that reported by many other researchers in waters leaving stormwater treatment systems.

As seen in Tables 4-3, 4-4, 4-6, and 4-7, a considerable variability was observed in the measured chemical characteristics of both rainwater and runoff between storm events. Attempts to explain this variability were conducted by performing correlations between runoff quality and storm event characteristics such as total rainfall, rainfall duration, antecedent dry period, and rain intensity as well as by ANOVA comparisons of rainfall and runoff quality during "wet" and "dry" seasons.

Most of the general water quality parameters as well as approximately half of the heavy metals were found to have significant correlations with total rainfall, but correlated poorly with rainfall duration, antecedent dry period, and rain intensity. Even though total rainfall was found to be significantly correlated with many runoff parameters, some of the correlations were negative, while the majority were positive, indicating that an increase in total rainfall results in an increase in runoff concentrations of these parameters. This relationship appears to violate the generally believed concept of "first flush" which predicts that concentrations of runoff constituents decrease with increasing rain amounts. However, it should be emphasized that the significant correlations observed were weak and explained in general only 5-37% of the variability in runoff characteristics.

The relatively poor ability of the correlation models to explain variations in runoff characteristics is indicative of the stochastic, poorly understood, and complex phenomenons regulating stormwater constituents and composition. These results are similar to those presented by Harper (1985) where poor correlations were found during attempts to correlate characteristics of highway runoff to parameters such as total rainfall, storm duration, antecedent dry period, and rain intensity, as well as work by Gupta et al. (1981), where poor correlations were found between metal concentrations in runoff and antecedent dry period.

A more conclusive examination of the effects of antecedent dry period on runoff characteristics can be obtained by examination of the ANOVA comparisons of rainwater and stormwater characteristics between "wet" and "dry" seasons. As seen in Table 4-5, only concentrations of copper and nickel were found to be significantly different in rainwater between "wet" and "dry" seasons, with copper found in greater concentrations during "wet" seasons and nickel greater in "dry" seasons. However, as seen in Table 4-10, virtually every runoff parameter measured was found in significantly greater concentrations during "dry" periods, characterized by long antecedent dry periods, than during "wet" periods of frequent rainfall. Accumulation of pollutants within the watershed between rain events with subsequent transfer to the runoff flow is readily apparent in this table, particularly for heavy metals.

<u>General Effects of Runoff Inputs</u> on the Hidden Lake Wetland

Effects on Surface Water

A summary of general characteristics of surface waters along the flowpath and control areas in the Hidden Lake wetland is given in Table 5-6. Upon entering the wetland flowpath, significant changes begin to occur for most of the parameters listed in Table 5-6. As seen in Figure 4-8, pH, alkalinity and dissolved oxygen all begin gradual declines in measured values with increasing distance along the flowpath.

SUMMARY OF GENERAL CHEMICAL CHARACTERISTICS OF SURFACE WATERS ALONG THE FLOWPATH AND CONTROL AREAS IN THE HIDDEN LAKE WETLAND

					FLO	WPATH				CONTROL
PARAMETER	UNITS	WEIR	10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA
pH	s.u.	6.54	6.53	6.25	6.19	6.02	5.92	5.87	5.65	4.88
Conductivity	µmho/cm	194	183	177	163	150	138	136	112	92
Diss. Oxygen	mg/l	7.4	6.7	4.0	2.8	2.0	1.6	1.3	1.7	0.9
ORP	mV	411	380	271	222	168	182	176	173	79
Alkalinity	mg/l	79	72	67	61	57	50	50	39	14
BOD	mg/l	1.7	1.5	1.8	1.4	1.5	1.3	1.1	1.4	0.9
Color	Pt-Co Units	73	94	. 101	109	126	150	172	226	505
Residue	mg/l	146	162	149	145	152	156	149	146	178
S.S.	mg/l	2.7	4.0	4.8	4.0	4.7	3.7	3.4	4.6	1.8
Turbidity	NTU	4.6	4.3	5.2	5.7	6.4	5.2	5.2	5.1	2.9
No. of Samples		20	10	11	8	8	8	7	7	8
Mean Travel Time to Sample Station (days)		0	0.04	0.90	1.80	2.69	3.59	4.49	5.39	

Declines in values of pH and alkalinity appear to be relatively linear with increasing flow distance. However, decreases in concentrations of dissolved oxygen appear to exhibit a more rapid logarithmic decline which is closely matched by corresponding decreases in redox potential. Measurements of dissolved oxygen and redox potential indicate a well oxidized and oxygenated water column entering the wetland which changes quickly to an oxygen depleted and reduced water column after a travel distance of approximately 50-75 meter. At the mean calculated surface flow velocity of 1.16 m/hour, water reaching the 50-75 m sample sites would have flowed through the wetland an average of 1.8-2.7 days.

Measured values of BOD, suspended solids, and turbidity were relatively unchanged during flow through the wetland and do not appear to be affected by the rapidly changing values of pH and redox potential. However, it should be noted that mean input concentrations of these parameters were extremely low initially and little additional improvement by the wetland could be expected.

An interesting relationship appears to exist between conductivity, residue, and color. As seen in Table 5-6, conductivity decreases steadily during travel through the wetland, suggesting a corresponding steady decrease in concentrations of dissolved ionic species in the water column. Assuming the relationship between conductivity and dissolved charged ions to be relatively linear, values of conductivity suggest an overall decrease in charged ionic species of approximately 23% after a travel distance of 75 m and 42% after 150 m. Apparently, the wetland is acting as an excellent scavenger for general ionic species. Unlike the gradual decline in values of conductivity, residue remained largely unchanged. Since concentrations of dissolved ions apparently decrease during flow, the lack of change in residue concentrations suggests that uncharged ions,

such as organic molecules, must be increasing as the charged ions decrease to maintain a fairly constant dissolved residue. Evidence for this increase in organic content is apparent in measured values of color which exhibit a steady increase with increasing flow distance. In general, it appears that the wetland flowpath is removing dissolved charged ionic species and releasing uncharged organic ions.

It seems likely that the rapid changes in chemical characteristics of input water during flow through the wetland is mediated primarily by the sediments. Bacterial activity and decomposition processes in the sediments are apparently very large. Bacterial activity is consuming oxygen very rapidly, as well as inorganic carbon, as evidenced by decreases in alkalinity and dissolved ions, as indicated by decreases in conductivity. The production of organic acids as a result of these decomposition processes is evidenced by increases in color and decreases in pH.

