

FATE OF HEAVY METALS FROM HIGHWAY
RUNOFF IN STORMWATER MANAGEMENT SYSTEMS

by

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ABSTRACT

The movement and fate of heavy metal inputs (Cd, Zn, Mn, Cu, Al, Fe, Pb, Ni and Cr) from highway runoff were investigated in a three-year study on a 1.3 hectare retention facility near the Maitland Interchange on Interstate 4, north of Orlando, Florida. Physical characteristics of the retention pond and surrounding watershed were defined and field instrumentation was installed. Stormwater samples were collected over a one-year period, representing a wide range of intensities and antecedent dry periods. Stormwater characteristics were compared with average retention pond water quality to determine removal efficiencies for heavy metals within the pond. A total of 138 core samples were collected in the pond over a three-year period to investigate the horizontal and vertical migrations of heavy metals within the pond. Sediment core samples were also carried through a series of sequential extraction procedures to examine the type of chemical associations and stability of each metal in the sediments. An apparatus was built which allowed sediments to be incubated under various conditions of redox potential and pH to investigate the effects of changes in sediment conditions on the stability of metal-sediment associations. Five groundwater monitoring wells were also installed to monitor metal movement and accumulations under stormwater management systems.

Heavy metal inputs from highway runoff were found to be predominantly particulate in nature, with dissolved fractions for most metals of only 25 percent. Upon entering the retention pond, most metal species settled into the sediments within 60-90 m of the inlet. Removal efficiencies for metals after entering the pond averaged 70-90 percent for particulate species and about 50 percent for dissolved species. Sediment concentrations of heavy metals were highest near the surface, with rapidly decreasing concentrations with increasing depth. Metal-sediment associations appear to be very strong for most metals, with the vast majority of metal inputs into the pond over the eight-year life still remaining in the top 10 cm.

Concentrations of all heavy metals measured were higher in groundwaters beneath the pond than in the pond water; but for most metals, the increases only extended to depths of 1-3 m beneath the pond. In general, metal concentrations beneath swale areas were significantly higher than concentrations beneath the retention pond. Due to slow groundwater movement in the area, the effects of increased metal concentrations are very localized. Evidence was presented to suggest that the mobilization of metals into groundwaters could substantially increase with time if maintenance procedures are not conducted.

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CHAPTER 1
INTRODUCTION

Within the past decade, a substantial amount of research has accumulated relating to the water pollution caused by the operation of motor vehicles. This concern is based largely on the potential aquatic toxicity of heavy metals such as lead, zinc, and chromium. Heavy metals have been proposed by several researchers as the major toxicant present in highway runoff samples (Shaheen 1975, Winters and Gidley 1980). Many heavy metals are known to be toxic in high concentrations to a wide variety of aquatic plants and animals (Wilber and Hunter 1977).

On a nationwide basis, the two most commonly used techniques for management of the pollution present in highway runoff are roadside swales and detention/retention facilities. Many states now require that specified amounts of excess rainfall from developed areas be collected and treated in such systems. Current (1985) regulations specified in Chapter 17-25 of the Florida Administrative Code require new developments in Florida to provide either retention or detention with filtration of the runoff from the first one inch of rainfall, or as an option, for projects with drainage areas less than 100 acres, facilities which provide retention or detention with filtration of the first one-half inch of runoff.

As these detention/retention facilities receive continual inputs of stormwater containing heavy metals, processes such as precipitation, coagulation, settling, and biological uptake will result in a large percentage of the input mass being deposited in the sediments. Over time, this continual accumulation may begin to present a toxicity or pollution potential to surrounding surface waters or groundwater, particularly if physical and chemical changes occur within the stormwater management facility which mobilizes certain species from the sediment phase into the water phase. With the large number of retention/detention facilities existing in Florida and other parts of the country, the potential for contamination of other waters by these systems is magnified if heavy metals become mobilized. No previous definitive studies have been conducted to determine the fate of toxic species, especially heavy metals, in these stormwater management systems.

The purpose of this research was to investigate the fate of heavy metals within stormwater management systems. The specific objectives were to:

1. Determine the extent to which dissolved heavy metals input by stormwater are removed from the water phase of the retention pond
2. Investigate the horizontal and vertical migration of particulate and settled heavy metals in the sediments of the retention pond
3. Determine fractions of heavy metals in the sediments which can be solubilized by various extraction procedures

4. Determine the specific changes in pH and redox potential which may result in mobilization of heavy metals from the sediments into the water phases
5. Determine the potential for metal transport into soils and possible contamination of groundwater

CHAPTER 2
LITERATURE REVIEW

Occurrence of Heavy Metals in Highway Runoff

Heavy metals in highway runoff have been reported to originate not only from the operation of motor vehicles and direct fallout, but also from the highway materials as well. Sources of metals include gasoline (Pb), exhaust emissions (Pb, Ni), crankcase and lubricating oils (Pb, Ni, Zn), grease (Zn, Pb), tire wear (Cd, Zn), wear on moving bearings (Cu, Pb), decorative and protective coatings (Al, Cd, Cu, Zn, Ni, Fe), brake lining wear (Cu, Cr, Ni), moving engine parts (Fe, Mn, Cr, Co), and asphalt paving wear (Ni, V) (Hopke et al. 1980, Novotny and Chesters 1981, and Portele et al. 1982). Christensen and Guinn (1979) indicated an average deposition of 0.0030 g zinc/vehicle/km predominantly from tire wear, and 0.0049 g lead/vehicle/km from lead in gasoline.

In a study on the contribution of urban roadway use to water pollution, Shaheen (1975) stated that the majority of solids deposited on roadways are vehicle dependent with over 95 percent of the material being inorganic in nature. He found that less than 5 percent of the solids deposited on the roadway originated from the vehicles themselves, and that vehicles act predominantly as a transport mechanism for pollutants picked up at other locations.

Several investigators have found close correlations between metal concentrations and total solids concentrations in highway runoff (Clark et al. 1981, and Portele et al. 1982). The combustion of lead containing fuels was reported by Goyer and Chisolm (1972) to be the primary source of lead in the atmosphere, resulting in a release of approximately 163,265 metric tons into the environment in 1971. Stinger and Hanson (1969) suggested that this source is thought to account for about 98 percent of all known atmospheric lead emissions with approximately half of these emissions being deposited within 30 meters of the highway. The U.S. Public Health Service (1966) reported atmospheric concentrations of lead in a typical urban area of 1 to 3 $\mu\text{g}/\text{m}^3$ and to to 40 $\mu\text{g}/\text{m}^3$ in air near heavily traveled roadways. However, the gradual removal of lead from gasoline during the 1980s may decrease this figure somewhat in future years.

The cadmium content of diesel fuels and heating oils was found to range from 0.07 to 1.0 ppm and from 0.42 to 0.54 ppm, respectively (Lagerwerff and Specht 1970). The cadmium concentration in motor oil was reported to average 0.48 ppm by the National Air Pollution Control Association (1969). Lagerwerff and Specht (1970) reported that the concentrations of cadmium in soil and vegetation beside major highways decreased with distance from the traffic. They stated that the cadmium concentrations in soil and vegetation were related to the average cadmium concentration in the motor oil and tires of the vehicles which travel the roadway.

The significance of the contribution of direct precipitation in contributing heavy metals to highway runoff has been studied with conflicting results. Wilber and Hunter (1977) found that concentrations of heavy metals in precipitation were insignificant in relation to the concentrations found in highway runoff. However, Larsen (1973) stated that bulk precipitation in western Washington contributed significant quantities of trace metals. Bourcier and Hindin (1979) conducted an investigation in which they measured deposition rates of heavy metals inside a viaduct to represent deposition due solely to operation of vehicles and compared these values to deposition rates at a control station outside the viaduct, in an area unaffected by highway traffic. A summary of their findings is presented in Table 2-1. They concluded that the relatively low loadings of metals at the control station compared to that for the viaduct indicate that the major source of heavy metal deposition is vehicle related. Each of the total metals found in the runoff existed primarily in particulate form with only a small percentage in the dissolved-colloidal fraction. They also concluded that a residual amount of metals will remain on the road surface after each storm.

Among the toxic metals, Pb, Zn, and Cu are the most abundant in highway runoff and have received the most study. Wilber and Hunter (1977) found that the major contributors of heavy metals in stormwater were lead, zinc, and copper. Together, these accounted

TABLE 2-1
DEPOSITION RATES OF METALS IN DUST SAMPLES
AT VIADUCT STATIONS AND CONTROL STATION

HEAVY METAL	MEAN (mg/m ² /day)	STANDARD ERROR OF THE MEAN	RANGE OF VALUES (mg/m ² /day)
Viaduct Stations ¹			
Fe	317.	60.8	61.3 - 1048.
Pb	2.92	0.67	0.377- 10.2
Cr	0.513	0.12	0.038- 1.58
Zn	42.2	12.3	1.08 - 163.
Control Stations ²			
Fe	6.78	3.93	0.380- 25.6
Pb	0.366	0.29	0.004- 1.83
Cr	0.222	0.09	0.002- 0.646
Zn	0.798	0.22	0.082- 1.38

NOTES: 1. n = 18
2. n = 6

SOURCE: Bourcier and Hindin (1979)

for approximately 90 to 98 percent of the total metals observed, with lead and zinc together accounting for as much as 89 percent. Nickel and chromium were found in considerably smaller quantities. It was also reported that peak concentrations of heavy metals were observed shortly after the initiation of runoff, usually within the first 30 minutes. They also reported a tendency for solids to settle out in the storm sewers during the latter stages of the storm flow.

The significance of average daily traffic (ADT), percent imperviousness, and dustfall to metal concentrations in highway runoff was examined by Gupta et al. (1981). Both simple and multiple correlations were performed between characteristics of the study site, such as average daily traffic, percent imperviousness, and dustfall and measured heavy metal concentrations. For the simple correlations, heavy metal concentrations were found to correlate best with percent imperviousness, although significant correlations were found with only Pb, Zn, and Cu. However, when multiple correlations were considered, the correlations improved considerably with the combination of all three site characteristics producing the best correlations.

The quantities of heavy metals in highway runoff, and the forms in which they exist, depend to a large degree on the physical and chemical behavior of the specific elements. Lead has been shown to exist on the highway in a predominantly insoluble particulate form which is largely inorganic in nature (Laxen and Harrison 1977). It was also found that most of the lead emitted from automobile exhaust occurs in two distinct particle sizes: less than 1 micron and 5 to 50 microns. Habibi (1970) found in wind tunnel experiments that between 50 percent to 60 percent of Pb particles greater than 9 microns are deposited within 7 m of the exhaust pipe. Wang et al. (1982), in a study conducted in Washington state, found that approximately 92 percent of the total lead present was associated with particles greater than 20 microns in size.

Actual concentrations and loading rates of heavy metals in highway runoff have been presented by numerous researchers from many areas of the country. Most of the data is highly site specific and reflects variations in dustfall, average daily traffic, land use in the area of the highway, as well as many other contributing parameters. However, one of the most extensive studies of metals in highway runoff was conducted by Gupta et al. (1981). Samples were collected at six highway sites in four states (Pennsylvania, Tennessee, Wisconsin, and Colorado), representing a wide range of ADT values, geographic locations, drainage areas and design characteristics, pavement types, and receiving water characteristics. A summary of highway runoff data for 159 storm events is listed in Table 2-2. In most highway runoff investigations it is found that Zn, Cu, and Cd are all considerably more soluble than Pb. Shaheen (1975) observed that dissolved Zn was almost always higher than dissolved Pb in roadway runoff, despite the fact that Pb was approximately eight times more abundant in materials deposited on the highway.

Effects of Heavy Metals on Aquatic Communities

In spite of the known toxic effects of numerous heavy metals, little research has been done to analyze the impact of these metals on the aquatic community (Portele et al. 1982). This analysis is complicated by the fact that heavy metals may exist in many

TABLE 2-2
 SUMMARY OF HEAVY METALS IN HIGHWAY RUNOFF
 AT SEVEN LOCATIONS DURING 1976-77

HEAVY METAL	METAL CONCENTRATION (mg/l)		METAL LOADINGS (Kg/ha/EVENT)		METAL LOADINGS (Kg/ha/cm RUNOFF)	
	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE	RANGE
Pb	0.96	0.02 -13.1	0.065	0.00-0.54	0.097	0.002 -1.31
Zn	0.41	0.01 - 3.4	0.025	0.00-0.13	0.041	0.0009-0.34
Fe	10.30	0.10 -45.0	0.56	0.00-3.9	1.03	0.01 -4.50
Cu	0.103	0.01 -0.88	0.0063	0.00-0.033	0.010	0.0009-0.088
Cd	0.040	0.010-0.40	0.0019	0.00-0.016	0.003	0.0009-0.040
Cr	0.040	0.10 -0.14	0.031	0.00-0.033	0.047	0.0009-0.014
Hg	0.003	0.001-0.067	0.0007	0.00-0.0024	0.32	0.0128-6.70

SOURCE: Gupta et al. (1981)

different chemical speciations, each of which exhibits a unique toxicity and method of movement in the environment. The majority of studies presenting data on heavy metals in highway runoff have presented results for total metals without regard for the physical state or chemical speciation of the metals present.

Although the effects of various heavy metals on algal growth has been extensively documented, very little is available concerning the specific effects of heavy metals in highway runoff on algal productivity. In one of the few studies which tested the effects of actual highway runoff on algal productivity, Harper et al. (1980) reported in bioassay experiments using Selenastrum capricornutum, that additions of highway runoff in concentrations less than 25 percent to Lake Eola water would stimulate and increase algal

production. However, in concentrations greater than 25 percent, a significant decline in total algal production was observed along with initial cell deaths ranging from 25 percent to 90 percent, depending on the relative concentration of highway runoff used.

In another recent study, Winters and Gidley (1980) concluded that lead and zinc appeared to be the factors responsible for the inhibition of algal growth in similar experiments. Portele et al. (1982), in algal bioassays conducted using Selenastrum capricornutum to assess the potential toxicity of runoff from I-5, found a definite trend toward reduced growth as the ratio of highway runoff to receiving water increased. It was suggested that higher concentrations of soluble zinc and copper were responsible for the observed toxic response. It was also reported that the toxicity of the stormwater could be reduced, as indicated by 96-hour toxicity tests, by travel or passage through a grassed channel. Reductions of 61 percent and 77 percent were reported for acid extractable concentrations of total zinc and lead, respectively, during travel through this grassed channel.

Bartlet and Rabe (1974) in a series of bioassay studies with Selenastrum reported that inhibition of algal growth would occur when the concentration of copper reaches 50 $\mu\text{g}/\text{l}$, when zinc reaches 30 $\mu\text{g}/\text{l}$, and when cadmium reach 50 $\mu\text{g}/\text{l}$. Complete inhibition was found at 90 $\mu\text{g}/\text{l}$ for copper, 120 $\mu\text{g}/\text{l}$ for zinc, and 80 $\mu\text{g}/\text{l}$ for cadmium. Braek et al. (1976) investigated the effect of synergistic or antagonistic actions of various heavy metals in combination on

toxicity. He concluded that for certain algal species the combination of copper and zinc produced antagonistic effects while producing synergistic reactions for other species.

The effects of various heavy metals on freshwater zooplankton have been examined by several researchers. Borgman et al. (1980) reported that concentrations of cadmium, mercury, and copper at considerably lower levels than necessary to produce mortality could significantly inhibit the growth of copepods. Biesinger and Christenson (1972) suggested that the toxic effects of heavy metals on zooplankton are due to covalent bonding of the metals at the cell surface. Gupta et al. (1981) reported no toxic response to Hexagenea (mayfly nymph), or Daphnia during a four-day exposure to undiluted highway runoff, whereas Gammarus (amphipod) was found to have a mortality of 40 percent. Portele et al. (1982) found that the toxic effects of highway runoff on zooplankton are related to the number of vehicles passing during the storm. In experiments using Daphnia, the 72-hour survival rate was 96.7 percent for a low traffic state road compared to only 13.3 percent for I-5.

The effects of heavy metals on fish have been investigated by numerous researchers. In one study, Skidmore (1964) reported that the hatching rate of rainbow trout eggs was reduced to zero at zinc concentrations as low as 40 µg/l. The survival rate of juvenile trout was reduced to only 46 percent at zinc concentrations of 10 µg/l. The tolerable concentration of zinc was found to increase as the fish matured to the point where the 48-hour LC₅₀ for trout

fingerlings increased to 600 µg/l zinc. Portele et al. (1982) conducted experiments on rainbow trout using both filtered and unfiltered highway runoff. Experiments performed with filtered water produced no toxic effects, while the impact was significantly increased with unfiltered stormwater. It is suggested that the mortalities were due to the presence of suspended solids or pollutants associated with the particulates.

Studies on the biotoxicity of lead on brook trout were conducted by Dorfman and Whitworth (1969) in a series of laboratory investigations. They found that a lead dosage of 25 mg/l reduced the growth of trout, but no effect could be detected on growth at lower lead levels.

In a similar study, Lloyd (1961) reported that the toxicity of lead, zinc, and copper salts to rainbow trout increased as the dissolved oxygen content of the water decreased. This increased toxicity was linked to an increase in exposure due to increased respiratory flow rather than a change in metal speciation due to a redox potential induced transformation.

Chemistry of Metal Ions in Aerobic Natural Waters

Metal ions in natural waters are present in many varied forms. These ions can exist in the free metal form, in complexes with inorganic species such as chlorides, sulfates, carbonates and phosphates, in organic complexes with a large number of natural and synthetic ligands, as well as in associations with other metal

species. Each of these complexes affect the solubility, movement, reactions, stability, and toxicity of the particular metal.

Inorganic Complexes

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. In equilibrium systems containing several metals and several ligands, the concentration as well as the distribution of any metal or ligand will depend on the total concentration of all the other constituents of the system. Metals and ligands combine to form complexes and solids, each one of which is a node in the network of interactions. For many ions these species form the limits for solubility of the metal. 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 Complexation

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 percent to 80 percent of the dissolved organic carbon and particulate organic carbon in fresh waters consists of humic substances.

Humic substances are basically polymers with molecular weights between 300 and 30,000 which contain phenolic OH and carboxylic groups along with some aliphatic OH groups (Stumm and Morgan 1981). Humic substances are usually divided into three fractions based on their solubility in alkaline and acid solutions:

1. Humic Acid: soluble in alkaline solution, but insoluble in acid solution
2. Fulvic Acid: the humic acid fraction that remains in the acidified solution
3. Humin: not soluble in either acid or base

The physical structures of the three fractions are thought to be quite similar with only small differences in molecular weight and functional groups (Stumm and Morgan 1981). Fulvic acid has probably the lowest molecular weight but contains more hydrophilic functional groups (Schnitzer 1969). 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 substance occurring naturally in water. A suggested structure of fulvic acid by Schnitzer (1969) is given in Figure 2-1.

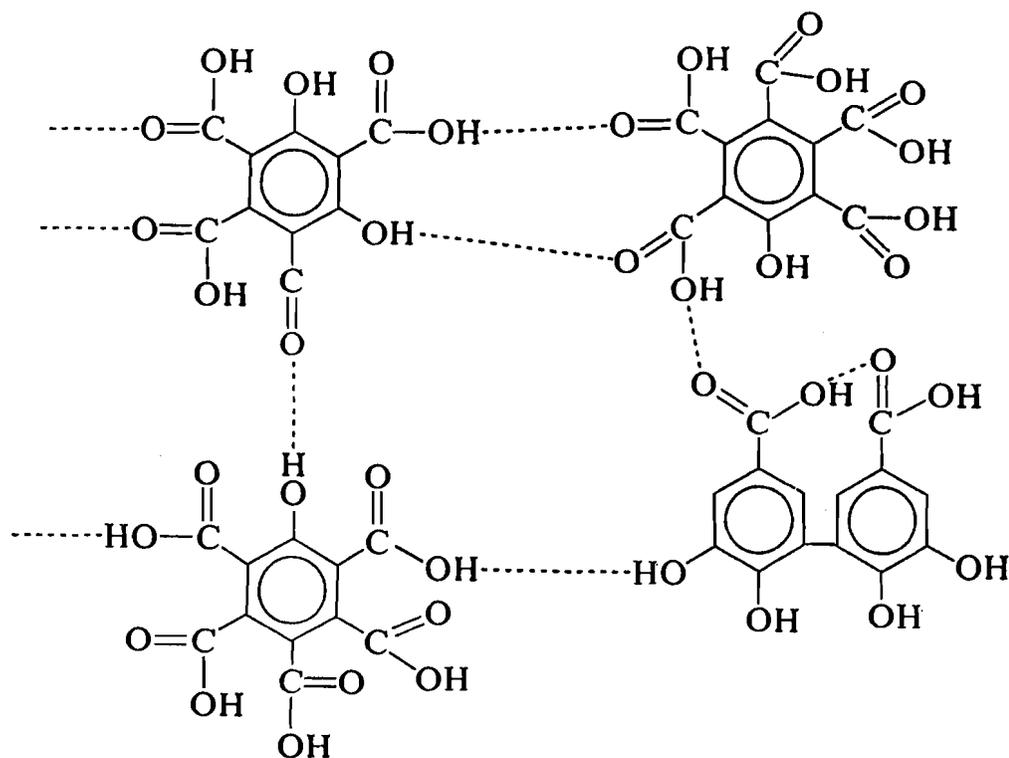


Figure 2-1. Proposed Structure of Fulvic Acid (Schnitzer 1969).

In addition to humic substances, tannins (which are derivatives of gallic acid) are often present in fresh waters where leaching of bark and leaf litter is abundant (see Figure 2-2). Tannins have chemical properties similar to those of humic substances (Stumm and Morgan 1981).

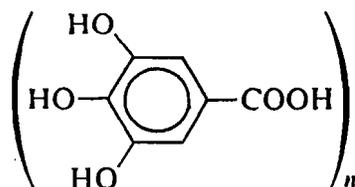


Figure 2-2. Structure of Tannic Acid (Stumm and Morgan 1981).

Black and Christman (1963) verified that fulvic acids, as well as most organic matter in surface waters, can be viewed as polyelectrolytic weak acids which carry a negative charge. The most probable reaction mechanism between humic compounds and metal ions is the formation of complex bonds with carboxyl and phenolic groups, some of which form quite stable combinations. However, it has been noted that all metal ions will not react in the same fashion with these acids. In general, the stability of humic complexes has been shown to increase with increasing pH due to the proposed ionization of more functional groups of the humic-polyelectrolyte molecule. An increase in the ionic strength of a water will result in a decrease in the measured stability of humic-metal complexes (Schnitzer and Hansen 1970).

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, developed by the U.S. Geological Survey

(1980), 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 showed 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, as indicated in Figure 2-3. Copper, however, exhibits a significant metal organic complex even at low concentrations of fulvate (Figure 2-4).

Until recently, the origin of organic compounds in natural waters has been strictly biogenic in nature. However, inputs of synthetic organic complexes in natural waters by man has increased significantly over the past few decades. This introduction of man-made substances into natural waters has resulted in a wide spectrum of new reactive chemical species.

The most common and widespread of these new organic complexes are nitrilotriacetate and citrate, both of which are used as substitutes for penta-sodium tri-polyphosphate in detergents. These compounds can be found today in virtually every water system which has been affected by the influence of man. Lerman and Childs (1973) state that nitrilotriacetate and citrate, as well as other man-made substances, are likely to be stronger complexing agents than naturally occurring ligands such as humic and fulvic acids.

By using a model fresh water system similar to that present in Lake Ontario and utilizing equilibrium constants of

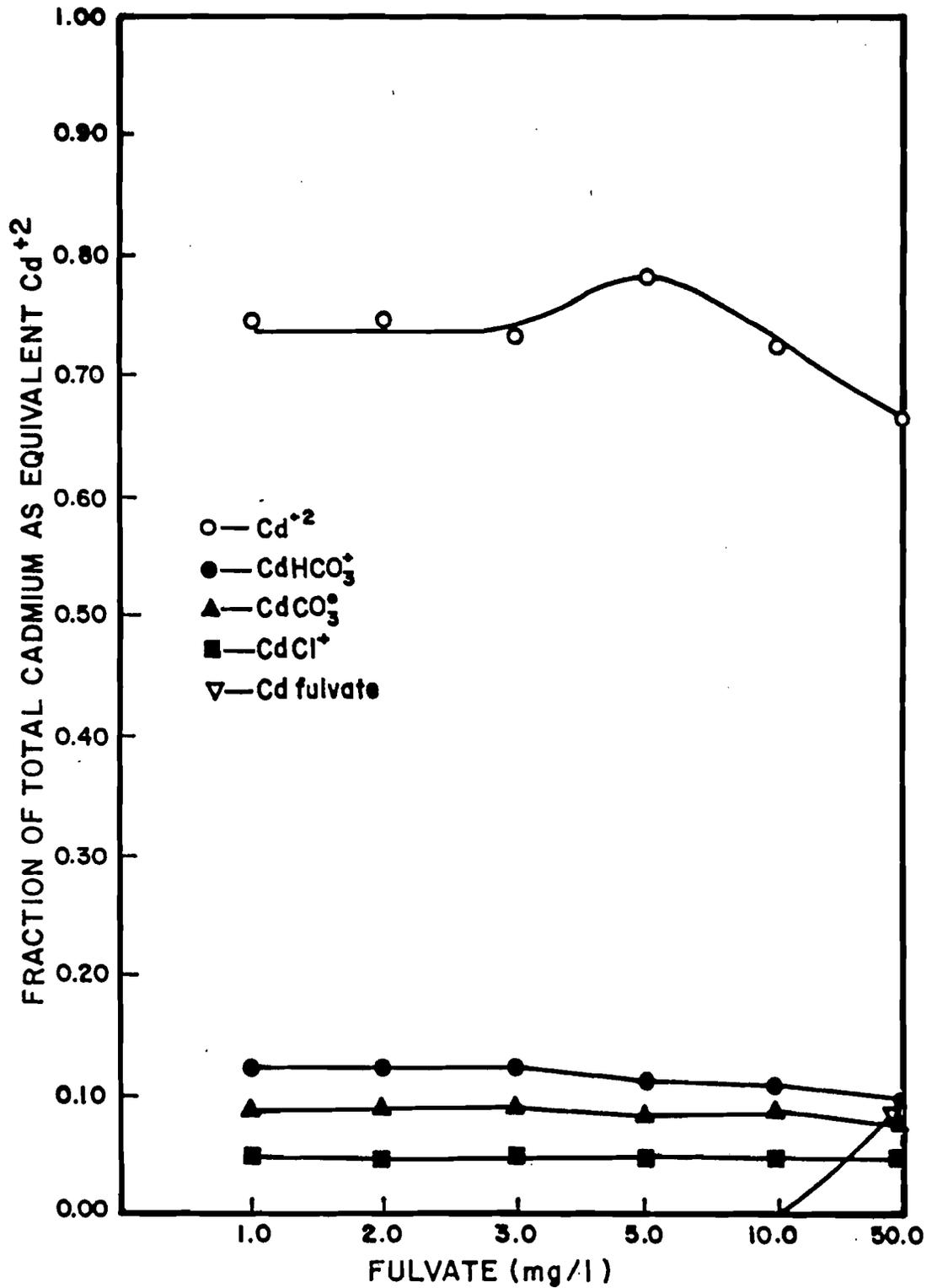


Figure 2-3. Cadmium Speciation as a Function of Fulvate Concentration (Temperature = 20°C, pH = 7.0) (Yousef et al. 1984).

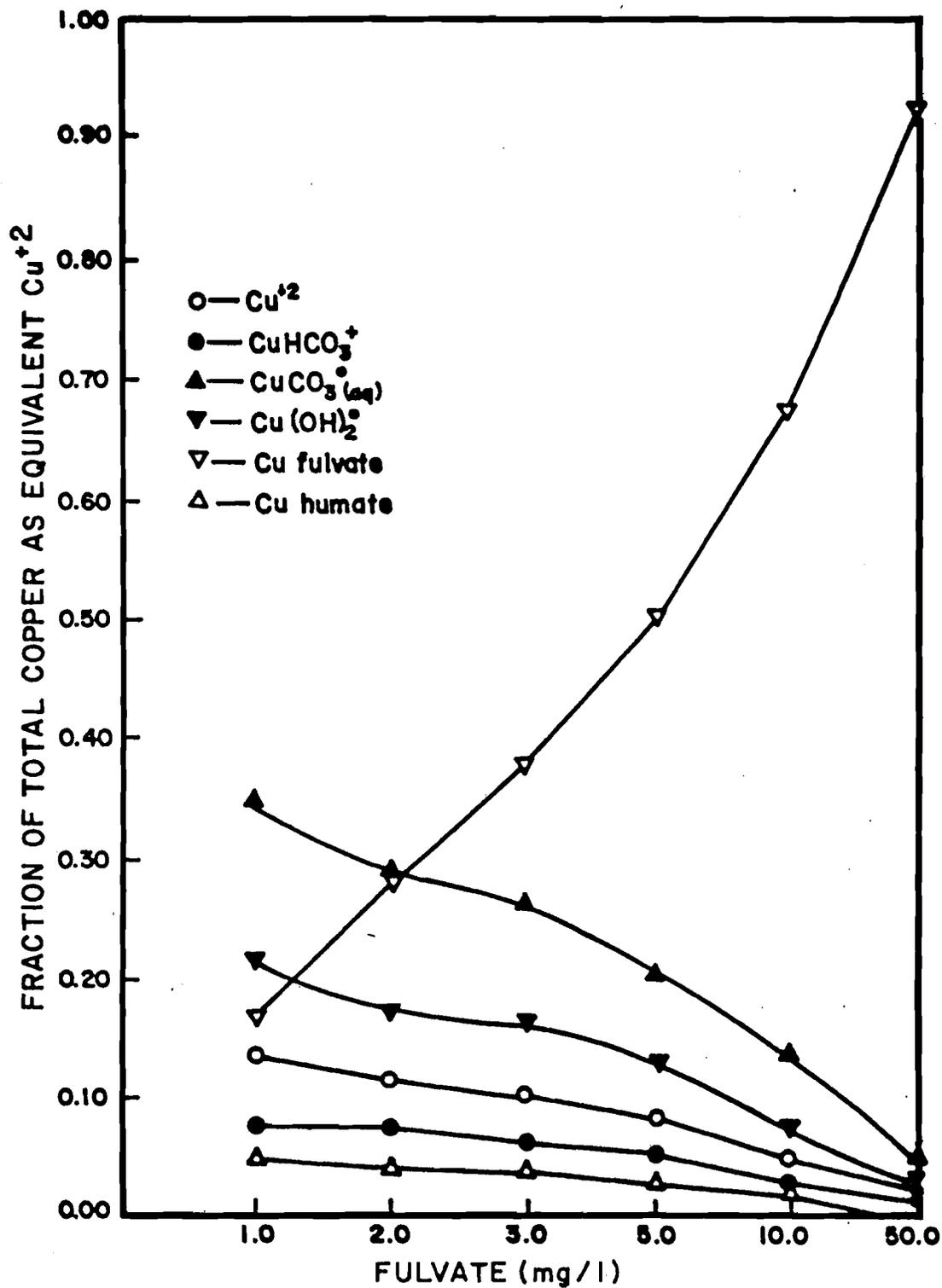


Figure 2-4. Copper Speciation as a Function of Fulvate Concentration (Temperature = 20°C, pH = 7.0) (Yousef et al. 1984).

nitrilotriacetate (NTA) and citrate complexes, Lerman and Childs were able to predict the importance of metal-NTA complexes and metal-citrate complexes for various heavy metals. Copper was found to preferentially complex with nitrilotriacetate at low concentrations of NTA almost to the exclusion of other metal species. As the concentration of NTA increases, the calcium-NTA complex becomes important. For citrate complexes both copper and iron were preferentially complexed with citrate at low concentrations of citrate with calcium complexation becoming significant at higher concentrations.

Schnitzer and Hansen (1970) conducted a study in which stability constants for nine divalent metal ion-fulvic acid complexes were measured. The values were given at pH values of 3.5 and 5.0 and are listed below:

log Ka, pH = 3.5:

Cu	>	Fe	>	Ni	>	Pb	>	Co	>	Ca	>	Zn	>	Mn	>	Mg
5.8		5.1		3.5		3.1		2.2		2.0		1.7		1.5		1.3

log Ka, pH = 5.0:

Cu	>	Pb	>	Fe	>	Ni	>	Mn	>	Co	>	Ca	>	Zn	>	Mg
8.7		6.1		5.8		4.1		3.8		3.7		2.9		2.3		2.1

It is apparent from these values that the stability constants increased as the pH increased from 3.5 to 5.0. This was attributed to the greater number of functional groups which ionize as pH

increases. In reducing sediments where the pH tends to approach 7, it follows that even more stable organo-metallic complexes may be present as a result of greater ionization of the organic material.

Consequential Species of Heavy Metals in Highway Runoff and Retention Ponds

One of the most extensive investigations into the speciation of heavy metals associated with highway runoff and stormwater management systems was conducted by Yousef et al. (1985). In this study the speciation model of Batley and Florence (1976) was used to divide samples of rainfall, highway runoff, and receiving body waters into three reactive or labile forms and four non-reactive or non-labile forms.

One of the two sample sites investigated by Yousef et al. (1985) was an intersection or interchange between Interstate 4 and Maitland Boulevard north of the city of Orlando, Florida. At this location, samples of rainfall, highway runoff, and the surface water in one of the retention ponds receiving runoff from the interchange were collected and carried through the speciation scheme. A summary of this speciation of rainfall, highway runoff, and retention pond water at the Maitland Interchange site is presented in Tables 2-3 through 2-5.

The speciation of Cd, Zn, Pb, and Cu in rainfall water collected at the Maitland site (Table 2-3) appears to be predominantly in the reactive inorganic (labile) state. Soluble

TABLE 2-3
 SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN RAINFALL WATER FROM MAITLAND INTERCHANGE SITE

DISSOLVED METAL FRACTION													
METAL	PARAMETER	LABILE (REACTIVE)				NON-LABILE (NON-REACTIVE)				TOTAL DISSOLVED METAL			
		ORGANIC		INORGANIC		ORGANIC		INORGANIC		SOL.	COLL.	SOL.	COLL.
		COLL.	SOL.	COLL.	SOL.	COLL.	COLL.	SOL.	COLL.	COLL.	SOL.	COLL.	
Cd	n	4	4	4	4	4	4	4	4	4	4	4	4
	x(µg/l)	0.01	1.69	0.44	0.003	0.015	0.32	0.015	0.015	0.015	0.32	0.015	2.49
	%	0.4	67.8	17.7	0.1	0.6	12.8	0.6	0.6	0.6	12.8	0.6	100.0
Zn	n	2	2	2	2	2	2	2	2	2	2	2	2
	x(µg/l)	0.0	3.90	3.73	0.0	0.0	0.52	0.0	0.0	0.0	0.52	0.0	8.15
	%	0.0	47.9	45.8	0.0	0.0	6.3	0.0	0.0	0.0	6.3	0.0	100.0
Pb	n	3	3	3	3	3	3	3	3	3	3	3	3
	x(µg/l)	3.6	9.67	11.4	1.03	0.83	3.07	0.83	0.83	0.83	3.07	7.97	37.6
	%	9.6	25.7	30.3	2.8	2.2	8.2	2.2	2.2	8.2	21.2	21.2	100.0
Cu	n	4	4	4	4	4	4	4	4	4	4	4	4
	x(µg/l)	14.9	16.0	24.6	10.4	0.01	0.2	0.01	0.01	0.2	0.2	0.01	66.1
	%	22.6	24.2	37.2	15.7	0.0	0.3	0.0	0.0	0.3	0.3	0.0	100.0

SOURCE: Yousef et al. (1985)

TABLE 2-4
SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN RUNOFF WATER FROM MAITLAND INTERCHANGE SITE

METAL	PARAMETER	DISSOLVED METAL FRACTION												TOTAL DISSOLVED METAL
		LABILE (REACTIVE)				NON-LABILE (NON-REACTIVE)				TOTAL				
		ORGANIC COLL.	SOL.	INORGANIC COLL.	SOL.	ORGANIC COLL.	SOL.	INORGANIC COLL.	SOL.	ORGANIC COLL.	SOL.	INORGANIC COLL.	SOL.	
Cd	n	6	6	6	6	6	6	6	6	6	6	6	6	6
	x(µg/l) %	0.02 1.2	0.81 50.5	0.53 33.0	0.05 3.1	0.0 0.0	0.16 10.0	0.035 2.2	1.61 100.0					
Zn	n	3	3	3	3	3	3	3	3	3	3	3	3	3
	x(µg/l) %	0.06 0.3	15.87 68.9	5.36 23.3	0.1 0.4	0.0 0.0	1.64 7.1	0.01 0.0	23.04 100.0					
Pb	n	5	5	5	5	5	5	5	5	5	5	5	5	5
	x(µg/l) %	0.33 0.8	19.9 48.9	9.34 23.0	1.01 2.5	4.91 12.1	1.93 4.7	3.25 8.0	40.7 100.0					
Cu	n	6	6	6	6	6	6	6	6	6	6	6	6	6
	x(µg/l) %	2.37 8.9	4.29 16.1	5.55 20.9	0.81 3.0	11.9 44.7	1.4 5.3	0.28 1.1	26.6 100.0					

SOURCE: Yousef et al. (1985)

TABLE 2-5
 SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN POND WATER FROM MAITLAND INTERCHANGE SITE

METAL	PARAMETER	DISSOLVED METAL FRACTION										TOTAL DISSOLVED METAL
		LABILE REACTIVE)				NON-LABILE (NON-REACTIVE)				TOTAL DISSOLVED METAL		
		ORGANIC		INORGANIC		ORGANIC		INORGANIC				
COLL.	SOL.	COLL.	SOL.	COLL.	SOL.	COLL.	SOL.	COLL.	SOL.			
Cd	n	8	8	8	8	8	8	8	8	8	8	8
	x(μg/l)	0.005	0.59	0.31	0.03	0.008	0.095	0.01	0.01	0.01	1.05	
Zn	n	4	4	4	4	4	4	4	4	4	4	4
	x(μg/l)	0.03	1.37	9.04	0.0	0.0	0.4	0.0	0.0	0.0	10.84	
Pb	n	7	7	7	7	7	7	7	7	7	7	7
	x(μg/l)	0.53	4.0	6.76	0.66	2.34	4.68	1.4	1.4	1.4	24.4	
Cu	n	8	8	8	8	8	8	8	8	8	8	8
	x(μg/l)	6.16	3.93	2.86	0.2	2.24	0.32	0.28	0.28	0.28	16.6	
	%	38.5	24.6	17.9	1.3	14.0	2.0	1.7	1.7	1.7	100.0	

SOURCE: Yousef et al. (1985)

metal fractions of species other than inorganic, in general, accounted for less than 5 percent of any given category with the exceptions of a soluble non-reactive (non-labile) inorganic cadmium fraction (12.8%), a colloidal non-reactive inorganic lead fraction (21.2%), and a colloidal reactive organic copper fraction (22.6%).

The speciation of metals in runoff water at the Maitland site (Table 2-4) was similar to that observed for rainfall. The dominant dissolved fraction was again reactive inorganic species comprising in excess of 75 percent of the total dissolved metal concentration for all metals except copper. The dominant form of copper in the runoff water, approximately 45 percent of dissolved metal, was a non-reactive organic colloidal species. Dissolved concentrations of cadmium and lead were similar in both rainwater and runoff water. However, total dissolved concentrations of zinc were approximately four times higher in runoff than in rainwater, while copper was approximately three times higher in rainwater than runoff.

A summary of the dissolved heavy metal speciation in the retention pond water at the Maitland site is given in Table 2-5. The speciation of cadmium in the pond water is similar to that observed for rainwater and runoff. The dominant form of zinc in this water is still a reactive inorganic species similar to that observed in rainwater and runoff, but the soluble portion of this species has been substantially reduced and the colloidal portion substantially increased. The speciation of lead in the retention

pond was observed to have undergone substantial changes from the rainwater and runoff. Although the reactive inorganic colloidal fraction is similar to that measured in rainfall and runoff, the soluble species was found to have decreased. This transformation seemed to have resulted in increased concentrations of non-reactive soluble inorganic forms. The speciation of copper in the pond was observed to be similar to highway runoff except that the dominant category of non-reactive organic colloidal species in runoff has been converted to reactive organic colloidal species in the retention pond.

Concentrations of total dissolved metal in the retention pond water were substantially reduced from those measured in highway runoff with a general reduction in concentration of approximately 50 percent for the samples measured. The retention pond water was also found to have lower dissolved metal concentrations than rainfall for all metals tested with the possible exception of zinc. Yousef et al. (1985) concluded that the retention pond was very efficient in the removal of heavy metals from highway runoff. It was suggested that after removal from the water column these metals accumulate in the retention pond sediments.

The Effects of pH on Metal Speciation and Solubility

The speciation and solubility of metal ions in aquatic systems is controlled by changes in pH values. As indicated previously, metal ions can exist in a free ionic form in complexes with

inorganic species such as hydroxides, carbonates, and sulfates, as well with a wide variety of organic ligands. The solubility of each of these species is regulated to a large degree by pH.

The importance of pH in regulating aquatic equilibria can be seen in the equilibrium expressions for metal species in natural environments. Many of these expressions involve reactions with dissociation products of H_2O such as H^+ or OH^- , dissociation products of a phosphate system such as $H_2PO_4^-$, HPO_4^{2-} , or PO_4^{3-} , or dissociation products of the system such as SO_4^{2-} , HS^- or S^{2-} . Since the dominance and concentration of each of these species is regulated by pH, the resulting speciation and equilibrium concentrations of complexes formed between these species and metal ions are correspondingly regulated.

The effects of pH on metal speciation and solubility in aerobic surface waters were investigated by Yousef et al. (1985). As a part of this study, numerous literature and reference sources were examined to obtain a complete list of thermochemical data possible in surface waters. Solubility diagrams were then constructed for each metal which predict the dominant metal species and limiting concentration for metal ions in an aquatic system. These solubility diagrams are given in Figures 2-5 to 2-10.

The solubility diagram for iron is presented in Figure 2-5. In an aerobic environment the ferric (Fe^{+3}) form is dominant. This form of iron is relatively insoluble in the pH range of 6 to 10. The dominant soluble species of iron was found to be $Fe(OH)_2^+$

between a pH of 4 and 8 and Fe(OH)_4^- between a pH of 8 and 14. The dominant solid species under most conditions is the hydroxide, Fe(OH)_3 .

Inorganic speciation for zinc is presented in Figure 2-6. The dominant inorganic dissolved species are the Zn^{+2} ions below a pH of 7.0, ZnCO_3^0 between a pH of 7.0 and 9.0, and Zn(OH)_3^- above a pH of 10. Solid phases are formed with the hydroxide (Zn(OH)_2), the carbonate (ZnCO_3), the phosphate ($\text{Zn(PO}_4)_2$), and the oxide (ZnO). Zinc has been shown to be one of the most mobile of the heavy metals (Khalid et al. 1977). They reported that zinc compounds formed with common ions are soluble in both acid and alkaline solutions.

The solubility diagram for copper is shown in Figure 2-7. Copper was shown to exhibit soluble forms with chlorides, carbonates, sulfates, and hydroxides, although the Cu^{+2} and Cu(OH)_2^0 forms are dominant. The equilibrium solid forms of copper are the oxide and a hydroxide-carbonate form. The chemistry of copper and zinc appear to be closely related, although in general, copper compounds are less soluble (Khalid et al. 1977). Organic complexes have been shown to play a more important role in the solubility of copper than zinc, since copper has been shown to form more stable complexes with fulvic acids than other metals.

As indicated in Figure 2-8, lead can exist with a multitude of inorganic species such as chlorides, sulfates, hydroxides, and carbonates. The dominant dissolved species below a pH of 7 is Pb^{+2} , PbCO_3^0 from a pH of 7 to 10, and Pb(OH)_3^- above a pH of 10.

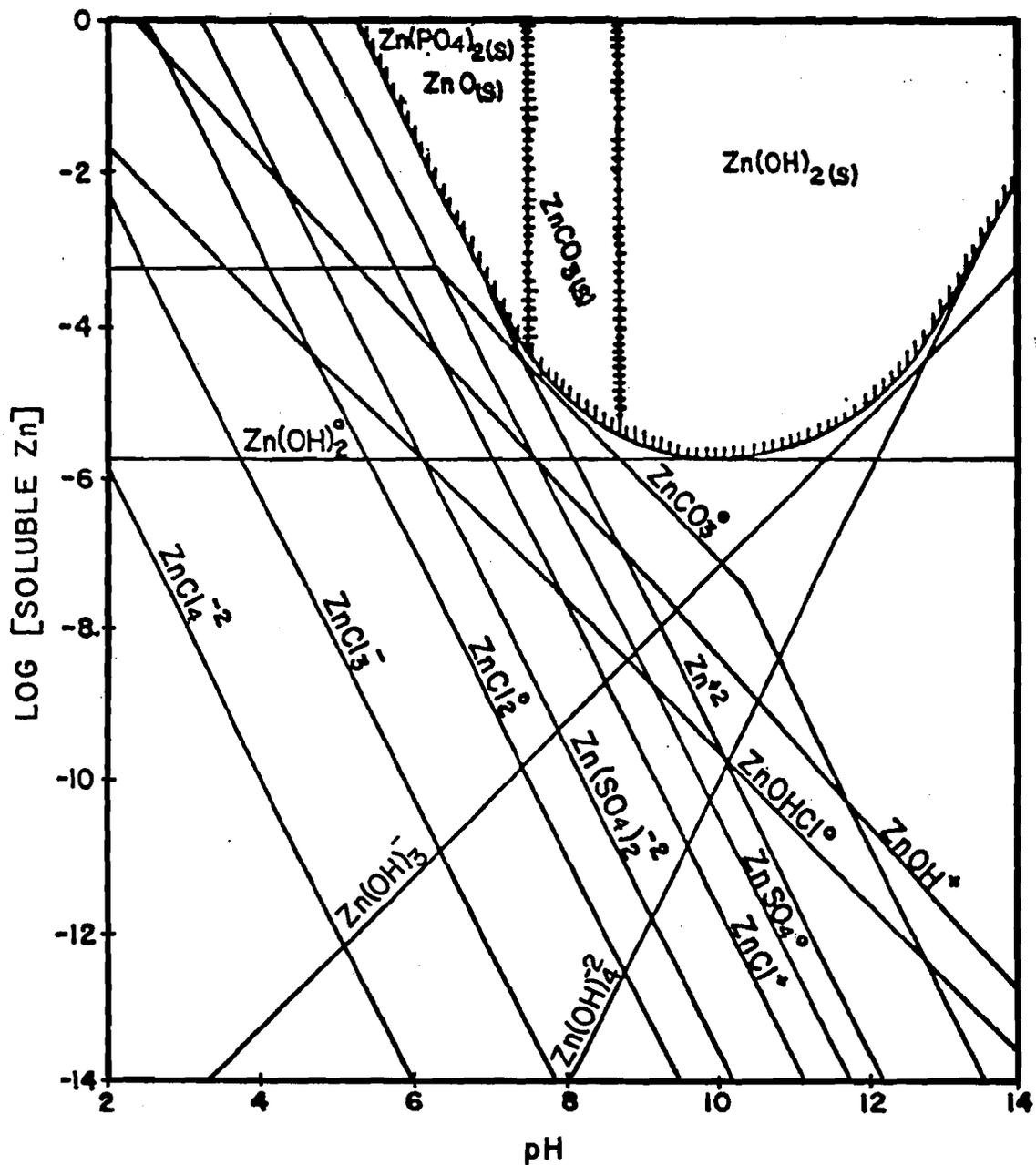


Figure 2-6. Solubility of Inorganic Zinc Ions in Natural Surface Waters (Assumptions: $C_T = 5 \times 10^{-4}$ M; $[Cl^-] = 5 \times 10^{-4}$ M; $[SO_4^{2-}] = 1 \times 10^{-4}$ M; and $[PO_4^{3-}] = 1 \times 10^{-5}$ M) (Yousef et al. 1985).

Important solid phases of lead are the hydroxide (Pb(OH)_2), the carbonate (PbCO_3), and the oxide (PbO).

In a similar study using a mathematical approach, Hahne and Kroontje (1973) examined the effects of hydroxide and chloride ions on the speciation of soluble inorganic lead. In chloride-free water, as pH was increased, divalent lead (Pb^{+2}) was found to dominate up to pH 5.0. The PbOH^+ form increased in importance to a pH of 6.0 where the two forms were equally important. Above a pH of 6.0, the dominant form was the hydroxide, PbOH^+ . At levels of pH where the Pb^{+2} ion was dominant, this form remained dominant up to chloride levels of 3500 mg/l. At greater chloride levels, the lead chloride, PbCl^+ , was the chief ionic form. In chloride levels approaching that of seawater, the uncharged PbCl_2^0 accounted for almost all of the total soluble concentration.

Inorganic speciation of cadmium ions is given in Figure 2-9. Cadmium can also exist as complexes with chlorides, sulfates, carbonates, and hydroxides. The dominant dissolved species is the Cd^{+2} ion below a pH of 8, CdCO_3^0 between a pH of 8 and 10, and Cd(OH)_2^0 above a pH of 10. Only two solid phases are important, the carbonate (CdCO_3) and the hydroxide (Cd(OH)_2).

Gardiner (1974), in a series of studies on the speciation of cadmium in rivers and lakes, reported that a substantial portion of the total cadmium present in rivers and lakes was present as the free metal ion, Cd^{+2} , with increasing importance as pH values

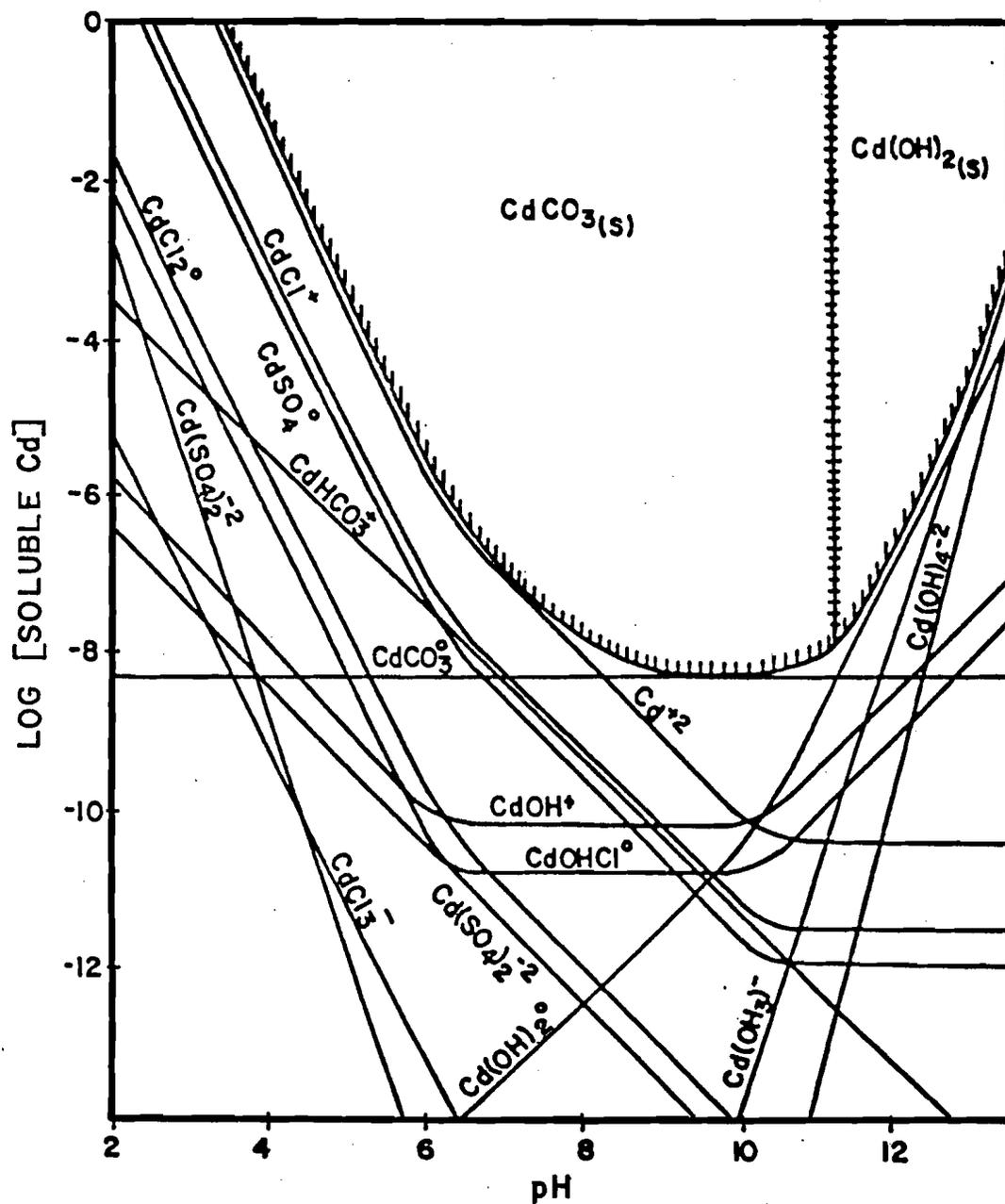


Figure 2-9. Solubility of Inorganic Cadmium Ions in Natural Surface Waters (Assumptions: $C_T = 5 \times 10^{-4}$ M; $[\text{Cl}^-] = 5 \times 10^{-4}$ M; $[\text{SO}_4^{2-}] = 1 \times 10^{-4}$ M; and $[\text{PO}_4^{3-}] = 1 \times 10^{-5}$ M) (Yousef et al. 1985).

decreased. It was also reported that cadmium can form stable complexes with carbonates and hydroxides as well as a wide variety of organic ligands.

The solubility diagram for nickel ions is presented in Figure 2-10. Nickel was shown to exhibit soluble species in complexes with chlorides, hydroxides, sulfates, and carbonates. Four dominant nickel species were found to be important: Ni^{+2} at pH values below 7, NiCO_3^0 at pH values between 7 and 10, $\text{Ni}(\text{CO}_3)_2^{-2}$ from pH values of 10 to 11, and $\text{Ni}(\text{OH})_3^-$ at pH values above 11. The dominant solid phases are the phosphate ($\text{Ni}_3(\text{PO}_4)_2$) and the hydroxide ($\text{Ni}(\text{OH})_2$).

The computer program, WATEQ2, was used by Yousef et al. (1985) to predict trace metal speciation in rainfall, highway runoff, and detention pond water from the Maitland Interchange. The dominant predicted species in Maitland rainfall for each of the tested metals, with the exception of copper, was the Me^{+2} form. This form accounted for 96 percent or more of the soluble forms of zinc, cadmium, lead, and nickel. Copper was split almost evenly between the Cu^{+2} form and the Cu-fulvate complex. These predicted values agreed with the actual measured concentrations presented in Table 2-3 from the laboratory speciation investigations by Yousef et al. (1985).

The dominant metal species present in Maitland runoff varied considerably from the predicted rainfall concentrations. Only zinc and cadmium still exhibited dominant Me^{+2} species in runoff with the MeHCO_3^+ and the MeCO_3^0 forms exhibiting fractions of 5 percent or

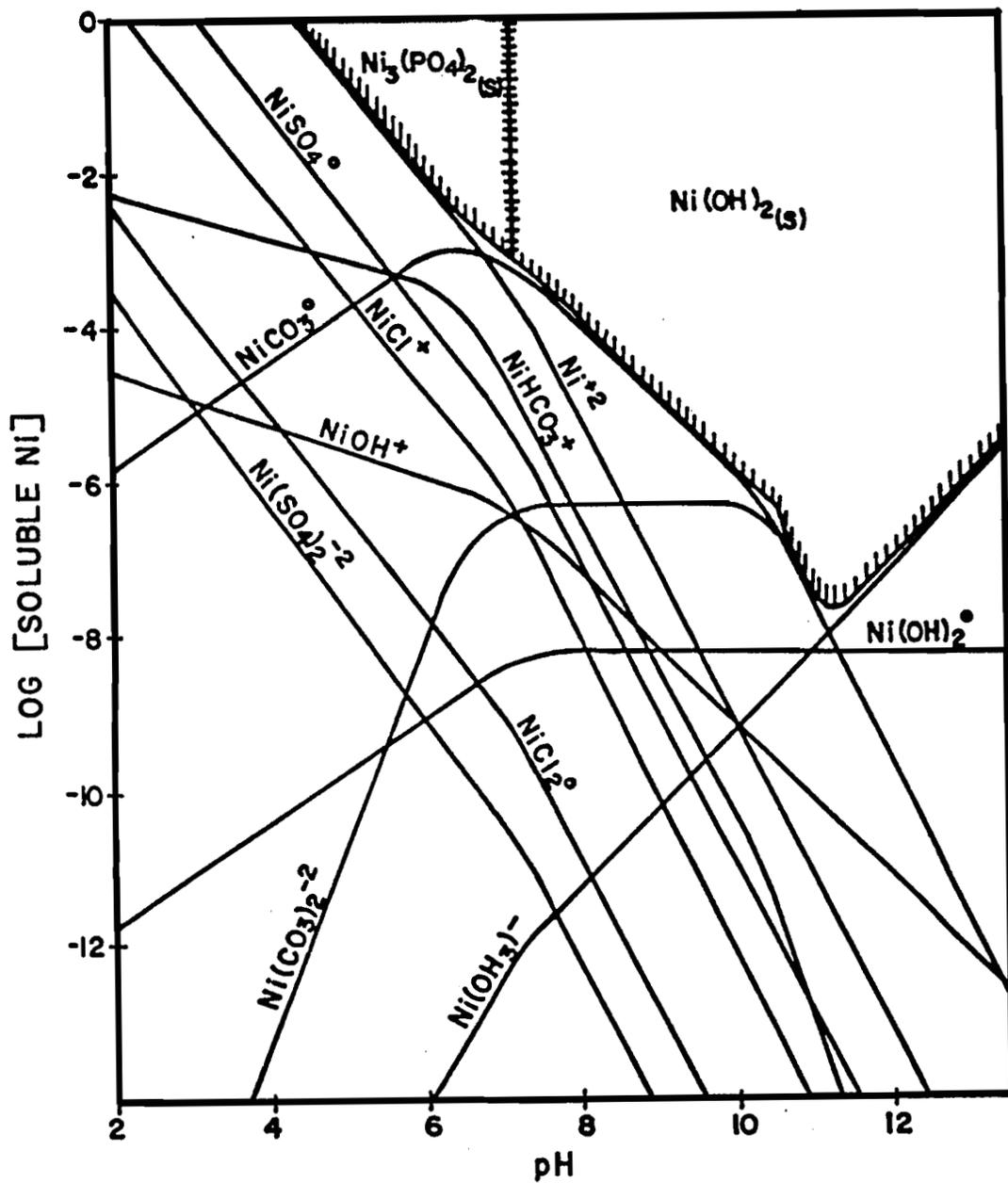


Figure 2-10. Solubility of Inorganic Nickel Ions in Natural Surface Waters (Assumptions: $C_T = 5 \times 10^{-4}$ M; $[\text{Cl}^-] = 5 \times 10^{-4}$ M; $[\text{SO}_4^{-2}] = 1 \times 10^{-4}$ M; and $[\text{PO}_4^{-3}] = 1 \times 10^{-5}$ M) (Yousef et al. 1985).

more. Lead was predicted to be present predominantly as PbCO_3^0 , with Pb^{+2} and PbHCO_3^+ of lesser importance. Copper was predicted to be present mainly as the Cu-fulvate complex, followed by CuCO_3^0 , Cu(OH)_2^0 , and with Cu^{+2} comprising only 9 percent of the total. Nickel was found to be present predominantly as the carbonate NiCO_3^0 , with a smaller fraction of Ni^{+2} .

Predicted speciation of metals in the pond water was virtually identical to the speciation predicted in highway runoff. Zinc and cadmium were present predominantly in the Me^{+2} forms, lead as PbCO_3^0 , copper as the Cu-fulvate complex, and nickel as NiCO_3^0 and Ni^{+2} .

In general, the predicted speciations obtained from WATEQ2 were very consistent with the measured values from the speciation experiments. More than 95 percent of the Zn, Cd, Pb, and Ni were found to be accounted for by reactive inorganic forms such as the Me^{+2} ion, metal carbonates, and bicarbonate species. The only deviation was noted for Pb which was found during the speciation experiments to have an organic complex that accounted for 15 percent of the total metal concentration, while the WATEQ2 model did not predict any. It was suggested by Yousef et al. (1985) that accurate reactions and thermodynamic data for Pb-organic complexes are not available and, therefore, not included in the WATEQ2 model.

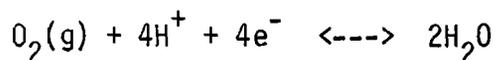
The Role of Redox Potential in Regulating
Metal Equilibria

Oxidation-Reduction Processes
in Aquatic Systems

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. Equilibrium expressions involving redox reactions should be viewed as a boundary condition toward which the system is proceeding (Stumm and Morgan 1981). A partial list of important redox processes in aquatic systems is given in Stumm and Morgan (1981).

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 often closely correlated with measurements of dissolved oxygen. This correlation is due to the fact that oxygen, when available, is used as the terminal electron acceptor by bacterial populations according to:



Sediments generally contain a considerable amount of partially decomposed organic matter which is derived primarily from the death and decay of both plant and animal matter. This organic matter is utilized as a food and energy source by predominantly heterotrophic bacterial populations in the oxidation process of respiration. If oxygen is available, bacterial populations utilize it as the preferred terminal electron acceptor. If the demand for oxygen exceeds the supply, first facultative and then anaerobic populations become active and reducible compounds such as nitrate, oxidized forms of iron and manganese, and other inorganic or organic species are reduced by microbial respiration. As oxygen is depleted in a 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 this sediment reduction is then indicated by the magnitude of the redox potential (Khalid et al. 1977).

Redox Potentials in Soils and Sediments

Patrick and Mahapatra (1968), however, suggested that redox potentials could be categorized into four general redox ranges. At a standard pH value of 7.0, soils characterized by a redox potential of +400 mv or more are considered to be oxidized, from +400 to +100 mv are moderately reduced, from +100 to -100 mv are reduced soils, and less than -100 mv are highly reduced soils. The oxidized layer at the sediment surface is usually very thin, and beneath this

oxidized layer the sediments become reduced quickly. This pattern was observed by Weiler (1973) during investigations on Lake Ontario. He observed that the overlying water column was well oxidized (greater than +400 mv). However, as the sediment-water interface is reached, the redox potential drops quickly, becoming strongly reduced (less than -100 mv) at a depth of 10 cm. He also observed that sediments which contained very little organic carbon were only moderately reduced (greater than +200 mv) at a depth of 10 cm.

The same general conclusions were reached by Mortimer (1971) who investigated the redox potential profiles across the sediment-water interface for Lake Windermere in England. The overlying water column had measured redox values between +200 and +300 mv. This potential dropped rapidly upon entering the sediments to a highly reduced value of -200 mv after only 4 cm. Mortimer also observed that coarse sediments containing little or no organic carbon were generally well oxidized while fine-textured sediments containing considerable organic carbon were highly reduced. It was also noted that during the winter months, the redox profiles shifted to values which were approximately 100 mv higher than during the summer months. He suggested that these seasonal fluctuations are a likely reflection of the temperature influence on biological activity.

Measurements of redox potential in the sediments of the Maitland Pond were conducted by Hvitved-Jacobsen et al. (1984). A summary of their findings for redox potentials at three stations in

the pond is given in Figure 2-11. Each of the three curves indicated in the figure represent an average value of redox potentials in two different core samples at each site.

The redox measurements indicate that the aerobic (oxidized) layer of the sediments is about 0.5 cm thick at two of the three stations. Extremely low redox potentials were not found in any of the anaerobic or reduced zones below this layer. The lack of extremely reduced conditions in these sediments was linked to the low oxygen demand of the sediments.

The Effects of Redox and pH on Metal Equilibria

Many equilibrium models based on thermodynamic data have been used to predict the chemical mobility of inorganic metal species in freshwater under various environmental conditions. Some of the more commonly used models are pH-redox potential diagrams which describe the stability fields of solids and predominant dissolved metal species in various systems, such as: $\text{CO}_2 + \text{S} + \text{H}_2\text{O}$. Such pE-pH stability field diagrams show, in a comprehensive way, how protons and electrons simultaneously shift the equilibria under various conditions and can indicate which species dominate under any given condition of pE and pH. The basic value of a pE-pH diagram is that it provides an aid in the interpretation of equilibrium constants by permitting the simultaneous representation of many reactions.

Under reduced environments, the solubility of many metal species is regulated by the $\text{SO}_4\text{-S}_{(s)\text{-H}_2\text{S}}$ system (Forstner and

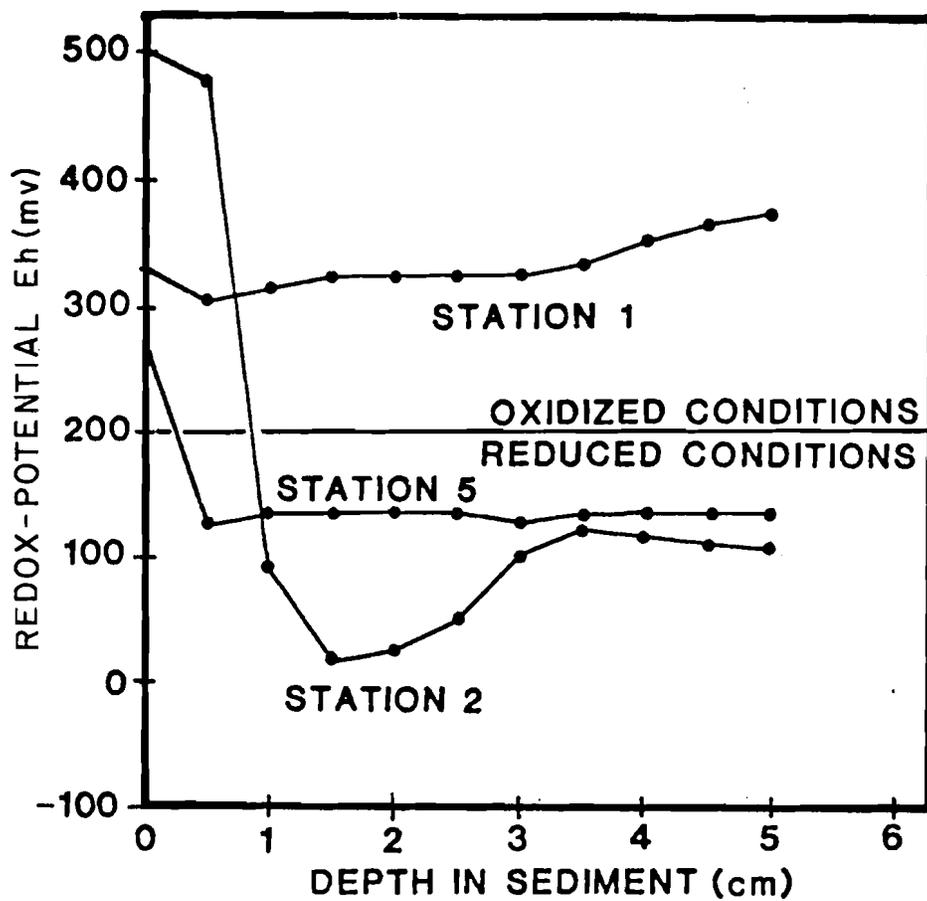
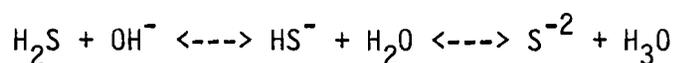


Figure 2-11. Redox Profiles Measured on Sediment Cores Collected From Maitland West Pond on 3/21/83 (Hvitved-Jacobsen et al. 1984).

Wittman 1979). A pE-pH diagram for this system is given in Figure 2-12 (Stumm and Morgan 1981). In general, the SO_4^{-2} species is dominant under oxidized conditions and at values of pH greater than 2.0. Under reduced and acidic conditions, SO_4^{-2} is reduced to H_2S which is in equilibrium with HS^- and S^{-2} by the following reactions:



Since the sulfide (S^{-2}) form of most heavy metals is highly insoluble, reduction to sulfide generally results in a decrease in concentrations of metal species which exhibit insoluble sulfides.

The redox potential-pH diagram for simple ions and hydroxides of iron is presented in Figure 2-13, (Krauskoph 1979). Under alkaline conditions for both oxidized and reduced states, iron exhibits rather stable solid phases such as Fe_2O_3 , FeCO_3 , $\text{Fe}(\text{OH})_3$, FeS_2 , and Fe_3O_4 . Under acidic conditions both the Fe^{+2} and Fe^{+3} forms are present with Fe^{+2} dominating at redox potentials less than 750 mv.

The E_h -pH diagram for lead showing the stability fields of the more important species in the presence of 10^{-3} M of both CO_2 (equivalent to 61 mg/l of HCO_3^-) and S (about 96 mg/l as SO_4^{-2}) is given in Figure 2-14 (Hem and Durum 1973). Equilibrium concentrations of dissolved lead are shown in Figure 2-14 by solid lines for the minimum amount considered, 1 $\mu\text{g/l}$, and for three higher values: 10, 100, and 1000 $\mu\text{g/l}$. The thermodynamic data

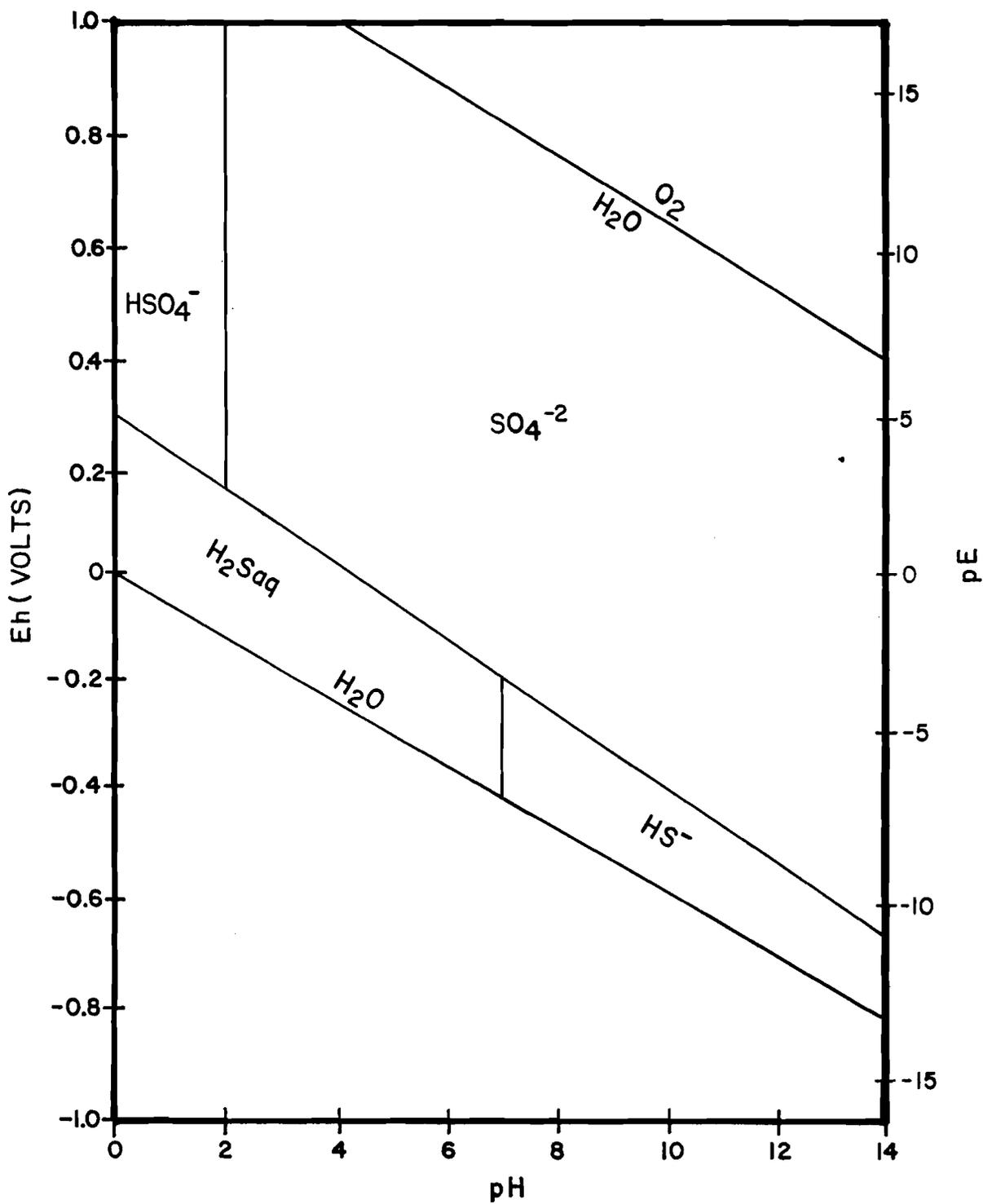


Figure 2-12. Equilibrium Distribution of Sulfur Species in Water at 25°C and 1 Atmosphere Total Pressure (Garrels 1960).

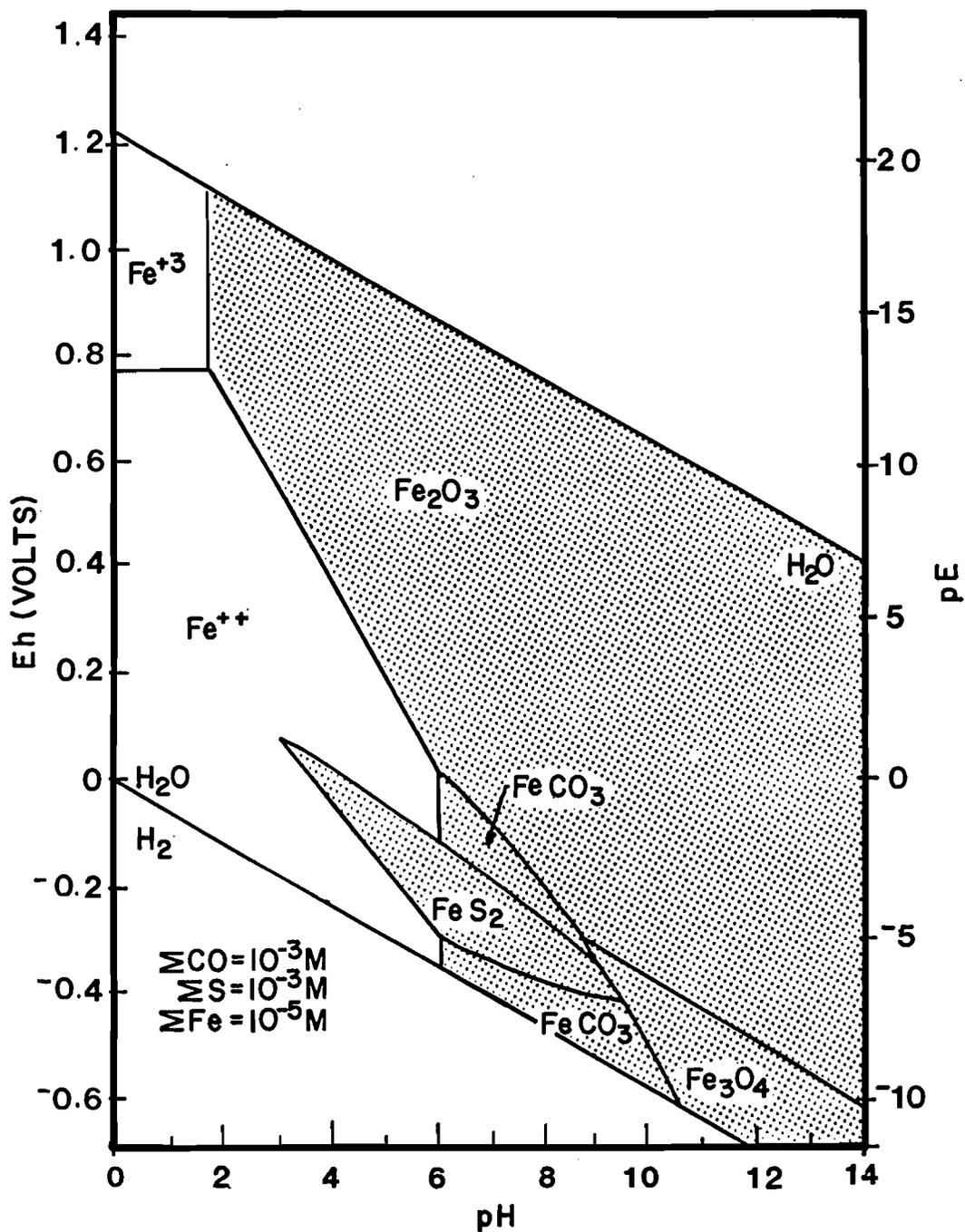


Figure 2-13. Stability Diagram for Iron Species in the System $\text{Fe} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$ at 25°C (Krauskopf 1979).

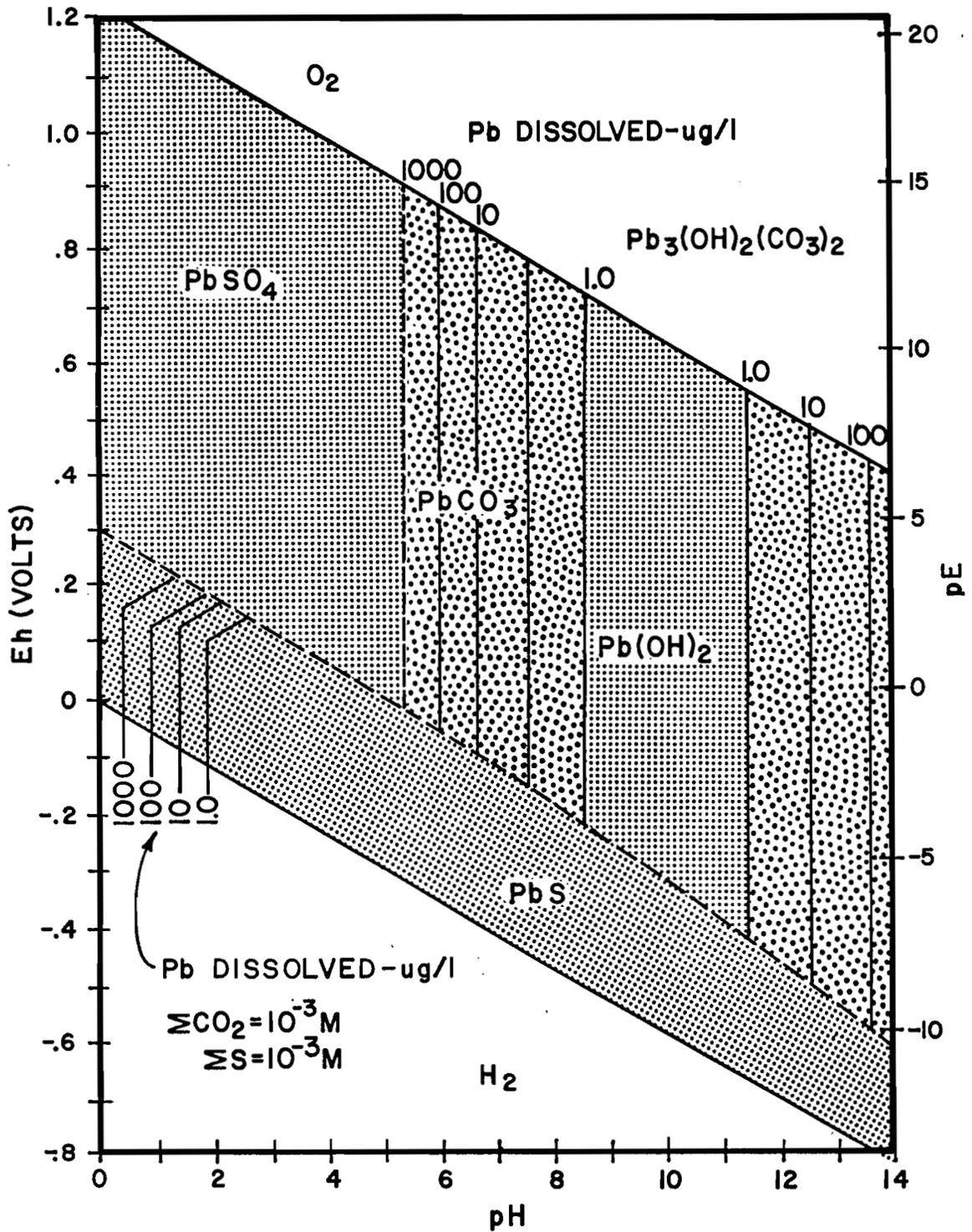


Figure 2-14. Stability Diagram for Lead Species in the System Pb + CO₂ + S + H₂O at 25°C (Stumm and Morgan 1981).

presented in Figure 2-14 show that there are five solid forms of lead which have fields of stability in this system. Under reducing conditions, the stable solid is PbS. This material has a low solubility, but is converted to lead hydroxide or carbonate when sulfur is oxidized to SO_4^{-2} . The partitioning between the hydroxide and carbonate forms are a function of the availability of dissolved carbon dioxide species. When the CO_2 is less than 0.8 mg/l as HCO_3^- , or when the partial pressure of CO_2 in the atmosphere is less than $10^{-3.44}$ atm (equal to ordinary air) the carbonate field is absent. The basic carbonate $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ is thermodynamically stable in only a small area in the system indicated in Figure 2-14.

The stability regions for zinc in the system: $\text{Zn} + \text{S} + \text{CO}_2 + \text{H}_2\text{O}$ are presented in Figure 2-15 (Hem 1972). Three solid species have stability fields in this system: the sulfide (sphalerite), the hydroxide, and the carbonate (smithsonite). Soluble species include the Zn^{+2} ion at low pH and the anionic forms $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{-2}$ at high pH values.

The pH- E_h diagram for copper is given in Figure 2-16 (Garrels and Christ 1965). Under strongly oxidized conditions and at pH values less than 7.0, the dominant copper form appears to be the Cu^{+2} ion. However, under alkaline conditions and ordinary atmospheric concentrations of CO_2 , the stable form is the solid, malochite. Under reduced concentrations of CO_2 , tenorite ($\text{CuO}_{(s)}$) may become the more stable form for certain pH- E_h conditions. The solubility of copper is dramatically decreased under reducing

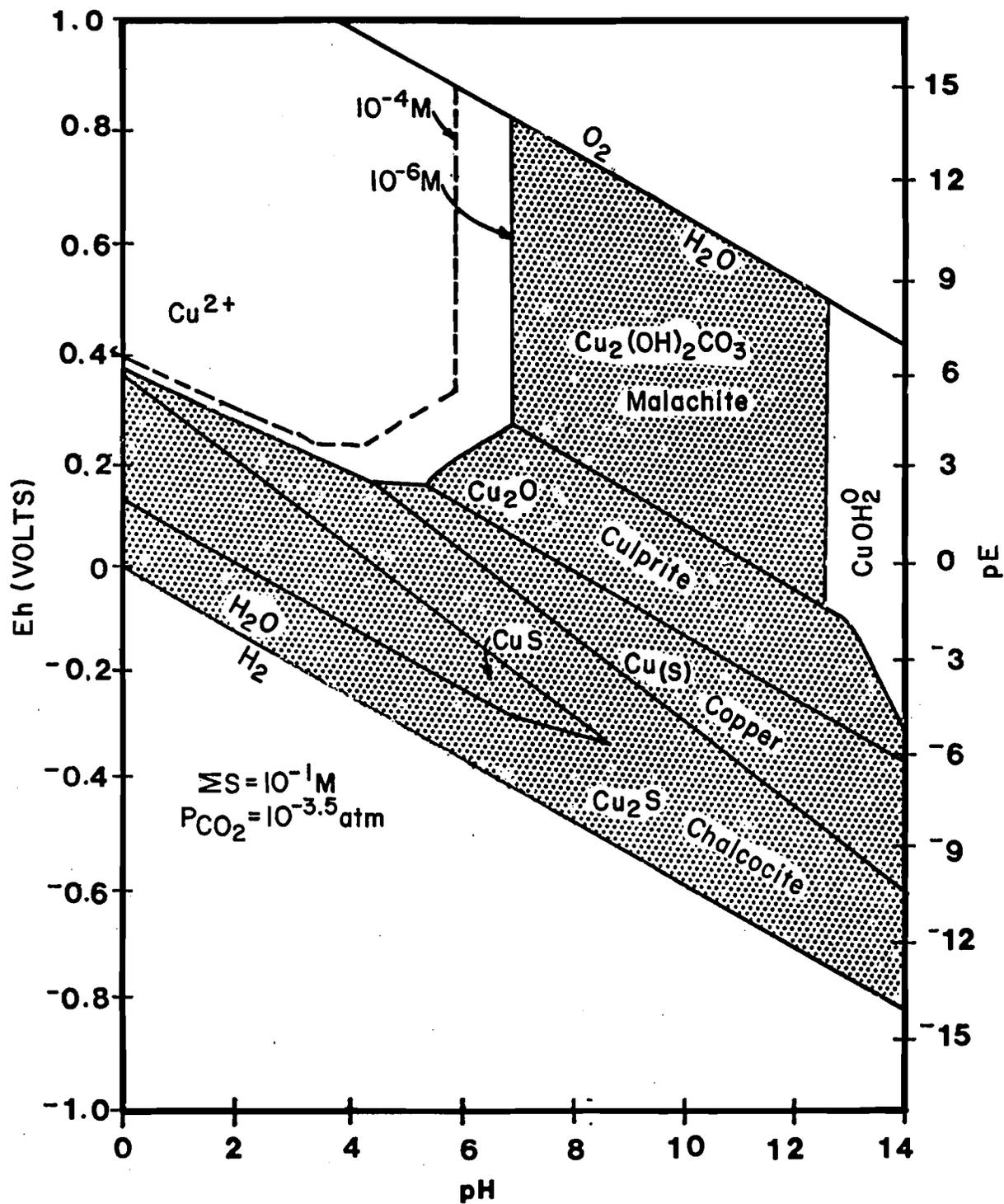


Figure 2-16. Stability Diagram for Copper Species in the System $\text{Cu} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$ at 25°C (Garrels and Christ 1965).

conditions. Under these conditions, copper is only slightly soluble with $\text{Cu}(\text{HS})_3^-$, CuCl_2^- , CuCl_3^{-2} , $\text{Cu}(\text{NH}_3)_2^+$, $\text{Cu}(\text{NH}_3)_3\text{OH}^+$, and $\text{Cu}(\text{NH}_3)_3^{+2}$ present in small amounts (Leckie and Davis 1979).

A pH- E_h diagram for inorganic cadmium species is presented in Figure 2-17 (Hem 1972). Under oxidized conditions and at pH values below 7.0, most of the cadmium was present in the free ionic form. As the pH approached 8.0 and above, the concentration of cadmium was governed by the solid CaCO_3 phase. Dissolved cadmium species in this system included Cd^{+2} , $\text{Cd}(\text{OH})_2^0$, and $\text{Cd}(\text{OH})_3^-$. Hem also reported that cadmium solubility would drop below 10 $\mu\text{g}/\text{l}$ at high pH values between 8.9 and 10.7 or in reduced systems with complete O_2 depletion. Hem compared the calculated equilibrium concentrations and observed concentrations of cadmium in river waters of the United States and concluded that the concentrations of this element that commonly occur in river waters were substantially below the equilibrium solubilities of the carbonate or hydroxide form of cadmium.

The stability fields for inorganic nickel in the system, $\text{Ni} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$, are presented in Figure 2-18. Under oxidized conditions at pH values less than 9, the Ni^{+2} ion is the dominant species. At pH values greater than 9 under oxidized conditions, the solid forms Ni_3O_4 and $\text{Ni}(\text{OH})_2$ become important up until a pH of 13. Under reduced conditions, the sulfide (NiS) is dominant at pH values greater than 2.