Even though inputs into the wetland were found to decrease in pH, dissolved oxygen, ORP, and alkalinity during travel along the flowpath, general water quality along the flowpath area, even at the most remote sample station (150 m), was substantially better than that measured in the control area which was isolated from runoff inputs. The control area was found to exhibit lower values of pH, dissolved oxygen, ORP, and alkalinity than those found along the flowpath and higher values of color and residue. Continual inputs of runoff and baseflow actually have improved mean wetland water quality by increasing mean values of pH, dissolved oxygen, ORP, alkalinity, and decreasing concentrations of color and residue.

The importance of hydrologic inputs on the chemistry of surface water is readily apparent in Table 4-18 where surface water characteristics were compared along the flowpath and in the control for "wet" and "dry" seasons. In general, differences between the flowpath and control areas were greatest during the "wet" season when inputs were larger in quantity and more frequent. During the "wet" season, 9 of the 15 parameters listed in Table 4-18 were significantly different between the flowpath and control areas, while only 6 of the 15 parameters were significantly different during the "dry" season.

Effects on Groundwaters

The changes in general chemical characteristics of surface waters along the flowpath caused by continual hydrologic inputs was found to extend into groundwaters as well. As seen in the general chemical characteristics of groundwaters given in Table 5-7 as well as in Figure 4-11, the effect of increased pH values extends to depths between 0.5-1.0 m and increased values of ORP extend to 0.1-0.5 m. Increased concentrations of alkalinity appear to extend to depths in excess of 1.0 m. Decreases in measured values of color also appear to extend to at least 1.0 m, with color levels in groundwaters in the control area generally 3-4 times greater than along the flowpath.

Fate of Nutrients in the Hidden Lake Wetland

A summary of mean nutrient concentrations measured in surface waters along the flowpath and control areas is given in Table 5-8 and concentrations measured in groundwaters are listed in Table 5-9. Each of the individual species listed in these tables will be discussed in the following sections.

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SUMMARY OF GENERAL CHEMICAL CHARACTERISTICS IN GROUNDWATERS AT THE HIDDEN LAKE WETLAND

PARAMETER	UNITS	UPS	STREAM VETLAN	OF D	FLC	WPATH 25 m	AT	FLC)WPATH 150 m	AT		CONTROL AREA	· · ·
		0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m
рН	s.u.	5.05	5.17	5.15	5.96	5.61	5.37	5.42	5.38	5.76	4.84	4.98	5.18
Conductivity	µmho/cm	137	118	115	229	153	128	139	158	290	100	111	135
Diss. Oxygen	mg/l	0.4	0.1	0.1	3.5	0.1	0.0	0.4	0.5	0.1	0.0	0.2	0.1
ORP	mV	78	76	68	139	83	52	77	107	83	57	72	27
Alkalinity	mg/l	29	38	42	100	54	42	50	48	122	16	18	32
BOD	mg/l	2.6	1.8	1.8	3.0	2.0	2.8	2.4	1.7	3.3	3.5	4.7	5.1
Color	Pt-Co Units	390	205	368	188	173	177	268	268	132	664	713	569
Residue	mg/l	187	142	172	211	156	126	141	163	238	169	182	201
No. of S	amples	11	12	12	10	11	12	10	11	11	11	12	12

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SUMMARY OF MEAN NUTRIENT CONCENTRATIONS IN SURFACE WATERS ALONG THE FLOWPATH AND CONTROL AREAS IN THE HIDDEN LAKE WETLAND

	LINTER				FLO	WPATH				CONTROL
PARAMETER	UNITS	WEIR	10 m	25 m	50 m	75 m	100 m	125 m	150 m	AREA
NH3-N	μg/l	44	41	54	90	95	80	61	56	48
NO3-N	μg/l	39	43	40	42	36	38	42	35	31
Organic N	μg/1	398	364	484	353	360	471	545	713	1163
Total N	μg/1	481	448	578	485	491	589	648	804	1242
Ortho-P	μg/1	28	20	29	32	49	61	54	76	130
Total P	μg/l	59	48	67	62	85	103	110	148	177
No. of Samples		20	10	11	8	8	8	7	7	8
Mean Travel Time to Sample Station (days)		0	0.04	0.90	1.80	2.69	3.59	4.49	5.39	

SUMMARY OF MEAN NUTRIENT CONCENTRATIONS IN GROUNDWATERS AT THE HIDDEN LAKE WETLAND

PARAMETER	UNITS	UPSTREAM OF WETLAND			FLOWPATH AT 25 m			FLOWPATH AT 150 m				,	
		0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m	0.1 m	0.5 m	1.0 m
NH3-N	μg/l	107	100	113	386	227	358	159	320	1131	445	982	1238
NO3-N	μg/l	76	40	46	60	43	83	41	61	68	14	42	19
Organic N	μg/l	572	122	210	300	311	432	567	575	378	1627	1456	1421
Ortho-P	μg/l	23	40	49	24	25	42	55	31	29	309	332	429
No. of S	amples	11	12	12	10	11	12	10	11	11	11	12	12

Fate of Nitrate

As seen in Tables 5-8 and 5-9, nitrate concentrations were generally low both in surface waters and groundwaters. Mean input concentrations of nitrate were generally less than 40 μ g/l, and little change was observed during flow through the wetland or in the control area. Groundwater concentrations were similar to those observed in surface waters, although concentrations measured in the control area groundwaters seem to be generally lower than those beneath the flowpath.

Although low input concentrations of nitrate made it difficult to examine the fate of nitrate in the wetland system, information can be obtained from the long-term and short-term rate experiments. As seen in Tables 4-32 and 4-34, nitrate is rapidly removed from the water column when present in concentrations characteristic of residential runoff measured in other studies. The importance of the sediments in removal of nitrate is clearly evident in Table 4-32 where removal was essentially complete (approximately 83%) in less than 24 hours, but required 2-4 days for a similar removal with no sediment contact. Removal of nitrate from the water column was observed to correlate closely to decreases in dissolved oxygen levels, suggesting that denitrification may be an important removal mechanism. However, reduction of nitrate to ammonia is also possible, especially since decreases in nitrate concentrations in Table 4-32 also correspond well to increases in ammonia. This same trend of decreasing concentrations of nitrate corresponding to increases in ammonia was observed in the channel experiments where nitrate was rapidly consumed while ammonia increased.

Fate of Ammonia and Organic Nitrogen

Similar to the trend observed for nitrate, input concentrations of ammonia were extremely low. Little change was observed in concentrations of ammonia during travel over the flowpath area, although concentrations appear to have increased slightly at the 50 m and 75 m stations. However, unlike nitrate ions, ammonium ions were significantly more concentrated in groundwaters than in surface waters and appear to increase substantially with increasing depth. Measured concentrations of ammonia in groundwaters beneath the control area were much larger than levels found along the flowpath. Concentrations of organic nitrogen, however, were found to increase with increasing retention time during travel through the wetland, accounting for most of the observed increases in total nitrogen. Concentrations of organic nitrogen in groundwaters were generally equal to or less than those observed for ammonia, concentrations of organic nitrogen were much higher in both surface waters and groundwaters in the control area.

The results of the isolation experiments suggest that ammonium ions are rapidly removed from the water phase in the absence of sediment content, presumably as a result of microbial activity. However, when sediment contact is present, this removal is overshadowed by a corresponding release from the sediments. This increase in ammonium ions is most likely caused by ammonification processes which break down the easily decomposable organic forms of nitrogen into ammonium ions. The net result is an initial decrease in organic nitrogen and a temporary increase in ammonium concentrations. This process apparently requires approximately 48 hours to complete, after which consumption of ammonium by the water phase reduces concentrations to equilibrium levels. As seen in Table 4-32, this entire process requires 4-6 days to complete.

Although conversions of organic nitrogen and ammonium ions required several days for completion, maximum reductions in total nitrogen were achieved in approximately 48 hours after which concentrations changed very little. Therefore, maximum removal of nitrogen can be achieved with retention periods of approximately 48 hours even though conversions between various compartments may still be occurring. With input concentrations of total nitrogen near 2 mg/l, a maximum reduction of approximately 42% was achieved after 48 hours. Retention periods longer than 48 hours did not result in additional removal of total nitrogen and may, in fact, result in increased concentrations, particularly if decomposition processes begin to add substantial amounts of organic nitrogen to the water column. As seen in Table 5-8, substantial increases in organic nitrogen, along with corresponding increases in total nitrogen, were observed at residence times in excess of approximately 3 days.

Fate of Phosphorus

Unlike nitrogen which is regulated primarily by biological reactions, phosphorus is regulated by both biological and chemical processes. As seen in Table 5-8, phosphorus inputs into the wetland changed very little during the first 50 m of travel. However, after the 50 m station, concentrations of soluble orthophosphorus increase rapidly, reaching a value at 150 m approximately three times greater than input values. Concentrations in the isolated control area averaged 4.6 times greater than input values.

Although orthophosphorus is an essential and often limiting ion in natural systems which is continuously being consumed by living matter, apparently processes of release within the wetland are overshadowing the uptake mechanisms, resulting in a net increase in concentrations. As seen in Tables 4-32 and 4-34, the sediments are clearly the dominant phase regulating uptake and release of phosphorus to the water column. Apparently, the uptake of phosphorus requires relatively quiescent conditions for maximum efficiency. As seen in Table 4-36, uptake of phosphorus by the sediments in the channel experiments was optimum at flow velocities of 1.20 m/hour or less, but was hindered at higher velocities.

Under aerobic conditions, adsorption of phosphorus onto the sediments is rapid and is essentially complete in 24 hours. In the absence of sediment contact, uptake by the water phase only is extremely slow. However, under anaerobic conditions, the uptake of phosphorus appears to decrease rapidly, and equilibrium water column concentrations are governed largely by the prevailing pH and redox potential. Since phosphorus is primarily attached to hydrous oxides of iron in the sediments, decreases in pH below 5.5 and redox potentials less than 200 mV, which solubilize iron compounds, also contribute to releases of phosphorus. This trend is clearly visible in Tables 5-6 and 5-7 where orthophosphorus concentrations increased along the flowpath from 32 μ g/l at 50 m to 49 μ g/l at 75 m as the ORP dropped from 222 mV to 168 mV.

Maximum retention of orthophosphorus in wetland sediments following the rapid initial uptake requires maintaining an aerobic and oxidized water column as well as pH values above 5.5. As seen in Table 5-6, these conditions were met by retention times of 48 hours or less, and under these conditions, phosphorus appeared to be retained in the sediments. However, retention times in excess of 48 hours contributed to decreases in redox potential below 200 mV and a subsequent release of phosphorus from the sediments.

Effects of Wetland Treatment on Algal Productivity in Receiving Waters

Two algal bioassay experiments were conducted to examine the effects of wetland treatment on algal productivity in receiving waters. Hidden Lake, a highly colored and nutrient rich water, and Lake Lee, a non-colored and generally nutrient poor water, were used as test waters. As seen in Figure 4-28, mixtures of Hidden Lake water with composite water samples collected along the flowpath were observed to decrease in algal productivity with increasing flow distance through the wetland. This figure should be viewed with caution since it suggests that the effect of discharges of wetland waters to a surface water would not produce increased algal production. The decreases in productivity illustrated in Figure 4-28 are more likely a result of inhibitory effects on algal growth caused by increasing concentrations of organic acids and other organic by-products which can act as natural algicides rather than an absolute reduction in productivity caused by nutrient limitation.

A more likely example of the effects of treated runoff on algal productivity is indicated in Figure 4-29 for Lake Lee. Additions of treated waters to a non-colored test water resulted in a dilution of organic compounds and a slight increase in algal productivity was observed with increasing flow distance.

Fate of Heavy Metals in the Hidden Lake Wetland

As discussed previously, input concentrations of heavy metals into the Hidden Lake wetland were extremely low, making conclusions concerning the removal potential of the wetland for metal species difficult. However, generalizations can be made by examination of mean water quality and sediment measurements along with speciation and redox experiments as well as the long-term and short-term isolation experiments.