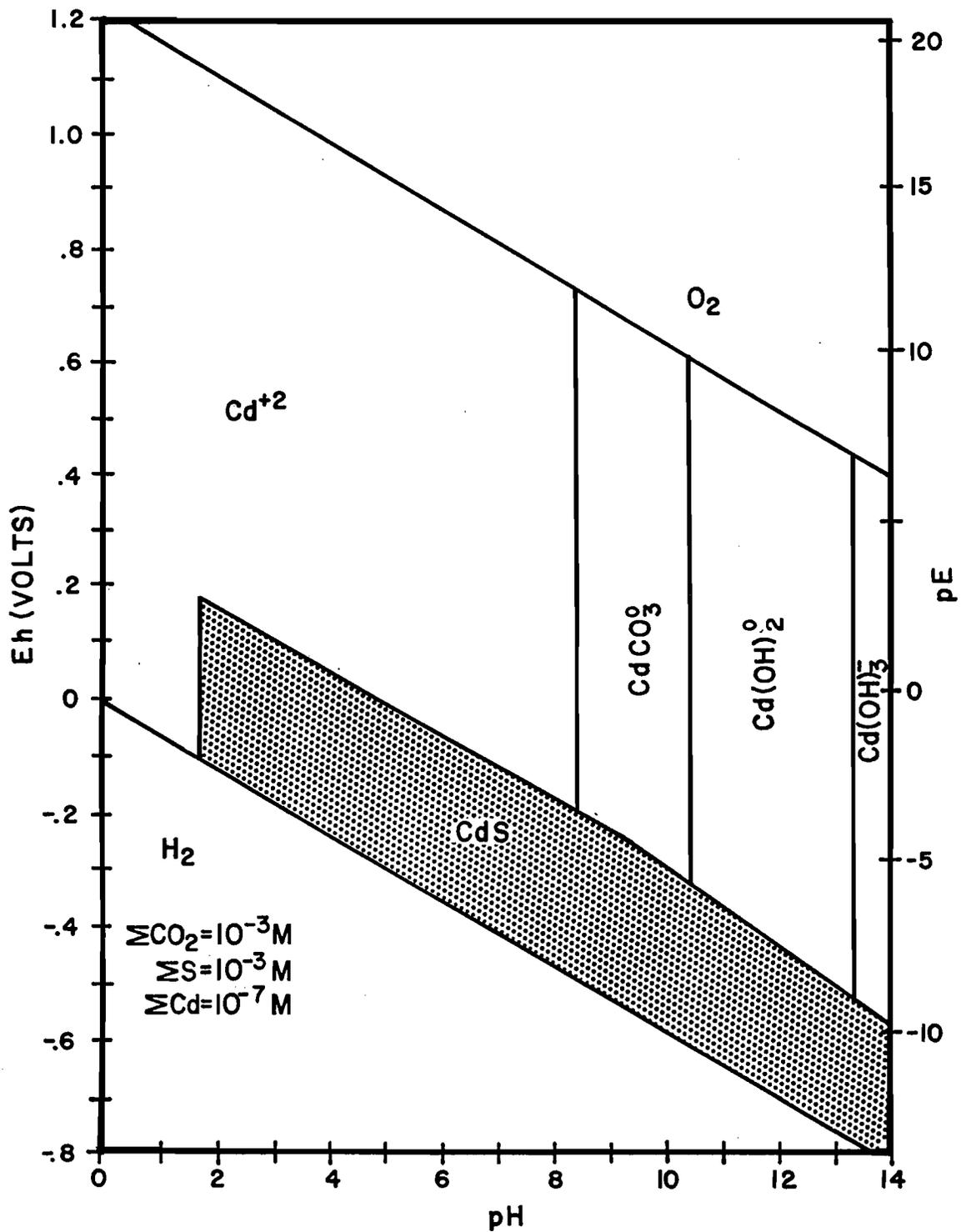


Figure 2-17. Stability Diagram for Cadmium Species in the System $\text{Cd} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$ at 25°C (Hem 1972).

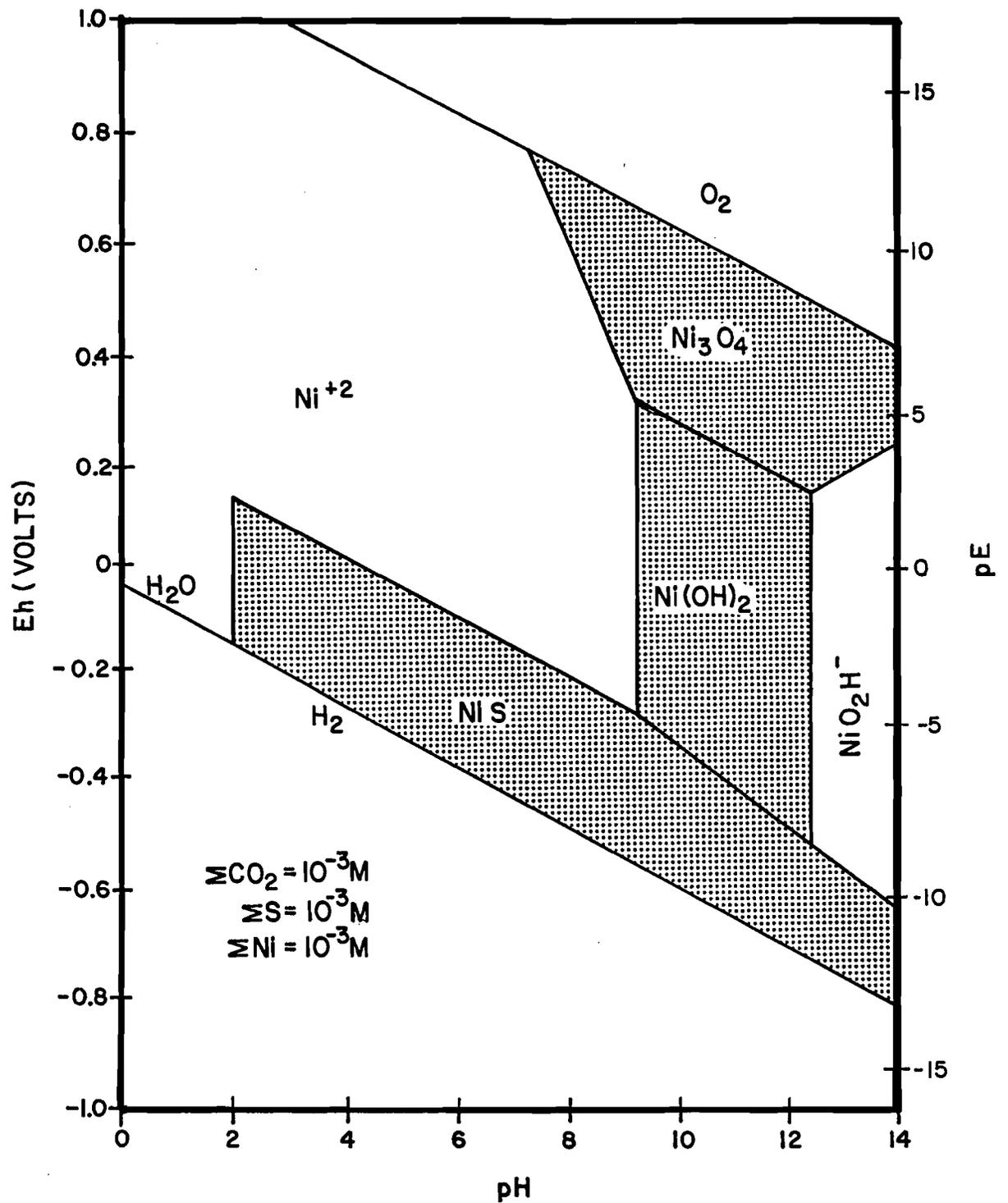
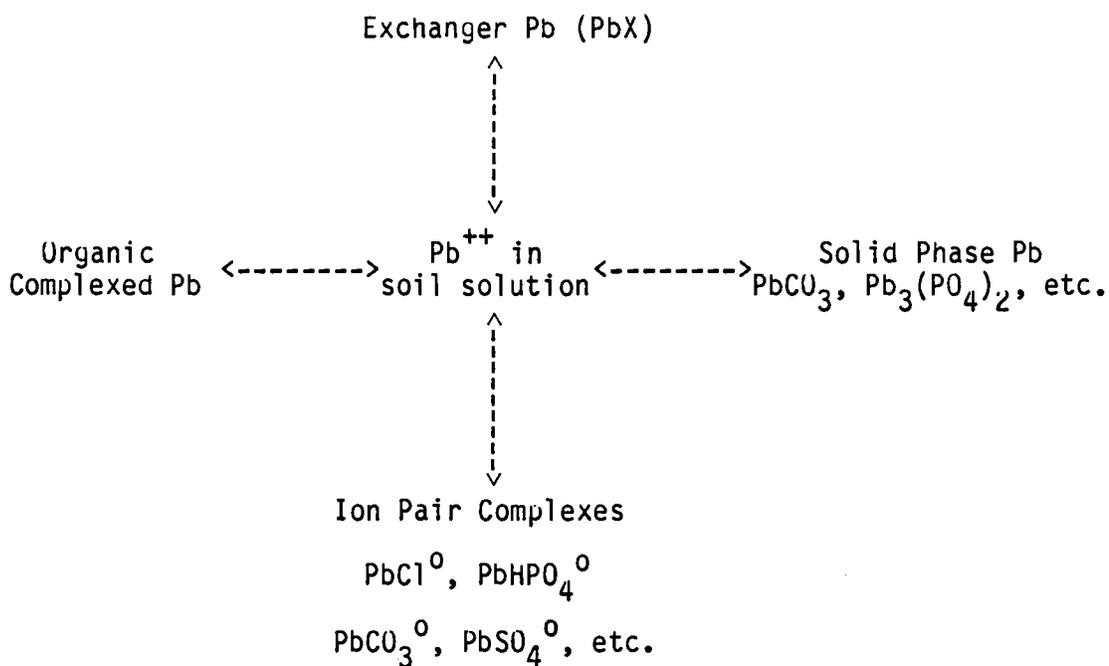


Figure 2-18. Stability Diagram for Nickel Species in the System $\text{Ni} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$ at 25°C (Garrels 1960).

A final pH- E_h stability diagram for inorganic species of manganese is given in Figure 2-19. In general, under oxidized conditions, the Mn^{+2} ion dominates in acidic solutions and the solid forms (MnO_2 , Mn_2O_3 , and $MnCO_3$) dominate in alkaline solutions under both oxidized and reduced conditions. The sulfide (MnS) is stable in only a small area between pH values of 8 and 10.

Previous Studies on the
Attenuation of Metal Species in Soils

In a soil-water system, heavy metal ions are assumed to be in equilibrium with the precipitated inorganic phase, the exchange phases, and the soil solution as described in the following diagram for lead, as an example:



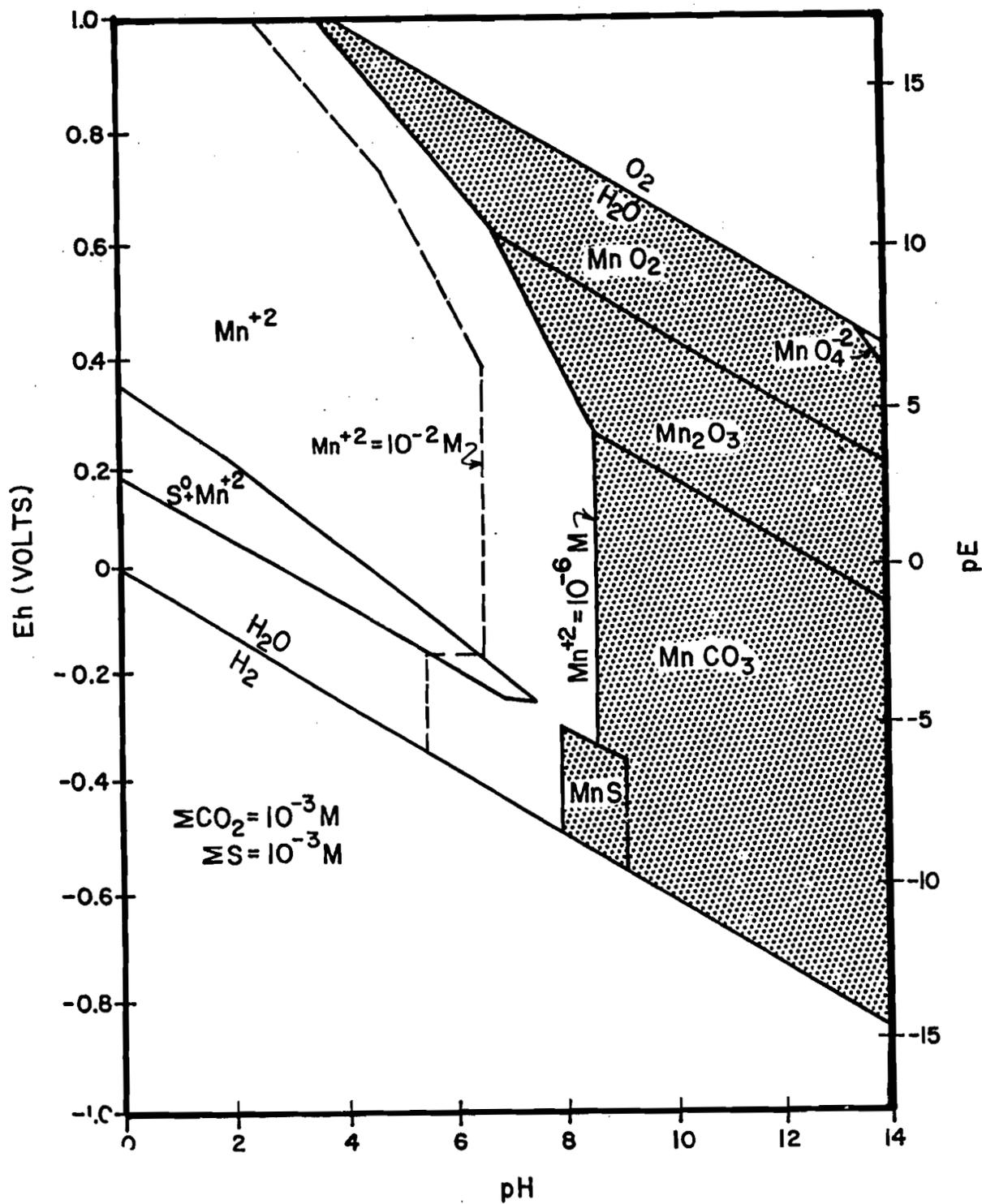


Figure 2-19. Stability Diagram for Manganese Species in the System $\text{Mn} + \text{CO}_2 + \text{S} + \text{H}_2\text{O}$ at 25°C (Garrels 1960).

Although this proposed model is written in terms of lead cations, it can be applied, with slight modifications, to any metal in a soil system.

Although no reference was found concerning any previous studies which dealt with the attenuation of heavy metals originating in stormwater management systems, numerous other studies have been conducted which investigated heavy metal attenuation from sources such as landfills and lake sediments, as well as in laboratory column studies using various soil types. A few of the more important investigations will be presented in the following section. A very detailed investigation into the attenuation of landfill leachate by soil types was conducted by Fuller (1978). A total of eleven different soil types, covering a wide range of textures, pH values, cation exchange capacities and bulk densities were tested for attenuation characteristics in column studies using a generated landfill leachate as a source of raw water. A partial summary of the heavy metal constituents measured in the solid waste generated leachate used for the column studies is given in Table 2-6, and a summary of the characteristics of the soils used in these experiments is presented in Table 2-7.

The soils were passed through a 2 mm sieve and then uniformly packed into 10 cm diameter x 20 cm long or 5 cm diameter x 10 cm long PVC columns for the studies. Leachate was pumped through each column in a CO₂ filled environment to simulate the anaerobic

TABLE 2-6

RANGES OF HEAVY METALS MEASURED IN THE
NATURAL LEACHATE GENERATED FROM MUNICIPAL SOLID
WASTE USED IN THE COLUMN STUDIES BY FULLER (1978)

HEAVY METAL	RANGE OF CONCENTRATIONS (mg/l)
Al	0.5
Ca	160-225
Cd	0.005
Cr	0.05
Cu	0.05
Fe	60-120
Mn	0.6-1.8
Pb	0.05
Zn	0.4-0.65

NOTE: Specific conductivity ranged from 2400-2600 μ mhos/cm

conditions which would be present in a subsurface soil. The flow was adjusted so that approximately one pore volume flowed from each column in 24 hours, and was continued until approximately 30 pore volumes had passed through a column.

The data obtained from any one soil column was found to fit one of the generalized curves shown in Figure 2-20. Curves A and B represent situations where an element is only weakly retained by the soil, resulting in a complete breakthrough where $C/C_0 = 1$. For curve A, the rapid rise in effluent concentration begins in the first sample; whereas, the breakthrough is delayed for curve B. The

TABLE 2-7
 CHARACTERISTICS OF THE SOILS USED IN SOIL-COLUMN RESEARCH BY FULLER (1978)

SOIL SERIES	SOIL ORDER	SOIL PASTE pH	CATION EXCH. CAPAC. (meg/100g)	ELECTRIC COND. OF EXTRACT ($\mu\text{mhos/cm}$)	COLUMN BULK DENSITY (g/cm^3)	PERCENT		TEXTURE CLASS	
						SAND	SILT CLAY		
Wagram	Ultisol	4.2	2	225	1.89	88	8	4	Loamy sand
Ava	Alfisol	4.5	19	157	1.45	10	60	31	Silty clay loam
Kalkaska	Spodosol	4.7	10	237	1.53	91	4	5	Sand
Davidson	Ultisol	6.2	9	169	1.89	19	20	61	Clay
Molokai	Oxisol	6.2	14	1262	1.44	23	25	52	Clay
Chalmers	Mollisol	6.6	26	288	1.60	7	58	35	Silty clay loam
Nicholson	Alfisol	6.7	37	176	1.53	3	47	49	Silty clay
Fanno	Alfisol	7.0	33	392	1.48	35	19	46	Clay
Mohave	Aridisol	7.3	10	615	1.78	52	37	11	Sandy loam
Mohave (Ca)	Aridisol	7.8	12	510	1.54	32	28	40	Clay loam
Anthony	Entisol	7.8	6	328	2.07	71	14	15	Sandy loam

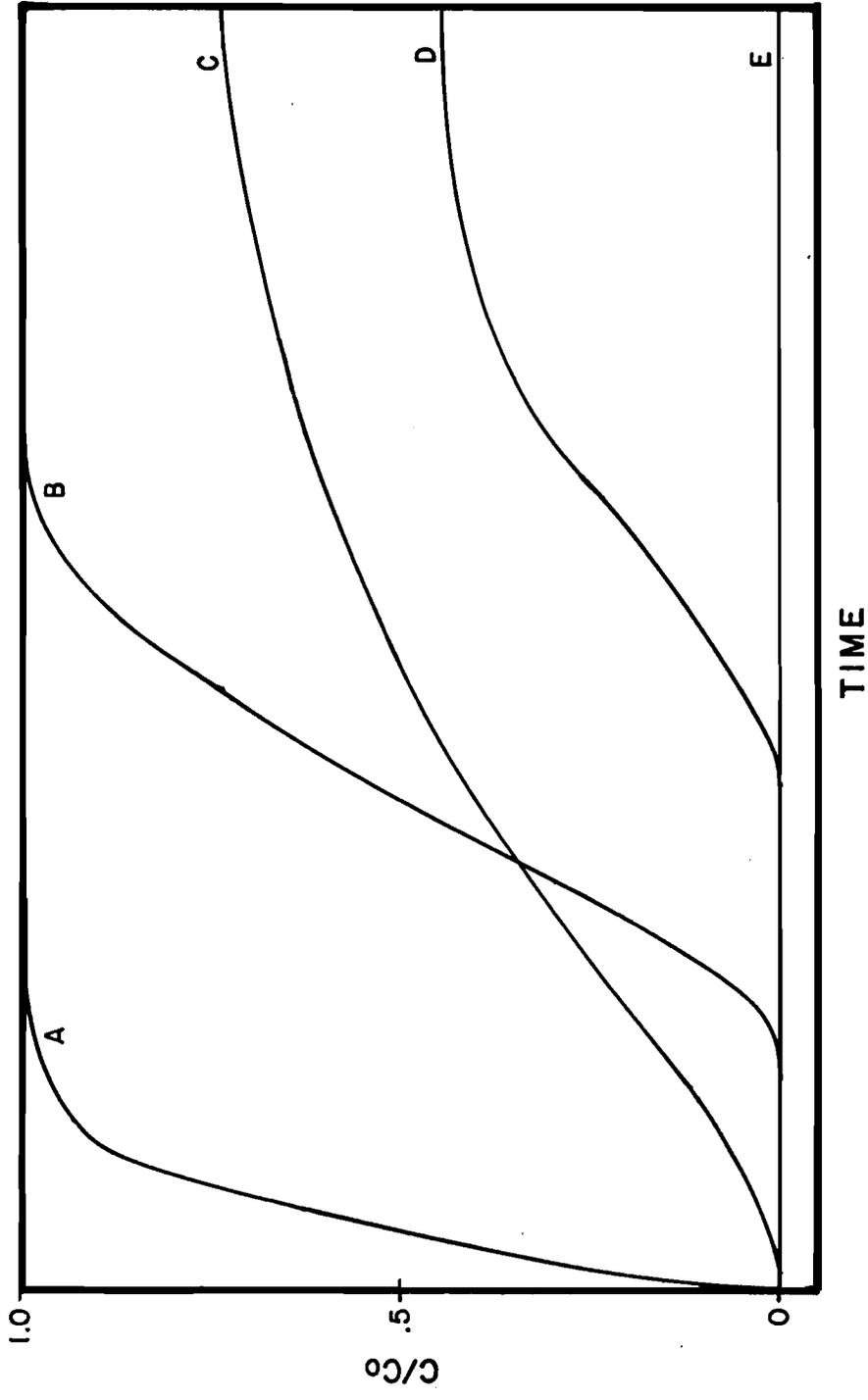


Figure 2-20. Generalized Breakthrough Curves Generated by Fuller (1978) for Absorption of Heavy Metals by Various Soils.

steady-state situation is represented by curves C and D. Curve E represents the extreme case where the concentration of the element in the effluent did not rise above $C/C_0 = 0.1$.

A summary of the type of adsorption curves found for the eleven soil types is given in Table 2-8. Sharp breakthroughs are seen most often for sandy soils with almost total retention observed in clay soils. An important exception was noted in the case of chromium in a soil containing free CaCO_3 at a relatively high pH. Although it has been reported that alkaline pH conditions decrease the mobility of trace elements, chromium appears to be an exception (John 1972).

A summary of the experimental results of Fuller indicating the relative mobility of trace elements and the relative effectiveness of the soils in attenuating them is given in Figure 2-21. In general, copper and lead were found to have low mobility in all soils, while zinc, cadmium, and nickel had low mobility in soils with a high clay fraction and highly mobile in soils with a high sand fraction.

On the basis of his results, Fuller was able to suggest a grouping of broad soil characteristics included in his studies which are important and unimportant in affecting attenuation by soils. These groups in summary form are:

TABLE 2-8
 DESIGNATION SHOWING TYPE OF CURVE GENERATED
 FROM EACH COLUMN FROM EXPERIMENTS BY FULLER (1978)

SOIL	As	Be	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Wagram (l.s.)*	A	C	A	A	E	A	A	B	A
Ava (si.c.l.)	C	D	A	C	D	B-C	A	D	A-B
Kalkaska (s.)	C	D	C	C	E	C	B	E	B
Davidson (c.)	C	D	C	E	E	C	B	E	D
Molokai (c.)	E	E	E	E	E	D	D	E	E
Chalmers (si.l.)	-	-	-	-	-	D	D-E	-	-
Nicholson (si.c.)	E	E	E	D	E	B-C	E	E	D
Fanno (c.)	C	E	E	C	E	C	E	E	C
Mohave (s.l.)	B	D	D	A	E	B	C	E	B
Mohave (Ca) (c.l.)	E	E	E	A	E	D	E	E	E
Anthony (s.l.)	A	D	A	A	D	A	A	D	B

*NOTE: l.s. - loamy sand; c.l. - clay loam; s. - sand; c. - clay; si.l. - silty loam; si.c. - silty clay; s.l. - sandy loam; and si.c.l. - silty clay loam

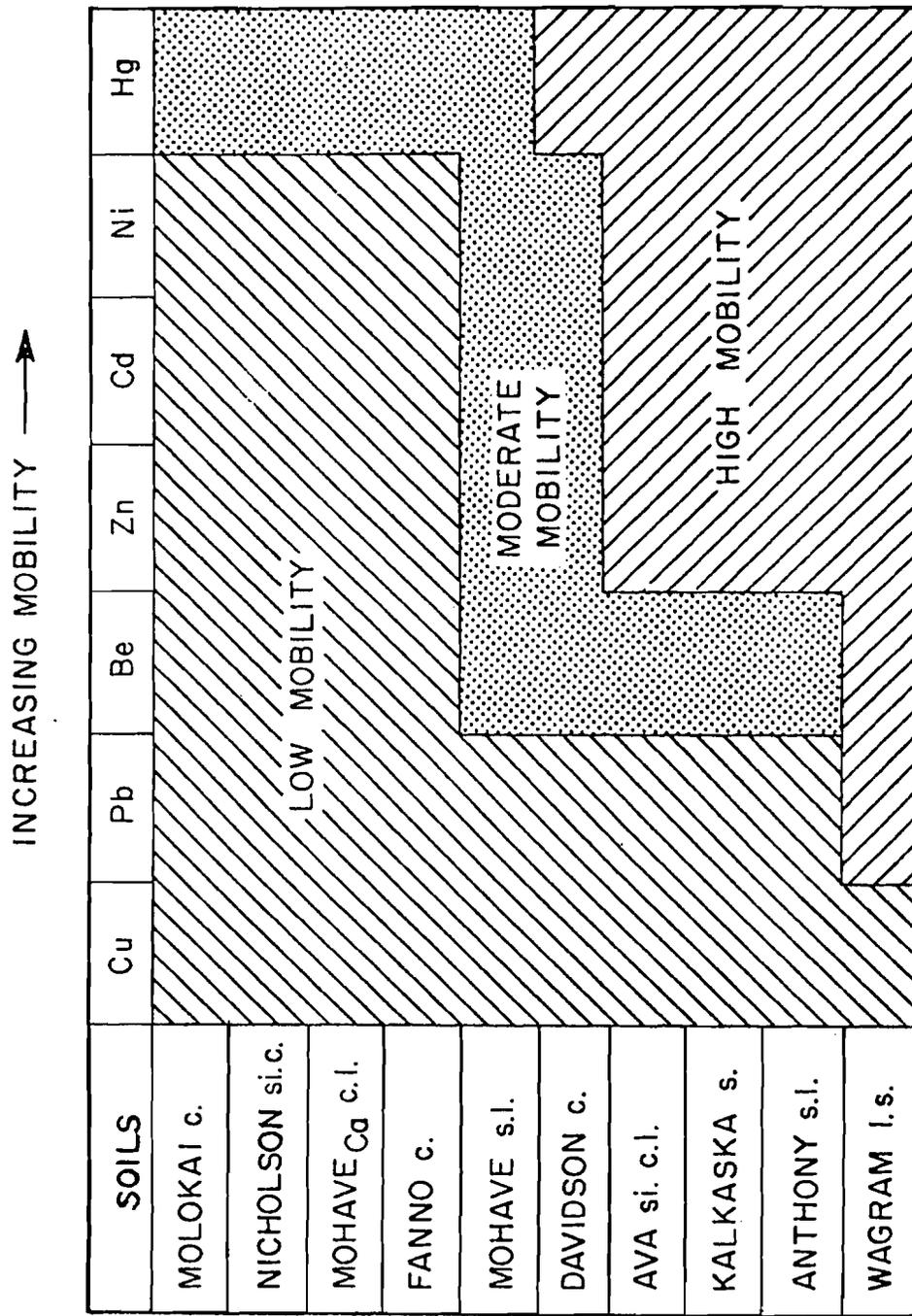


Figure 2-21. Relative Mobility of Cation Forming Elements in Soils (Fuller 1978).

1. Most Important Factors in Retention
 - a. clay content
 - b. free iron oxide content
 - c. soil lime content
 - d. solution flux or flow rate through the soil (hydraulic conductivity)

2. Least Important Factors in Retention
 - a. sand
 - b. kind of clay material
 - c. cation exchange capacity
 - d. soil pH

Correlation coefficients between various heavy metals and selected soil properties were given by Fuller and are listed in Table 2-9. The percentage of clay-sized particles in the soil stands out as the most useful means of predicting whether a soil will retain a particular element. This correlation does not seem to be a reflection of cation exchange capacity and suggests that cation exchange capacity is not necessarily related to heavy metal fixation. Surface area and the percentage of free iron oxide provide the best correlations next to the clay fraction. The best relationships with surface area was found with those elements which exist as a M^{+2} cation. Those elements present in the leachate as anions correlate more strongly to free iron oxides than to surface area.

TABLE 2-9
 CORRELATION COEFFICIENTS OF MASS ADSORBED PER GRAM OF
 SOIL WITH SOIL PROPERTIES FROM THE SOIL EXPERIMENTS BY FULLER (1978)

ELEMENT	CLAY	pH	CEC	SURFACE AREA	Fe ₂ O ₃	Mn
Arsenic	.88 ^{***}	.22	.42	.66 [*]	.60	.52
Beryllium	.78 [*]	.47	.62 [*]	.81 ^{**}	.52	.52
Cadmium	.67 [*]	.48	.60	.71 ^{**}	.46	.45
Chromium	.56	-.43	.21	.10	.75 ^{**}	.65 [*]
Nickel	.69 [*]	.51	.79 ^{**}	.88 ^{***}	.27	.24
Selenium	.71 [*]	-.30	.44	.39	.68 [*]	.57
Vanadium	.84 ^{***}	.16	.55	.61 [*]	.69 [*]	.49
Zinc	.83 ^{**}	.52	.71 [*]	.84 ^{**}	.50	.48

* = significant at .05 level
 ** = significant at .01 level
 *** = significant at .001 level

Finally, Fuller presented a modification to the partial differential equation for uni-directional steady flow in groundwater presented previously, which accounts for both adsorption and desorption kinetics for trace elements in soils. The modification given was:

$$\frac{\Delta S}{\Delta t} = k_1 C - k_2 n$$

change in storage of solute in soil
adsorption term
desorption term

where:

k_1 = adsorption rate (1/day)

C = concentration of solute (mg/cm^3)

k_2 = desorption rate (1/day)

n = concentration of solute in the solid phase (mg/cm^3)

This model assumes first-order rate terms for both forward and backward reactions which are effective reaction rates rather than mechanic desorptions of the reactions taking place. Estimates of k_1 and k_2 , as well as the dispersion coefficients, D , and flow velocities, V , from the experiments by Fuller, are given in Table 2-10.

An investigation into the chemistry and transport of lead and cadmium in soils was conducted by Jurinak et al. (1974). In this study, models for the speciation of lead and cadmium were developed

TABLE 2-10
 PARAMETERS ESTIMATED FROM THE SOIL EXPERIMENTS BY FULLER (1978)

ELEMENT	SOIL	D (cm ² /day)	K ₁ (1/day)	K ₂ (1/day)	V (cm/day)
Arsenic	Anthony (s.l.)*	9.9244	0.3916	0.09893	8.58
	Kalkaska (s.)	9.9305	0.3572	0.06337	7.04
	Wagram (l.s.)	9.9185	0.6748	0.24570	8.39
Cadmium	Anthony (s.l.)	9.9067	0.5611	0.10250	8.64
	Ava (si.c.l.)	9.9214	0.2940	0.11730	5.22
Beryllium	Davidson (c.)	9.8293	2.2983	0.28120	8.45
Lead	Wagram (l.s.)	9.9750	1.2386	0.30440	9.47
Mercury	Anthony (s.l.)	9.8136	4.2171	1.44020	10.80
	Nicholson (si.c.)	9.8780	0.3749	0.10480	12.10
	Wagram (l.s.)	9.9316	0.2972	0.05206	9.24
Vandium	Anthony (s.l.)	10.0010	1.4621	0.40440	13.20
Nickel	Anthony (s.l.)	10.5400	2.1257	0.50180	13.30
	Kalkaska (s.)	9.8660	1.4866	0.40500	7.78
	Wagram (l.s.)	9.8690	0.5029	1.91770	13.40
Zinc	Ava (si.c.l.)	9.8909	0.6705	0.15040	6.68
	Wagram (l.s.)	9.9207	0.3980	0.19450	13.1

*NOTE: l.s. - loamy sand; c.l. - clay loam; s. - sand; c. - clay; si.l. - silty loam; si.c. - silty clay; s.l. - sandy loam; and si.c.l. - silty clay loam

from thermodynamic data and a FORTRAN computer program was written which was similar to WATEQ2 for only two metals. The model was then tested for sensitivity by conducting a series of column studies and comparing the predicted and measured effluent concentrations of Pb and Cd. The computer model included data on dissociation constants and solubility products, as well as kinetic data.

An analysis of thermodynamic data combined with the column study results indicated that the main mechanism regulating lead solubility in a non-calcareous soil system can be attributed to the precipitation of $\text{Pb}(\text{OH})_2$ and $\text{Pb}_5(\text{PO}_4)_3\text{OH}$. Calcareous soils were found to be excellent scavengers of lead as well. Cadmium was found to be approximately 100 times more soluble than lead in the pH range of 5 to 9 and correspondingly more mobile in soils. It was reported that cadmium was retained in the soil mainly by adsorption or exchange at both the organic and inorganic interfaces and was not regulated by precipitation reactions.

The column studies also indicated that basic soils of arid and semi-arid regions constitute essentially an infinite sink for lead. The movement of lead in percolating water in these soils was essentially zero, even in the presence of large amounts of excess salt. It was suggested that arid soils could be an excellent medium for scavenging lead and other chemically similar heavy metals from industrial waste with minimal danger of groundwater pollution. Cadmium was found to be far less efficiently removed from percolating waters by these soils.

In general, the computer model developed from thermodynamic data was effective in predicting the movement of Cd and Pb in soil after the initial 15-20 pore volumes of effluent passed through the soil columns. Less accurate prediction was obtained during the initial stages of effluent flow. This was ascribed to the difficulty encountered by the main model in handling the pH change caused by the addition of the acidic heavy metal solution to the soil columns.

The mechanisms controlling the transport of cadmium and chromium in natural water systems were evaluated by Gilbert et al. (1976) in laboratory studies of adsorption/desorption behavior and the interaction of these metals with phytoplankton. In this study, adsorption of cadmium and chromium onto three inorganic clay minerals was investigated in batch studies.

The adsorption of chromium onto inorganic particles was found to be highly dependent on its valence state. Chromium entering fresh water systems in the hexavalent state will not be appreciably adsorbed by suspended inorganic particulates such as clay particles, and hydrous iron and manganese oxides. However, Cr(VI) is apparently reduced to Cr(III) in fresh waters under anoxic environments. The trivalent form can then be strongly absorbed by most inorganic particulates, with the exception of hydrous manganese oxides.

Cadmium was also found to be adsorbed by clay minerals as well as hydrous manganese oxides. However, the adsorption appears to be

an exchange reaction and should, therefore, be reversible under some conditions.

Gilbert et al. (1976) predicted that metals associated with bottom sediments will undergo other geochemical transformations which further reduce their availability to the aqueous phase. As a result, short-term resuspension of the bottom sediment does not appear to release substantial levels of cadmium or chromium at a pH of 6.5. However, as the pH decreases and the sediments become more reduced, chromium was found to be stable, while cadmium exhibited some release.

The final study to be presented was one by Nelson (1972) on the fate of trace metals in subsoils as related to the quality of groundwater. In this study, laboratory experiments were conducted to evaluate the metal adsorptive capacities of six soils. Disturbed samples of each of the six soil types were placed in 2.2 cm diameter x 15.2 cm long acrylic columns, and solutions of various heavy metals at constant pH were infiltrated through the columns until breakthrough occurred.

The adsorption patterns of all six soil types were found to resemble the Langmuir and/or Freundlich adsorption isotherms and indicated that each of the six soils tested were capable of complexing metals and rendering them insoluble regardless of the organic matter content, genesis, and physical and chemical properties of the soil. However, the degree to which a particular soil exhibited adsorption was dependent on the above factors as well

as on the nature of the metal which is rendered insoluble. Complexation was found to decrease in the following order: multivalent > divalent > monovalent. It was observed that the former ones could replace the latter ones from a complex. If the major mechanism for complexation of the metal is precipitation, then the above series would not necessarily apply.

In soils with a high organic content, Nelson (1972) reported that chelation and surface adsorption are the mechanisms mainly responsible for rendering heavy metals insoluble. If there is very little or no organic matter, then diffusion and entrapment were found to be primarily responsible.

Partition coefficients were presented by Nelson for a soil-water mixture for various heavy metals. A summary of these values is given in Table 2-11. In general, a pattern appears to be present in which the partition coefficient for a given metal species decreases with decreasing organic content of the soil. For the case of Pb and Zn, the adsorption process appears to be approximately 40 percent in an exchange phenomenon with the remainder bound into an exchangeable form which would presumably be more permanent. Chromium, manganese, and cadmium were almost totally in an exchangeable form with some soils exhibiting release of cadmium and manganese rather than an uptake.

The maximum adsorptive capacities of the four soils tested were also calculated and are presented in Table 2-12. The same general trend of decreasing partition coefficient with decreasing organic

TABLE 2-11
 SUMMARY OF PARTITION COEFFICIENTS (LOG K_d VALUES) FOR
 SOIL-METAL SYSTEMS AS PRESENTED BY NELSON (1972)

SOIL TYPE*	Cr		Pb		Mn		Cd		Zn	
	TOTAL ADS.	EXCH. ADS.								
Muck	2.93	2.75	8.71	4.83	2.62	2.36	2.42	1.13	12.10	12.10
Hoytville	5.23	4.70	5.54	3.36	1.20	1.14	0.90	0.47	7.90	5.00
Nebraska	4.03	2.17	3.97	2.81	1.71	0.77	0.55	-1.77	9.67	5.11
Norfolk	2.49	2.36	2.19	1.80	0.45	-0.60	-2.01	-2.55	1.44	1.40

*In order of decreasing organic matter

TABLE 2-12
 SUMMARY OF MAXIMUM ADSORPTION (VALUES $\times 10^{-5}$ MOLES/gm OF SOIL)
 FOR SOIL-METAL SYSTEMS AS PRESENTED BY NELSON (1972)

SOIL TYPE*	Cr		Pb		Mn		Cd		Zn	
	TOTAL ADS.	EXCH. ADS.								
Muck	28.26	27.28	43.00	41.80	29.03	20.37	14.97	11.12	21.61	18.80
Hoytville	17.16	15.29	32.40	28.80	26.04	18.90	11.49	6.37	12.71	11.40
Nebraska	16.72	15.64	20.40	17.40	9.82	6.78	3.27	1.68	13.90	11.20
Norfolk	3.57	2.75	11.00	8.42	6.36	4.46	0.97	0.77	2.54	2.16

*In order of decreasing organic content

)

content was observed for maximum adsorption, with a decreasing maximum adsorption with decreasing organic content. Lead was adsorbed to the largest degree, followed by chromium and manganese, and zinc and cadmium. However, determination of the metal content of the soils prior to the column studies indicated that current concentrations were far below the maximum measured value for each soil type. Nelson suggested that, given the current rate of deposition of heavy metals into these soil types, it was doubtful that the maximum values would ever be reached.

CHAPTER 3
FIELD AND LABORATORY INVESTIGATIONS

Site Description

The site selected for these investigations is located at the Maitland Interchange on Interstate 4 (I-4). This interchange, located north of the city of Orlando, Florida, was constructed in 1976 to provide access onto Maitland Boulevard for both northbound and southbound interstate traffic. A schematic of this interchange is given in Figure 3-1. Maitland Boulevard crosses over Interstate 4 by means of a bridge overpass created during construction of the interchange. The Maitland Boulevard bridge consists of two sections, one carrying two lanes of eastbound traffic plus one exit lane, with the other section carrying two lanes of westbound traffic plus one exit lane. Traffic volume on Maitland Boulevard is approximately 15,800 ADT (Average Daily Traffic) eastbound and 15,600 westbound. Traffic volume on I-4 through the Maitland Interchange is approximately 51,000 ADT eastbound and westbound (Harrell 1984).

During the construction process, three borrow pits were excavated to provide fill material for construction of the overpass and exit lanes. After completion of the interchange, the excavated pits were shaped and utilized as stormwater detention/retention facilities. The drainage system for Interstate 4 surrounding the

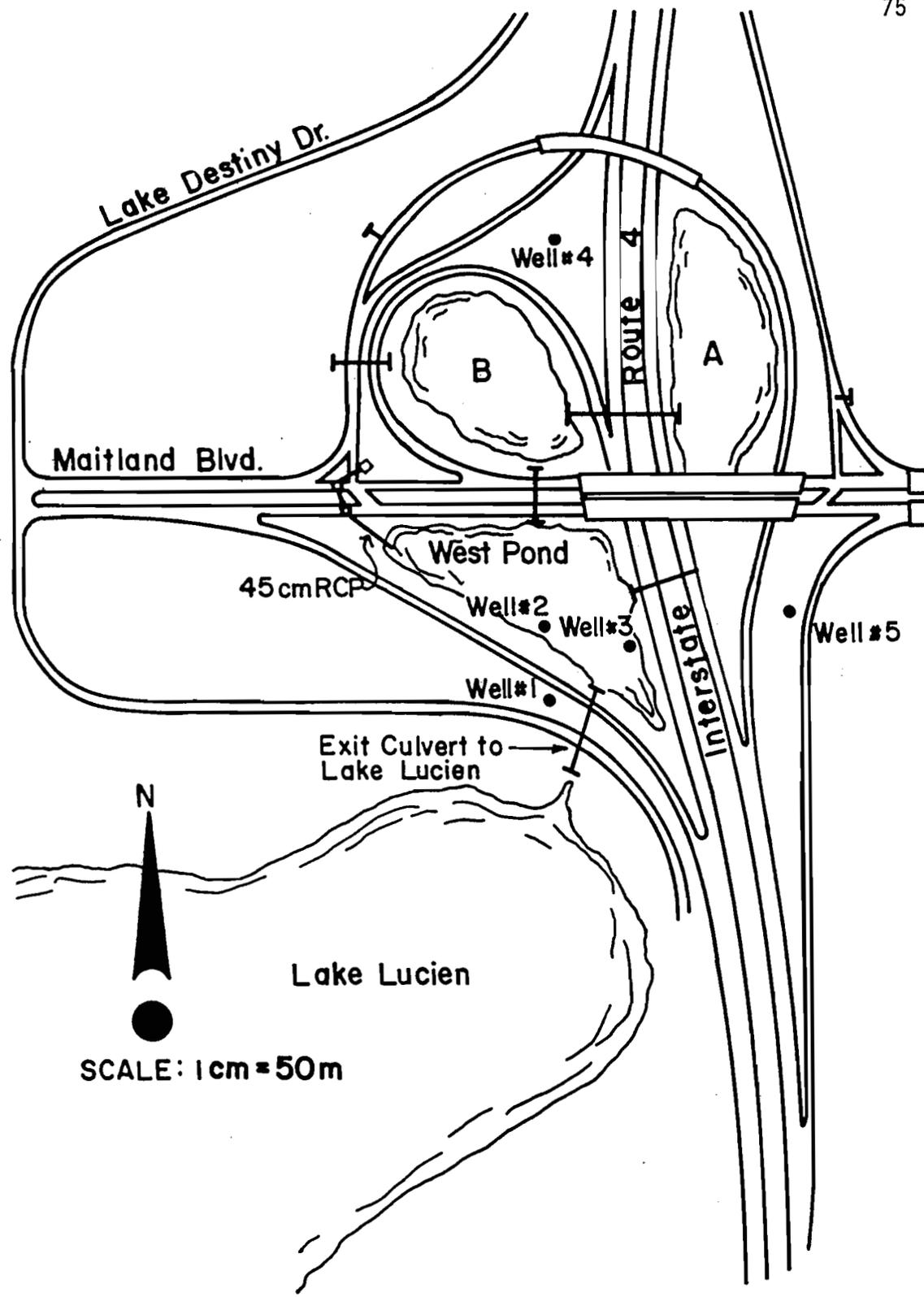


Figure 3-1. Study Site at Maitland Interchange.

interchange was designed so the highway runoff would flow by gravity to the center grassy median. Stormwater inlets were constructed at various points along the median to collect and divert the flow under the highway to the large grassy swale on the east side of the northbound lane. Stormwater then flows through this swale, passing under entrance and exit ramps by way of concrete culverts, and finally reaches the eastern pond (designated as Pond A in Figure 3-1).

Pond A is connected to Pond B by way of large culverts so that when Pond A exceeds its design capacity, it can discharge to the northwestern pond (Pond B). The northwestern pond has the capability to discharge to the southwestern pond (referred to hereafter as the West Pond) by way of three 90 cm reinforced concrete pipe culverts when design elevations are exceeded. The total design drainage area which discharges into the three ponds is 19.8 hectares, most of which is discharged to Ponds A and B. However, since the available volumes of both Pond A and Pond B are quite large relative to their receiving watersheds, it is anticipated that a discharge from Ponds A or B to the West Pond would only occur as a result of an extreme rainfall event. The largest direct input into the West Pond other than precipitation is highway runoff from a watershed of approximately 1.6 ha (3.95 acres) that includes much of the Maitland Boulevard overpass. Stormwater runoff from this watershed is discharged into the west end of the pond through a 45 cm concrete pipe culvert located at the northwest

tip of the triangular pond. The remaining inputs into the West Pond are predominantly highway runoff subjected to overland and swale flow, along with a small watershed on the east side which drains directly from I-4 into the pond.