A comparison of dissolved heavy metal concentrations in surface waters and groundwaters between the flowpath and control areas is given in Table 5-10. Metals such as zinc, manganese, copper, aluminum, and iron appear to be more soluble. Apparently, the chemical changes in surface waters caused by inputs of runoff and baseflow have created conditions which increased the adsorption of zinc, manganese, copper, aluminum, and iron, while decreasing the adsorption of cadmium, lead, nickel, and chromium.

However, in spite of the fact that certain metals are more soluble under conditions present in the flowpath than in the control area, the flowpath sediments are clearly retaining a large portion of the metal inputs. As seen in Figure 4-16, sediment concentrations of nickel, chromium, aluminum and iron in the flowpath area are much greater than concentrations found in the control site, especially near the surface. These differences in sediment concentrations indicate an ability of the flowpath sediments to provide long-term retention for metal inputs.

As seen in Figure 4-17, zinc is also retained well in the flowpath area. However, conditions in the flowpath appear to lower the retention of lead from that found in the control area. Sediment concentrations of cadmium and copper were the lowest of all

COMPARISON OF SURFACE AND SHALLOW GROUNDWATER FOR FLOWPATH AND CONTROL AREAS

HEAVY	SURFACE (µį	E WATER g/l)	GROUNDWATER (µg/l)			
METAL	FLOWPATH	CONTROL AREA	FLOWPATH	CONTROL AREA		
Cd	3.92	2.30	5.93	3.88		
Zn	3.90	6.57	20.9	37.3		
Mn	3.10	7.57	18.0	9.80		
Cu	19.9	28.7	30.3	28.0		
Al	176	296	290	710		
Fe	105	389	868	11 72		
Pb	24.7	15.9	35.8	21.6		
Ni	2.71	1.91	5.84	3.24		
Cr	2.78	1.89	3.69	2.80		

metals found. The general lack of a pronounced peak in concentration near the sediment surface suggests that neither of these metals are retained well in wetland sediments, especially under conditions typical of the flowpath area.

The curves presented in Figures 4-16 and 4-17 suggest two important conclusions concerning heavy metals. First, with the possible exceptions of cadmium and copper, wetland soils appear capable of adsorbing and retaining metal inputs with the majority of inputs retained very near the surface in the top 5 cm. Second, the general changes in water characteristics caused by continuous inputs of runoff and baseflow appear to create sediment conditions which improve the ability of the sediments to retain metals, with the exception of lead, over natural conditions found in the isolated control area.

The apparent inability of the wetland sediments to retain cadmium, copper, and lead can be explained partially by examination of metal speciations in the sediments. A summary of mean heavy metal speciations in the top 20 cm of flowpath and control areas at the wetland site is given in Table 5-11. Cadmium was found to exist in wetland sediment associations with a weak exchange bond. This weak bonding mechanism was more prevalent in the flowpath than in the control area, perhaps explaining the inability of the flowpath area to accumulate cadmium in excess of the control area. Similar bonding mechanisms were found for lead. As seen in Figures 4-18 and 4-19, both cadmium and lead were found to be less soluble under reduced conditions typical of the control area and more soluble under oxidized conditions found in the flowpath. These results also predict a lessened ability of flowpath sediments to retain these metal species.

A comparison of metal speciation in the top 20 cm of the sediment in a wet detention facility receiving highway runoff at the Maitland Interchange in Orlando,

5-32

COMPARISON OF HEAVY METAL SPECIATION IN THE HIDDEN LAKE WETLAND AND THE WET DETENTION POND AT THE MAITLAND INTERCHANGE

SOLUBLE				EXCHANG	3	BOUND	TO CARB	ONATES	Fe	/Mn OXID	ES	ORG	ANIC BOU	JND	
HEAVY	weri	LAND	WET	wer	LAND	MICT	WETI	LAND		WETI	AND		WETI	LAND	
METAL	FLOW- PATH	CONT.	DET.	FLOW- PATH	CONT.	DET.	FLOW- PATH	CONT.	DET.	FLOW- PATH	CONT.	WET DET.	FLOW- PATH	CONT.	WET DET.
Cd	3	6	15	72	59	52	11	9	12	9	15	10	6	12	11
Zn	2	5	4	22	17	1	12	17	4	35	26	81	30	35	10
Mn	0.1	0.2	1	57	53	9	16	19	1	17	17	86	10	10	3
Cu	4	3	1	5	6	3	3	5	1	13	25	89	75	62	7
Al	0.5 ·	0.3	< 1	0.4	0.7	< 1	2	2	< 1	14	10	74	82	88	26
Fe	0.2	0.2	< 1	1	0.9	5	0.6	0.5	< 1	40	32	52	59	67	43
Pb	0.9	2	1	73	46	44	13	22	1	6	11	52	8	20	2
Ni	2	6	4	46	37	8	2	0.1	< 1	9	8	82	42	50	6
Cr	1	2	2	13	10	5	1	0.1	1	4	3	73	· 81	86	19

SOURCE: Harper (1985)

 ${\cal C}^{(1)}$

Florida is also given in Table 5-11. In general, with the possible exception of cadmium, metals in the sediments of the wet detention pond appear to be associated primarily with relatively stable Fe/Mn oxides and exhibit very little association with the less stable soluble, exchange, and carbonate fractions. Metals in the wetland were found to associate strongly in normally stable organic fractions. However, the rapid rates of decomposition found in wetland sediments makes the long-term stability of these organic associations questionable. Therefore, it appears that heavy metals are perhaps more stable in the sediments of the wet detention facility than in the wetland.

Another method of examining the stability of metal-sediment associations is to compare the rates of attenuation of metal concentrations between two sediments. Metals which exhibit a rapid attenuation with increasing depth are assumed to be retained primarily at the surface with little tendency for downward migration. However, a low attenuation coefficient would indicate an inability to retain metals at the surface or suggest a downward migration of metals previously deposited at the surface.

A comparison of attenuation coefficients (K values) for a semi-log model of metal retention in the Hidden Lake wetland and in the Maitland wet detention pond (Harper 1985) are given in Table 5-12.