Discharge from the West Pond into Lake Lucien is possible and is regulated by a flashboard riser system and earthen berm. However, the flashboard risers were constructed to fit very loosely into the exit structure, and water seeps freely around and between these boards. As a result, the earthen berm located downstream from the outlet culvert, actually controls discharges from the pond. The minimum elevation necessary to cause a discharge from the earthen berm is 27.43 m above MSL (89.67 ft). Upon discharging from the bermed area, pond water is retained in a very small shallow wetland area. A water elevation of 27.48 m MSL (90.14 ft) is necessary to cause a discharge from the wetland area to Lake Lucien.

Since the pond surface area is quite large in relation to the contributing watershed, stormwater inputs under normal conditions do not cause large changes in water level. Pond elevations have been continuously monitored with a Stevens Model A-72 water level recorder since 7/1/83. A summary of this record for a one-year period is presented in Figure 3-2. According to this record, the exit elevation of 27.48 m (90.14 ft) is exceeded only a small portion of the time, and as a result, discharges from the pond into Lake Lucien occur infrequently. Because of the relatively

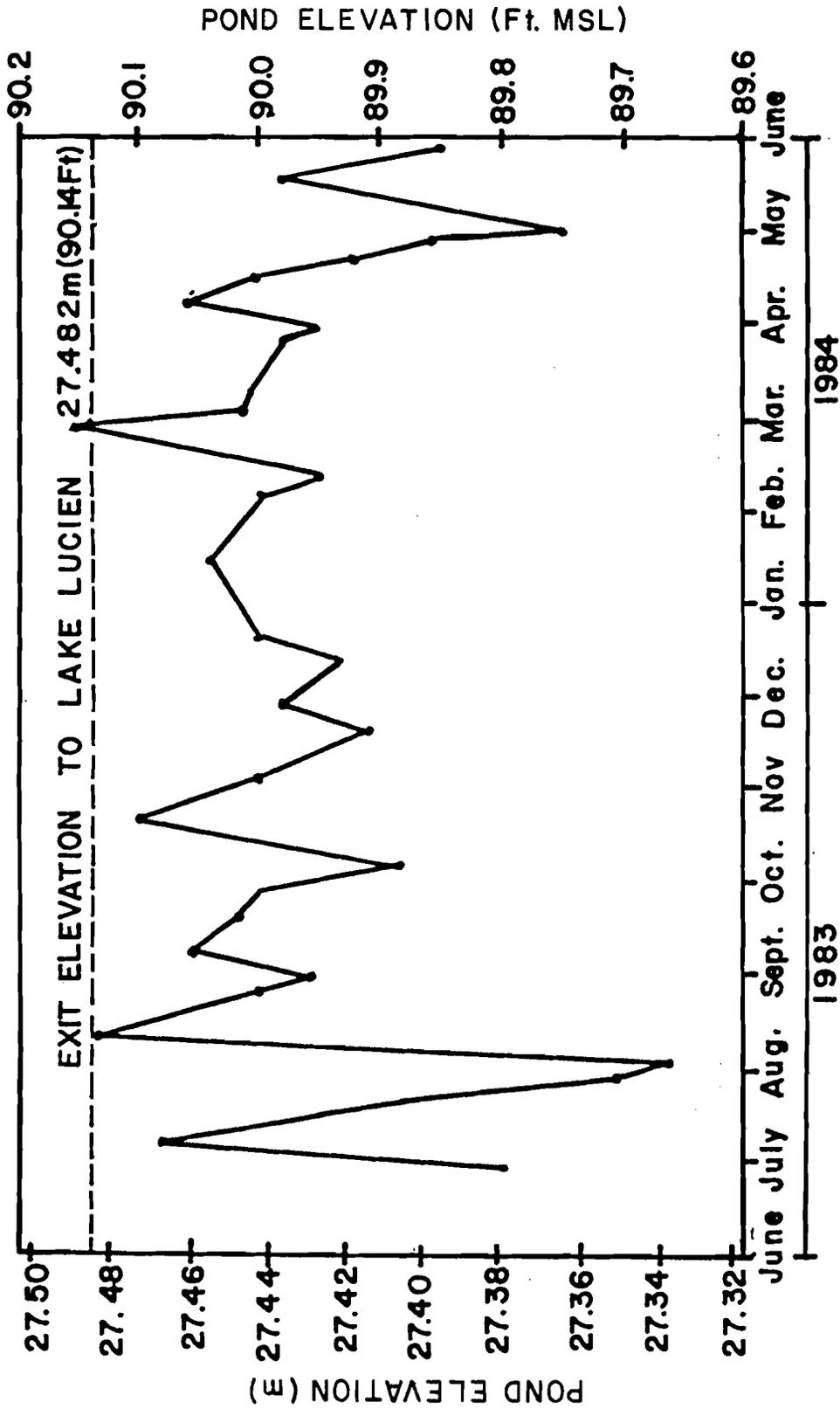


Figure 3-2. Fluctuations in Water Level with Time for the West Pond During 1983-84.

well-defined nature of both the inputs and outputs of the West Pond, this system was chosen for the investigation.

Physical Characteristics of the West Pond

Morphometric characteristics of the West Pond were determined during August and September 1982 through a series of field measurements. A map of the shoreline contour was produced using a two-point triangulation technique as described in Lind (1974), and contour depths and profiles were estimated by depth soundings collected at nine transects across the pond. The results of the shoreline and depth contour mappings are shown in Figure 3-3, and calculated contour areas and frustrum volumes are listed in Table 3-1. Plots of surface area and volume versus water elevation are shown in Figures 3-4 and 3-5. As evident in these figures, the West Pond has a triangular shape with relatively steep sides and an approximately flat bottom. These physical characteristics are presumably a result of the origin of the pond as a borrow pit.

The West Pond has an approximate surface area of 1.3 ha and an average depth of 1.5 m. Water clarity in the pond is normally quite good with visibility extending easily to the bottom. Concentrations of nutrients, especially phosphorus, are typically low. The pond maintains a population of Eichornia crassipes (water hyacinths) which normally reach a peak in numbers during the summer, covering approximately 30-50 percent of the pond surface. However, during

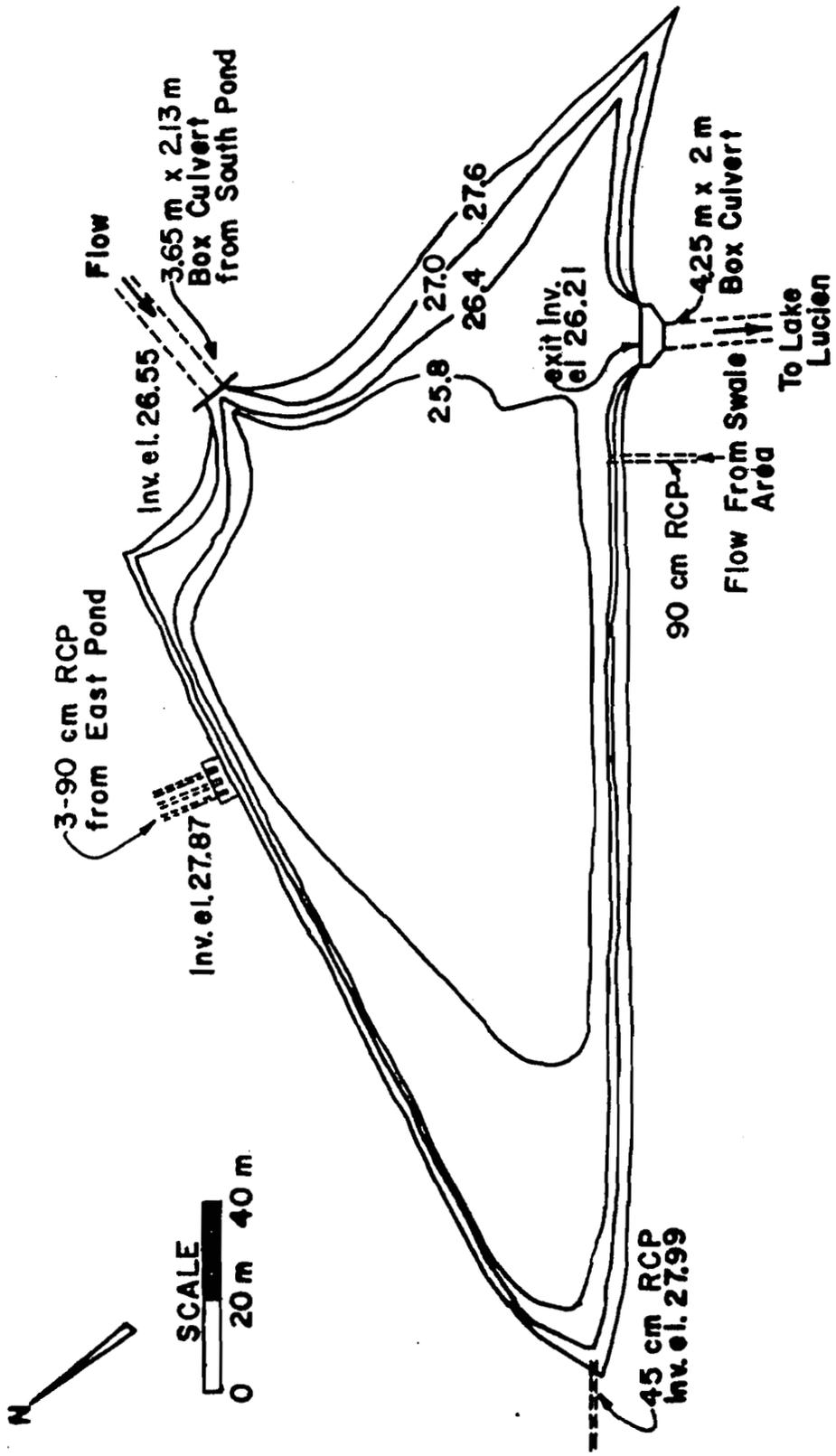


Figure 3-3. Contour Map of the West Pond Showing Connecting Drainage Lines.

TABLE 3-1
MORPHOMETRIC CHARACTERISTICS OF THE WEST POND AT
MAITLAND INTERCHANGE ON 9/1/82

CONTOUR LEVEL, FT (MSL)	CONTOUR AREA		FRUSTRUM VOLUME	
	m ²	ft ²	m ³	ft ³ gal
92.1	15,425	166,037	-	-
91.5	15,057	162,074	2,787	98,431 736,264
90.5	14,038	151,589	4,440	156,802 1,172,879
89.5	13,124	141,265	4,145	146,397 1,095,050
88.5	12,408	133,563	3,891	137,396 1,027,722
87.5	11,734	126,308	3,679	129,918 971,787
86.5	11,050	118,942	3,472	122,606 917,093
85.5	9,889	106,450	3,189	112,638 842,532
84.5	7,158	77,052	2,587	91,365 683,410
TOTALS:			28,190	995,544 7,446,669

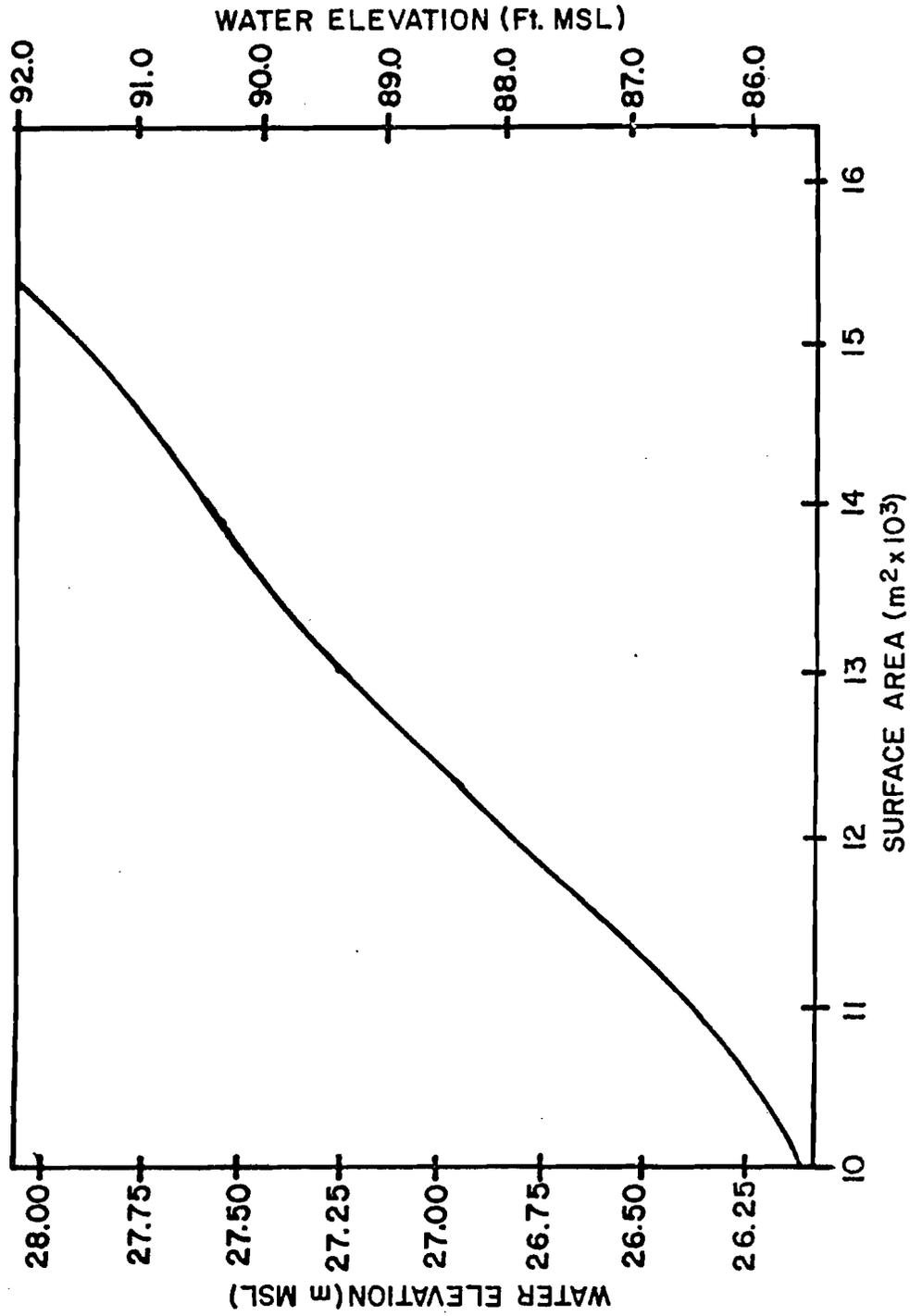


Figure 3-4. Maitland Pond Surface Area as a Function of Water Surface Elevation.

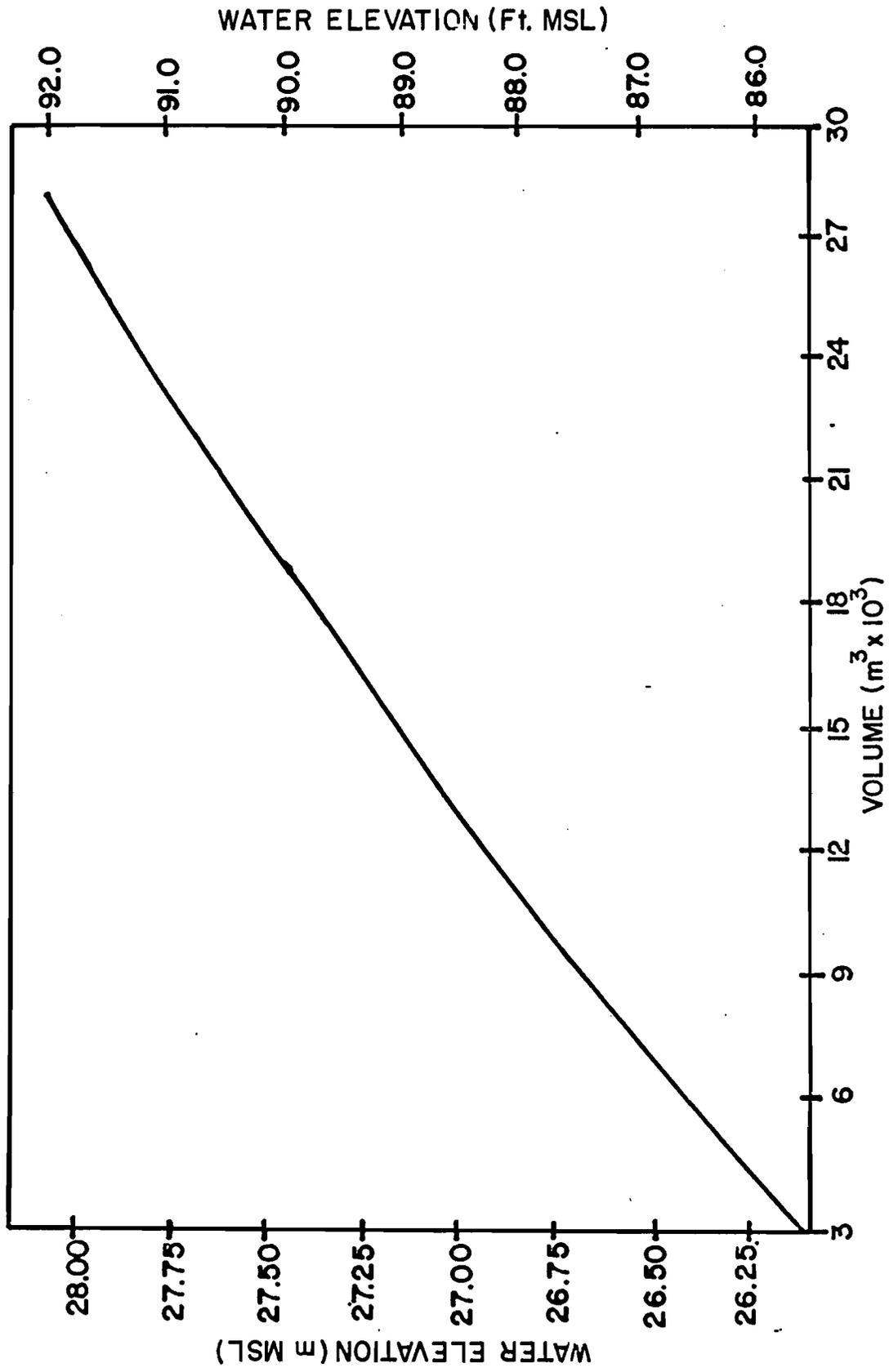


Figure 3-5. Maitland Pond Volume as a Function of Water Surface Elevation.

the winter months, these plants die back to a coverage of less than 10 percent. The pond maintains a large standing crop of the macro-algae Chara virtually year-round. In certain portions of the pond, particularly the central and western areas, this species has filled the entire available water column. In many places the Chara is intermixed with filamentous algae, such as Spirogyra. A large and diverse fish population was observed with several large bass and gar, along with an abundance of smaller species such as sunfish and mosquito fish. A colony of African cichlids (an imported tropical fish species) had become established on the southern shoreline, undoubtedly released there by someone either intentionally or accidentally. Large soft-shell turtles were also seen on several occasions. Because of the shallow water depth and large amount of algal production, the pond waters remain in a well oxygenated state. Sediment material is predominantly sand which is covered by a thin layer of organic matter, approximately one centimeter thick.

Field Investigations

Field investigations conducted during 1982-1984 at the West Pond were divided into the following tasks: (1) determination of the quantity of heavy metals entering the West Pond by way of stormwater runoff, (2) determination of the average heavy metal concentrations in the retention basin water, (3) assessment of the horizontal and vertical accumulation of heavy metals in the sediments of the pond,

and (4) monitoring of heavy metal concentrations in groundwater beneath the retention basin. Each of these tasks is described in the following sections.

Characterization of Stormwater Runoff

To determine the quantity of heavy metals entering the West Pond by way of stormwater runoff, an ISCO automatic refrigerated sampler was installed in a trailer adjacent to the 45 cm stormsewer input on the west end of the pond. A tygon sample tube was extended from the trailer to the stormsewer. A 60 cm x 60 cm plywood box, 1.25 m long, was attached to the end of the exit pipe, and a 90° V-notch weir was placed on the end of the box. The sample collection tube was attached inside the wooden box. Water elevations discharging from the V-notch weir were monitored by an ISCO pressure transducer and converted to a volumetric flow by a pre-programmed ISCO flow meter. A record of stormwater volumes entering the pond was made for each storm event.

Flow weighted composite samples were collected with the automatic refrigerated sampler over a 13-month period for 15 separate storm events, representing a wide range of rainfall intensities and antecedent dry periods. The automatic sampler was programmed to collect a one-liter sample of runoff for every 1830 liters (100 cubic feet) of flow. Samples were collected as soon as possible following storm events and returned to the laboratory for nutrient and heavy metal analyses.

Characterization of Retention Basin Water

Water samples were collected periodically within the West Pond from June 1982 to February 1983. An acrylic four-liter Kemmerer water sampler was used for sample collection. Composite samples were formed by combining samples collected at depths of 0.5 and 1.0 meters from five fixed stations selected initially at random within the pond. The locations of these stations are indicated in Figure 3-3. Each of the five samples were analyzed separately for nutrients and heavy metals, and an average value was calculated for each parameter on each sampling date. In addition, depth profiles of water temperature, pH, dissolved oxygen, specific conductivity, and oxidation-reduction potential were recorded at 0.5 m intervals at each station on each date, using a Hydrolab Series 8000 Water Quality Monitor, to provide background information for possible use in data analysis.

Characterization of Heavy Metals in Sediments

The horizontal and vertical distribution of heavy metals in the sediments of the West Pond was investigated by collection of a series of 2.5 cm diameter core samples to a depth of approximately 13 cm. A schematic of the core sample collection device is shown in Figure 3-6. Core sample tubes were constructed of clear polycarbonate pipe approximately 20 cm long with a beveled edge for ease in sediment penetration. The sample tube was attached with

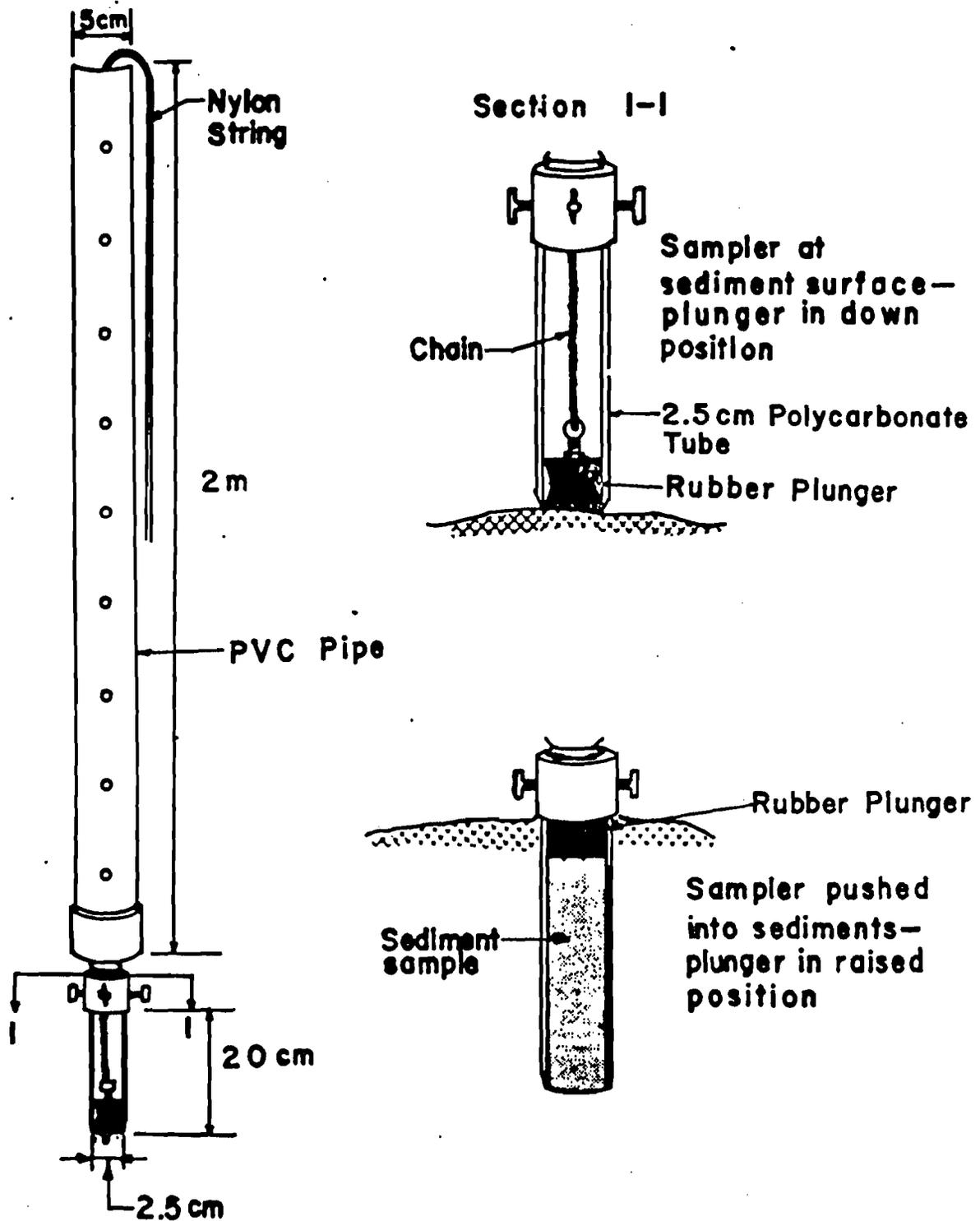


Figure 3-6. Core Sampler Apparatus Used for Collection of Sediment Cores.

holding screws to the end of a 3 m long, 3.8 cm diameter PVC pipe. A suction plunger, constructed from rubber stoppers, was placed inside the core tube at the bottom near the beveled edge. A nylon string was attached to an eyehook in the rubber plunger. As the core tube was inserted into the sediments, the rubber plunger was simultaneously pulled up the tube with the string so that the plunger and sediment material moved up the tube close together and at the same rate. This technique created a partial vacuum in the core tube above the sediments so that the loose sediment would not fall out of the tube after it was extracted.

Core samples were collected on 10/15/82, 10/15/83 and again on 4/15/84 in order to estimate accumulations of heavy metals over this period. On each date, 43 separate core samples were collected in the West Pond at 7.5 m intervals along 10 transects, as shown in Figure 3-7. The use of transects allowed collection of core samples on each collection date from locations very close to where the other sets were collected, so that accumulation rates of heavy metals in the sediment could be estimated.

Upon return to the laboratory, the core samples were frozen to facilitate handling of the loose sediments. The frozen cores were removed from the tubes and sectioned into the following layers: 0-1 cm, 1-3.5 cm, 3.5-6 cm, 6-8.5 cm, and 8.5-13 cm. Sediment layers were stored in polyethylene bottles under refrigeration until analysis. Metal concentrations in the 0-1 cm layer were used to investigate horizontal movement of heavy metals from the point of

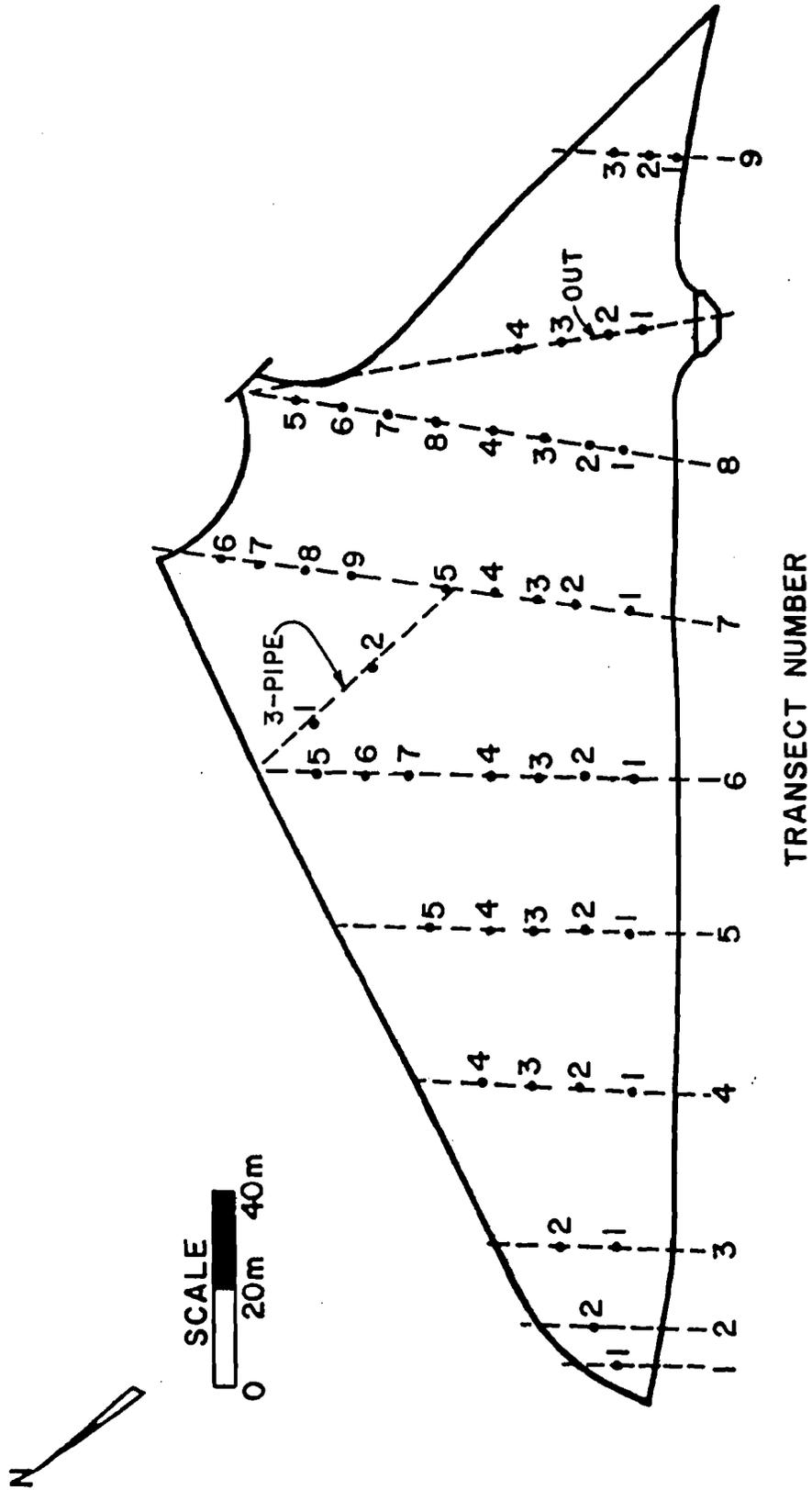


Figure 3-7. Sampling Locations for Bottom Sediment Cores in the West Pond.

discharge into the pond. The extent of vertical migration of heavy metals was determined using all five layers. For the set of core samples collected on 10/15/82, each of the 43 core samples was analyzed for heavy metals separately at each of the five layers, for a total of 215 sediment samples. Samples collected on 10/15/83 were divided into the five layers and then combined together by layer to form a composite sample for each layer. Each of the five resulting samples were analyzed in triplicate. A similar technique was used for the samples collected on 4/15/84.

Groundwater Monitoring

To investigate the possibility of groundwater contamination by leaching of heavy metals from stormwater management systems, five multiport monitoring wells were installed at locations indicated in Figure 3-1. Wells designated as numbers 2 and 3 were installed at the edges of the West Pond to monitor possible vertical movement of heavy metals beneath the pond. The remaining three monitoring wells were installed at various locations surrounding the stormwater management system. Well number 1 was located in a grassy "dry" swale area approximately 40 m south of the pond to provide for groundwater monitoring in an area receiving periodic stormwater infiltration. Well number 4 was placed in an isolated area which receives no direct stormwater discharges and is normally dry. Well number 5 was located east of I-4 in a low "wet" swale area. Since normal groundwater flow in this area is toward the east and

northeast, any contaminants leaving the West Pond and migrating with groundwater might possibly be detected at this location.

The well design was such that all sample ports were housed in a single two-inch polyethylene pipe. A schematic of the multiport sampling devices is shown in Figure 3-8. 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 such as cluster wells. 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 mesh plastic screen to prevent particles from entering the tubing. The well casing was constructed of 5 cm PVC pipe. Sample ports were inserted in the casing at depths of 0.1 m, 0.5 m, 1.0 m, 3.0 m, and 6.0 m below the water table elevation at the time of placement. Polyethylene tubing was extended from each sample port 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 multiport wells were drilled by Ardaman and Associates of Orlando, Florida, using a rotary bit to a depth of approximately 7 meters. A six-inch casing was extended in 2 m sections as the drilling progresses to hold the bore hole open. No drilling fluids of any kind, except water, were used during drilling. Once the drilling process was completed, the hole was backwashed until the wash water was clear and free of suspended

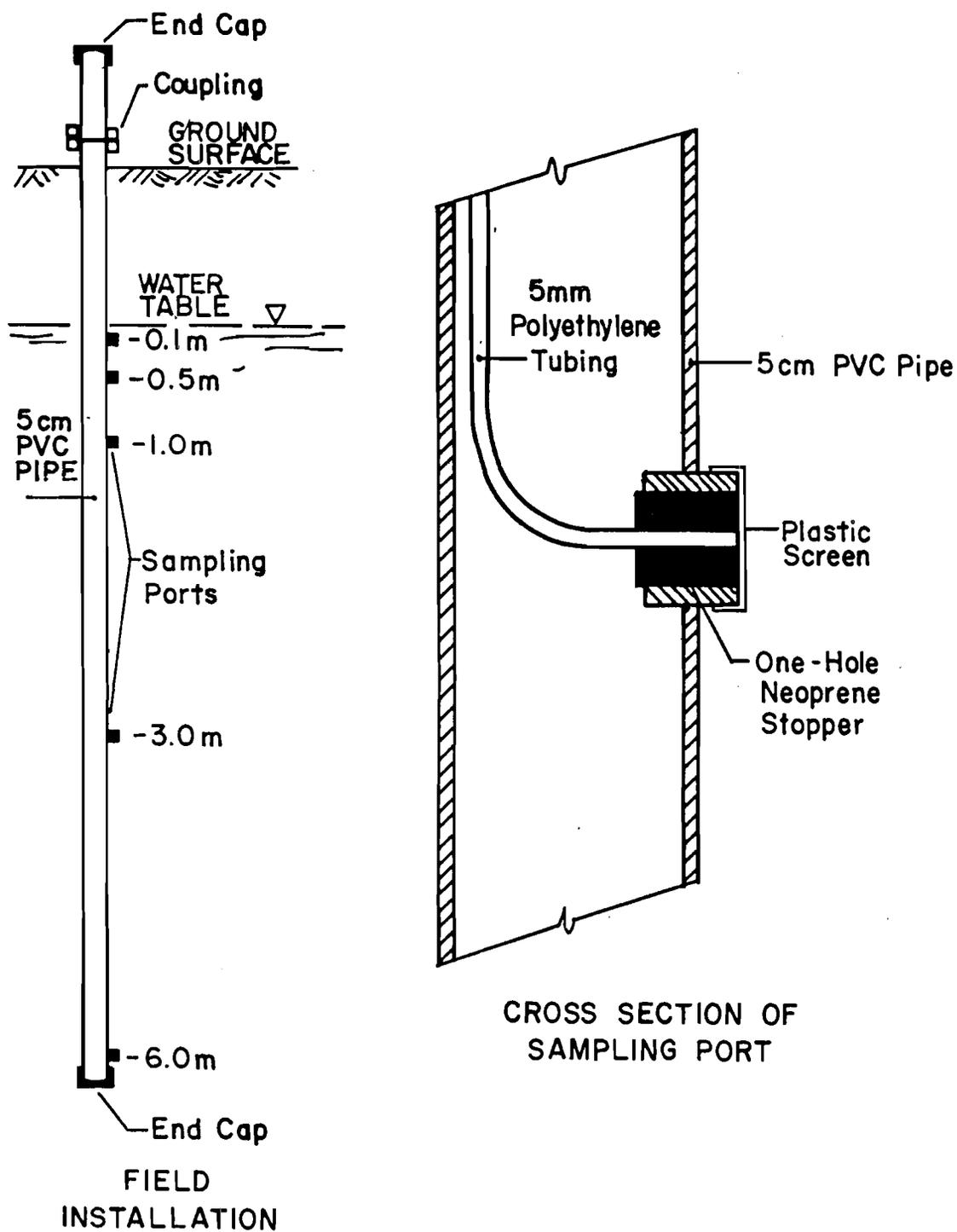


Figure 3-8. Schematic Diagram of the Multiport Groundwater Sampling Device.

solids. The monitoring well's polyethylene housing was inserted, and backfilling with clean silica sand (20-30 grade) was begun. After approximately 1.5 meters of backfill had been placed, the drill casing was raised and a section was removed. Bentonite seals, approximately 20 cm thick, in the form of 0.75 cm pellets, were placed mid-way between the 3 m and 6 m sample ports, and between the 1.0 and 3 m ports. No seals were placed between the upper ports since these ports were very close together and clogging of a port by the bentonite seal was a possibility. An additional seal was placed around the monitoring well casing at the ground surface to minimize seepage of water around the sides of the PVC pipe. A removable end cap cover was installed on each well to protect the sample tubes.

After construction was completed in March 1983, no samples were collected for analysis for approximately 60 days to allow for groundwater disturbances created during the installation process to dissipate. In addition, during the first six months following construction, each port on each of the five wells was pumped for 10 minutes on a weekly basis with a peristaltic pump to remove any remaining groundwater which may have been disturbed during construction. This process removed approximately 20 liters from each sample port on each weekly visit.

Groundwater samples were collected for analysis on a monthly basis beginning in May 1983. Samples were collected using a portable battery-powered peristaltic pump. Approximately 10 liters of groundwater was pumped and discarded from each port before a

sample was collected. Samples were collected in one-liter polyethylene bottles. The sample bottle was allowed to overflow approximately 3 volumes before the sample was accepted. Beginning in December 1983, the 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 measurement of temperature, conductivity, pH, dissolved oxygen and oxidation-reduction potential as the sample was being collected. These field measurements are accurate for certain parameters such as pH, dissolved oxygen and oxidation-reduction potential which are subject to rapid change during storage. Collected samples were returned to the laboratory for analysis of nutrients and heavy metals.

Laboratory Investigations

Laboratory investigations during this research were divided into the following tasks: (1) analyses of dissolved and total heavy metal concentrations in the retention pond water, stormwater, and monitoring well samples, (2) analysis of heavy metal concentrations in sediment core samples from the West Pond, (3) an extraction process which allowed determination of the chemical speciation of heavy metals in sediment core samples, and (4) a series of investigations to determine the influence of pH and redox potential on the chemistry of heavy metals in sediments. Each of these procedures is described in the following sections.

Heavy Metal Analysis in Water Samples

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 was 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 was first deionized then glass distilled, followed by a final deionization through a Barnstead Nanopore 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, an average value, and a standard deviation for each metal. A standard solution and a distilled water blank were analyzed before and after each set of 6 to 8 samples. A computer program was written and used to correct the average values for each sample for drift in measurements of both the standard solution and blank solution.

Analysis of Heavy Metals in Sediments

Acid extractable heavy metal analyses were conducted on the core samples collected on 10/15/82, 10/15/83, and 4/15/84 for each of the nine metals listed previously. Each core section was first dried at 103° to determine moisture content followed by ignition at

550°C to determine organic content. The ashed sample was ground with a mortar and pestle, and approximately 0.4 g of sediment (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.

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 particulate trace metals. This 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. Soluble - metal ions contained in water which are trapped in interstitial pore spaces
2. Exchangeable - metal ions which are specifically adsorbed and are ion exchangeable

3. Bound to Carbonates - metal ions which are associated with sediment carbonates as a precipitate or co-precipitate
4. Bound to Iron and Manganese Oxides - iron and manganese oxides may exist as nodule, cement between particles
5. Bound to Organic Matter - this includes metals 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-gram samples from each composite core layer collected on 10/15/83 were taken through the following metal speciation steps. All extractions were conducted in 50 ml polypropylene centrifuge tubes to minimize losses of solid material.

Soluble. A 2 g sample of finely ground sediment (weighed to the nearest 0.1 mg) 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 min. The supernatant was carefully decanted and prepared for metal analysis.

Exchangeable. The sediment residue from above was extracted at room temperature (20°C) with 16 ml of 1 M MgCl₂ (ph 7.0) with continuous agitation for 1 hour. The supernatant was removed with a pipet and prepared for metal 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 for a particular layer were combined and later analyzed for heavy metals. The mass of heavy metals measured in the wash water was added to the amount released during the extraction step since heavy metals 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 M NaOAc (pH 5.0) with continuous agitation at room temperature (20°C) for 5 hours. Following extraction, the mixture was centrifuged at 3000 rpm for 30 min. The supernatant was removed for analysis and the residue washed with 16 ml of distilled/deionized water as before. Wash waters were combined and analyzed for metals as described previously.

Bound to Fe-Mn Oxides. The residue from above was extracted with 40 ml of 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ 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.

Bound to Organic Matter. To the residue from above were added 6 ml of 0.02 M HNO_3 and 10 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 . The mixture was heated to 85°C for 2 hours with occasional agitation. A second 6 ml aliquot of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was then added and the sample was heated again to 85°C for 3 hours with intermittent agitation. After cooling, 10 ml of 3.2 M NH_4OAc in 20% HNO_3 (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 Chemistry of Heavy Metals in Sediments

The effects of changes in pH and redox potential on release of 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 kettle was used to contain sediment suspensions under selected conditions. The apparatus used for incubating sediment suspensions is shown in Figure 3-9. 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 suspension.

Sediment material for use in the incubation studies was collected as a composite sample from six randomly selected stations in the West Pond using an Eckman dredge. Two dredge samples were collected from each station, combined in a large polyethylene container, and covered with approximately 25 cm of pond water. This composite sample was used for all incubation studies. Sediments were mixed by stirring prior to sample collection to insure a homogeneous sample. Moisture content and organic content were determined on the mixed sample used in each incubation experiments.

To begin an experiment, approximately 300 g of wet sediment was placed in the acid-washed reaction kettle along with 1800 ml of pond water from the West Pond collected prior to the start of the experiment. A separate sample of pond water was collected for initial metal analysis. The reaction vessel was closed and the

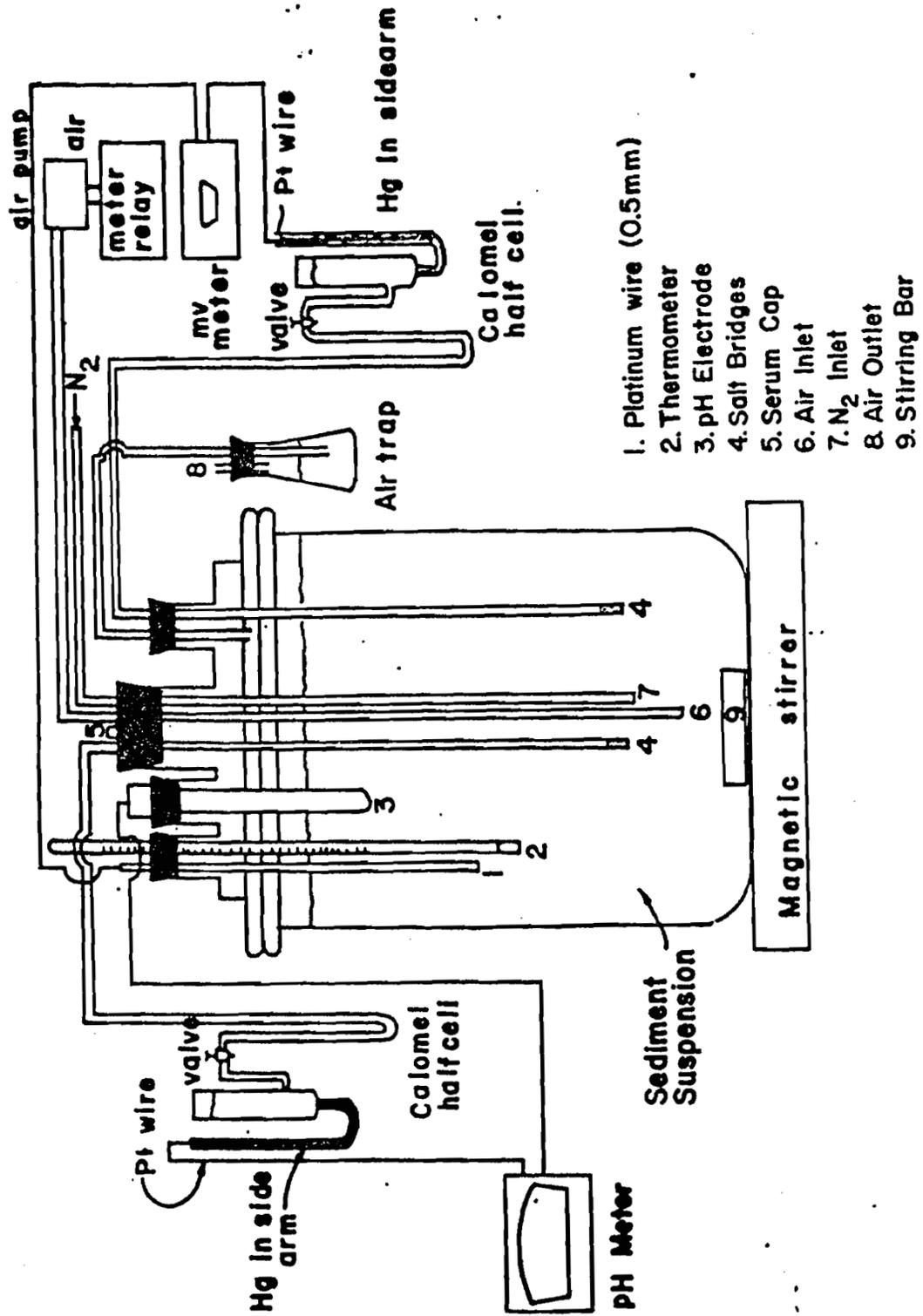


Figure 3-9. pH and Redox Potential Control Apparatus for Incubating Sediment Suspensions.

suspension stirred 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 adjusted to the desired level. For highly oxidized redox potentials several days were often required to achieve the desired levels. Reduced conditions were obtained more quickly. The suspension pH was adjusted at this time to the proper level, and further refinement of pH and redox potential continued for 2 to 5 additional days. Sediment suspensions were then incubated for 5 days after the desired pH and redox potentials had been reached. Each experiment conducted at a specified pH included four redox potentials ranging from highly oxidized to highly reduced: +500 mv, +250 mv, 0 mv, and -150 mv. Values for pH which were tested included: 5.0, 6.5, and no control which produced values in the range of 7.5-8.0.

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 mercury and connected to the reference side of the meter. 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 small stream of air to the reaction vessel when the redox potential of the suspension dropped below the desired level. The desired level for activation of the

pump could be set internally in the relay so that any desired redox potential could be selected. 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 CO_2 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. Adjustments were made using 30% Suprapur hydrochloric acid or 12 N sodium hydroxide through the serum cap located in the center rubber stopper. The pH was measured continuously on a Corning Model 12 Research pH Meter using a glass pH electrode and a saturated calomel electrode as described previously. 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. Gambrell found that possible metal sulfide precipitation in the fritted ceramic junction of the silver-silver chloride combination electrode contributed a junction potential to the electrode system which was not constant with time. The stability of this separate calomel and glass electrode system was verified in these investigations. Virtually no drift was measured in pH calibration even in suspensions which were maintained in a highly reduced state for 30 days or more. Adjustments to the calibration were less than 0.02 units in all experiments with several requiring no adjustments at all.

During incubation of suspensions, the temperature was maintained at $30^{\circ}\text{C} \pm 1^{\circ}$. The incubation temperature was an equilibrium between the heat generated by the stirring motor and the room temperature. If the suspension temperature increased above 30°C , the temperature was reduced by inserting thin sheets of polyethylene as required between the reaction kettle and the warm stirrer platform to maintain the desired temperature.

The incubation apparatus, illustrated in Figure 3-9, performed remarkably well throughout the entire experimental period. Once the calomel electrodes with the agar tips had become equilibrated, they produced extremely trouble-free continuous reference cells for both

pH and redox potential. At the beginning of the first set of experiments, the pH calibration was checked daily. Adjustments were rarely necessary and were in all cases less than 0.1 unit. Because of this stability, the pH calibration became less frequent until finally it was conducted on a bi-weekly basis. Adjustments, even after this extended period, were infrequent. The agar plugs on the calomel electrodes never required replacement and provided a quick response which was similar to a pre-manufactured calomel electrode.

Measurements of redox potential using a shiny platinum electrode and a calomel reference electrode were also virtually trouble-free. The only problem encountered was a periodic fluctuation in values which was most pronounced when the air pump was injecting air into the system. Apparently, the air bubbles were affecting either the platinum or calomel electrodes. The only difficulty which was encountered with the incubation apparatus was that the stirring bar would seem to lose its magnetic attraction over time and require replacement. However, this was only a minor inconvenience.

At the termination of an incubation period, a 100 ml sample of circulating sediment suspension was withdrawn from the reaction vessel using a siphon into a sealed 250 ml polycarbonate bottle. 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 may cause changes in redox potential that could result in

immediate oxidation of metal ions to insoluble forms. Thus, laboratory air may be a potentially serious contaminant during chemical extractions, and considerable care must be exercised to minimize oxidation of sediment material during extractions. To minimize potential 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 3-10. A syringe connected to a low pressure nitrogen source was inserted through the serum cap. A polyethylene pipet 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 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.

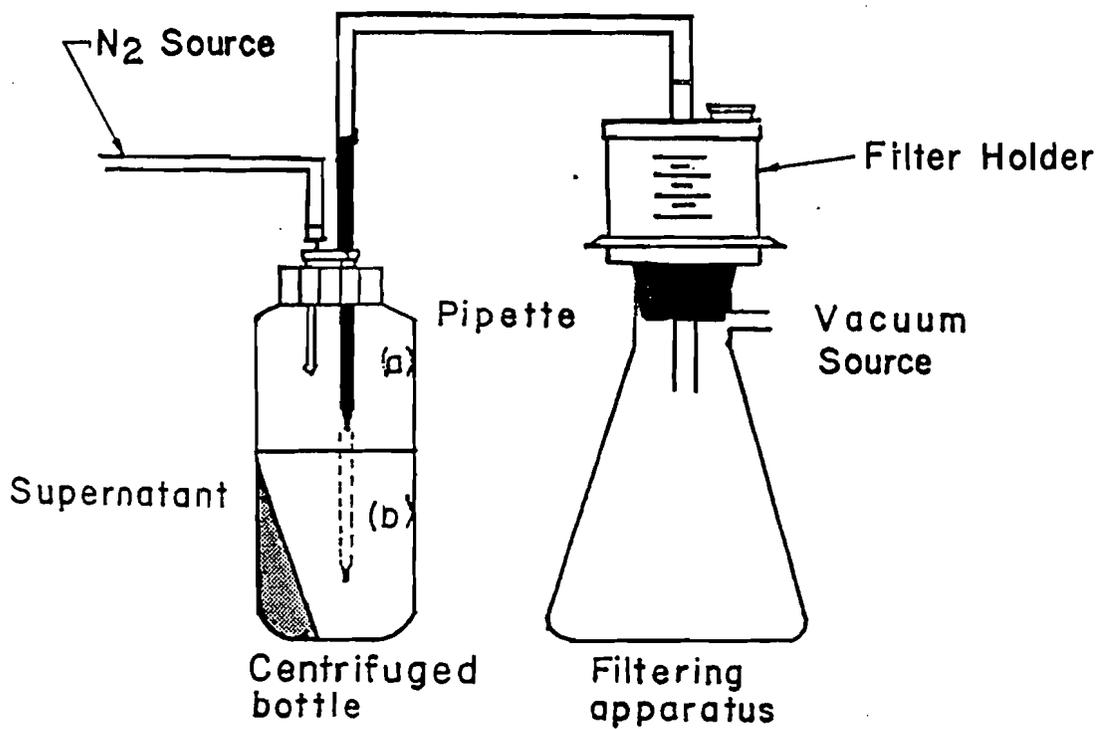


Figure 3-10. Apparatus for Filtering Supernatant Solutions Under a Nitrogen Atmosphere: (a) Pipette in N₂ Purge Position and (b) Pipette in Filtering Position.

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 analyses to provide least-square estimates to various linear regression models.

Although most of the procedures listed above were reasonably straightforward, regression analyses involved a number of steps, and as a result, will be discussed in more detail. The purpose of the regression analyses was to determine the "best fit" least-square equation between various response and predictor variables. Since the objective in most cases was to determine the importance of significant predictor variables in regulating heavy metal concentrations, the "best fit" regression model was defined to be the model which included the largest number of predictor variables

which were all significant at the 0.10 level or better. Regression analyses were conducted on stormwater, sediment, and groundwater data sets to examine both predictive relationships between concentrations of heavy metals and various predictor variables, as well as to examine the relative importance of significant predictor variables in regulating heavy metal concentrations.

The first step in a regression analysis was to examine the functional forms of the response and predictor variables. Plots of residuals and partial residuals versus each of the predictor variables were used to test for linearity or the presence of higher order effects. When functional forms were correctly specified, studentized residuals were used to detect outliers in the response variables, and values of Cook's D were used to detect outliers in the predictor variables. Observations with studentized residuals in excess of 2.5, or a value of Cook's D in excess of 0.400, were discarded as outliers. Most regression analyses resulted in the removal of very few data points as outliers. PROC REG was used to obtain values for the studentized residuals and Cook's D. Plots of raw residuals versus the predicted values of the response variables were examined as a test for homoscedasticity (equality of variances). A random scattering of the points with a slope of zero was used to indicate equality of variances.

In most analyses, the purpose of the regression procedures was for model specification and estimation of the regression coefficients. As a result, PROC REG was used with the full model to

examine correlations and multicollinearities. The correlation matrix indicated predictor variables which were strongly correlated and unnecessary variables were removed from the model. The presence of multicollinearities was examined using eigenvalues and eigenvectors along with the variance inflation factor. In general, values of the variance inflation factor in excess of 10 were used to indicate the presence of multicollinearities. Variables which were strongly correlated or involved in multicollinearities were removed from the model. Variables not producing a significant test for $B=0$ at the 0.10 level or better were also discarded from the model. Improvements in MSE (mean square error) and changes in the values of R-square were observed after removal of each variable. The model producing the best combination of a large value of R-square with a small value of MSE with no significant multicollinearities was chosen as the "best fit" model. Following selection of the model, a test for normality was conducted from a normal probability plot of raw residuals. A straight line on this plot indicated a normally distributed data set. A runs-test was also used to check for correlation of the error terms.

Two types of regression equations were calculated during this research. One equation was the least-squares "best fit" predictor equation. The other equation was the unit length standardized form of the "best fit" equation which has the form:

$$Y = u + B_1 * W_1 + B_2 * W_2 + \dots + B_n * W_n$$

where \bar{u} is the mean value of Y , B_1^* is the standardized least-squares estimator, and W_1 is the X_1 variable scaled to the unit length form with W equal to zero and a standard deviation equal to one. This type of standardized equation is more informative in determining the relative effects of the predictor variables since it is independent of units, and the magnitude of the standardized estimates is a direct reflection of their importance in predicting Y .

CHAPTER 4
EXPERIMENTAL RESULTS

Characteristics of Highway Runoff
at the Maitland Site

To establish a record of the concentrations of various heavy metals entering the West Pond by way of highway runoff, flow weighted runoff samples were collected at the 45 cm inlet with a refrigerated Isco automatic sampler from April 23, 1983 to May 28, 1984 over a wide range of rainfall intensities, durations, and antecedent dry periods. A total of 16 storm events, including a total of 150 separate runoff samples were collected and analyzed over this period for both dissolved and total heavy metals. Total rainfall amounts for sampled storm events ranged from 0.33 to 3.23 inches with antecedent dry periods of 0.24 to 25.4 days. Average flow rates in the 45 cm stormsewer, an indirect measure of rainfall intensity, ranged from 0.085 to 59.4 liters/sec.

Measured concentrations of heavy metals during each of the individual storm events are given in Appendix I for sequential stormwater samples collected at intervals of 2831 liters (100 ft³) over the runoff hydrographs. A summary of these heavy metal concentrations is presented in Table 4-1. Of the heavy metals which

TABLE 4-1
 HEAVY METAL CONCENTRATIONS IN SEQUENTIAL HIGHWAY RUNOFF SAMPLES
 COLLECTED AT THE MAITLAND WEST POND DURING 1983-84

PARAMETER	NUMBER OF SAMPLES	MEAN ($\mu\text{g/l}$)	PERCENT DISSOLVED (%)	STANDARD DEVIATION	MINIMUM VALUE ($\mu\text{g/l}$)	MAXIMUM VALUE ($\mu\text{g/l}$)
LEAD:						
Dissolved	150	33.0		40.2	7.0	413
Total	150	181	18.2	331	11.0	3,596
ZINC:						
Dissolved	150	40.0		42.6	1.0	324
Total	150	73.9	54.1	71.2	5.0	372
COPPER:						
Dissolved	150	28.6		24.7	6.0	175
Total	150	38.6	74.1	28.8	6.0	176
NICKEL:						
Dissolved	150	2.5		2.4	0.5	15
Total	150	3.4	73.5	2.8	0.5	18
CHROMIUM:						
Dissolved	150	2.5		2.2	0.5	16
Total	150	4.2	59.5	3.2	0.5	18

TABLE 4-1 -- CONTINUED

PARAMETER	NUMBER OF SAMPLES	MEAN (µg/l)	PERCENT DISSOLVED (%)	STANDARD DEVIATION	MINIMUM VALUE (µg/l)	MAXIMUM VALUE (µg/l)
IRON:						
Dissolved	150	77.9		59.7	11.0	466
Total	150	378	20.6	354	44.0	2,172
ALUMINUM:						
Dissolved	150	125		124	19.0	832
Total	150	561	22.3	563	53.0	3,499
MANGANESE:						
Dissolved	150	2.70		6.7	<1	59
Total	150	9.53	28.3	10.8	<1	62
CADMIUM:						
Dissolved	150	1.7		2.0	<1	12
Total	150	2.2	77.3	2.4	<1	12
pH	101	6.30	--	0.88	4.95	8.49

were measured at the Maitland site, the following order was observed in terms of dissolved concentrations:

$$\text{Al} > \text{Fe} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Mn} > \text{Ni} = \text{Cr} > \text{Cd}$$

Total concentrations observed the following order:

$$\text{Al} > \text{Fe} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Mn} > \text{Cr} > \text{Ni} > \text{Cd}$$

With the exceptions of lead, iron, manganese, and aluminum, all heavy metals in the highway runoff samples appeared to be present predominantly in a dissolved form. Cadmium, nickel, and copper were all present in dissolved fractions which were near 75 percent of the total metal measured. On the other extreme, lead, iron, manganese, and aluminum were predominantly particulate in nature with dissolved fractions of only approximately 20 percent. Zinc and chromium appeared to be approximately equal in dissolved and particulate forms.

As seen in the raw data presented in Appendix I, as well as in the summary data listed in Table 4-1, a considerable variability was found for most heavy metal concentrations not only between the various storm events but during individual storm events as well. Several heavy metals exhibited a variability in concentrations for both dissolved and total species which covered several orders of magnitude. This variability was especially apparent for lead,

copper, zinc, iron, and aluminum. As a result, flow-weighted metal concentrations were calculated for each storm event which allowed a rainfall event to be represented by a single concentration for each metal. These flow weighted concentrations were calculated by dividing the total metal mass transported during a storm event by the total flow of runoff.

Average flow-weighted concentrations of heavy metals are presented in Table 4-2 for dissolved species and in Table 4-3 for total metal species. In general, the variability of mean flow-weighted dissolved metal concentrations appears to be much less than that observed for total metal concentrations, with most dissolved species exhibiting a five-fold difference between the low and high concentrations, while total concentrations exhibited over a ten-fold range in most cases.

As observed previously for the sequential hydrograph samples, flow-weighted concentrations of heavy metals (with the exceptions of lead, iron, manganese, and aluminum) are all predominantly in a dissolved state. Cadmium, nickel, and copper were all present in dissolved fractions near 75 percent with lead, iron, and aluminum existing predominantly in a particulate form with dissolved fractions of only approximately 20 percent.

Probability distributions of mean flow-weighted heavy metal concentrations in the 16 measured storm events are presented in Figures 4-1 to 4-3, where the metal concentration is plotted on the y-axis on a log scale. Total concentrations of heavy metals appear

TABLE 4-2

MEAN FLOW-WEIGHTED CONCENTRATIONS OF DISSOLVED HEAVY METALS IN HIGHWAY RUNOFF
COLLECTED AT THE 45 CM INLET TO THE MAITLAND WEST POND DURING 1983-84

DATE	AVERAGE WEIGHTED RAINFALL EVENT CONC. ($\mu\text{g/l}$)										TOTAL RAIN (in)	ANT. DRY PERIOD (days)
	Pb	Zn	Cu	Fe	Ni	Cr	Al	Mn	Cd			
4/23/83	25.8	22.2	14.2	34.2	2.2	3.6	62.9	0.9	3.0	1.44	10.1	
6/8/83	22.7	21.0	13.4	90.9	1.8	1.7	60.9	1.2	1.0	1.53	0.38	
7/1/83	14.6	18.3	19.8	65.7	1.2	1.4	54.9	1.0	0.7	1.96	9.75	
7/29/83	25.0	36.5	30.7	30.7	1.5	1.7	45.5	1.1	0.9	0.38	1.96	
8/7/83	15.2	18.1	10.3	27.7	1.6	1.1	56.5	0.8	1.0	1.16	0.99	
9/2/83	21.3	42.9	63.8	97.3	4.0	2.5	98.0	1.0	0.7	0.56	0.38	
9/21/83	40.5	30.1	29.1	80.9	2.9	2.9	213	2.0	0.5	0.82	0.91	
10/19/83	30.1	12.8	21.0	55.6	4.6	33.3	122	0.5	1.2	0.42	2.75	
2/12/84	18.3	35.6	23.7	212.	1.6	2.0	93.6	3.8	1.4	0.82	25.4	
2/21/84	19.7	23.0	28.3	149	0.9	1.2	75.1	2.2	0.9	0.42	10.2	
2/22/84	13.1	18.9	16.3	53.8	1.1	1.0	40.5	1.4	0.8	0.46	0.24	
3/22/84	51.9	80.9	43.7	88.0	1.4	3.0	245	3.0	1.5	1.09	9.42	

TABLE 4-2 -- CONTINUED

DATE	AVERAGE WEIGHTED RAINFALL EVENT CONC. ($\mu\text{g/l}$)										TOTAL RAIN (in)	ANT. DRY PERIOD (days)
	Pb	Zn	Cu	Fe	Ni	Cr	Al	Mn	Cd			
5/22/84	128	134	55.3	105	8.3	7.7	439	18.2	7.2	0.58	0.66	
5/23/84	54.3	59.4	31.5	98.8	4.0	2.8	212	3.0	5.2	0.33	1.06	
5/25/84	28.0	44.8	11.5	49.6	1.6	2.5	105	2.1	1.5	3.23	1.96	
5/28/84	28.1	47.9	10.4	255	3.1	3.7	120	2.2	1.7	1.45	2.08	
AVG.	33.5	40.4	26.4	93.4	2.6	2.6	128	2.8	1.8	1.04	4.89	

TABLE 4-3

MEAN FLOW-WEIGHTED CONCENTRATIONS OF TOTAL HEAVY METALS IN HIGHWAY RUNOFF
COLLECTED AT THE 45 CM INLET TO THE MAITLAND WEST POND DURING 1983-84

DATE	AVERAGE WEIGHTED RAINFALL EVENT CONC. ($\mu\text{g/l}$)										TOTAL RAIN (in)	ANT. DRY PERIOD (days)
	Pb	Zn	Cu	Fe	Ni	Cr	Al	Mn	Cd			
4/23/83	379	121	43.3	796	4.2	8.2	1,263	37.4	3.2	1.44	10.1	
6/8/83	376	64.9	22.4	477	2.9	3.4	500	8.7	1.0	1.55	0.38	
7/1/83	147	39.6	30.9	334	1.5	2.8	516	4.6	0.7	1.96	9.75	
7/29/83	326	173	46.0	690	3.5	6.3	663	15.0	2.0	0.38	1.96	
8/7/83	114	38.2	16.9	235	1.8	2.3	221	3.1	1.6	1.16	0.99	
9/2/83	198	84.1	82.5	467	5.3	4.5	587	6.0	0.9	0.56	0.38	
9/21/83	69.1	30.9	32.4	113	3.2	3.0	379	3.0	0.9	0.82	0.91	
10/19/83	39.3	12.8	22.2	91.8	4.7	3.0	158	3.6	2.8	0.42	2.75	
2/12/84	84.9	58.2	28.1	629	2.0	2.7	311	7.4	1.8	0.82	25.4	
2/21/84	41.8	32.1	32.7	279	2.1	1.6	225	3.2	1.7	0.42	10.2	
2/22/84	29.7	19.2	26.4	145	1.1	1.3	144	2.2	1.0	0.46	0.24	
3/22/84	92.6	99.4	47.9	172	1.6	3.3	442	15.9	1.5	1.09	9.42	

TABLE 4-3 --- CONTINUED

DATE	AVERAGE WEIGHTED RAINFALL EVENT CONC. ($\mu\text{g}/\text{l}$)										TOTAL RAIN (in)	ANT. DRY PERIOD (days)
	Pb	Zn	Cu	Fe	Ni	Cr	Al	Mn	Cr	Cr		
5/22/84	231	171	100.7	281	10.1	9.7	1,040	21.8	8.9	8.9	0.58	0.66
5/23/84	113	67.2	45.3	158	5.0	3.8	424	8.2	8.5	8.5	0.33	1.06
5/25/85	247	93.9	11.8	558	3.0	6.0	1,077	11.0	1.4	1.4	3.23	1.96
5/28/84	124	30.3	10.4	25.9	2.7	2.3	475	6.7	1.8	1.8	1.45	2.08
AVG.	163.1	71.0	37.5	340.8	3.4	4.0	527	9.8	2.5	2.5	1.04	4.89
% DISSOLVED	20.5	56.9	70.4	27.4	76.5	65.0	24.2	28.6	72.0	72.0	--	--

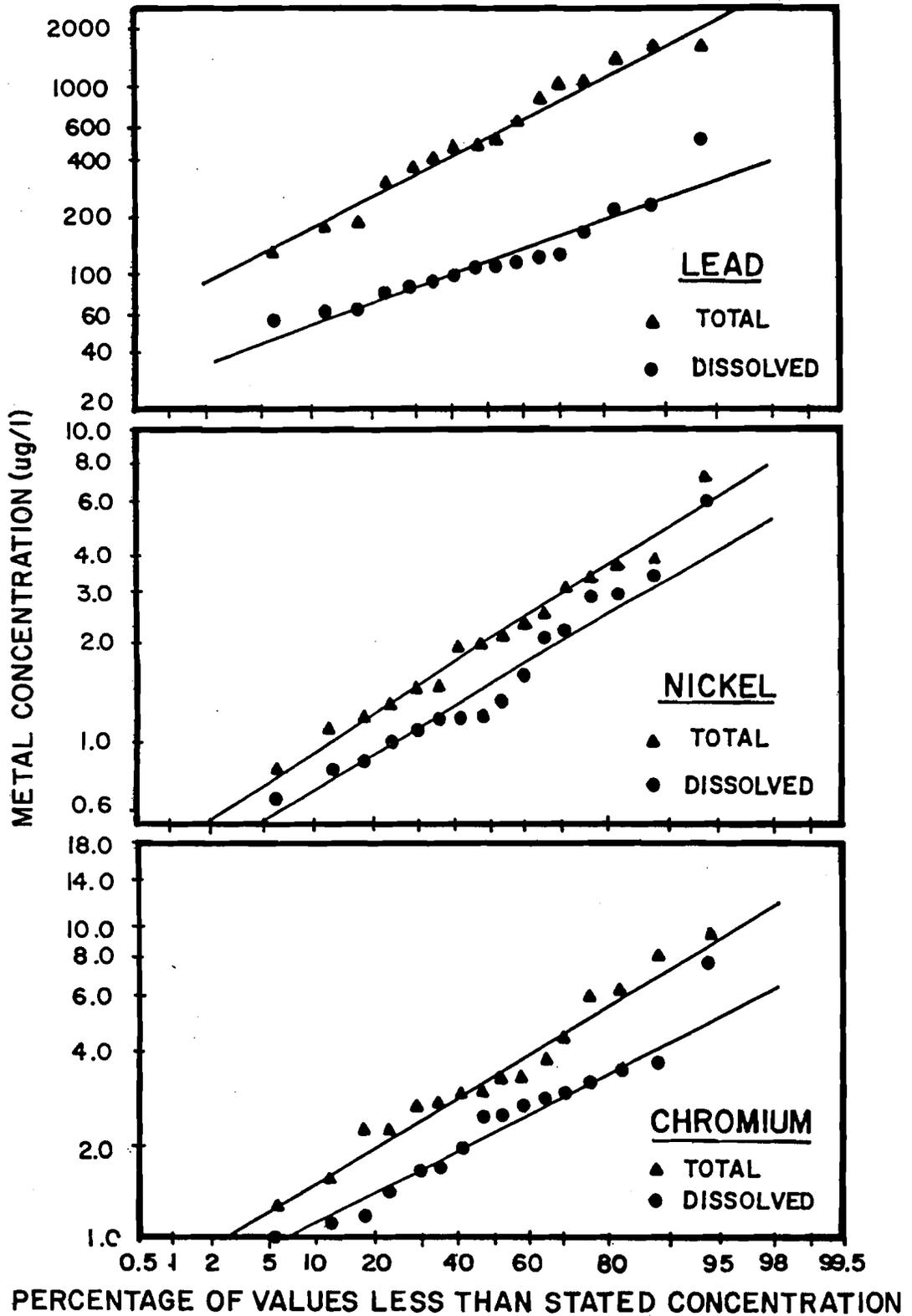


Figure 4-1. Distribution of Lead, Nickel and Chromium in Highway Runoff Entering the West Pond at Maitland During 1983-84.

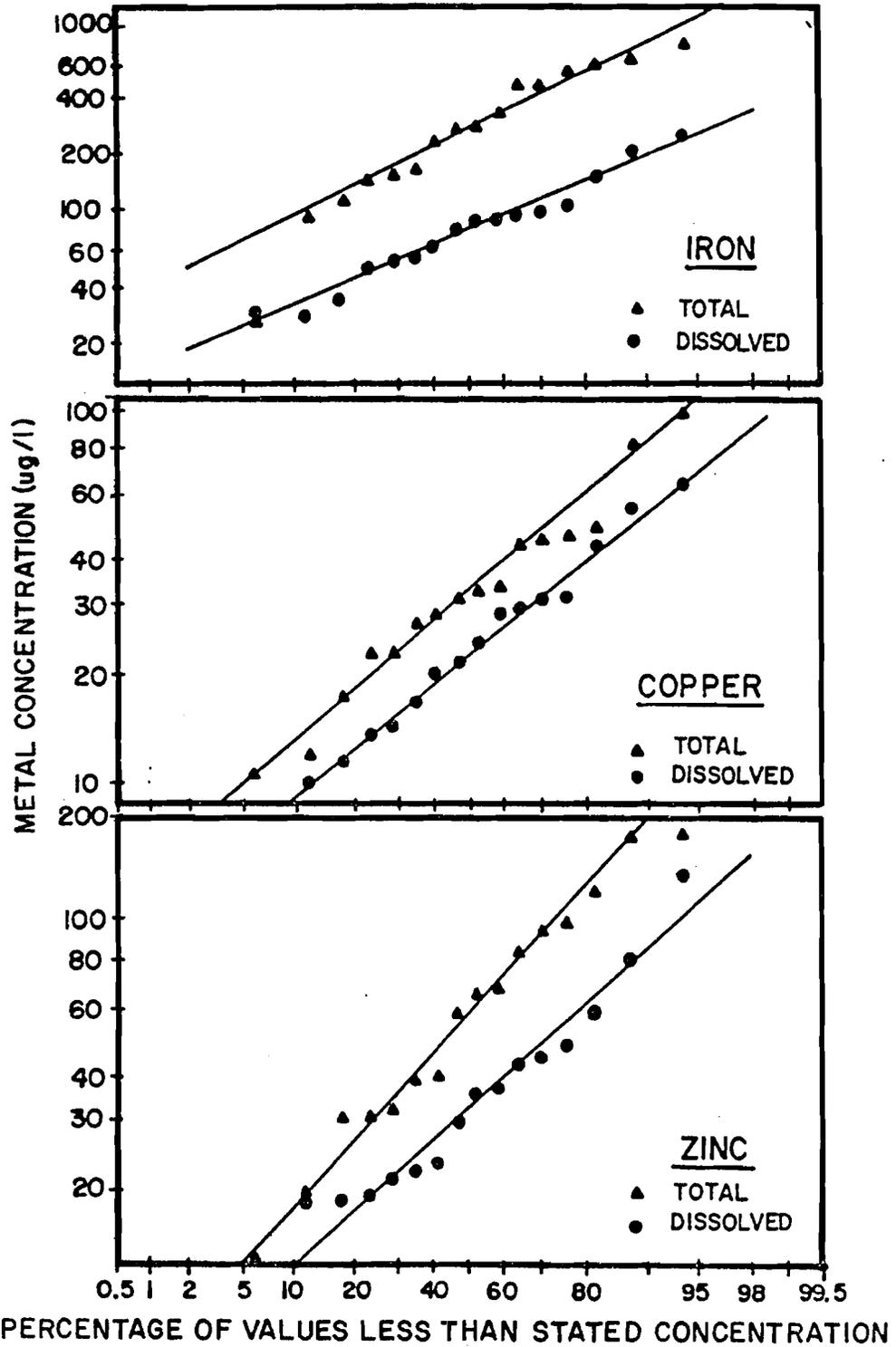


Figure 4-2. Distribution of Iron, Copper, and Zinc in Highway Runoff Entering the West Pond at Maitland During 1983-84.

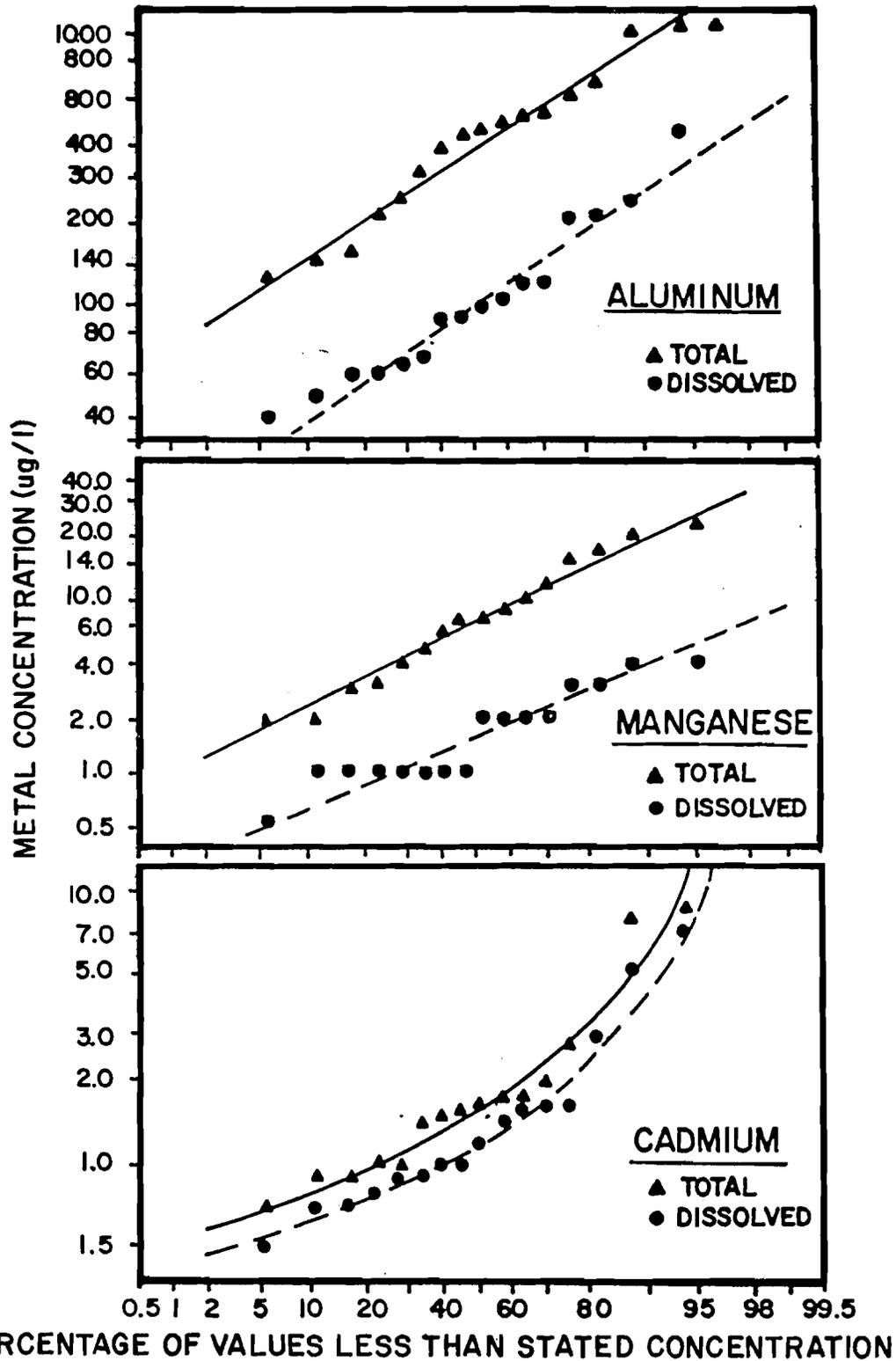


Figure 4-3. Distribution of Aluminum, Manganese, and Cadmium in Highway Runoff Entering the West Pond at Maitland During 1983-84.

to approximate a straight line relationship indicating a log-normal distribution of concentrations for the events measured. A linear fit to a log-normal distribution generally indicates a positively skewed data distribution when plotting the probability of occurrence on the y-axis versus metal concentration on the x-axis. This suggests that the majority of events are represented by concentrations which are on the lower end of the range of values, with the more concentrated events making up a much smaller percentage of the total measured concentrations. Dissolved concentrations also seem to approximate a log-normal distribution. However, cadmium appears to exhibit a convex curvilinear relationship. This behavior indicates that a higher order exponential function may be more appropriate for describing this distribution.

A series of correlation analyses were run with the SAS statistical package using the PROC CORR routine (Ray and Sall 1982) to determine if relationships exist between concentrations of heavy metals in highway runoff and various factors such as runoff pH, runoff flow rate (an indirect measure of rainfall intensity), cumulative time since start of a rainfall event, and antecedent dry period. For these analyses, all 150 data points for each heavy metal concentration were used and correlations with the various physical parameters (which were measured simultaneously with the sample collection) were determined. Since measured concentrations

of cadmium were near the limits of detection in most samples, this metal was not included in these analyses.

The first correlations which were attempted were correlations between selected heavy metal concentrations and measured runoff flowrates. Correlations were performed for the following combinations of heavy metal concentrations and runoff flowrates: (1) concentration versus runoff flowrate, (2) concentration versus the log of runoff flowrate, and (3) log of concentration versus log of runoff flowrate. These correlations are intended to detect those metals which can be mobilized by increasing flow rates and rainfall intensities. A summary of these correlations is given in Table 4-4.

Maximum values of the correlation coefficients were found for most metals with the combination of metal concentration and the log of flowrate. Iron was apparently the only exception to this generality. Maximum correlations were achieved for both dissolved and total iron when iron was correlated with the untransformed value of the runoff flowrate. The significant correlations (with the exception of iron) were negative, indicating that metal concentrations decrease with increasing rainfall intensity. It should be noted, however, that even though significant correlations were found, calculated values for R-square indicate that the regression of rainfall intensity against dissolved heavy metal concentrations was capable of explaining only approximately 20 percent or less of the variability in the measured dissolved heavy metal concentrations.

TABLE 4-4

CORRELATIONS BETWEEN SEQUENTIAL HYDROGRAPH CONCENTRATIONS OF
VARIOUS HEAVY METAL SPECIES AND RUNOFF FLOWRATE
(n = 142 samples)

HEAVY METAL SPECIES	CONC. VS. FLOWRATE		CONC. VS. LOG FLOWRATE		LOG CONC. VS. LOG FLOWRATE	
	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION
DISSOLVED:						
Lead	-0.302	99.9	-0.451	99.9	-0.563	99.9
Zinc	-0.166	95.2	-0.329	99.9	-0.234	99.5
Manganese	-0.174	96.1	-0.357	99.9	-0.391	99.9
Copper	-0.106	79.1	-0.218	99.1	-0.212	98.9
Aluminum	-0.313	99.9	-0.430	99.9	-0.450	99.0
Iron	0.202	98.4	0.071	59.9	-0.040	36.6
Nickel	-0.247	99.7	-0.367	99.9	-0.298	99.9
Chromium	-0.317	99.9	-0.412	99.9	-0.439	99.9
Cadmium	-0.246	99.7	-0.338	99.9	-0.274	99.9
TOTAL:						
Lead	-0.025	23.0	-0.193	97.9	0.002	2.3
Zinc	-0.060	52.3	-0.243	99.4	-0.089	71.1
Manganese	-0.132	88.4	-0.315	99.9	-0.176	96.4
Copper	-0.068	57.8	-0.175	94.2	-0.147	91.9
Aluminum	0.026	24.5	-0.122	85.2	-0.055	48.7
Iron	0.271	99.9	0.132	88.3	0.234	99.5
Nickel	-0.194	97.9	-0.324	99.9	-0.252	99.7
Chromium	-0.053	46.7	-0.149	92.2	-0.147	92.0
Cadmium	-0.258	99.8	-0.348	99.9	-0.300	99.7

Significant negative correlations between the log of runoff flow rate and total heavy metal concentrations were found at the 0.05 level for lead, zinc, manganese, nickel, and cadmium. These regressions against rainfall intensity produced calculated values of R-square which were equal to 0.10 or less and, therefore, were capable of explaining only approximately 10 percent or less of the variability in the measured total metal concentrations. In general, it appears that significant but weak correlations are present at the Maitland site for most total or dissolved species of heavy metals when correlated with the log of rainfall intensity.

It should be noted that several metal species exhibited a slightly higher correlation coefficient for the combination of log of metal concentration versus the log of the runoff flowrate. Dissolved concentrations of lead, manganese, aluminum, and chromium were all found to be correlated to a larger degree using a log-log relationship for runoff flowrate.

Correlations between runoff metal concentrations and cumulative time since the start of a runoff are listed for dissolved and total species in Table 4-5. These correlations were designed to examine the "first flush" phenomenon to determine if heavy metal concentrations decline with cumulative rainfall time. Correlations were tested between the following combinations of runoff concentrations and cumulative time: (1) metal concentrations and cumulative time, (2) metal concentrations and the log of cumulative time, (3) the log of metal concentration and cumulative time, and (4) the log of metal concentration and the log of cumulative time.

TABLE 4-5

CORRELATIONS BETWEEN RUNOFF METAL CONCENTRATIONS
AND CUMULATIVE RUNOFF TIME
(n = 150 samples)

HEAVY METAL SPECIES	CONC. & CUM. TIME		CONC. & LOG CUM. TIME		LOG CONC. & TIME		LOG CONC. & LOG TIME	
	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION
DISSOLVED SPECIES:								
Lead	0.227	99.5	0.306	99.9	0.420	99.9	0.522*	99.9
Zinc	0.166	9.58	0.228*	99.5	0.182	97.4	0.216	99.2
Manganese	0.142	91.6	0.142	91.8	0.271	99.9	0.168	96.0
Copper	0.053	48.4	0.150*	93.3	-0.024	22.6	0.108	81.4
Aluminum	0.277	99.9	0.365	99.9	0.336	99.0	0.437*	99.9
Iron	-0.030	28.4	-0.131*	88.9	0.091	73.3	0.022	20.8
Nickel	0.182	97.4	0.266	99.9	0.213	99.1	0.275*	99.9
Chromium	0.208	98.9	0.333	99.9	0.285	99.9	0.441*	99.9
Cadmium	0.261	99.9	0.304*	99.9	0.259	99.8	0.282	99.9
TOTAL SPECIES:								
Lead	0.187*	97.8	0.102	78.8	0.130	88.7	0.058	52.0
Zinc	0.122	86.4	0.097	76.5	0.160*	94.9	0.110	81.8
Manganese	0.181	91.4	0.218	99.2	0.259*	99.9	0.252	99.8
Copper	0.025	24.3	0.116*	84.2	-0.055	49.4	0.059	52.9
Aluminum	0.050	45.2	0.135	91.0	0.109	81.7	0.178*	97.0
Iron	-0.087	71.0	-0.190	98.0	-0.149	93.1	-0.272*	99.9
Nickel	0.165	95.6	9.229*	99.5	0.170	96.3	0.228	99.5
Chromium	0.050	45.7	0.135	90.1	0.109	81.4	0.201*	98.6
Cadmium	0.229	99.5	0.274	99.9	0.205	98.8	0.239	99.7

*Indicates highest value of correlation coefficient.

The strongest correlation for dissolved metal species was found for lead using the log-log transformations. This correlation was significant at the 0.001 level and, as indicated by the value of R-square, explained approximately 27 percent of the variability in the measured values for dissolved lead. This type of positive relationship suggests that lead concentrations peak very quickly after the initiation of the rain event. A significant correlation (0.005 level) was also found for dissolved zinc when the zinc concentration was regressed against the log of cumulative time. However, this regression was able to account for only 5 percent of the data variability. No significant correlations (at the 0.05 level) were found for either dissolved copper or iron. Significant correlations for both dissolved nickel and chromium (both at the 0.001 level) were found between the log of the metal concentration and the log of cumulative time. This relationship was able to explain approximately 8 percent of the variability in the dissolved nickel concentrations and 19 percent of the variability in the dissolved chromium concentrations. This type of correlation indicates that these metal concentrations peak quickly during a storm event and drop off rapidly.

Correlations between cumulative rainfall event time and total metal concentrations were, in general, less significant than correlations measured for dissolved species. Total lead concentrations were found to correlate most closely with a linear positive relationship between concentration and cumulative time.

However, the calculated value of R-square indicated that this relationship was only able to explain less than 4 percent of the variability in total lead concentrations. Similar correlations were observed for the remaining total metal concentrations for various combinations of concentration and cumulative time. However, these regressions were in general capable of explaining less than 5 percent of the variability in the measured total metal concentrations.

Correlations between measured values of runoff pH and heavy metal concentrations were also performed. A summary of these correlations is given in Table 4-6. Significant correlations between pH and the log of the dissolved metal concentration were observed at the 0.05 level for zinc, iron, and nickel, although these regressions were able to explain at most 10 percent of the data variability and in general less than 5 percent.

Therefore, in general it appears that while sequential hydrograph measured concentrations of both total and dissolved heavy metals in highway runoff at the Maitland site did produce significant correlations with certain combinations of rainfall intensity, pH, and antecedent dry period, the correlations were able to explain only a small fraction of the variability measured in the data set. In most cases this regression accounted for less than 10 percent of the total variability and these factors are not the major factors regulating concentrations of heavy metals measured at the Maitland site.

TABLE 4-6

CORRELATIONS BETWEEN pH AND SEQUENTIAL HYDROGRAPH CONCENTRATIONS
OF VARIOUS METAL SPECIES IN HIGHWAY RUNOFF
(n = 101 samples)

PARAMETER	CORR. BETWEEN pH AND METAL CONC.		CORR. BETWEEN pH AND LOG OF CONC.		CORR. BETWEEN H ⁺ AND METAL CONC.		CORR. BETWEEN H ⁺ AND LOG OF CONC.	
	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION	r	PROB. OF CORRELATION
Lead	0.148	85.9	0.174*	91.8	-0.077	55.6	-0.063	46.9
Zinc	0.262	99.2	0.342*	99.9	-0.131	80.6	-0.159	88.7
Copper	-0.021	16.7	-0.073*	53.4	-0.027	20.8	-0.013	10.7
Iron	0.323	99.9	0.369*	99.9	-0.176	92.2	-0.202	95.7
Nickel	-0.107	71.4	-0.251*	98.9	0.035	27.1	0.127	79.5
Chromium	-0.041	31.3	-0.128*	79.9	0.013	10.4	0.054	40.6

DISSOLVED SPECIES:

* Indicates highest value of correlation coefficient

Correlations were also examined using the composite flow-weighted runoff concentrations of dissolved and total metals calculated for each of the 16 storm events. Correlations were tested between total runoff volume and total rainfall for each event, mean rainfall intensity, rainfall duration, and antecedent dry period to test whether relationships exist between these parameters and measured heavy metal concentrations. When these correlations were performed, no significant correlations at the 0.05 level were found between any of the four parameters and any total or dissolved heavy metal concentrations. However, flow-weighted concentrations of both dissolved copper and total copper had a significant correlation with total runoff volume at the 0.06 level with a correlation coefficient of -0.487 for dissolved copper and -0.451 for total copper. These negative correlations suggest a general decline in copper concentrations with increasing runoff volume. Dissolved cadmium was positively correlated with total rainfall at the 0.06 level with a correlation of 0.479. This correlation suggests that cadmium concentrations increase when the total rainfall volume increases.