Mass Balance for Inputs to the Hidden Lake Wetland

Estimates of loading rates to the 1.0 hectare wetland treatment area were calculated for selected measured parameters for inputs due to direct rainfall, stormwater runoff, and baseflow during 1985. Calculations were performed by multiplying the total yearly hydrologic input for rainfall, runoff, and baseflow listed in Table 4-1 times the

COMPARISON OF REGRESSION STATISTICS FOR METAL ATTENUATION IN WETLAND SOILS AND SOILS OF WET DETENTION SYSTEMS

HEAVY	SEMI-LOC In (Metal Conc.	G MODEL) = -K (Depth)	SEMI-LOG M WET DE	MODEL FOR TENTION	RATIO OF METAL SOLUBILITY IN WETLAND	
METAL	SLOPE (K)	VALUE OF R ²	SLOPE (K)	VALUE OF R ²	SEDIMENTS TO WET DETENTION SEDIMENTS	
Cd	0.033	0.162	0.374	0.821	11.2	
Zn	0.100	0.582	0.398	0.898	3.98	
Cu	0.034	0.101	0.286	0.877	8.41	
Al	0.132	0.639	0.311	0.902	2.36	
Fe	0.039	0.245	0.549	0.821	14.1	
Pb	0.022	0.147	0.272	0.910	12.4	
Ni	0.047	0.406	0.304	0.890	6.47	
Cr	0.076	0.502	0.346	0.913	4.55	
Mn	0.045	0.527	0.327	0.895	7.27	

mean measured concentrations of chemical parameters in each input. A summary of loading rates for selected parameters is given in Table 5-13. In general, mass inputs from runoff and baseflow were approximately equal for most parameters, comprising together approximately 70-98% of total yearly inputs. Contributions due to direct rainfall were generally very small for most parameters, except for nitrate, where direct rainfall contributed 31% of total inputs; zinc, accounting for 33% of total input; and copper, where rainfall contributed 75% of the total input mass.

A mass balance for selected stormwater pollutants in the Hidden Lake wetland during 1985 is given in Table 5-14. Outflow mass was calculated by multiplying the volumes discharged to Hidden Lake, summarized in Table 5-1, times the corresponding mean surface water concentration in the control area adjacent to Hidden Lake during the period over which the outflow occurred.

Estimates of mass loadings given in Table 5-14 indicate that substantial percentages of the input mass of both ammonia and nitrate were retained in the wetland. However, the rather large increase in organic nitrogen measured in the control area produced in a net export of organic nitrogen from the system, resulting in a small net export of total nitrogen from the system. A similar situation was observed for phosphorus.

It should be noted that the removal efficiencies listed in Table 5-14 were based on input concentrations for most parameters which were extremely low compared to values normally measured in stormwater runoff. It was clearly shown in the isolation experiments that the sediments have the ability to absorb much larger concentrations of ammonia, nitrate, orthophosphorus, and most dissolved metals than those input to the

SUMMARY OF LOADING RATES FROM RAINFALL, RUNOFF, AND BASEFLOW TO THE 1.0 HECTARE FLOWPATH AREA IN THE HIDDEN LAKE WETLAND

PARAMETER			LOADING RATE: (kg/	S TO WETLAND year)	
		RAINFALL	RUNOFF	BASEFLOW	TOTAL
NH	I ₃ -N	0.63	1.40	1.49	3.52
NO3-N		1.35	1.70	1.32	4.37
Orga	nic N	0.48	12.14	13.44	26.06
Ort	ho-P	0.08	0.70	0.95	1.73
To	al P	0.09	1.80	1.99	3.88
В	DD	10.89	64.8	57.4	133.1
S	s.	10.89	154.6	91.2	256.7
Cd	Diss. Total	0.03 0.03	0.12 0.13	0.16 0.17	0.31 0.33
Zn	Diss. Total	0.14 0.14	0.12 0.14	0.16 0.16	0.42 0.44
Mn	Diss.	0.04	0.06	0.10	0.20
	Total	0.04	0.10	0.12	0.26
Cu	Diss.	0.27	0.49	0.36	1.12
	Total	0.27	0.66	0.45	1.38
Al	Diss. Total	0.24 0.24	0.51 13.96	4.83 7.77	5.58 21.97
Fe	Diss. Total	0.12 0.12	1.68 2.84	2.37 3.12	4.17 6.08
РЬ	Diss. Total	0.04 0.04	0.74 0.80	1.09 1.13	1.87 1.97
Ni	Diss. Total	0.01 0.01	0.08 0.09	0.12 0.13	0.21 0.23
Cr	Diss. Total	0.01 0.01	0.08 0.09	0.13 0.13	0.22 0.23

MASS BALANCE FOR SELECTED STORMWATER POLLUTANTS AT THE HIDDEN LAKE WETLAND

			MASS LOADING (kg/year)		PERCENT OF
		INPUT	SURFACE OUTPUT TO HIDDEN LAKE	RETAINED IN WETLAND	RETAINED
NH	I ₃ -N	3.52	1.33	2.19	62.2
NC	D ₃ -N	4.37	0.87	3.50	80.2
Orga	nic N	26.06	32.31	- 6.25*	- 24.0*
Tot	al N	33.95	34.51	- 0.56	- 1.6*
Ort	ho-P	1.73	3.61	- 1.88	- 109*
To	tal P	3.88	3.61	0.27	7.0
В	OD	133.1	24.9	108.2	81.3
s	.s.	256.7	43.9	212.8	82.9
Cd	Diss.	0.31	0.064	0.25	79.4
	Total	0.33	0.097	0.23	70.7
Zn	Diss.	0.42	0.18	0.24	57.1
	Total	0.44	0.26	0.18	40.9
Mn	Diss.	0.20	0.22	- 0.02	- 10.0*
	Total	0.26	0.24	0.02	7.7
Cu	Diss.	1.12	0.80	0.32	28.6
	Total	1.38	0.83	0.55	39.9
Al	Diss.	5.58	7.00	- 1.42	- 25.4*
	Total	21.97	8.11	13.86	63.1
Fe	Diss.	4.17	9.64	- 5.47	- 131*
	Total	6.08	11.56	- 5.48	- 90.1*
РЬ	Diss.	1.87	0.82	1.05	56.1
	Total	1.97	0.89	1.08	54.8
Ni	Diss.	0.21	0.064	0.15	69.5
	Total	0.23	0.069	0.16	70.0
Cr	Diss.	0.22	0.056	0.16	74.5
	Total	0.23	0.063	0.17	72.6

* Indicates a net export of this parameter from the wetland.

 wetland. Had input concentrations of many parameters been greater, the performance of the treatment system, as reflected in the mass retention percentages in Table 5-14, would have been much improved.