Heavy Metal Concentrations in the Maitland Pond Waters

Water samples were collected periodically from 6/82 to 2/83 to characterize average concentrations of heavy metals in the West Pond. A total of 40 depth composite water samples were collected at five fixed stations during this period, and heavy metal analyses

were conducted on 30 of these samples. Concentrations of heavy metals measured in these depth composite samples at each of the five sample stations on each sample collection date are listed in Appendix II.

A summary of heavy metal concentrations in the West Pond during the sampling period is presented in Table 4-7. Mean values of most heavy metals, with the exceptions of iron and aluminum, were near or below a level of 20 $\mu\text{g}/\text{l}$. Most metal species also varied within a relatively narrow range of concentrations during this period, with maximum concentrations for all species except total iron and total aluminum near or less than 100 $\mu\text{g}/\text{l}$. Nine of the 20 metal species (dissolved and total zinc, dissolved and total nickel, dissolved and total chromium, dissolved manganese, and dissolved and total cadmium) never exceeded 20 $\mu\text{g}/\text{l}$ as a maximum value. As seen in Table 4-6, the major fraction of all metal species (except iron, aluminum, and manganese) was in the dissolved state, with dissolved fractions of about 65 percent or greater. Zinc, copper, and cadmium exhibited dissolved fractions of approximately 80 percent or greater.

A summary of field measured values of pH, dissolved oxygen, and ORP at the time of sample collection are also listed in Table 4-7. The mean pH value of the retention pond water was slightly alkaline at a value of 7.46. The measured range of pH values covered approximately two pH units with values between 6.62 and 8.46. Measurements of dissolved oxygen indicated an aerobic water column

TABLE 4-7
SUMMARY OF HEAVY METAL CONCENTRATIONS IN THE MAITLAND WEST POND FROM 6/82 TO 2/83

PARAMETER	NUMBER OF SAMPLES	MEAN (µg/l)	STANDARD DEVIATION	MINIMUM VALUE (µg/l)	MAXIMUM VALUE (µg/l)	PERCENT DISSOLVED (%)	FRACTION OF MEAN RUNOFF CONCENTRATION
LEAD:							
Dissolved	30	15.0	8.5	<1	32.0		0.46
Total	30	22.2	11.0	3.0	60.0	67.6	0.12
ZINC:							
Dissolved	30	4.7	2.6	<1	12.0		0.12
Total	30	6.0	3.2	<1	17.0	78.3	0.08
COPPER:							
Dissolved	30	14.4	7.9	<1	38.0		0.50
Total	30	16.7	8.6	<1	38.0	86.2	0.43
NICKEL:							
Dissolved	30	1.6	1.2	<1	5.0		0.64
Total	30	2.2	1.6	<1	7.0	72.7	0.65
CHROMIUM:							
Dissolved	30	2.2	1.8	<1	8.0		0.88
Total	30	3.5	2.8	<1	13.0	62.9	0.83

TABLE 4-7 -- CONTINUED

PARAMETER	NUMBER OF SAMPLES	MEAN (µg/l)	STANDARD DEVIATION	MINIMUM VALUE (µg/l)	MAXIMUM VALUE (µg/l)	PERCENT DISSOLVED (%)	FRACTION OF MEAN RUNOFF CONCENTRATION
IRON:							
Dissolved	30	18.4	15.1	<1	79.0		0.24
Total	29	63.1	79.7	16.0	420	29.2	0.17
ALUMINUM:							
Dissolved	30	58.0	19.4	13.0	108		0.46
Total	29	156	164	48.0	888	37.1	0.28
MANGANESE:							
Dissolved	30	4.5	4.2	<1	16.0		1.67
Total	30	17.1	10.6	4.0	94.0	26.3	1.79
CADMIUM:							
Dissolved	30	0.73	0.34	<1	2.0		0.43
Total	30	0.82	0.40	<1	2.0	89.0	0.37
pH	40	7.46	0.43	6.62	8.46		
D.O. (mg/l)	25	5.6	1.8	2.8	9.1		
ORP (mv)	25	523	34	479	600		

on all sample collection dates. The mean value for dissolved oxygen was 5.6 mg/l with a range between 2.8 and 9.1. Measurements of ORP also indicated an oxidized environment with most measured values in excess of 500 mv(Eh).

A comparison of mean pond concentrations with mean runoff concentrations is listed in the last column of Table 4-7. As indicated by the relatively low fractions of heavy metals remaining, pond concentrations of most heavy metals, except manganese, are substantially lower than in the runoff water. Pond concentrations of total lead and total zinc were only approximately 10 percent of the mean concentrations in the incoming water. Total metal concentrations for all metals except manganese were reduced to a greater degree than the dissolved portions. The order for reduction of total runoff concentrations upon entering the West Pond is:

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

Dissolved concentrations of heavy metals in highway runoff were also reduced upon entering the retention pond, although not to the degree noted for particulate species. The order for reduction of dissolved runoff species upon entering the West Pond is:

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

Concentrations of both dissolved and total manganese increased in the retention pond water over concentrations measured in highway runoff.

A summary of mean heavy metal concentrations at each of the individual sample stations in the Maitland West Pond is given in Table 4-8. These concentrations were investigated to determine if changes in heavy metal concentrations could be detected during travel through the retention pond from the point of input to the discharge. The SAS PROC GLM procedure (Ray and Sall 1982) was used to conduct an analysis of variance for the heavy metal data by station for the sample period. Those parameters which produced a significant F-test at the 0.05 level were subjected to the multiple comparison technique of Tukey to detect where the differences occurred.

The analysis of variance procedure produced a significant F-test at the 0.05 level only for concentrations of dissolved and total zinc. Differences between pond stations for dissolved zinc were significant at the 0.015 level and total zinc was significant at the 0.031 level. The multiple comparison technique of Tukey found Station 1 near the stormwater inlet to be different from the other four stations. Thus, it appears that there is evidence to indicate that concentrations of total and dissolved zinc may be different at Station 1 than at the other four stations. As seen in Table 4-8, the mean value for zinc concentrations at Station 1 is approximately twice as high as the other measured stations.

TABLE 4-8

SUMMARY OF MEAN HEAVY METAL CONCENTRATIONS AT INDIVIDUAL SAMPLE STATIONS
 IN THE MAITLAND WEST POND FROM 6/82 TO 2/83
 (Percent dissolved fractions are listed in parentheses)

PARAMETER	MEAN VALUE ($\mu\text{g/l}$ EXCEPT WHERE NOTED)				
	STATION 1	STATION 2	STATION 3	STATION 4	STATION 5
LEAD:					
Dissolved	14.3	12.8	13.2	14.4	20.4
Total	23.5 (60.9)	26.0 (49.2)	16.5 (80.0)	23.0 (62.6)	21.8 (93.6)
ZINC:					
Dissolved	7.7	3.6	3.6	3.7	5.0
Total	9.5 (81.1)	4.6 (78.3)	4.5 (80.0)	5.8 (63.8)	5.3 (94.3)
COPPER:					
Dissolved	16.8	13.2	14.7	10.3	17.2
Total	18.7 (89.8)	14.7 (89.8)	17.5 (84.0)	13.4 (76.9)	19.2 (89.6)
NICKEL:					
Dissolved	2.2	1.3	1.4	1.3	1.9
Total	3.0 (73.3)	2.3 (56.5)	1.7 (82.4)	2.0 (65.0)	1.9 (100)
CHROMIUM:					
Dissolved	2.3	2.3	1.2	2.0	3.3
Total	3.8 (60.5)	4.1 (56.1)	2.6 (46.2)	3.4 (58.8)	3.4 (97.1)
IRON:					
Dissolved	28.8	15.8	12.6	18.8	16.0
Total	52.5 (54.9)	57.2 (27.6)	69.2 (18.2)	96.3 (19.5)	41.3 (38.7)

TABLE 4-8 -- CONTINUED

PARAMETER	MEAN VALUE ($\mu\text{g/l}$ EXCEPT WHERE NOTED)				
	STATION 1	STATION 2	STATION 3	STATION 4	STATION 5
ALUMINUM:					
Dissolved	54.7	57.5	57.2	62.2	58.3
Total	116 (47.0)	105 (54.9)	257 (22.3)	110 (56.8)	186 (31.4)
MANGANESE:					
Dissolved	7.5	2.6	4.0	4.4	3.8
Total	14.3 (52.4)	26.0 (10.0)	9.2 (43.5)	21.3 (20.7)	14.5 (26.2)
CADMIUM:					
Dissolved	0.58	0.75	0.75	0.67	0.92
Total	0.67 (86.6)	0.75 (100.0)	0.92 (81.5)	0.83 (80.7)	0.92 (100.0)
pH	7.34	7.80	7.33	7.36	7.46
D.O. (mg/l)	5.1	7.6	4.9	5.2	5.0
ORP (mv)	522	545	512	515	523

Accumulation of Heavy Metals in the Sediments
of the Maitland West Pond

The horizontal and vertical distributions of heavy metals in the sediments of the Maitland West Pond were characterized by collection and analysis of multiple core samples. Core samples were collected in the West Pond on 10/15/82, 10/15/83, and 4/15/84. On each date a total of 46 separate core samples were collected at specified intervals along 11 fixed transects. On the first sample date (10/15/82), the 46 core samples were analyzed individually by sectioning each sample into the following layers: 0-1 cm, 1-3.5 cm, 3.5-6 cm, 6-8.5 cm, and 8.5-13 cm. The heavy metal concentrations in the 0-1 cm layer were used to characterize horizontal metal distributions, while average concentrations in each of the separate layers were used to investigate vertical migration. On the last two sample collection dates (10/15/83 and 4/15/84), the 46 separate samples were combined together by layer so that average concentrations at each layer were obtained for vertical migration studies. Raw measured values of sediment heavy metal concentrations for each of the three sample dates are listed in Appendix III. The results of the horizontal distributions and vertical migrations are discussed separately in the following sections.

Horizontal Distributions of Heavy Metals

An analysis of the horizontal distributions of heavy metals in the sediments of the West Pond is useful in characterizing the settling patterns of various heavy metals upon entering the

retention pond water. As seen in the data given in Appendix III, concentrations of heavy metals in the 0-1 cm layer appear to be highest for most metals near the influent points for stormwater runoff, with rapid decreases in concentrations as the distance from the input increases. The greatest surface concentrations for most metals were measured near the 45 cm inlet on the west end of the pond which is assumed to be the major input into the system. However, elevated concentrations were also found near other input points such as the small concrete channel in the northeast corner which receives direct runoff from a small portion of I-4, along the northern shore where several stormsewer lines drain small portions of the adjacent bridge area (Maitland Boulevard), and along the southern shore where periodic flow from the swale area enters through a 90 cm RCP line. In general, elevated concentrations of Pb, Ni, Cr, and Al near inlet pipes were approximately twice as high as the average pond concentration, while sediment concentrations of Cd, Cu, and Fe were approximately 1.5 times as great as mean values. Concentrations of Zn near inlet pipes were approximately three times the average sediment Zn concentrations.

A summary of average sediment metal concentrations in the 0-1 cm layer along transects at various distances from the 45 cm RCP inlet is given in Table 4-9. These values represent the mean concentrations for each metal measured in each of the first six transects. Transects 7, 8, and 9 were not included since these transects are influenced by inputs from the swale area as well as the channel in the northeast corner.

TABLE 4-9

AVERAGE SEDIMENT METAL CONCENTRATIONS IN THE 0-1 CM LAYER
ALONG THE FLOW PATH OF THE 45 CM RCP INLET TO THE MAITLAND POND
(samples collected on 10/15/82)

HEAVY METAL	AVERAGE SEDIMENT METAL CONCENTRATION ($\mu\text{g/g}$ DRY WEIGHT)							AVERAGE POND CONC. IN TOP 1 CM
	7.5 m	15 m	30 m	60 m	90 m	120 m		
Cd	0.95	0.60	0.58	0.70	0.28	0.45	0.65	
Zn	84	176	84	93	45	19	59	
Cu	5	20	14	24	14	7	15	
Al	8,363	41,796	85,802	58,701	20,258	21,494	51,059	
Fe	887	4,012	6,908	5,159	2,513	1,405	4,735	
Pb	75	226	134	141	59	40	119	
Ni	3	14	29	15	7	5	16	
Cr	9	36	74	55	23	19	47	
Mn	7	35	31	51	39	--	--	
ORGANIC CONTENT (%)	5.3	18.4	19.3	13.7	7.8	5.0	13.30	

The distributions of selected heavy metals as a function of distance from the 45 cm RCP inlet are indicated in Figure 4-4. Concentrations of Pb and Zn appear to peak quickly after a distance of 15 m from the inlet with a rapid decline in sediment concentration with increasing distance. Concentrations of Cr and Ni appear to reach a peak less quickly with maximum values measured at a distance of approximately 30 m from the inlet. The decline in concentration with increasing distance for these two metals is much less pronounced than that observed for Pb and Zn. Concentrations of Cu appear to be relatively evenly distributed with only a small peak observed between 15 and 60 m.

The distributions of Fe and Al as a function of distance from the outfall are shown in Figure 4-5. Both Fe and Al appear to peak at a distance of 30 m from the inlet with gradual declines observed with increasing distance.

Vertical Distribution of Heavy Metals

The vertical distribution of heavy metals in the sediments of the Maitland West Pond was characterized by analysis of average sediment metal concentrations on each of the three sample dates. A summary of the mean concentrations at each sample depth on each sample date is presented in Table 4-10. Aluminum was the most abundant metal present in the Maitland Pond sediments at all depths, with average aluminum concentrations several orders of magnitude larger than most of the other metals. The second most abundant metal present was iron with average concentrations at all depths

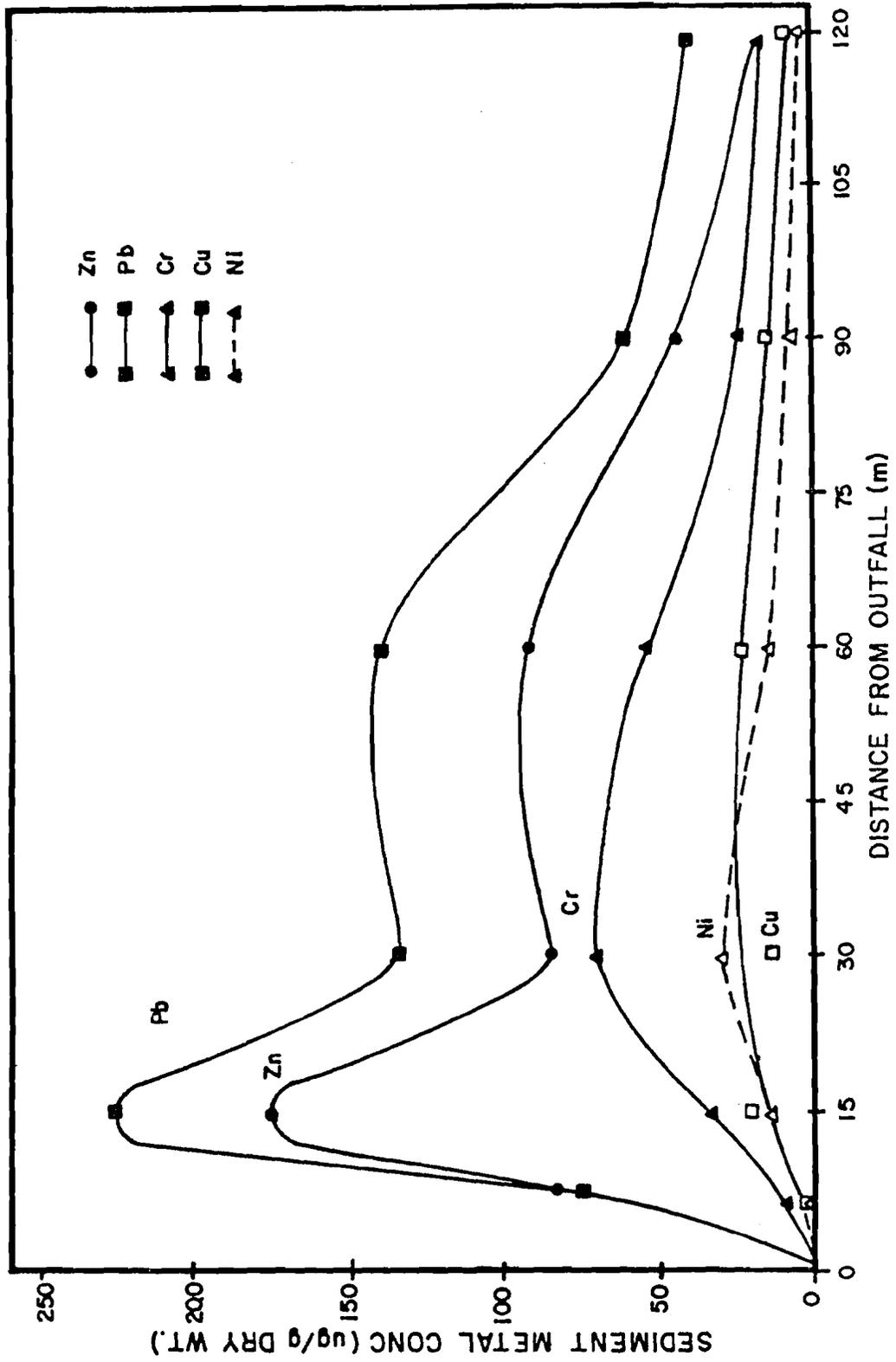


Figure 4-4. Sediment Concentrations of Selected Heavy Metals in the Top 1 cm of the Maitland West Pond as a Function of Distance from the Outfall.

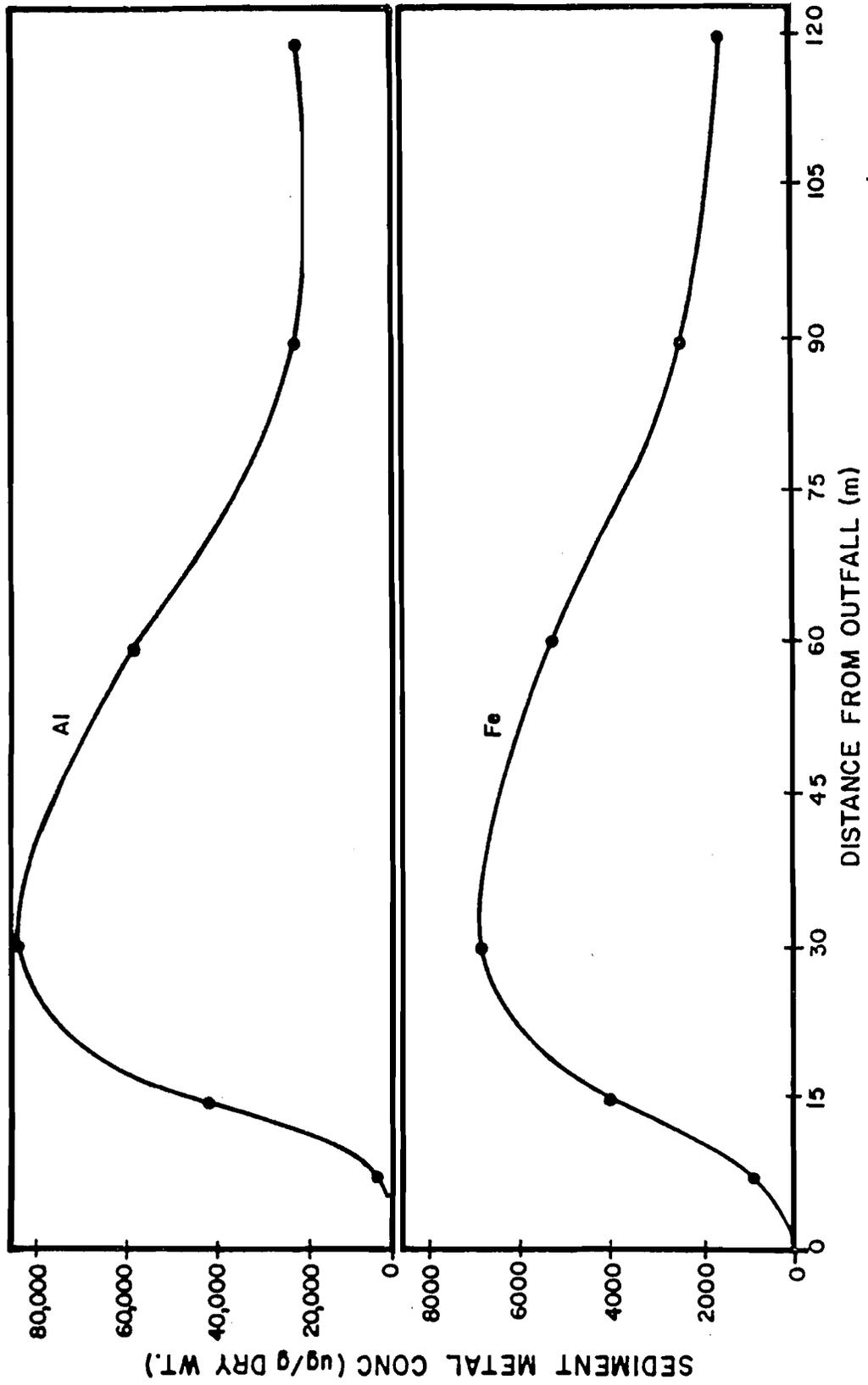


Figure 4-5. Sediment Concentrations of Iron and Aluminum in the Top 1 cm of the Maitland West Pond as a Function of Distance from the Outfall.

TABLE 4-10
 SUMMARY OF MEAN HEAVY METAL CONCENTRATIONS IN SEDIMENT CORE SAMPLES
 COLLECTED IN THE MAITLAND WEST POND FROM 1982-1984

SAMPLE DEPTH (cm)	DATE COLLECTED	SEDIMENT METAL CONCENTRATION ($\mu\text{g/g}$ DRY WT)										MOISTURE CONTENT (%)	ORGANIC CONTENT (%)
		Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	Mn			
0-1.0	10/15/82	0.65	58.6	15.0	51,059	4735	118.6	16.1	47.2	--	65.3	13.3	
	10/15/83	3.34	32.8	24.9	44,413	3917	105.2	15.7	38.2	38.3	61.4	8.4	
	4/15/84	2.61	44.8	17.3	53,807	5010	114.4	17.6	48.6	49.5	72.6	12.0	
	AVERAGE	2.20	45.4	19.1	49,760	4554	112.7	16.5	44.7	43.9	66.4	11.2	
1.0-3.5	10/15/82	0.44	11.3	6.72	25,304	1813	36.7	5.86	20.8	--	34.4	4.9	
	10/15/83	1.41	9.61	15.1	23,919	1785	44.7	7.13	18.9	12.3	37.1	3.6	
	4/15/84	0.81	11.1	6.51	24,499	1685	31.4	6.47	18.2	12.5	36.5	3.7	
	AVERAGE	0.89	10.7	9.44	24,574	1761	37.6	6.49	19.3	12.4	36.0	4.1	
3.5-6.0	10/15/82	0.40	8.73	4.12	16,272	1408	30.3	4.39	16.0	--	25.8	2.7	
	10/15/83	0.93	4.60	14.4	21,201	1376	25.9	4.83	17.6	7.84	30.4	2.4	
	4/15/84	0.36	6.14	3.97	17,294	1125	17.3	3.22	12.5	5.88	25.7	2.2	
	AVERAGE	0.56	6.49	7.50	18,256	1303	24.5	4.15	15.4	6.86	27.3	2.4	
6.0-8.5	10/15/82	0.37	6.88	3.30	16,251	1067	22.8	3.64	13.1	--	24.1	2.6	
	10/15/83	0.53	2.67	9.03	17,701	658	15.8	4.65	6.17	6.58	29.2	2.6	
	4/15/84	0.44	4.38	2.87	17,663	898	12.5	3.80	13.1	4.52	23.9	1.9	
	AVERAGE	0.45	4.64	5.07	17,205	874	17.0	4.03	10.8	5.55	25.7	2.4	
8.5-13.0	10/15/82	--	--	--	--	--	--	--	--	--	--	--	
	10/15/83	0.47	1.39	5.22	15,487	609	16.7	3.65	4.34	6.12	26.7	2.3	
	4/15/84	0.85	4.92	3.09	9,482	355	10.2	2.97	3.67	3.80	25.3	1.9	
	AVERAGE	0.66	3.16	4.16	12,485	482	13.5	3.31	4.01	4.96	26.0	2.1	

measured approximately one order of magnitude larger than other metals. Lead was the third most abundant heavy metal present, followed by zinc and chromium, copper and nickel, and finally cadmium. Concentrations of cadmium were generally very small with many measured values, especially in the lower sediment depths, approaching the limits of detection.

In general, concentrations of all heavy metals were highest in the surface layer with a rapid decrease in concentration with increasing depth. The same general trend was also observed for moisture content and organic content as well. Sediment concentrations of zinc, iron, lead and chromium appear to be attenuated at the most rapid rate while cadmium, copper, aluminum, and nickel seem to be attenuated less quickly. The attenuation of heavy metal concentrations in the sediments is shown in Figure 4-6.

The attenuation of heavy metals through the retention pond sediments was modeled using the PROC GLM package of SAS (Ray and Sall 1982) with a variety of models such as metal concentration versus depth, log of metal concentration versus depth, metal concentration versus log of depth, log of metal concentration versus log of depth, as well as various other combinations of inverse functions of the metal concentration and depth. Of the relationships tested, the best values of R-square and MSE (mean square error) were obtained for both individual sample dates as well as for the combined data using semi-log and log-log relationships. A summary of the regression statistics for the semi-log model is listed in Table 4-11.

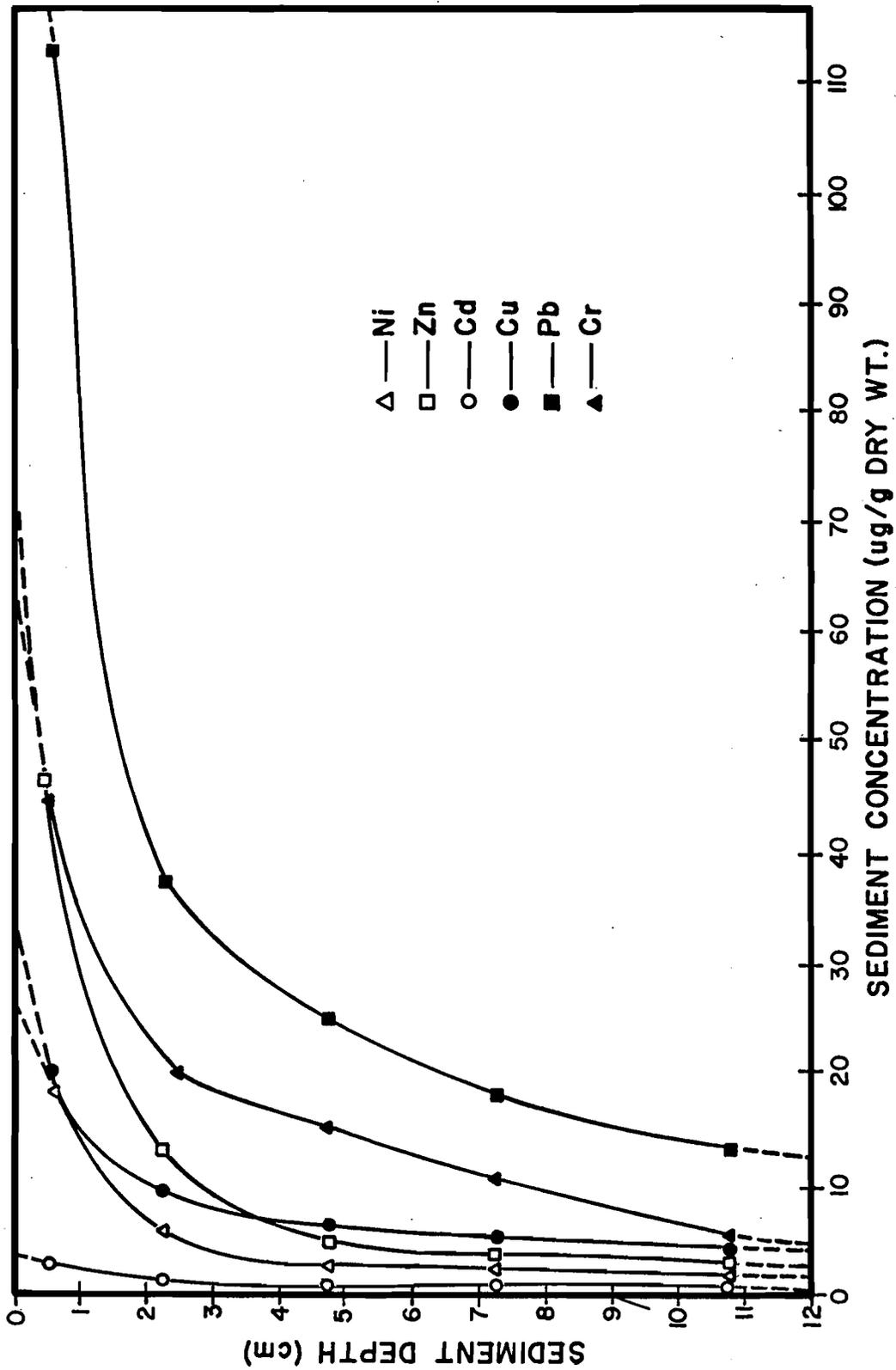


Figure 4-6. Attenuation of Heavy Metals in the Bottom Sediments of the Maitland Pond for Samples Collected 10/15/82.

TABLE 4-11
 SUMMARY OF REGRESSION STATISTICS FOR HEAVY METAL ATTENUATION
 IN THE TOP 13 cm OF THE MAITLAND POND FOR
 THE MODEL: $\ln(C/Co) = K \times (\text{Depth})$

HEAVY METAL	10/15/82		10/15/83		4/15/84		COMBINED DATA	
	SLOPE (K)	R ²	SLOPE (K)	R ²	SLOPE (K)	R ²	SLOPE (K)	R ²
Cd	-0.098	0.912	-0.237	0.953	-0.207	0.710	-0.201	0.787
Zn	-0.381	0.888	-0.360	0.969	-0.297	0.885	-0.338	0.913
Cu	-0.257	0.954	-0.156	0.983	-0.228	0.903	-0.203	0.900
Al	-0.207	0.920	-0.128	0.919	-0.189	0.942	-0.167	0.895
Fe	-0.253	0.928	-0.223	0.959	-0.282	0.964	-0.253	0.945
Pb	-0.285	0.907	-0.236	0.932	-0.302	0.921	-0.272	0.910
Ni	-0.260	0.915	-0.178	0.914	-0.227	0.884	-0.212	0.881
Cr	-0.220	0.928	-0.235	0.978	-0.257	0.952	-0.242	0.955
Mn	--	--	-0.238	0.892	-0.325	0.914	-0.282	0.885
Organic Content	-0.295	0.922	-0.161	0.870	-0.245	0.880	-0.219	0.843

following five fractions: soluble, exchangeable, bound to carbonates, bound to iron and manganese oxides, and bound to organic matter. It is generally believed that the stability of metal-soil associations increases in the following order: soluble < exchangeable < bound to carbonates < bound to iron and manganese oxides < bound to organic matter. A summary of the extraction results is presented in Table 4-12.

As seen in Table 4-12, only a small portion of the total metals present were extracted with the soluble fraction. This fraction indicates metal ions which are trapped in interstitial pore spaces and not bound to the sediments. Zinc appeared to be present in this soluble form to the largest degree of all metals measured, although the measured values were relatively small when compared to the total metal concentrations present. Most of the heavy metals measured (with the exceptions of cadmium, iron and manganese) exhibited large increases in soluble concentrations in the 8.5-13 cm layer.

When the sediment suspension was tested for adsorbed or ion exchangeable metal species, many of the heavy metals measured (such as zinc, copper, nickel, and chromium) exhibited exchangeable values similar to those measured for the soluble or interstitial fraction. However, significantly higher concentrations of cadmium, aluminum, iron, and lead were measured in the exchangeable fractions than in the soluble fraction. While most of these increases measured were on the order of 2 to 10 times greater than was measured for the soluble portion, iron and lead were present in an exchangeable form

TABLE 4-12

SPECIATION OF HEAVY METALS IN THE TOP 13 cm OF THE WEST RETENTION POND AT MAITLAND INTERCHANGE
(all numbers represent an average of 3 separate analyses on sediment samples collected 10/15/83)

SEDIMENT CORE DEPTH (cm)	MOISTURE CONTENT (%)	ORGANIC CONTENT (%)	HEAVY METALS ($\mu\text{g/g}$ DRY SEDIMENT)									
			Mn	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	
SOLUBLE												
0-1.0	61.4	8.4	0.09	0.03	0.40	<0.01	<1	<1	0.11	<0.01	<0.01	<0.01
1.0-3.5	37.1	3.6	0.36	0.25	0.06	<0.01	<1	<1	0.54	<0.01	<0.01	0.12
3.5-6.0	30.4	2.4	0.07	0.04	0.03	<0.01	<1	<1	0.62	0.04	0.04	0.08
6.0-8.5	29.2	2.6	<0.01	0.01	<0.01	0.10	<1	<1	0.60	0.07	0.07	0.14
8.5-13	26.8	2.3	<0.01	<0.01	0.35	0.13	18	<1	0.90	0.30	0.30	0.33
EXCHANGEABLE												
0-1.0	61.4	8.4	4.01	0.30	0.06	<0.01	2	50	19.2	0.08	0.08	0.33
1.0-3.5	37.1	3.6	0.32	0.27	0.09	<0.01	10	59	16.1	0.08	0.08	0.56
3.5-6.0	30.4	2.4	0.31	0.16	0.05	<0.01	1	44	17.3	0.04	0.04	0.10
6.0-8.5	29.2	2.6	0.28	0.16	<0.01	<0.01	<1	41	15.2	0.05	0.05	0.21
8.5-13	26.8	2.3	0.34	0.32	0.04	0.74	48	6	24.0	0.57	0.57	0.50
CARBONATE BOUND												
0-1.0	61.4	8.4	0.32	0.11	0.02	<0.01	24	1	0.43	<0.01	<0.01	0.08
1.0-3.5	37.1	3.6	0.21	0.13	0.23	<0.01	13	<1	0.28	<0.01	<0.01	0.13
3.5-6.0	30.4	2.4	0.13	<0.01	0.03	<0.01	13	2	<0.01	<0.01	<0.01	<0.01
6.0-8.5	29.2	2.6	0.11	<0.01	0.15	<0.01	12	1	<0.01	<0.01	<0.01	<0.01
8.5-13	26.8	2.3	0.03	<0.01	0.61	<0.01	5	<1	0.60	<0.01	<0.01	<0.01

TABLE 4-12 -- CONTINUED

SEDIMENT CORE DEPTH (cm)	MOISTURE CONTENT (%)	ORGANIC CONTENT (%)	HEAVY METALS (µg/g DRY SEDIMENT)								
			Mn	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr
Fe/Mn BOUND											
0-1.0	61.4	8.4	25.1	0.11	16.7	8.03	5209	584	42.4	4.41	6.68
1.0-3.5	37.1	3.6	10.6	0.05	2.23	3.41	3970	436	32.0	1.28	4.45
3.5-6.0	30.4	2.4	6.70	0.03	0.27	8.42	4675	534	15.7	1.48	4.75
6.0-8.5	29.2	2.6	5.23	0.03	0.29	4.16	4256	475	14.5	0.93	4.20
> 8.5	26.8	2.3	3.61	0.01	0.07	1.96	5220	109	3.0	0.73	3.25
ORGANIC BOUND											
0-1.0	61.4	8.4	1.13	<0.01	0.65	0.93	3473	783	0.42	0.46	0.28
1.0-3.5	37.1	3.6	0.43	0.02	1.01	0.21	1364	462	0.20	0.01	<0.01
3.5-6.0	30.4	2.4	0.16	0.05	0.17	0.62	1057	272	0.66	0.05	1.77
6.0-8.5	29.2	2.6	0.19	0.10	0.35	<0.01	1207	238	1.16	0.08	2.14
> 8.5	26.8	2.3	0.06	0.08	0.19	0.31	939	44	0.89	0.09	1.93

approximately 50 times greater than they were in a soluble form. For those metals which exhibited elevated concentrations as an exchangeable fraction, the measured concentrations appeared to be highest near the sediment surface and decreased with increasing sediment depth. However, the decrease with depth of the exchange fraction was not as rapid as the decrease in metal concentrations discussed previously for the soluble fraction. The rather large increase in concentrations which was noted in the bottom layer of the soluble portion was present in the exchange fractions as well.

Metal species bound to carbonates are also indicated in Table 4-12. This test separates those metal ions which are associated with sediment carbonates as a precipitate or co-precipitate. In general, concentrations of most heavy metals bound to carbonates were similar to concentrations measured as a soluble form, and were less than concentrations in the exchange fraction. This decline in concentrations is particularly evident for cadmium, iron, and lead which exhibited large increases in the exchange fraction. The only heavy metal which produced any increased concentrations in the carbonate fraction was aluminum which increased several fold over concentrations measured in the exchange fraction. The substantial increase in concentrations which was very apparent in the bottom layers of the soluble and exchange fractions was less pronounced for the carbonate extractions.

Heavy metal associations with iron and manganese oxides were, for most heavy metals tested, substantially larger than any other

association. The only exception to this generality was for cadmium which exhibited its major association with the exchangeable fraction. Concentrations of other heavy metals bound to iron and manganese oxides were several orders of magnitude larger than any previous association. The same general trend was observed where the largest concentrations of Fe/Mn bound metals were measured at the surface with slight decreases with increasing depth.

The final association, bound to organic matter, resulted in larger concentrations for most metals than were measured for the soluble, exchangeable, or carbonate fractions, but were generally less than those measured for iron and manganese oxides. The only exception to this generalization was for iron which had concentrations in the organic fraction similar to the fraction associated with iron and manganese oxides.

Fractional distributions of the total extracted heavy metals for each of the five extracted species are presented in Table 4-13. Most of the metal species tested, with the exceptions of lead, iron, and cadmium, appear to be predominantly associated with only one major fraction. For most metals, the dominant fraction is the one which is bound to Fe/Mn oxides. However, cadmium is predominantly associated with the exchangeable fraction. Lead also has a major association with this fraction. Aluminum and iron appear to have significant fractions with organic particles. Very few of the heavy metals present in the sediments appear to be present in a dissolved or carbonate form although cadmium, zinc and nickel had dissolved

TABLE 4-13
 SPECIATION OF TOTAL HEAVY METAL CONCENTRATIONS IN THE SEDIMENTS
 OF THE MAITLAND WEST POND AS A FRACTION OF THE TOTAL METAL PRESENT

HEAVY METAL	PERCENT OF TOTAL EXTRACTED METAL CONCENTRATION					TOTAL
	SOLUBLE	EXCHANGABLE	CARBONATE	BOUND TO Fe/Mn OX.	BOUND TO ORGANICS	
Cadmium	15	52	12	10	11	100
Zinc	4	1	4	81	10	100
Copper	1	3	1	89	7	100
Aluminum	<1	<1	<1	74	26	100
Iron	<1	5	<1	52	43	100
Lead	1	44	1	52	2	100
Nickel	4	8	<1	82	6	100
Chromium	2	5	1	73	19	100
Manganese	1	9	1	86	3	100

fractions of approximately 10 percent. Cadmium was also present as a carbonate with a total fraction of 12 percent.

A comparison of total acid-extractable sediment metal concentrations for core samples collected on 10/15/83, as determined through the nitric acid digestion procedure and the sum of the extracted metal concentrations obtained during the sequential extraction procedure, is presented in Table 4-14. The total sediment metal concentrations, as determined by the rigorous nitric acid digestion technique, provide a good estimation of the total metal content of the sediments, with the possible exception of metals bound into sand or silica particles. A more rigorous and dangerous hydrofluoric acid digestion procedure would be necessary to dissolve these particles. Assuming that the extraction procedures were substantially complete, the differences between the two techniques can be attributed largely to metal ions present in a bound crystalline form.

As seen in Table 4-14, the percent recovery of most metal species present in the top layer (with the exceptions of zinc, lead, and manganese) is less than 50 percent. Therefore, a large fraction of the metal species appears to be bound in a crystalline form and was not extracted even by the somewhat rigorous techniques involved during the organic oxidation steps. There also appears to be a general trend for the extracted percentage to increase as the sediment depth increases and organic fraction decreases. Manganese and cadmium seem to exhibit the largest extractable fractions, while

TABLE 4-14

COMPARISON OF TOTAL SEDIMENT METAL CONCENTRATIONS AND TOTAL EXTRACTED
SEDIMENT CONCENTRATIONS DURING THE SPECIATION PROCESS

SAMPLE DEPTH (cm)	METAL CONCENTRATION	METAL CONCENTRATION ($\mu\text{g/g}$ DRY SEDIMENT)									
		Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	Mn	
0-1.0	Total Concentration	3.34	32.8	24.9	44,413	3917	105.2	15.7	38.2	38.3	
	Extracted	0.56	17.8	8.99	8,709	1419	62.6	4.97	7.38	30.7	
	% Extracted	16.8	54.3	36.1	19.6	36.2	59.5	31.7	19.3	80.2	
1.0-3.5	Total Concentration	1.41	9.61	15.1	23,919	1785	44.7	7.13	18.9	12.3	
	Extracted	0.72	3.62	3.65	5,358	959	49.1	1.39	5.27	11.9	
	% Extracted	51.1	37.7	24.2	22.4	53.7	109.8	19.5	27.9	96.7	
3.5-6.0	Total Concentration	0.93	4.60	14.4	21,201	1376	25.9	4.83	17.6	7.84	
	Extracted	0.29	0.55	9.07	5,747	853	34.3	1.62	6.71	7.37	
	% Extracted	31.2	12.0	63.0	27.1	62.0	132.4	33.5	38.1	94.0	
6.0-8.5	Total Concentration	0.53	2.67	9.03	17,701	658	15.8	4.65	6.17	6.58	
	Extracted	0.31	0.80	4.29	5,477	756	31.5	1.14	6.70	5.52	
	% Extracted	58.5	30.0	47.5	30.9	114.9	199.4	24.5	108.6	88.4	
8.5-13.0	Total Concentration	0.47	1.39	5.22	15,487	609	16.7	3.65	4.34	6.12	
	Extracted	0.43	1.26	3.15	6,230	161	29.4	1.70	6.02	4.05	
	% Extracted	91.5	90.6	60.3	40.2	26.4	176.0	46.6	137.8	66.2	

aluminum and nickel appear to have the smallest. Extracted concentrations of lead, iron, and in some cases, chromium were greater in certain samples than the total nitric acid extracted sediment concentration.

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

A summary of heavy metal concentrations released from the sediment suspension under various redox potentials at an average suspension pH of 5.0 is presented in Table 4-15. Unlike the other two experiments, the minimum redox potential could not be achieved at this somewhat acidic pH of 5.0. After approximately 20 days of continuous purging, the redox potential could not be reduced below -90 mv. As a result, this value was selected as the minimum and a sample was collected at that point. Under the other two pH values (6.5 and 7.5-8.5), the minimum redox potential of -150 mv was achieved after approximately 5-7 days of continuous purging with nitrogen gas.