<u>Anticipated Treatment Levels</u> <u>Achieved by Hardwood Wetland Systems</u>

Two basic approaches were undertaken to examine the ability of the hardwood wetland at Hidden Lake to provide treatment for runoff inputs. First, a year-long monitoring program was conducted to document quality of inputs to the system and surface water quality along the treatment flowpath. However, as indicated previously, concentrations of most constituents in the input flows were extremely low and the efficiency of the system to treat higher concentrations was not tested. As a result, both long-term and short-term isolation experiments were conducted to examine the ability of the system to reduce inputs with substantially higher initial concentrations.

A summary of initial and final concentrations for selected parameters in the isolation experiments as well as mean values measured along the flowpath is given in Table 5-15. Examination of the data summarized in this table reveals an important conclusion concerning the ability of the wetland to treat pollutant inputs. Although input values of orthophosphorus varied between 28 and 274 μ g/l, final equilibrium concentrations were in the range of 33-60 μ g/l.

The trend noted previously was especially apparent for dissolved heavy metals. Input concentrations of cadmium ranged from 4.6-19 μ g/l, with equilibrium concentrations between 3-4 μ g/l; zinc ranged from 4.6-80 μ g/l initially, with equilibrium

SUMMARY OF ANTICIPATED TREATMENT LEVELS FOR WETLAND TREATMENT AT HIDDEN LAKE

PARAMETER	UNITS	MEAN WETLAND VALUES		18-DAY RATE EXPERIMENT		24-HOUR RATE EXPERIMENT		ANTICIPATED TREATMENT	TREATMENT LEVEL IN
		STORMWATER INPUTS	125 m STATION	INITIAL	FINAL	INITIAL	FINAL	LEVELS IN WETLAND	MAITLAND POND ¹
pH Conductivity Diss. Oxygen Alkalinity ORP NH N	s.u. µmho/cm mg/l mg/l mV ua/l	5.91 143 7.4 66 411	5.87 136 1.3 50 176 61	6.51 176 6.4 68.4 247 239	6.21 208 1.1 58.0 246 5	6.47 175 71.0 285	6.18 148 53.7 332	5.8-6.2 135-210 1-2 50-60 175-250 5-330	7.46 170 5.6 57.2 523 30
NO ₃ -N Organic N Total N Ortho-P	μg/1 μg/1 μg/1 μg/1 μg/1	68 487 611 28	42 545 648 54	239 282 1397 1918 274	41 1150 1196 33	233 278 674 1237 216	106 458 896 57	40-110 450-1150 650-1200 33-60	40 830 900 4
Dissolved Metals Cd Zn Mn Cu Al Fe Pb Ni Cr	μg/l μg/l μg/l μg/l μg/l μg/l μg/l μg/l	4.6 4.6 2.5 19.6 20.6 67.3 29.5 3.2 3.1	3.7 5.7 4.6 25.6 193 176 25.3 2.9 2.8	19 80 22 106 181 258 110 24 22	4.2 22 17 22 145 206 46 5.2 4.6	6.2 37 7 57 103 56 43 19 9.6	4.1 10 2 34 181 118 30 3.9 7.1	3-4 5-22 2-17 22-34 150-200 120-210 25-45 3-5 3-7	$\begin{array}{c} 0.7 \ (0.8)^2 \\ 4.7 \ (6.0) \\ 4.5 \ (17.1) \\ 14.4 \ (16.7) \\ 58.0 \ (156) \\ 18.4 \ (63.1) \\ 15.0 \ (22.2) \\ 1.6 \ (2.2) \\ 2.2 \ (3.5) \end{array}$

1. SOURCE: Harper (1985). Receives highway runoff, n = 30 samples.

2. Total metal concentrations are given in parentheses.

values between 5-22 μ g/l; and inputs of nickel ranged from 3.2-24 μ g/l, with final values between 3-5 μ g/l. Similar trends were observed for the other dissolved metals as well.

Treatment levels measured in a wet detention system receiving highway runoff at the Maitland Interchange in Orlando, Florida during 1982-1985 by Harper (1985) are given in the last column of Table 5-15 for comparison. Treatment levels achieved by the wet detention system were, in general, more neutral in pH and higher in dissolved oxygen and redox potential. Mean values of ammonia and nitrate appear to be lower in the wet detention system, although organic nitrogen and total nitrogen are similar in the two systems. However, the wet detention system was able to produce substantially lower mean values of orthophosphorus and dissolved metals, especially cadmium, zinc, copper, aluminum, lead, iron, nickel, and chromium. A large portion of the observed differences in treatment efficiencies can be explained simply by differences in pH. Many metal species exhibit maximum solubility in the pH range of 4.5-5.5 which is similar to wetland values and exhibit minimum solubility in the pH range of 7.5-8.5 which is similar to values measured in the detention facility. However, regardless of the apparent explanation, wet detention systems will likely provide a better treatment level for runoff than a wetland system similar to that studied at Hidden Lake.
CHAPTER 6

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The movement and fate of nutrient and heavy metal inputs from residential stormwater runoff were investigated in a 1.0-hectare hardwood wetland treatment system near Sanford, Florida. Physical characteristics of the wetland, an adjacent lake, and the surrounding watershed were defined, and field instrumentation was installed. The wetland receives stormwater runoff from a large residential community through a small shallow canal and provides treatment prior to discharge to Hidden Lake.

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Field investigations were begun in 1984 and were divided into the following tasks: (1) assessment of the quantity of nutrients and heavy metals entering the wetland by way of stormwater runoff; (2) measurement of the attenuation of these pollutants during travel through the wetland; (3) monitoring of the concentrations of nutrients and heavy metals in groundwaters; (4) accumulation of nutrients and heavy metals in the sediments of the wetland; (5) examination of the typical chemical associations binding nutrients and heavy metals to the sediments using sequential extraction procedures; (6) investigation of the importance of redox potential and pH on metal-sediment stability with regard to the release of phosphorus and heavy metals from wetland sediments; and (7) a detailed hydrologic balance of inputs and outputs at the wetland.

From the results obtained in these investigations, the following specific conclusions were reached:

1. Approximately 70% of the total direct inputs into the wetland during 1985 from baseflow, runoff, and direct rainfall were retained in the wetland and lost by a combination of evapotranspiration and groundwater seepage. During six months of the study period, 100% of the direct inputs were totally retained and in 9 of the 12 months, retention within the wetland was in excess of 80% of total direct inputs.

2. Losses due to transpiration from plant surfaces were the greatest output from the wetland, far exceeding losses by evaporation. Excluding groundwater seepage, transpiration losses accounted for 92% of the direct losses during spring, 96% of direct losses during summer, and 81% during the fall/winter.

3. Measured transpiration rates in the hardwood wetland were approximately one order of magnitude greater than those reported by other researchers in cypress domes, while rates of evaporation in the hardwood wetland were several times less than those measured in cypress domes. However, the combined losses due to evapotranspiration were 5-10 times greater in the hardwood wetland than in a cypress dome.

4. Continuous seepage of baseflow into the wetland through the inflow canal constituted the largest single input to the wetland during the study period. This virtually continuous input was found to increase the average hydroperiod to approximately 320 days. Normal hydroperiods for hardwood wetlands range between 200-250 days.

5. Alterations of hydroperiod in the wetland may be hindering the ability of certain canopy species to reproduce, especially red maple, and may be slowly altering the canopy dominance.

6. Wetland systems with longer natural hydroperiods, such as cypress domes, bayheads, or marshes, appear better suited for modification as stormwater management systems than those with shorter hydroperiods. 7. Groundwater movement beneath the wetland appears to flow from both Hidden Lake and the inflow area to the center of the wetland and dissipate at that point by transpiration losses or seepage to deeper groundwaters.

8. Rainwater collected at Hidden Lake exhibited a mean pH of 4.76 and was found to be relatively dilute and low in concentration for all general parameters with the possible exception of nitrate. Mean rainfall concentrations were also dilute for all heavy metals with the exception of copper, which was the most concentrated heavy metal measured, averaging 27 μ g/l. Mean concentrations of cadmium, manganese, lead, nickel, and chromium in rainfall were less than 4 μ g/l.

9. Travel of rainwater over the residential watershed was found to contribute substantial quantities of alkalinity, turbidity, organic nitrogen, phosphorus, residue, suspended solids, and TOC to the flow stream. However, concentrations of ammonia and nitrate were lower in runoff than in rainwater. Movement through the watershed was found to increase concentrations of cadmium, aluminum, iron, lead, nickel, and chromium while decreasing concentrations of zinc from those measured in direct rainfall.

10. Excluding aluminum and iron, lead, copper and zinc were the most abundant heavy metals in runoff water, together accounting for 80% of dissolved heavy metals and 79% of total heavy metals.

11. Mean chemical characteristics of runoff waters measured at Hidden Lake are substantially lower than those measured at other residential sites in Florida. In general, constituents at other sites were found in concentrations 5-10 times greater than those measured at Hidden Lake. Many of these differences may be due to the pre-treatment effect of the swale drainage system used at Hidden Lake, but differences in activity levels may also be important. 12. Mass loading rates of pollutants from the residential watershed at Hidden Lake were also extremely low and as much as a factor of 10 times lower than values measured at another central Florida residential site near Lake Eola. The initially low runoff concentrations combined with the low watershed runoff coefficient of 0.11 result in substantially reduced loadings from the watershed.

13. Attempts to correlate stormwater quality characteristics with rainfall characteristics such as rainfall amount, rainfall duration, rainfall intensity, and antecedent dry period were largely unsuccessful. The lack of strong correlations between runoff quality and rainfall characteristics is indicative of the stochastic, poorly understood, and complex phenomenon regulating stormwater composition.

14. Continuous inputs of runoff and baseflow produced substantial increases in pH, alkalinity, dissolved oxygen, and redox potential in both surface waters and groundwaters in the flowpath area over those measured in the isolated control area which was unaffected by normal runoff inputs. Elevated levels of pH extended to a depth of 0.5-1.0 m beneath the sediment surface, increased concentrations of alkalinity appear to extend to depths in excess of 1.0 m, while ORP remained elevated to depths between 0.1-0.5 m.

15. Upon entering the wetland flowpath, alkalinity, dissolved oxygen, ORP, and pH all begin gradual declines with increasing flow distance. Measured values along the flowpath as well as the results of isolation chamber experiments suggest that oxygenated inputs become anaerobic and reduced after 48 hours of wetland flow. The sediments are clearly the primary driving force for these rapid changes.

16. Mean input concentrations of nitrate to the flowpath were extremely low, averaging less than 40 μ g/l, and little change was observed in concentrations during flow in the wetland. However, information obtained from the long-term and short-term isolation experiments conducted at nitrate concentrations more typical of residential runoff suggested that nitrate is rapidly removed from the water column by the sediments under reduced conditions.

17. Ammonium ions were found to be rapidly removed from the water phase in the absence of sediment contact. However, when sediment contact is present, the rate of removal of ammonia from the water phase is overshadowed by a corresponding release from the sediments most likely caused by ammonification processes. The net result is an initial decrease in organic nitrogen and a temporary increase in ammonia concentrations.

18. Maximum removal of total nitrogen was found to occur after 48 hours even through conversions between various compartments may still be occurring. Retention times in excess of 48 hours may result in increases in concentrations of total nitrogen.

19. Uptake of phosphorus in the wetland is primarily a sediment mediated phenomenon which appears to be optimum at flow velocities of 1 m/sec or less. Phosphorus is adsorbed rapidly by the sediments under aerobic conditions but released under reduced conditions and pH levels less than 5.5. Maximizing retention of phosphorus in a wetland requires maintaining an aerobic and oxidized water column as well as pH values above 5.5.

20. Metals such as zinc, manganese, copper, aluminum, and iron appear to be less soluble in surface and groundwaters along the flowpath, while cadmium, lead, nickel, and chromium appear to be more soluble along the flowpath than in the control area.

21. In spite of the increased solubilities of certain metals in the flowpath area, the flowpath sediments are clearly retaining a large portion of metal inputs. Sediment concentrations of nickel, chromium, aluminum, and iron were much greater along the flowpath than in the control area, especially near the surface. General changes in water characteristics caused by continuous inputs of runoff and baseflow appear to create sediment conditions which improve the ability of the sediments to retain metals over natural sediment conditions found in the control area. However, general chemical characteristics in the flowpath area appear to lower the retention of lead from that observed in the control area.