Adjustment of pH during the three experiments was achieved by manual additions of ultra-pure HCl in drop form. Measurements of pH were recorded continuously on a strip chart recorder so that the rate of change could be monitored. Fluctuations in pH for all experiments occurred generally very slowly. Adjustments were made whenever the monitored pH values deviated by more than 0.1 unit from the desired value. In general, adjustments were required more

TABLE 4-15
 RELEASE OF HEAVY METALS FROM THE MAITLAND POND SEDIMENTS UNDER
 VARIOUS REDOX POTENTIALS AT A CONTROLLED pH OF 5.0

REDOX POTENTIAL (mv)	HEAVY METALS RELEASED ($\mu\text{g/g}$ DRY SEDIMENT)									
	Cd	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr	
-90	0.57 (21.7)	1.87 (3.7)	42.33 (82.0)	0.37 (1.5)	17.70 (<0.01)	88.54 (1.3)	8.78 (6.0)	0.69 (4.0)	0.82 (1.6)	
0	0.62 (23.6)	1.12 (2.2)	48.09 (93.2)	0.58 (2.3)	18.41 (<0.01)	93.15 (1.3)	9.61 (6.6)	0.73 (4.2)	0.84 (1.6)	
250	0.69 (26.2)	1.06 (2.1)	48.33 (93.7)	0.35 (1.4)	19.86 (<0.01)	3.48 (<0.01)	10.46 (7.2)	0.81 (4.7)	0.87 (1.6)	
500	0.91 (34.6)	0.85 (1.7)	58.61 (113.6)	0.19 (0.8)	21.65 (<0.01)	2.75 (<0.01)	11.46 (7.8)	1.06 (6.1)	0.83 (1.6)	
Total Conc. in Pond Water Used ($\mu\text{g/l}$)	2	1	3	3	155	1	19	4	2	
Total Sediment Concentration ($\mu\text{g/g}$ dry wt)	2.63	51.1	51.6	24.7	72,179	7,077	146	17.4	52.9	

Released metal concentrations as a percentage of the total sediment metal concentrations are in parentheses.

frequently during the initial days of an incubation and decreased in frequency as the incubation time increased. However, adjustments were necessary throughout the entire incubation period, even though the frequency may have decreased to once every few days. The general tendency was for the sediments to increase in pH value with time toward their initial value. The incubation at a pH of 5.0 required an addition of approximately 20 ml of HCl over the entire period, while the incubation at a pH of 6.5 required an addition of only about 8 ml.

As seen in Table 4-15, heavy metal release followed basically three major patterns: metals which were released at a greater rate during conditions of low redox potential, metals which were released at a greater rate during conditions of high redox potential, and metals which were released in a fashion which appeared to be independent of redox potential. At a pH of 5.0, cadmium, manganese, aluminum, lead, and nickel all appeared to exhibit their lowest release potential under conditions of low redox potential and highest release potential under highly oxidized conditions. Zinc and iron seemed to be more soluble under conditions of low redox potential with decreasing solubility under oxidized conditions. Copper and chromium appeared to be relatively unaffected by changes in redox potential at the test pH value of 5.0. Although most of the metals tested exhibited a range of release values of approximately 2 between the maximum release and minimum release, the release of iron covered a range of approximately 50. The maximum

release of iron, approximately 90 $\mu\text{g/g}$, occurred at reduced potentials of -90 and 0 mv. Upon entering the oxidized region, the release of iron dropped to about 2-3 $\mu\text{g/g}$ sediment.

Although the largest physical release rates at a pH of 5.0 were obtained with manganese, aluminum, iron, and lead, the quantity released (with the exception of manganese) was only a small fraction of the total sediment metal concentration present. Values for the fraction of total metal released at each redox potential are listed in parentheses in Table 4-15. With the exceptions of manganese and cadmium, the fraction of total metals released was less than 5-7 percent for most metals, with many in the 1-2 percent range. However, manganese was released virtually completely at each redox potential. Cadmium was released in amounts ranging between 0 and 35 percent of the total metal present, depending upon the redox potential.

The release of heavy metals from Maitland sediments under various redox potentials at an average pH of 6.5 is presented in Table 4-16. The total release of most metals was similar to or less than the release measured at a pH of 5.0, although many of the trends for increasing or decreasing concentrations with changes in redox potential were not present at this pH. The release of cadmium at a pH of 6.5 was still observed to increase with increasing redox potential, although the magnitude of the increase was substantially reduced from the increase measured at a pH of 5.0. The release of zinc was again shown to decrease with increasing redox potential but the rate of decrease was much less.

TABLE 4-16

RELEASE OF HEAVY METALS FROM THE MAITLAND POND SEDIMENTS UNDER
VARIOUS REDOX POTENTIALS AT A CONTROLLED pH OF 6.5

REDOX POTENTIAL (mv)	HEAVY METALS RELEASED ($\mu\text{g/g}$ DRY SEDIMENT)									
	Cd	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr	
-150	0.47 (14.3)	1.23 (2.1)	30.43 (49.9)	0.38 (1.4)	10.23 (<0.1)	10.00 (0.1)	5.32 (3.0)	0.49 (2.4)	0.77 (1.5)	
0	0.53 (16.5)	1.50 (2.6)	40.05 (65.7)	0.15 (0.6)	12.18 (<0.1)	8.74 (0.1)	6.10 (3.5)	0.95 (4.6)	0.90 (1.8)	
250	0.54 (16.5)	1.23 (2.1)	31.07 (50.9)	0.34 (1.3)	15.31 (<0.1)	2.24 (<0.1)	6.02 (3.4)	0.56 (2.7)	0.83 (1.6)	
500	0.61 (18.6)	0.92 (1.6)	29.36 (48.1)	0.08 (0.3)	10.98 (<0.1)	1.90 (<0.1)	5.99 (3.4)	0.59 (2.8)	0.80 (1.6)	
Total Conc. in Pond Water Used ($\mu\text{g/l}$)	4	8	2	4	384	44	15	3	2	
Total Sediment Concentration ($\mu\text{g/g}$ dry wt)	3.28	57.9	61.0	26.3	82840	8364	175	20.8	51.2	

Released metal concentrations as a percentage of the total sediment metal concentrations are indicated in parentheses.

The release of iron from the sediments at a pH of 6.5 was also still found to decrease with increasing redox potential. However, the magnitude of the releases of iron at each redox potential was much smaller than that observed at the lower pH. The remaining heavy metals measured (manganese, copper, aluminum, lead, nickel, and chromium) seemed to be fairly independent of changes in redox potential at the test pH of 6.5, although several of these metals exhibited a maximum release near a redox value of 0 mv with decreased release rates both above and below this value.

The final experiment to be conducted was a sediment incubation at various redox potentials in which the pH was not controlled and was allowed to fluctuate freely. This experiment, without pH control, was essentially conducted twice, once when the experimental apparatus was first constructed to test its operation, and again at a later date. During the first experiment, no sediment samples were collected. However the suspension was carried through each of the redox potential changes, and the pH was recorded continuously during these changes. The second experiment was carried out in the fashion described previously with samples collected at the appropriate intervals.

The initial sediment pH value at the start of the incubation period after the sediment slurry had reached equilibrium was approximately 7.3 for both of the experiments. As the sediments were purged with nitrogen and the sediment redox value began to decrease toward the first desired setting of -150 mv, a general slow

increase in pH value was observed in each case. By the time the redox potential had reached an equilibrium at -150 mv, the suspension pH had increased to a fairly stable value of 7.8. The general increase in pH value continued as the sediment redox potential was increased to 0 mv, although at a much slower rate, reaching an equilibrium value of 8.1-8.2. However, when the sediment suspension was aerated into an oxidized state at 250 mv, the pH value decreased sharply, reaching a fairly stable equilibrium at a value of 8.0 for the first experiment and a value of 7.6 for the second. This decline in pH value continued as the sediments were oxidized to 500 mv, reaching a final equilibrium pH of 7.8 for the first and 7.3 for second at the end of the 25-28 day incubation period. The changes in pH with incubation time and redox potential are illustrated in Figure 4-7 for each of the two experiments.

The release of heavy metals from the sediment suspension under conditions of no pH control is shown in Table 4-17. Several familiar patterns are apparent in this data. First, the release of cadmium from the sediments was found to increase with increasing redox potential as observed in both of the two previous experiments. However, the release rates were substantially lower than observed previously, with less than 10 percent of the total cadmium concentrations released. Second, as observed in the first experiment conducted at a pH of 5.0, the release of lead increased and the release of iron decreased with increasing redox potential, although the total release as well as the fractions released were

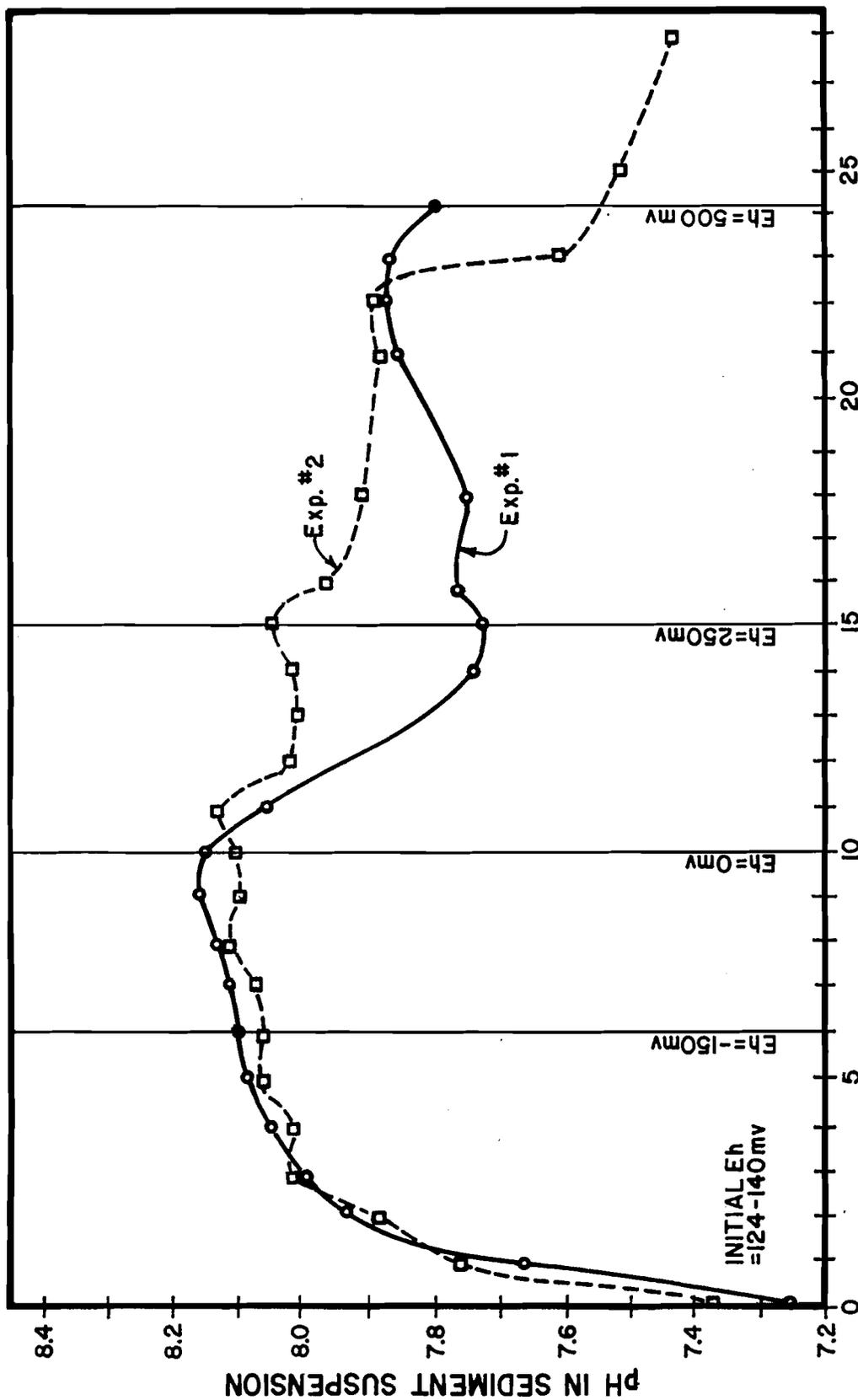


Figure 4-7. Variations in Sediment Suspension pH with Changes in Redox Potential in the Incubation Experiment with no pH Control.

TABLE 4-17

RELEASE OF HEAVY METALS FROM THE MAITLAND POND SEDIMENTS
UNDER VARIOUS REDOX POTENTIALS WITH NO pH CONTROL

REDOX POTENTIAL (mv)	HEAVY METALS RELEASED ($\mu\text{g/g}$ DRY SEDIMENT)									
	Cd	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr	
-150	0.16 (5.3)	0.39 (0.9)	0.49 (1.3)	0.12 (0.3)	131.4 (0.7)	8.63 (0.2)	0.99 (0.9)	0.08 (0.6)	0.14 (0.3)	
0	0.22 (7.3)	0.41 (1.0)	0.47 (1.3)	0.15 (0.9)	144.04 (0.3)	9.29 (0.2)	1.13 (1.0)	0.14 (1.1)	0.17 (0.4)	
250	0.28 (9.3)	0.32 (0.8)	0.09 (0.2)	0.10 (0.6)	50.66 (0.1)	3.62 (0.1)	1.26 (1.1)	0.13 (1.0)	0.10 (0.2)	
500	0.29 (9.7)	0.34 (0.8)	0.08 (0.2)	0.11 (0.6)	14.29 (<0.1)	1.28 (<0.1)	1.57 (1.4)	0.14 (1.1)	0.09 (0.2)	
Total Conc. in Pond Water Used ($\mu\text{g/l}$)	3	6	2	2	277	36	12	2	2	
Total Sediment Concentration ($\mu\text{g/g}$ dry wt)	3.00	41.4	37.6	17.3	45,603	4293	112	12.9	40.8	

Released metal concentrations as a percentage of the total sediment metal concentrations are indicated in parentheses.

less than those observed in the other experiments. The release of manganese and aluminum also decreased with increasing redox potential at these pH values, although the measured amounts of manganese were the lowest and the aluminum the highest of any of the three experiments. No obvious patterns were apparent for zinc, copper, nickel, or chromium, all of which were released in amounts generally less than 1% of the total metal sediment concentrations.

A summary of the fractional release rates of the total sediment metal concentrations of cadmium, zinc, and manganese is presented in Figure 4-8. A general pattern appears to exist for all three metals for maximum release to occur at a pH of 5.0, minimal release under uncontrolled conditions of pH, and a release somewhere between these two extremes for a pH of 6.5. Cadmium appeared to exhibit a trend for release rates to be higher under highly oxidized conditions and lower during highly reduced conditions. Release of zinc from sediments appeared to decrease with decreasing redox potential at a pH of 6.5, and remain a constant value at a natural pH of 7.5-8.5. Manganese was generally more soluble under reduced conditions and less soluble under oxidized conditions.

Fractional release rates for copper, aluminum, and iron are presented in Figure 4-9. Copper and iron seemed to follow a similar pattern with maximum release at low pH values and low redox potential, although the trends for iron were substantially more pronounced. Release rates for pH values of 6.5 and 7.5-8.5 appeared to be very close for both metals. Aluminum exhibited virtually no

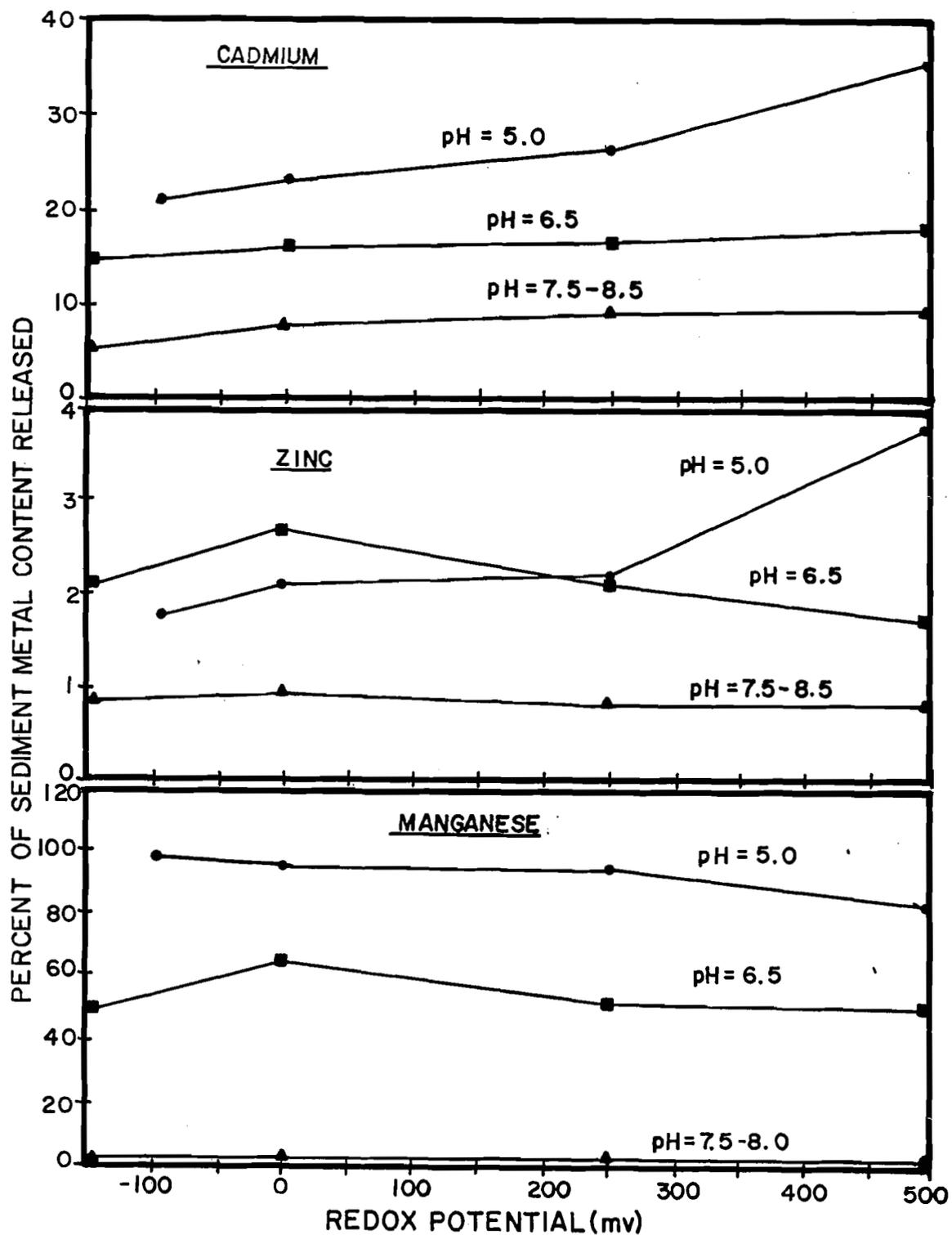


Figure 4-8. Fraction of Total Sediment Metal Concentrations of Cadmium, Zinc, and Manganese Released at Various Values of Redox Potential and pH.

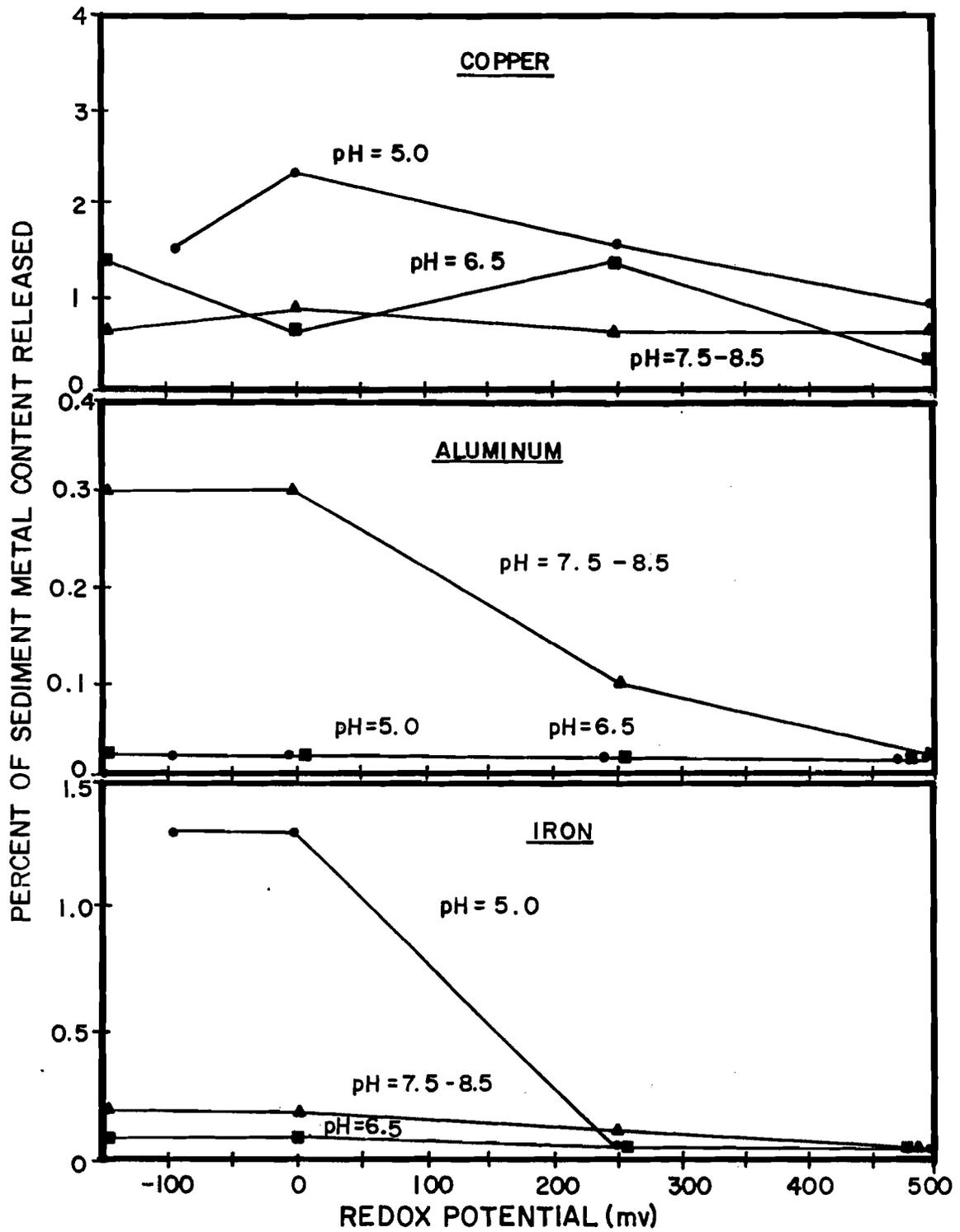


Figure 4-9. Fractions of Total Sediment Concentrations of Copper, Aluminum, and Iron Released at Various Values of Redox Potential and pH.

release at pH values of 5.0 and 6.5 over the entire range of redox values. However, a large release was observed under reduced conditions in the pH range of 7.5-8.5. This release was essentially zero under oxidized conditions at the same pH.

A final summary of release rates for lead, nickel, and chromium is presented in Figure 4-10. Release rates for lead and nickel followed the familiar trend of maximum release at low values of pH with a small release under natural conditions of pH. Chromium was released equally well at pH values of 5.0 and 6.5 with little release under natural pH. No obvious differences were noted for release under various conditions of redox potential.

Heavy Metals in Groundwater Flow

The movement of heavy metals in groundwater beneath the West Pond and in swale areas at the Maitland Interchange was monitored using five groundwater monitoring wells installed at various locations, as described in Chapter 3. A complete listing of concentrations of heavy metals measured in these monitoring wells at each of the sample ports is given in Appendix IV.

A summary of average heavy metal concentrations in each well at each sample port over the 16 month period is given in Table 4-18. Although a substantial amount of variability is present in these mean values, a general trend appears to exist for most heavy metals to decrease in concentrations as the sample depth increases. This trend is especially apparent for cadmium, manganese, lead, nickel,

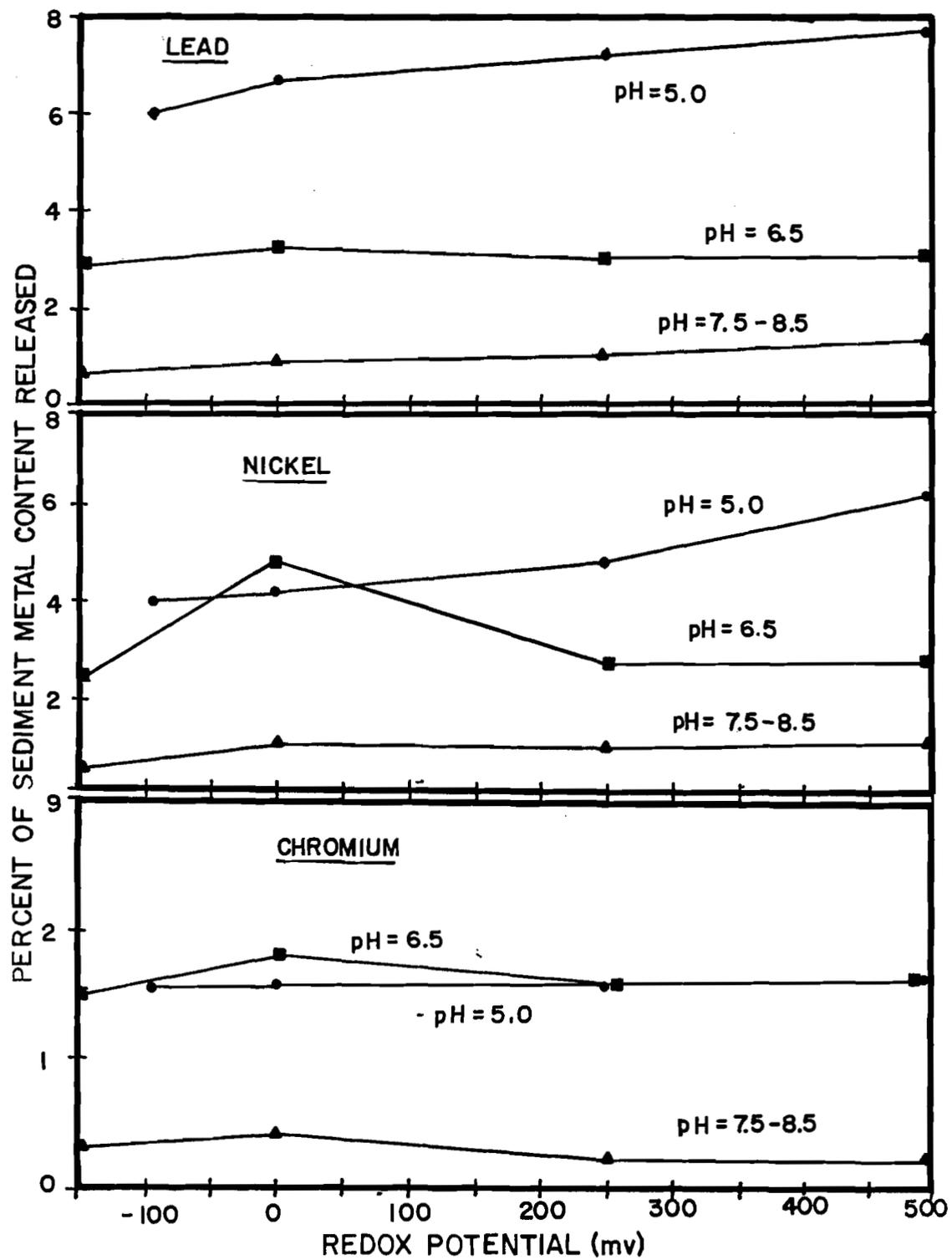


Figure 4-10. Fractions of Total Sediment Concentrations of Lead, Nickel, and Chromium Released at Various Values of Redox Potential and pH.

TABLE 4-18

SUMMARY OF AVERAGE HEAVY METAL CONCENTRATIONS IN GROUNDWATER MONITORING
WELLS AT THE MAITLAND INTERCHANGE DURING 1983-1984
(n = 13 observations)

SAMPLE DEPTH (m)	HEAVY METAL CONCENTRATION ($\mu\text{g/l}$)									
	Cd	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr	
WELL 1:										
0.1 m	2.15	30.6	40.9	18.9	831	3304	25.9	33.8	7.92	
0.5 m	1.15	26.4	60.0	10.9	1426	4633	19.2	4.81	6.00	
1.0 m	1.73	45.8	77.2	15.7	2304	5350	22.0	4.00	6.00	
3.0 m	1.19	30.0	61.9	15.8	107	1383	11.2	3.77	1.62	
6.0 m	1.54	31.3	96.9	9.9	171	3859	16.0	4.81	2.00	
WELL 2:										
0.1 m	1.73	27.3	41.5	6.7	811	1745	17.4	3.27	2.85	
0.5 m	2.69	21.7	37.8	8.4	1365	797	18.5	2.85	5.08	
1.0 m	1.92	24.0	24.6	12.6	168	717	18.7	1.77	2.42	
3.0 m	1.27	20.9	151.3	14.5	745	672	13.5	1.77	1.15	
6.0 m	0.88	24.7	31.3	14.5	602	2808	9.4	1.78	1.42	
WELL 3:										
0.1 m	1.23	18.1	66.2	12.1	607	964	31.5	2.50	3.19	
0.5 m	1.42	15.3	50.5	12.2	214	872	31.0	2.42	3.23	
1.0 m	1.04	13.2	21.9	5.3	219	820	22.5	2.21	2.79	
3.0 m	1.08	17.2	6.6	9.0	104	922	8.9	2.12	1.42	
6.0 m	1.12	14.3	109.1	11.7	483	1016	12.5	2.50	1.65	

TABLE 4-18 -- CONTINUED

SAMPLE DEPTH (m)	HEAVY METAL CONCENTRATION ($\mu\text{g}/\text{l}$)									
	Cd	Zn	Mn	Cu	Al	Fe	Pb	Ni	Cr	
WELL 4:										
0.1 m	1.67	19.9	5.0	14.8	401	77	19.0	2.88	2.00	
0.5 m	1.15	19.3	12.6	13.9	94	111	12.7	1.85	1.62	
1.0 m	1.31	23.4	28.8	9.7	44	134	14.5	2.00	2.12	
3.0 m	1.12	21.0	21.9	15.9	71	115	10.4	1.69	1.54	
6.0 m	1.00	19.4	5.9	8.6	112	908	7.7	1.88	1.96	
WELL 5:										
0.1 m	2.31	21.7	55.0	13.3	265	587	51.8	3.92	6.00	
0.5 m	2.12	18.1	47.7	31.2	256	355	47.8	3.23	5.54	
1.0 m	2.27	18.2	41.8	14.7	201	183	42.2	3.62	5.08	
3.0 m	2.42	23.5	43.6	15.7	178	217	26.6	3.15	4.23	
6.0 m	1.85	29.5	23.5	18.8	161	1155	19.2	4.00	6.00	

and chromium and less apparent or nonexistent for zinc, aluminum, iron, and copper. There also appears to be a trend for average metal concentrations to be higher at wells 1 and 5 which represent swale areas. The statistical significance of these trends will be examined in the following sections.

Comparisons Between the Monitoring Wells

The first analysis to be conducted was a test of differences in mean values between the five wells for each heavy metal. For this first analysis each of the sample ports for a single well were grouped together so that the wells could be tested independently of the sample ports.

A summary of the test statistics resulting from the GLM procedure is given in Table 4-19. The multiple comparison technique of Tukey was used to detect where significant differences or similarities occurred between the various wells. Tukey's test is generally considered to be conservative and will produce significant differences more frequently than other multiple comparison techniques such as Bonferonni or Scheffe.

As seen in Table 4-19, significant differences between the various wells were found at the 0.01 level for all metals except copper and nickel. Several general patterns appear to be present in this statistical summary. First, for each of the heavy metals exhibiting significant probabilities of unequal means the wells in swale areas had the highest mean concentrations and were

TABLE 4-19

SUMMARY OF ANOVA PROCEDURE FOR HEAVY METAL
CONCENTRATIONS IN WELL SAMPLES WITH ALL
SAMPLE PORTS COMBINED
(n = 65 observations)

HEAVY METAL	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY	
Cd	98.9	5 (S)*	2.19	A**	
		2 (P)	1.70	A	B
		1 (S)	1.55	A	B
		4 (C)	1.24		B
		3 (P)	1.80		B
Zn	99.7	1 (S)	32.8	A	
		2 (P)	23.7	A	B
		5 (S)	22.2	A	B
		4 (C)	20.6		B
		3 (P)	15.6		B
Mn	99.9	1 (S)	67.3	A	
		2 (P)	57.3	A	B
		3 (P)	51.0	A	B
		5 (S)	42.3		B
		4 (C)	14.9		
Cu	84.4	5 (S)	15.1		
		1 (S)	14.2		
		4 (C)	12.5		
		2 (P)	11.3		
		3 (P)	10.1		
				NSD***	
Al	99.9	1 (S)	970	A	
		2 (P)	580	A	B
		3 (P)	327		B
		5 (S)	213		B
		4 (C)	140		B
Fe	99.9	1 (S)	970	A	
		2 (P)	580	A	B
		3 (P)	327		B
		5 (S)	213		B
		4 (C)	140		B

TABLE 4-19 -- CONTINUED

HEAVY METAL	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY		
Pb	99.9	5 (S)	37.5	A	B	C
		3 (P)	21.3			
		1 (S)	18.8			
		2 (P)	15.5			
		4 (C)	12.8			
Ni	82.9	1 (S)	10.2	NSD		
		5 (S)	3.59			
		3 (P)	2.35			
		2 (P)	2.29			
		4 (C)	2.05			
Cr	99.9	5 (S)	5.37	A	B	C
		1 (S)	4.71			
		2 (P)	2.58			
		3 (P)	2.45			
		4 (C)	1.84			

* Well types are denoted by the following symbols:
S = swale, P = pond, and C = control

** Means within the same groupings are not statistically different at the 0.05 level

*** NSD = No significant differences

statistically different from the other wells by each of the three multiple comparison techniques. Second, metal concentrations in monitoring wells beneath the retention pond were smaller in magnitude for most metals, but not statistically different from the concentrations in swale areas. Third, concentrations of heavy metals in the control well were, in general, lower than in wells beneath either swales or the retention pond.

For those heavy metals which exhibited significant differences in Table 4-19, an additional analysis of variance procedure was conducted between the various wells for each metal at each sample port using PROC GLM to determine where the differences detected in Table 4-19 might occur. Even though Cd and Zn showed significant differences at the 0.05 level with all ports combined, they did not produce any significant differences between the various wells when analyzed at each port separately. Of the remaining metals, Mn, Al, Fe, Pb, and Cr, significant differences were observed in most cases between the various wells for a particular sample port at the 0.01 significance level or better. Summary statistics for metals exhibiting significant differences between the various sample ports are listed in Table 4-20.

The analysis of variance for manganese at the various sample ports produced the same general trends which were observed previously. At most of the sample depths the swale and pond wells had manganese concentrations which were several times higher than the control concentrations. In most cases, the control

TABLE 4-20

SUMMARY OF ANOVA PROCEDURE FOR HEAVY METAL
CONCENTRATIONS IN THE FIVE MONITORING
WELLS AT EACH SAMPLE PORT
(n = 13 observations)

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Cd	0.1	29.5	5 (S)*	2.31	NSD***
			1 (S)	2.15	
			2 (P)	1.73	
			4 (C)	1.67	
			3 (P)	1.23	
	0.5	63.2	2 (P)	2.69	NSD
			5 (S)	2.12	
			3 (P)	1.42	
			1 (S)	1.15	
			4 (C)	1.15	
	1.0	66.5	5 (S)	2.27	NSD
			2 (P)	1.92	
			1 (S)	1.70	
			4 (C)	1.31	
			3 (P)	1.04	
	3.0	77.3	5 (S)	2.42	NSD
			2 (P)	1.27	
			1 (S)	1.19	
			4 (C)	1.12	
			3 (P)	1.08	
6.0	85.6	5 (S)	1.85	NSD	
		1 (S)	1.54		
		3 (P)	1.12		
		4 (C)	1.00		
		2 (P)	0.88		

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Zn	0.1	31.4	1 (S)	30.6	NSD
			2 (P)	27.3	
			5 (S)	21.7	
			4 (C)	19.9	
			3 (P)	18.1	
	0.5	42.5	1 (S)	26.4	NSD
			2 (P)	21.7	
			4 (C)	19.3	
			5 (S)	18.1	
			3 (P)	15.3	
	1.0	76.9	1 (S)	45.8	NSD
			2 (P)	24.0	
			4 (C)	23.4	
			5 (S)	18.2	
			3 (P)	13.2	
	3.0	38.5	1 (S)	30.0	NSD
			5 (S)	23.5	
			4 (C)	21.0	
			2 (P)	20.9	
			3 (P)	17.2	
6.0	76.1	1 (S)	31.3	NSD	
		5 (S)	29.5		
		2 (P)	24.7		
		4 (C)	19.4		
		3 (P)	14.3		

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY			
Mn	0.1	99.9	3 (P)	66.2	A			
			5 (S)	55.0	A			
			2 (P)	41.5	A			
			1 (S)	40.9	A			
			4 (C)	5.0		B		
	0.5	99.9	1 (S)	60.0	A			
			3 (P)	50.5	A			
			5 (S)	47.7	A			
			2 (P)	37.8	A	B		
			4 (C)	12.6		B		
	1.0	99.9	1 (S)	77.2	A			
			5 (S)	41.8		B		
			4 (C)	28.8		B		C
			2 (P)	24.6				C
			3 (P)	21.9				C
	3.0	99.9	2 (P)	151.3	A			
			1 (S)	61.9		B		
			5 (S)	43.6		B		C
			4 (C)	21.9				C
			3 (P)	6.6				C
6.0	99.9	3 (P)	109.1	A				
		1 (S)	96.9	A				
		2 (P)	31.3		B			
		5 (S)	23.5		B			
		4 (C)	5.9				C	

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY	
Al	0.1	45.1	1 (S)	831		
			2 (P)	811		
			3 (P)	607		NSD
			4 (C)	401		
			5 (S)	265		
	0.5	99.7	1 (S)	1426	A	
			2 (P)	1365	A	
			5 (S)	256	A	B
			3 (P)	214	A	B
			4 (C)	94.2		B
	1.0	99.9	1 (S)	2304	A	
			3 (P)	219		B
			5 (S)	201		B
			2 (P)	168		B
			4 (C)	44.2		B
	3.0	99.9	5 (S)	178	A	
			1 (S)	107	A	B
			3 (P)	104		B
			2 (P)	74.5		B
			4 (C)	70.7		B
6.0	99.9	2 (P)	602	A		
		3 (P)	483	A		
		1 (S)	171		B	
		5 (S)	161		B	
		4 (C)	112		B	

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY		
Fe	0.1	99.9	1 (S)	3304	A		
			2 (P)	1745		B	C
			3 (P)	964		B	C
			5 (S)	587		B	C
			4 (C)	76.8			C
	0.5	99.9	1 (S)	4633	A		
			3 (P)	872		B	
			2 (P)	797		B	
			5 (S)	355		B	
			4 (C)	111		B	
	1.0	99.9	1 (S)	5350	A		
			3 (P)	820		B	
			2 (P)	717		B	
			5 (S)	183		B	
			4 (C)	134		B	
	3.0	98.2	1 (S)	1383	A		
			3 (P)	922	A	B	
			2 (P)	672	A	B	
			5 (S)	217		B	
			4 (C)	115		B	
6.0	99.9	1 (S)	3859	A			
		2 (P)	2808	A			
		5 (S)	1155		B		
		3 (P)	1016		B		
		4 (C)	908		B		

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY		
Pb	0.1	99.9	5 (S)	51.8	A		
			3 (P)	31.5		B	
			1 (S)	25.9		B	
			4 (C)	19.0		B	
			2 (P)	17.4		B	
	0.5	99.9	5 (S)	47.8	A		
			3 (P)	31.0		B	
			1 (S)	19.2		B	C
			2 (P)	18.5		B	C
			4 (C)	12.7			C
	1.0	99.9	5 (S)	42.2	A		
			3 (P)	22.5		B	
			1 (S)	22.0		B	
			2 (P)	18.7		B	
			4 (C)	14.5		B	
	3.0	99.9	5 (S)	26.6	A		
			2 (P)	13.5		B	
			1 (S)	11.2		B	
			4 (C)	10.4		B	
			3 (P)	8.9		B	
6.0	99.9	5 (S)	19.2	A			
		1 (S)	16.0	A	B		
		3 (P)	12.5	A	B	C	
		2 (P)	9.4		B	C	
		4 (C)	7.7			C	

TABLE 4-20 -- CONTINUED

HEAVY METAL	SAMPLE PORT DEPTH (m)	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY	
Cr	0.1	95.7	1 (S)	7.92		
			5 (S)	6.00		
			3 (P)	3.19		NSD
			2 (P)	2.85		
			4 (C)	2.00		
	0.5	98.4	1 (S)	6.00	A	
			5 (S)	5.54	A	B
			2 (P)	5.08	A	B
			3 (P)	3.23	A	B
			4 (C)	1.62		B
	1.0	99.9	1 (S)	6.00	A	
			5 (S)	5.08	A	B
			3 (P)	2.79		B
			2 (P)	2.42		B
			4 (C)	2.12		B
	3.0	99.9	5 (S)	4.23	A	
			1 (S)	1.62		B
			4 (C)	1.54		B
			3 (P)	1.42		B
			2 (P)	1.15		B
6.0	99.0	5 (S)	6.00	A		
		1 (S)	2.00		B	
		4 (C)	1.96		B	
		3 (P)	1.65		B	
		2 (P)	1.42		B	

* Well types are denoted by the following symbols:
S = swale, P = pond, and C = control

** Mean within the same groupings are not statistically different at the 0.05 level

*** NSD = No significant differences

concentrations were smaller and statistically different from the other wells by each of the multiple comparison techniques. Significant differences for aluminum were found between the wells for all sample ports except the top 0.1 m port. In general, concentrations of aluminum at the control well were lower than the swale area or pond area at all depths.

Significant differences were also observed at all sample depths for iron concentrations. Maximum concentrations of iron at all depths occurred in Well 1 located in the dry swale area. These iron concentrations were in general several times greater than concentrations in any of the other wells and were statistically different from the other wells at most depths. Concentrations of iron beneath the retention pond followed the dry swale area in terms of magnitude. The next lowest concentrations of iron were observed in the wet swale area at Well 5. These concentrations were similar to and statistically the same as the control well at most depths.

Similar to the trends observed for iron, maximum concentrations of lead were observed at each sample depth in a swale area well. However, unlike iron which had highest concentrations in the dry swale area, lead concentrations were highest in the wet swale well. These concentrations were statistically different from the remaining wells at all depths measured. The two pond wells and the dry swale well had similar concentrations which were in general only 50-70 percent of the wet swale concentrations. Concentrations of lead in the control well were the lowest concentrations measured at most depths.

Significant differences were observed for chromium between the five wells at all depths measured. Concentrations measured in swale areas were greater than under the pond or control area. The highest mean concentrations of chromium were measured beneath Well 1 in the dry swale at depths of 0.1, 0.5, and 1.0, while Well 5 in the wet area had higher concentrations at the 3.0 and 6.0 m levels. Concentrations of chromium in the pond and control wells were similar at all depths with mean concentrations approximately 50% less than the swale area.

Comparisons of Wells in Swale, Pond, and Control Areas

A more detailed comparison of heavy metal concentrations in swale, pond, and control areas was conducted by grouping Wells 1 and 5 into a general category of "swale" areas, wells 2 and 3 into a "pond" category, and well 4 as the control. An analysis of variance procedure was conducted first with all the sample ports combined. The ANOVA procedure of GLM was used for the analysis. The results of this analysis are presented in Table 4-21.

With the exceptions of nickel and copper significant differences were detected at the 0.05 level between the three well types for each metal tested. For each metal exhibiting a significant difference the swale area concentrations were the highest. In the cases of aluminum, iron, lead, and chromium, these concentrations were as much as twice the concentrations measured

TABLE 4-21

SUMMARY OF ANOVA PROCEDURES BETWEEN METAL CONCENTRATIONS
IN GROUNDWATER MONITORING WELLS BY WELL TYPE

HEAVY METAL	PROB. OF UNEQUAL MEANS	WELL TYPE	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY		
Cd	96.0	S*	1.87	A		
		P	1.44	A	B	
		C	1.24		B	
Zn	96.2	S	27.4	A		
		C	20.6	A	B	
		P	19.8		B	
Mn	99.9	S	54.9	A		
		P	54.2	A		
		C	15.0		B	
Cu	94.3	S	14.6			
		C	12.6			NSD**
		P	10.8			
Al	99.7	S	630	A		
		P	412	A	B	
		C	140		B	
Fe	99.9	S	2147	A		
		P	1089		B	
		C	272			C
Pb	99.9	S	28.2	A		
		P	18.3		B	
		C	12.8			C
Ni	82.1	S	6.88			
		P	2.31			NSD
		C	2.05			
Cr	99.9	S	5.05	A		
		P	2.48		B	
		C	1.84		B	

* Well types are denoted by the following symbols:

S = swale, P = pond, and C = control

** NSD = No significant differences

beneath the pond and approximately 3-10 times higher than concentrations in the control well. In all cases except zinc, the pond groundwater concentrations were second in magnitude behind the swale areas. The control area concentrations were in general lower and statistically different from the other well types.