22. Cadmium and copper do not appear to exhibit a great affinity for wetland sediments in either the flowpath area or control area and do not appear to be retained to a substantial degree in either area.

23. With the exceptions of cadmium, copper and lead, metal species appear to be bound to sediments along the flowpath in relatively stable organic associations. However, cadmium, copper and lead are primarily bound by relatively weak exchange associations which is largely responsible for the apparent inability of these metals to be retained in the sediments.

24. In spite of the differences in sediment retention between the flowpath and control areas, the long-term and short-term isolation experiments indicated that the wetland has the capability to reduce input concentrations of all metals, except possibly aluminum and iron. As observed for dissolved phosphorus, initial uptake of heavy

metals from the water phase is largely a sediment mediated phenomenon. For some metals, such as nickel and zinc, the uptake is rapid and essentially complete in less than 24 hours. However, other metals such as cadmium, copper and chromium required as much as 4 days or more for maximum removal to occur, although the majority was complete after 48 hours.

25. A comparison of metal speciation in the wetland sediments with that measured in a wet detention basin in Orlando, Florida receiving highway runoff suggests that metals are perhaps more stable in the sediments of a wet detention facility than in the wetland. The sediments of the wet detention facility generally had smaller fractions of the less stable soluble, exchange and carbonate associations and larger fractions of more stable Fe/Mn and organic associations than the wetland.

26. In general, metal concentrations appear to be attenuated much more rapidly in the sediments of the wet detention basin than in the wetland sediments. Most metals in the sediments of the wet detention pond have remained near the surface, while metals in the wetland sediments appear to be migrating to lower sediment depths. These differences in sediment behavior appear to be greatest for cadmium, iron and lead which are attenuated 11-14 times more rapidly in the wet detention sediments than in the wetland.

27. On a mass balance basis, substantial percentages of the input mass of both ammonia and nitrate were retained in the wetland. However, increases in organic nitrogen during travel through the wetland resulted in a net export of organic nitrogen, producing no net retention of nitrogen mass in the system.

6-7

28. Substantial increases in concentrations of orthophosphorus near the point of discharge resulted in a net loss of orthophosphorus mass from the wetland of approximately 109%. However, retention of particulate phosphorus within the system was sufficient to offset the loss of orthophosphorus, producing a net mass retention for total phosphorus of 7%. In general, it appears that neither nitrogen or phosphorus were retained within the wetland to a significant degree. Treatment schemes designed to remove and retain nitrogen and phosphorus inputs must be designed with high levels of retention for hydrologic inputs.

29. Even though the wetland treatment did not appear to retain nitrogen or phosphorus, other parameters were retained to substantial degrees. Input masses of both BOD and suspended solids were retained in excess of 80%. Total inputs of cadmium, nickel and chromium were retained in excess of 70%, while total zinc, copper, aluminum and lead were retained between 40-60%. Only total iron was found to exhibit a net export from the system.

30. Regardless of the wide range of input values tested, both in the wetland and in the isolation experiments, the final treatment levels for pollutants appear to be very similar regardless of the initial input value. This trend is particularly apparent for orthophosphorus and heavy metals. This behavior suggests that the results of this research may extend relatively well to other systems with similar sediment characteristics.

31. Some of the anticipated pollutant treatment levels from the Hidden Lake wetland may exceed criteria listed in Chapter 17-3.121 for Class III Recreational Waters. Cadmium can be expected to exceed the freshwater limit of 0.8 μ g/l; copper may exceed

the freshwater limit of 30 μ g/l; lead may exceed the freshwater limit of 30 μ g/l; and pH values may possibly be depressed in effluent waters below the minimum level of 6.0 listed in the general criteria of Chapter 17-3.061. The minimum criterion for dissolved oxygen of 5 mg/l may be violated much of the time.

32. Comparison of treatment efficiencies achieved in a wet detention system receiving highway runoff with the anticipated treatment levels achieved by wetland treatment suggests that wet detention systems will likely provide a better level of treatment for runoff than a hardwood wetland system with hydrologic characteristics similar to that studied at Hidden Lake.

In view of the results obtained in this research, the following recommendations and design criteria are given for wetland treatment systems:

1. Wetland systems best suited for modification as stormwater management systems are those which already exhibit relatively long hydroperiods such as hardwood hammocks, cypress domes, and marshes.

2. Runoff inputs into wetland treatment systems should be attenuated and released slowly into the system to avoid problems with erosion or high travel velocities which reduce opportunity for adsorption processes. A detention or equalization basin should be constructed to receive initial runoff inputs and release these slowly into the treatment path. This initial detention system will also aid in deposition of solids and oxygenation of the water column which will not only produce a well oxidized influent, but may result in some initial conversion of ammonia to nitrate through nitrification.

3. Runoff inputs should be discharged from the detention system into a spreader swale or other system which distributes the water evenly over the flowpath area.

4. If the system is operated primarily as a flow-through system, the detention time should not exceed 48 hours. Retention times in excess of 48 hours were shown to create reductions in ORP and pH which not only reduce the uptake potential of the sediments but may cause releases of some parameters back into the water column.

5. Mean flow velocities in the wetland treatment path should not exceed 1 m/hour under normal conditions. Flow velocities in excess of this value were shown to significantly limit the uptake of phosphorus and many heavy metals into the sediments. Flow velocities substantially less than 1 m/hour may be deoxygenated more quickly, producing conditions of low dissolved oxygen along the flowpath. A flow rate of 1 m/hour combined with a retention period of 48 hours would result in a treatment path approximately 50 m long.

6. Hardwood wetlands have the ability to evapotranspirate large quantities of hydrologic inputs, particularly in the summer months, and large wetland systems may act as total retention systems. Based on measurements of evapotranspiration in the Hidden Lake wetland, the required hardwood wetland area necessary to totally retain runoff inputs from a typical residential watershed with a runoff coefficient of 0.25 during the wet summer months in Central Florida is approximately 1.1 hectare of wetland/hectare of watershed/inch of rainfall treated on a monthly basis.

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