Comparison of Groundwater Concentrations in Wet and Dry Swale Areas

A comparison was also conducted of heavy metal concentrations in groundwater beneath the "wet" and "dry" swale areas. An initial comparison was conducted by combining all sample ports together in order to detect the presence of significant differences. The ANOVA procedure of PROC GLM was used for this analysis. The summary statistics from this analysis are given in Table 4-22. Significant differences were found between the two areas for manganese, aluminum, iron, and lead. The first three metals, manganese, aluminum, and iron exhibited much larger and statistically different concentrations in the dry swale area while lead had a larger concentration in the wet area.

Comparison of Groundwater Concentrations Beneath the Retention Pond

A final comparison was conducted of heavy metal concentrations in the two groundwater monitoring wells beneath the retention pond. One of these monitoring wells, Well 3, was located approximately 20 m from the edge of Interstate 4, while the other, Well 2, was

TABLE 4-22

SUMMARY OF ANOVA BETWEEN METAL CONCENTRATIONS
IN GROUNDWATER MONITORING WELLS BENEATH
WET AND DRY SWALE AREAS WITH
ALL SAMPLE PORTS COMBINED

HEAVY METAL	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Cd	91.1	5 (wet) 1 (dry)	2.19 1.55	NSD*
Zn	94.5	1 (dry) 5 (wet)	32.8 22.2	NSD
Mn	99.9	1 (dry) 5 (wet)	67.4 42.3	A B
Cu	25.8	5 (wet) 1 (dry)	15.1 14.2	NSD
Al	99.9	1 (dry) 5 (wet)	970 213	A B
Fe	99.9	1 (dry) 5 (wet)	3742 499	A B
Pb	99.9	5 (wet) 1 (dry)	37.5 18.8	A B
Ni	72.3	1 (dry) 5 (wet)	10.2 3.59	NSD
Cr	50.8	5 (wet) 1 (dry)	5.37 4.71	NSD

* NSD = No significant differences

located on a entrance ramp on the southern shore of the pond. An initial comparison was conducted by combining all sample ports together in order to detect significant differences. The ANOVA procedure of PROC GLM was used to test this multivariate model. A summary of the ANOVA statistics is given in Table 4-23. Significant differences between the two retention pond wells were found for zinc, iron, and lead. Zinc and iron were found to have greater concentrations and to be statistically different in Well 2 while lead was found to have higher concentrations in Well 3.

Heavy Metal Concentrations in Subsurface Soils at Monitoring Well Sites

During the installation of the monitoring wells, core samples were collected using a 5 cm diameter stainless steel split spoon core sampler at the surface and at each 1.5-2.0 m interval to a final depth of 6.5 m. A total of five core samples were collected in each well boring. Each of the 0.5 m long core samples were mixed thoroughly in a polyethylene container, and a single 0.5 liter sample was collected. Analyses of moisture content, organic content, and heavy metals were conducted on each sample. The results of these analyses are listed in Table 4-24.

Measurements of moisture and organic content were similar in each of the soil samples. The only layer which differed substantially in these two parameters was the 4.5-5.0 m layer at Well 5. This layer exhibited elevated values of both moisture and

TABLE 4-23

SUMMARY OF ANOVA BETWEEN METAL CONCENTRATIONS
IN GROUNDWATER MONITORING WELLS
IN THE MAITLAND WEST POND

HEAVY METAL	PROB. OF UNEQUAL MEANS	WELL NO.	MEAN CONC. ($\mu\text{g/l}$)	MULTIPLE COMPARISON TECHNIQUE OF TUKEY
Cd	90.9	2	1.70	NSD*
		3	1.18	
Zn	97.4	2	23.7	A B
		3	15.6	
Mn	53.0	2	57.3	NSD
		3	51.1	
Cu	45.4	2	11.3	NSD
		3	10.1	
Al	93.4	2	580	NSD
		3	327	
Fe	96.5	2	1348	A B
		3	920	
Pb	99.8	3	21.3	A B
		2	15.5	
Ni	18.8	3	2.35	NSD
		2	2.48	
Cr	28.3	2	2.58	NSD
		3	2.45	

* NSD = No significant differences

organic content which were approximately twice the values observed at other locations. During the drilling process at this location, a dense layer of gray clay, approximately 1 m thick, was encountered at this depth.

Concentrations of heavy metals in soil samples collected at each of the well sites were similar with several noticeable exceptions. First, the surface concentrations of zinc appeared to be higher at Well 2 than at any of the other locations. Concentrations at this location were approximately 2-6 times greater than at the other locations. Second, concentrations of zinc, aluminum, iron and chromium as well as organic content seemed to be elevated in the 4.5-5.0 and 6.0-6.5 m samples collected at Well 4. And finally, substantially higher concentrations of zinc, aluminum, iron, and chromium were found in the clay layer at a depth of 4.5-5.0 m at Well 5.

TABLE 4-24
 CONCENTRATIONS OF HEAVY METALS IN SOIL LAYERS IN MONITORING WELLS
 SITES AT THE MAITLAND INTERCHANGE IN APRIL 1983

SAMPLE	MOISTURE CONTENT (%)	ORGANIC CONTENT (%)	HEAVY METALS ($\mu\text{g/g}$ DRY SOIL)																	
			Mn	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr									
<u>Well #1</u>																				
Surface	21.7	8.2	15.8	0.45	13.1	4.3	3888	517	19.4	1.2	3.9									
1.5-2.0 m	20.2	3.4	2.0	0.37	1.8	3.0	15339	676	11.0	2.8	12.7									
3.0-3.5 m	21.9	3.0	2.3	0.29	1.5	1.8	16180	572	14.0	2.4	12.5									
4.5-5.0 m	17.5	1.2	2.2	0.10	2.2	1.7	13440	878	8.5	2.5	8.8									
6.0-6.5 m	21.2	1.7	3.0	0.10	4.8	2.1	20125	1534	14.2	3.2	15.9									
<u>Well #2</u>																				
Surface	21.1	4.4	2.7	0.01	42.2	3.7	4766	580	11.1	1.9	5.2									
1.5-2.0 m	23.8	1.6	1.4	0.01	0.9	1.5	4572	129	7.9	2.0	1.7									
3.0-3.5 m	18.6	1.4	1.1	0.19	1.2	2.8	13560	520	11.4	3.7	8.4									
4.5-5.0 m	20.0	1.1	2.0	0.33	2.0	1.5	12004	859	7.4	1.6	8.2									
6.0-6.5 m	19.1	1.3	2.0	0.37	2.0	1.8	7891	514	3.9	1.2	2.5									

CHAPTER 5

DISCUSSION

The discussion of experimental results contained in this chapter is intended to present a logical progression of the fate of heavy metals in stormwater management systems. It will begin with a review of the characteristics of highway runoff collected at the Maitland site and provide comparisons with other nationally published studies. The fate and settling characteristics of the stormwater related heavy metals upon entering the retention pond will be examined.

Metal-sediment interactions will be used to evaluate the metal fixation onto the sediment layers and the potential for resolubilization. Finally, the potential for groundwater contamination by heavy metals originating in highway runoff will be evaluated.

Characterization of Highway Runoff

The most common vehicle related heavy metals measured in highway runoff at the Maitland site were lead, zinc, and copper in ratios of 4.70:1.91:1.0, respectively, for total concentrations, and ratios of 0.85:1.04:1.00, respectively, for dissolved species. Together these three metals accounted for approximately 91 percent of the dissolved heavy metals present and 94 percent of the total metal concentrations, excluding aluminum, iron, and manganese.

The large percentages of dissolved and total species of lead, zinc, and copper found in highway runoff at the Maitland site are very similar to results reported by Wilbur and Hunter (1977) for stormwater runoff collected from a highway site in Lodi, New Jersey. After monitoring eleven storm events, they concluded that lead, zinc, and copper accounted for approximately 90 to 98 percent of the total metals observed, with lead and zinc alone accounting for 89 percent. Nickel and chromium were usually found in considerably smaller quantities and accounted for approximately 2 to 10 percent of the total metals in highway runoff.

A comparison was made of mean total metal concentrations measured at the Maitland site with five highway sites monitored by Gupta (1981). Measured concentrations of total heavy metals at the Maitland site are substantially lower than those measured in large urban areas by Gupta and other researchers and for certain metals even lower than rural locations. There are several reasons which could be speculated at to why this difference exists. First, the Orlando area enjoys a larger number of storm events and higher runoff volumes during much of the year. Repeated rainfall events serve to keep the road surfaces relatively clean so that measured concentrations in any particular event would be relatively low. In addition, the Maitland site is relatively flat resulting in slower runoff velocities and less scouring and movement of particles than would be expected in a more Northern location where the Gupta studies were conducted.

Another somewhat obvious factor affecting the measured heavy metal concentrations in highway runoff is the degree and type of industrial activities present in the areas near the sample sites. The Milwaukee, Harrisburg, Nashville, and Denver areas measured by Gupta are all characterized by dense areas of relatively heavy industry while the Orlando area is not. Particulate emissions from heavily industrialized areas as well as the increased heavy truck traffic associated with this industry undoubtedly contribute to the increased loadings measured at these locations.

A final factor affecting the quality of runoff in northern locations is the use of salt to de-ice roadways during the winter months. Heavy metals are likely contaminants in the salt crystals which are used, and this could serve to increase the yearly mean metal concentrations in runoff. The tendency for increased concentrations of heavy metals during the winter months was readily apparent in the seasonal data given by Gupta (1981) for the five northern sites. At the Milwaukee site, for example, average non-winter runoff concentrations of lead, zinc, iron, copper, cadmium, and mercury were approximately 50 percent less than concentrations measured in winter periods. In addition to the use of salt, Gupta suggested that the smaller winter runoff quantities, the length of time between winter runoff events, and the retention of metals in snow may also be responsible for the increased winter concentrations.

In summary, it appears that measured concentrations of heavy metals in highway runoff collected at the Maitland site are substantially lower than comparable northern areas measured by Gupta. The primary factors responsible for these lower concentrations appear to be the increased rainfall frequency in the Orlando area, the lack of high intensity industrial and manufacturing operations which contribute to dustfall and increased traffic of large trucks, and the lack of de-icing activities in the winter months.

Another characteristic of the highway runoff collected at the Maitland site is the large variation in the percent of mean dissolved measured concentrations for various metals. The heavy metals can be divided into three general groups according to the percent dissolved fraction present: those metals with dissolved portions of 20-25 percent (including lead, iron, aluminum, and manganese), metals with dissolved portions of approximately 50 percent (including zinc and chromium), and metals with dissolved fractions of 75 percent (including copper and cadmium).

Probably the most important factor regulating the solubility of dissolved species of heavy metals in stormwater runoff is the chemical speciation of the street dust and dirt which contributes the loadings. Investigations into the distribution and speciation of heavy metals in street sweepings have been conducted by Gibson and Farmer (1983) and Harrison et al. (1981). In these studies, street sweepings were collected at various locations in urban areas

in Glasgow, Scotland and in Lancaster, England. The sweepings were analyzed for total metal content then carried through a sequential extraction procedure similar to that used in this research to define the following chemical associations: exchangeable, carbonate bound, bound to Fe/Mn oxides, and organic bound. A summary of their findings is given in Table 5-1.

The low solubility of lead in highway runoff is explained by Gibson and Farmer (1981) and Harrison et al. (1981), at least in part, by the relatively small potentially soluble exchangeable fraction found in street sweepings. The remaining fractions are predominantly carbonate and Fe/Mn bound which exhibit rather stable characteristics. Similar findings were reported by Hamilton et al. (1983) who found lead in street sweepings to be primarily associated with carbonate and Fe/Mn oxides with only a small exchangeable portion.

The speciation of zinc in street sweepings was found to have a somewhat larger exchangeable fraction than lead which may be responsible for the larger dissolved fraction of zinc measured in highway runoff. Copper was found to be one of the most soluble heavy metals in the runoff collected at Maitland. Copper was found to be associated to a large degree with organic complexes in street sweepings. Since the affinity of copper ions for soluble organic compounds similar to humic and fulvic acids is well documented, the large solubility of copper may be due to its associations with these organic ions.

TABLE 5-1
DISTRIBUTIONS OF HEAVY METALS IN STREET SWEEPINGS

SAMPLE	PERCENT OF TOTAL CONCENTRATIONS				
	Pb	Zn	Cu	Cd	
Exchangeable:					
1	13	10	11	27	
2	1.5	20	7	2	
Carbonate:					
1	28	23	4	19	
2	43	38	18	44	
Fe/Mn Oxides:					
1	32	25	11	16	
2	38	28	4.5	43	
Organic:					
1	14	16	43	22	
2	7.5	8	58	7.5	
Residual:					
1	13	26	31	16	
2	10	6	12	4.5	

1. Gibson and Farmer (1981)
2. Harrison et al. (1981)

Cadmium was found to have the largest percent solubility of any measured heavy metal at the Maitland site. Cadmium was reported to have a low exchangeable portion in street sweepings which is probably not of sufficient magnitude to cause the large degree of solubility found. The relatively large fractions of cadmium associated with carbonates and organic matter may contribute to the solubility in ways which are not clearly understood.

In a similar investigation involving the distribution of trace metals in street sweepings, Wilbur and Hunter (1979) found iron to have virtually no associations with exchangeable fractions (0.005%) and an almost total speciation with Fe/Mn oxides (96.02%). This speciation is consistent with the low solubility of iron found in the current study.

In summary, it appears that the speciation of heavy metals in the particles deposited on the street surface is responsible for regulating the relative amounts of dissolved and particulate species in highway runoff. The low dissolved fractions of both lead and iron are explained well by the low percentage of exchangeable associations of iron and lead in street sweepings. The increased solubility of zinc over lead can also be explained by the increased percentage of exchangeable associations of zinc. The large degree of solubility observed for copper was attributed to associations with soluble organics.

As discussed previously, various correlations were performed to determine if runoff metal concentrations were correlated with

factors such as runoff pH, runoff flow rate (an indirect measure of rainfall intensity), cumulative time since start of a rainfall event, or antecedent dry period. The first correlations which were computed were correlations between selected heavy metal concentrations and measured runoff flow rates to detect those metals which can be mobilized by increasing flow rates and rainfall intensities.

As indicated in Table 4-4, relatively small but significant correlations were found at the 0.05 level between runoff flowrate and dissolved heavy metal concentrations for all metals with the exception of copper. However, the correlations (with the exception of iron) were negative indicating a decline in concentrations with increasing rainfall intensity. Also, significant correlations were found between runoff flowrate and total metal species of iron, nickel and cadmium, with nickel and cadmium exhibiting negative correlations and iron exhibiting a positive correlation. These negative correlations suggest that increases in runoff flowrates produce a decline in metal concentrations.

A possible explanation of the decline in metal concentrations with increasing flowrates can be obtained by examination of runoff patterns measured at the Maitland site. Dimensionless mass curves of total event runoff versus cumulative duration for each of the storm events measured at the Maitland site were superimposed on a single graph using the PROC PLOT procedure of SAS. This plot is summarized in Figure 5-1. Three very distinct rainfall patterns

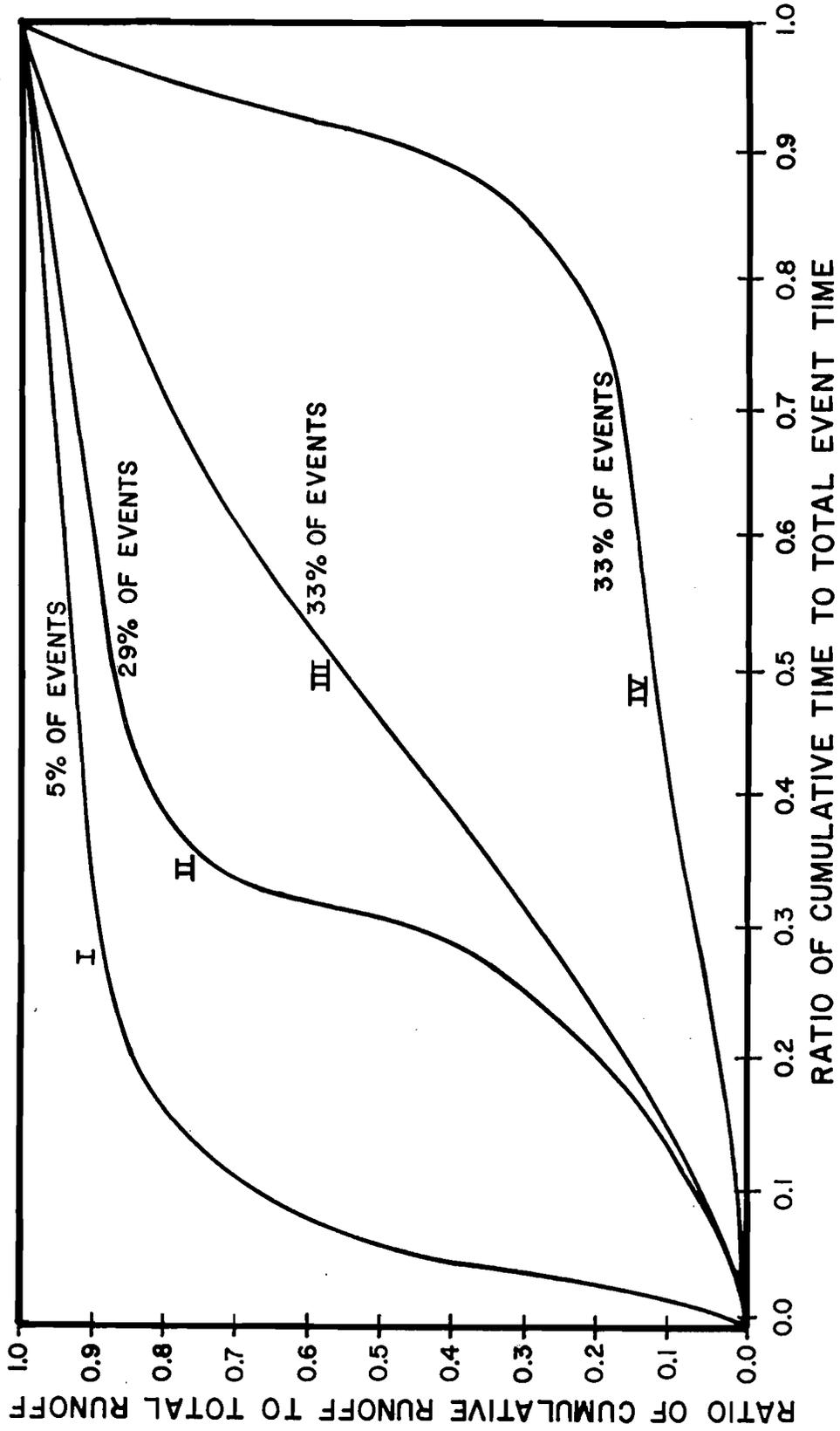


Figure 5-1. Generalized Patterns of Rainfall Distributions Observed at the Maitland Site During 1983-84.

(representing 95 percent of the events measured at the Maitland site) and one less dominant pattern are apparent in this figure. Both curves III and IV (representing 66 percent of the total events measured) indicate rainfall patterns which increase gradually in intensity in the early portions of the rain event, with maximum intensity occurring at later portions of the event. For rainfall events of this type, most of the deposited heavy metals could have been mobilized and transported with the initial lower intensity rainfall. When the high intensity portions of the storm arrived, the majority of the heavy metals would be removed and relatively clean runoff water would be present. This type of behavior would cause negative correlations to occur between metal concentrations and rainfall intensity since the largest concentrations would be present during the periods of lowest intensity, and reduced concentrations would be present during periods of high intensity.

The behavior discussed in the previous section suggests that a "first flush" effect would be present in which the majority of heavy metals should be mobilized and transported with the early portions of the rainfall event. To test this suggestion, measured concentrations of lead, copper, zinc, iron, and aluminum for each of the 16 monitored storm events were scaled by expressing each as a ratio of concentration over maximum concentration for a particular storm event. This converted all metal concentrations to a number between 0 and 1 for each event, representing each sample by the fraction of the maximum event concentration. These values were

plotted versus similarly scaled values of cumulative event time using the PROC PLOT program of SAS. Scaled plots were constructed separately for total and dissolved species of the metals listed above with all 16 storm events superimposed on a single graph. These plots provided information on the general relative behavior of each metal species for the events monitored.

Upon examination of these plots, no apparent trends were present for dissolved species of any of the five metals tested. Relative concentration patterns appeared to be somewhat random; however, the plots of total metal concentrations indicated very similar trends for lead, zinc, iron, and aluminum. Those patterns are indicated in Figure 5-2. A first flush effect is apparent for total concentrations of the four metals. In general, maximum concentrations were maintained through approximately 20 percent of the storm duration, followed by a rapid decline in concentrations for 20-30 percent of the duration, with substantially reduced concentrations for the remainder of the storm. These plots suggest a strong first flush effect with maximum concentrations in the first quarter of any event.

The total mass of heavy metals mobilized during various portions of a rain event were estimated by graphical integration of the area under the curve given in Figure 5-2. Approximately 47 percent of the total metal mass of lead, zinc, iron, and aluminum were found to be transported with the first quarter of a storm event. The second quarter was found to transport 22 percent of the

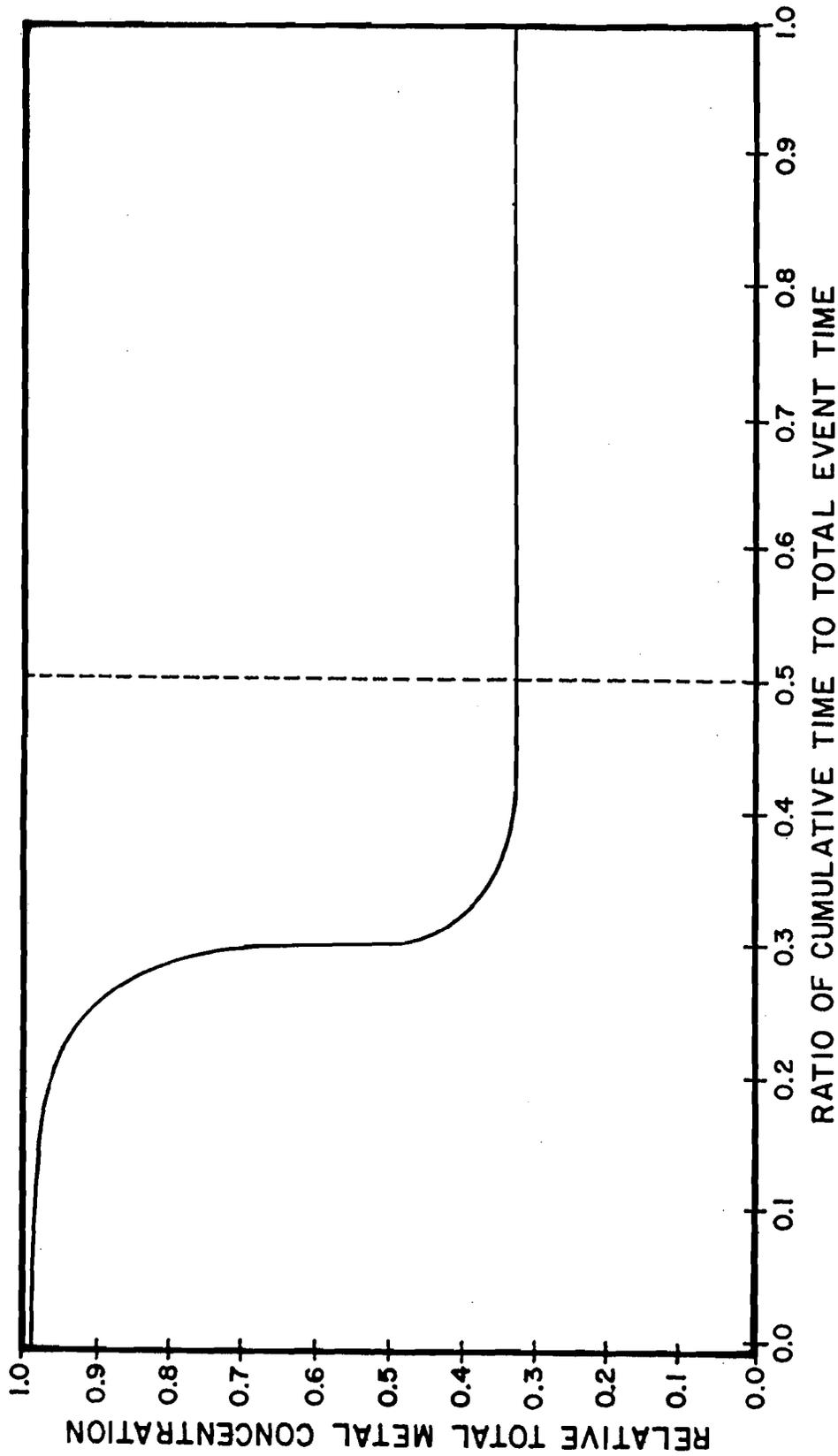


Figure 5-2. Generalized Pattern of Total Concentrations of Zinc, Lead, Iron, and Aluminum in Highway Runoff at the Maitland Site During 1983-84.

total mass, with the third and fourth quarters contributing approximately 15 percent each. If these percentages are expressed in a cumulative manner, then approximately 47 percent of total metal mass for these four metals would be transported during the first quartile of an event, 69 percent by the median or second quartile event, and 85 percent by the third quartile.

Total metal concentrations were found to exhibit a first flush effect while dissolved species did not. With the exception of zinc, approximately 80 percent of the total concentrations of the four metals listed above are in a particulate form. Zinc was present in a particulate form of about 50 percent. Chemical or physical reactions which are responsible for the release and mobilization of dissolved species from the road surface are not immediate and may occur slowly, causing a gradual release over the entire rain event. Factors such as rainfall intensity and runoff pH among others can affect these reaction times.

Correlations between pH and sequential hydrograph concentrations of various heavy metals in highway runoff were presented in Table 4-6. Significant positive correlations were observed between pH and the log of the metal concentration at the 0.01 level for dissolved zinc and iron, and a negative correlation was observed at the 0.01 level for dissolved nickel. However, these correlations were relatively weak with R-square values of 0.10 or less. Apparently, the pH of the runoff water plays only a small role in explaining concentrations of metal species with the range of pH values measured (4.95-8.49).

Since correlations between sequential hydrograph heavy metal concentrations and parameters such as runoff flowrate and cumulative rainfall event time were able to explain only small fractions of the variability in metal concentrations, regression analyses were conducted using metal concentrations as the response variable and runoff flowrate, cumulative time, and antecedent dry period as predictor variables. Functional forms of the relationships between the response and predictor variables were determined through examination of plots of residuals versus the various predictor variables using the PROC PLOT procedure of SAS.

In general, values of R-square for the best fit models of dissolved metal concentrations were relatively low. The highest values of R-square for the selected best fit models were found for manganese and lead with a value of 0.410 for lead and 0.281 for manganese. Cumulative time and runoff flowrate were approximately of equal importance in predicting dissolved lead values, although cumulative time was found to have a positive slope and flowrate a negative slope. Antecedent dry period was not important in predicting dissolved lead values. Dissolved concentrations of manganese were found to be influenced to the largest degree by flowrate with a negative slope, followed by antecedent dry period with a positive slope and cumulative time with a negative slope.

Although the calculated R-square values for the remaining predictive equations indicated a relatively poor ability to predict dissolved metal concentrations, it is nevertheless interesting to

note that flowrate was present in all of the final equations except those for iron and nickel. All of the slopes for the flowrate predictor variables were negative. Cumulative event time was important in six of the nine equations, while antecedent dry period was present in four of the final equations. Both antecedent dry period and cumulative event time had positive and negative slopes associated with their presence in the models.

Regression equations for total metal species were, in general, not as good as those for corresponding dissolved species and were very poor in their ability to explain the variability in the measured metal concentrations. Values of R-square for these equations were less than 0.20 in all cases, with many less than 0.05. Apparently, the parameters of antecedent dry period, runoff flowrate, and cumulative time are only slightly important in regulating concentrations of total heavy metals in runoff at the Maitland site.

The relatively poor ability of the predictive models to explain variations in heavy metal concentrations is indicative of the stochastic and poorly understood and complex phenomena regulating stormwater constituents and composition. These results are similar in some respects to those presented previously by Gupta et al. (1981). Gupta found poor correlations between metal concentrations and the parameters of average daily traffic and dustfall which are both indirectly related to antecedent dry period.

In a final attempt to examine causative relationships for heavy metals in highway runoff, correlations were conducted between the

flow-weighted runoff concentrations of dissolved and total heavy metals listed in Table 4-2 and 4-3 and total rainfall, mean rainfall intensity, rainfall duration, and antecedent dry period. However, when these correlations were performed, no significant correlations were found at the 0.05 level between any of the four predictor variables and any total or dissolved flow-weighted metal concentrations.

In summary, concentrations of both dissolved and total heavy metals in highway runoff were found to exhibit considerable variability both within a single event as well as between events. Attempts to correlate this variability with other runoff related characteristics such as flowrates, antecedent dry period, cumulative event time, runoff pH, rainfall duration, and rainfall intensity were not conclusive. Runoff flowrate appeared to be somewhat important in regulating concentrations of virtually all metals, while cumulative time and antecedent dry period were important in regulating only a few metal species. These findings emphasize the poorly understood phenomena which regulate runoff characteristics and suggest that further research is necessary in this area.

Short-Term Fate of Heavy Metals Upon Entering the Maitland Retention Pond

From the data presented in Chapter 4, it appears that (with the possible exception of manganese) the Maitland pond is very efficient in the removal of heavy metals in highway runoff entering the pond. A comparison of summary statistics for highway runoff and Maitland

pond water is given in Table 5-2. Heavy metal concentrations in this table have been given in terms of the concentrations of dissolved and particulate species rather than dissolved and total species. This was done so that the removal characteristics of soluble and particulate species could be examined separately.

Upon entering the Maitland retention pond, chemical, physical, and biological processes begin to occur which, for most metal species, results in substantial reductions in concentrations. The most noticeable removals for heavy metals occurs for the particulate species. Particulate species of lead and zinc are reduced in excess of 95 percent, cadmium and iron near 85 percent, with copper and aluminum averaging near 75 percent. Reductions of particulate nickel and chromium, however, were much less, with a removal of only 25-35 percent.

A partial explanation of the above phenomenon can be found in the chemical associations and speciations of heavy metals in highway deposits which are then transported by the runoff flow. As indicated in Table 5-1, lead, zinc, copper, and cadmium were found in studies by both Harrison et al. (1981), and Gibson and Farmer (1981) to exhibit relatively small residual fractions in roadway deposits. Residual fractions are indicative of metals which are tightly bound to larger particles such as sand or dirt. These particles should settle rapidly. Assuming that the chemical speciations of heavy metals in road deposits at the Maitland site are similar to those reported in the two previous studies, the large

TABLE 5-2

COMPARISON OF SUMMARY STATISTICS FOR HIGHWAY RUNOFF
AND MAITLAND RETENTION POND WATER

PARAMETER	STORMWATER RUNOFF ¹		RETENTION POND WATER ²		PERCENT REMOVAL IN POND	STATE OF FLA. CLASS III WATERS CRITERIA (2/1/83)
	MEAN (µg/l)	PERCENT OF TOTAL	MEAN (µg/l)	PERCENT DISSOLVED		
Lead:						
Dissolved	33.0	18.2	15.0	67.6	54.5	
Particulate	148	81.8	7.2	32.4	95.1	30 (Total)
Zinc:						
Dissolved	40.0	54.1	4.7	78.3	88.3	
Particulate	33.9	45.9	1.3	21.7	96.2	30 (Total)
Copper:						
Dissolved	28.6	74.1	14.4	86.2	49.7	
Particulate	10.0	25.9	2.3	13.8	77.0	30 (Total)
Nickel:						
Dissolved	2.5	73.5	1.6	72.7	36.0	
Particulate	0.9	26.5	0.6	27.3	33.0	100 (Total)
Chromium:						
Dissolved	2.5	59.5	2.2	62.9	12.0	
Particulate	1.7	40.5	1.3	37.1	23.5	50 (Total)
Iron:						
Dissolved	77.9	20.6	18.4	29.2	76.4	
Particulate	300	79.4	44.7	70.8	85.1	1000 (Total)

TABLE 5-2 -- CONTINUED

PARAMETER	STORMWATER RUNOFF ¹		RETENTION POND WATER ²		PERCENT REMOVAL IN POND	STATE OF FLA. CLASS III WATERS CRITERIA (2/1/88)
	MEAN (µg/l)	PERCENT OF TOTAL	MEAN (µg/l)	PERCENT DISSOLVED		
Aluminum:						
Dissolved	125	22.3	58.0	37.1	53.6	
Particulate	436	77.7	98.0	62.9	77.5	None
Manganese:						
Dissolved	2.7	28.3	4.5	26.3	-66.7 ³	
Particulate	6.8	71.7	12.6	73.7	-85.3 ³	None
Cadmium:						
Dissolved	1.7	77.3	0.73	89.0	57.1	
Particulate	0.5	22.7	0.09	11.0	82.0	0.8 (Total)

NOTES:

1. Number of observations = 150
2. Number of observations = 30
3. Denotes an increase

removal rates of particulate species in runoff water upon entering the pond can be explained by rapid settling of these relatively small residual fractions.

Whipple and Hunter (1981) conducted a survey of the settling characteristics of urban runoff collected at five locations in New Jersey. A 30 cm x 183 cm glass column was used for the settling tests. Samples were collected periodically from depths of 45 cm and 140 cm, and a composite sample was formed from the two. Their data indicated a maximum settlement for total lead, including both dissolved and particulate species, of about 60 percent in 32 hours. Zinc, copper, and nickel all appeared to settle out initially at very high rates for the first two hours, achieving a removal of total concentrations of about 30 percent in this time. Settlement after that time was much slower, with reductions of approximately 35 percent after 32 hours.

A more detailed study into the settling characteristics of urban runoff was conducted by Wanielista et al. (1982). In this investigation, stormwater samples were collected at four locations in the Lake Eola watershed and examined for settleability in a series of laboratory column studies using a 30 cm diameter by 2 m long plexiglass column. Samples were collected at sample ports located at various intervals on the column for a period of two hours. Removal of heavy metals during this detention period was found to be poor, with maximum removals not exceeding 20 percent for any metal species. This poor settleability can be explained, at

least in part, by the high dissolved fraction of most heavy metals in the stormwater used in these studies. This is undoubtedly a contributing factor to the low removal rates obtained in these short-term studies.

It appears, therefore, that particulate forms of lead, zinc, copper, iron, aluminum, and cadmium are associated with particles which exhibit good settling characteristics in the Maitland retention pond. However, nickel and chromium exhibited removal rates for particulate species in the range of 25-35 percent. Since nickel and chromium are generally present in highway runoff in small quantities, they have received little attention by most researchers, and as a result, the chemical associations of these metals in street sweepings or in stormwater runoff are poorly understood. It is possible that they may both be associated with relatively small diameter particles which exhibit poor settling characteristics even after prolonged periods. However, it should be noted that the concentrations of these metals measured in both stormwater runoff and in the retention pond water were near the limits of detection for the plasma emission spectroscopic technique used to measure these metals. As a result, the lack of precision at these low levels may be partially responsible for these results.

Although a substantial removal of particulate metal species was expected in the retention pond, the significant removal of dissolved metal species was surprising. Dissolved forms of zinc were removed to the greatest degree with an average removal of almost 90 percent.

Dissolved iron was removed at a rate of 75 percent, followed by lead, copper, aluminum, and cadmium with removals of dissolved species ranging from 50-60 percent. Removal rates for dissolved nickel and chromium were very poor, however, with average removals of only 36 and 12 percent, respectively.

An investigation into the chemical speciation of soluble metal species in both highway runoff and the retention pond water at the Maitland pond was conducted by Yousef (1985) and was previously discussed in Chapter 2. Removal of dissolved metal species is closely related to the speciation of the metal species in the runoff water and retention pond water. Those metals which were present with large fractions of reactive species (such as zinc, cadmium, and lead) were found to be removed efficiently. Other metal species which were not present as reactive species or were bound to organics were removed to a lesser degree.

Although not specifically evaluated in this research, the importance of biological uptake in the removal of dissolved metal ions should not be underestimated. Yousef et al. (1984) measured concentration factors for heavy metals in various aquatic plants and algae in an urban lake in central Florida receiving highway runoff. Concentration factors were calculated as the ratio of metal concentration in mg/g of oven dry weight of plant matter to the concentration of the same metal in mg/ml of the surrounding water column. The results of this study are presented in Table 5-3.

TABLE 5-3
 AVERAGE CONCENTRATION FACTORS OF HEAVY
 METALS BY PLANTS AND ALGAE

PLANT SPECIES	CONCENTRATION FACTOR (ml/g)						
	Cd	Zn	Ni	Cu	Fe	Pb	Cr
<u>Hydrilla</u>	363	5145	4104	5024	12103	3522	9700
<u>Spirogyra</u>	336	3047	3516	13483	25434	52375	7398
<u>Typha</u>	54	555	255	539	2322	444	610

SOURCE: Yousef et al. (1984)

The results presented by Yousef et al. (1984) indicate a significant ability of plant species to uptake and concentrate heavy metals in their cells. This concentrating ability was especially obvious for the algal species Spirogyra, which was an abundant species in the Maitland pond. Since these plant species are characterized by relatively rapid turnover rates for biomass, metal species incorporated into their cells are eventually deposited into the sediments. In ponds with an abundance of plant biomass, such as the Maitland pond, this type of concentration, followed by later deposition into the sediments, may be an important mechanism for removal of dissolved metal species from the water column.

A series of investigations into the fate of dissolved metal species in retention ponds was presented by Yousef et al. (1985).

In their research, isolation chambers were placed in a newly constructed retention pond near Epcot Center. The isolation chambers were constructed of inverted polyethylene 200-liter barrels which isolated a 0.25 m² area of the sediment and the overlying water column. Chambers were constructed with both open and sealed bottoms to investigate the effects of sediments on heavy metal concentrations. The chambers were first installed then dosed with a solution of heavy metals. Periodic samples were analyzed for metal content. A summary of their work is presented in Table 5-4.

Soluble concentrations of copper, zinc, iron, and lead were added to two of the test chambers in concentrations between 0.5 and 1 mg/l on 4/1/83. However, when the next sample was collected on 4/4/83, concentrations of copper, zinc, and lead had been substantially reduced by an average of 90 percent; and by 4/18/83 (the next sample collection date) were indistinguishable from the control which received no metal additions. No change was noted either with or without sediment contact in these metal concentrations throughout the test period, even when anaerobic conditions were established.

Soluble concentrations of iron, however, did not follow the pattern of reduction established by the other metals. Iron concentrations decreased slightly in the aerobic state inside the chambers with sediment contact, but began to increase again as soon as anaerobic conditions became established. This behavior is consistent with the widespread belief that iron is bound into the

TABLE 5-4

UPTAKE AND RELEASE OF HEAVY METALS INSIDE ISOLATION CHAMBERS AT EPCOT POND

CHAMBER DESIGNATION	METAL	TOTAL METALS CONCENTRATION BY DATE IN 1983 (µg/l)											
		4-1	4-1*	4-4	4-18	4-21	4-25	5-5	5-9	5-12	5-19	5-24	
Sediment	Cu	23	-	15	17	27	8	11	9	13	15	22	
Contact-	Zn	7	-	9	5	6	4	4	3	4	4	4	
Control (no metals added)	Fe	596	-	614	455	596	743	781	916	904	1118	1267	
	Pb	23	-	32	26	23	27	24	28	26	23	23	
Sediment	Cu	21	683	71	17	19	24	24	26	20	19	46	
Contact	Zn	14	857	82	10	10	11	10	5	12	5	10	
(metals added)	Fe	744	790	648	499	772	1059	1282	1703	2008	1654	1666	
	Pb	24	904	93	23	29	41	27	39	37	29	22	
No Sediment	Cu	23	590	61	19	17	22	14	64	28	28	41	
Contact	Zn	13	749	50	3	10	4	5	7	7	7	10	
(metals added)	Fe	401	468	720	617	788	612	360	341	535	269	300	
	Pb	27	724	56	30	32	45	30	48	38	25	33	
Pond	Cu	22	-	35	16	25	26	26	27	24	28	29	
	Zn	12	-	4	0	6	4	3	2	3	4	3	
	Fe	603	-	855	454	820	484	423	404	371	421	174	
	Pb	28	-	52	21	36	48	46	49	51	44	45	

<-----Diffused Air-----> <-----Diffused Air was Shut-off----->
was Supplied

* After addition of nutrient and heavy metal solution.

SOURCE: Yousef et al. (1985)

sediments as $\text{Fe}(\text{OH})_3$ under aerobic conditions. However, under anaerobic conditions, iron is converted from the Fe^{+3} form to the Fe^{+2} form which is substantially more soluble, and release from the sediments occurs. The chamber with no sediment contact did not indicate the increased concentrations of iron.

A final comment should be made concerning the ANOVA tests which were conducted to detect differences between metal concentrations at the various sample stations within the pond. The only significant differences which were detected by these tests were for dissolved and total concentrations of zinc which were shown to be higher at station 1 than at the other stations by the multiple comparison test of Tukey (Ray and Sall 1982). Station 1 had a mean zinc concentration of 7.7 $\mu\text{g}/\text{l}$ for dissolved and 9.5 $\mu\text{g}/\text{l}$ for total species compared to values approximately one-half of those at the other stations. This finding is not surprising and can be explained by the reactive nature of zinc. Apparently zinc is being taken up quickly during movement through the pond by mechanisms discussed previously. The rapid nature of these reactions may account for the rapid decline in concentrations during movement through the pond.

In summary, it appears that the Maitland pond is very effective in removal of heavy metals measured in highway runoff with the exception of manganese. Particulate species of heavy metals were found to be removed to a larger degree than dissolved species. The order of removal of particulate species of heavy metals in highway runoff was determined to be: $\text{Zn} > \text{Pb} > \text{Fe} > \text{Cd} > \text{Al} = \text{Cu} > \text{Ni} > \text{Cr}$.

A large portion of particulate metal species appears to settle near the input source.

Removal of dissolved metal species was related to the speciation of the metal species in the runoff water and retention pond water. Those metals which were present with large fractions of reactive species (such as zinc, cadmium, and lead) were found to be removed efficiently. Other metal species which were not present as reactive species or were bound to organics were removed to a lesser degree. Although not specifically investigated in this research, uptake and concentration of heavy metals in aquatic plants and algae is certain. Studies conducted by Yousef et al. (1985) suggest that the removal of dissolved metal species is rapid, with 90 percent removal occurring in four days in isolation chamber experiments. The measured order of removal efficiency for dissolved metal species at the Maitland pond was: $Zn > Fe > Cd > Pb = Al > Cu > Ni > Cr$.

Horizontal Distributions of Heavy Metals in the Sediments of the Maitland Pond

Distributions of heavy metals in the top 1 cm of the Maitland pond sediments (presented in Figures 4-4 and 4-5) suggest that upon entering the receiving water body, the majority of heavy metals associated with highway runoff settle out quickly and are deposited near the point of input for the runoff. Most of the metals in the runoff water entering the Maitland pond were retained in the pond sediment within a distance of 60-90 m from the inlet to the pond.

These results are similar to conclusions reached by Yousef et al. (1984) in an investigation of sediment metal concentrations beneath bridges with and without scupper drains. Concentrations of Zn, Pb, Ni, and Fe were found to be significantly higher in the sediments beneath bridges with scuppers. It was concluded that heavy metals associated with particulates, especially lead, will settle out and become immobilized in the sediments near the point of input.

The results of the horizontal analyses of heavy metals suggest important design parameters for use in designing retention basins to optimize removal of heavy metals. Many of the particulate metals were found to settle quickly near the point of input, with sediment metal concentrations reduced to levels substantially below mean concentrations at a point 60-90 m from the inlet. Although the characteristics of the particulate species were important in regulating this sedimentation, the design of the inlet end of the Maitland pond may be a contributing factor. As seen in Figure 3-3, the inlet end is at the corner of the triangle shape. As water enters the pond at this point, it quickly spreads out over an increasingly larger area, and the flow velocity begins to slow. Under these conditions, discrete particle settling as well as flocculation processes can occur, resulting in sedimentation of metals. This design aids in settling of particles and may be a reason why the metals settle so close to the inlet. Retention or detention pond designs which provide large wide areas where the flow velocity becomes very small would optimize particulate metal removal.

It is recommended, therefore, that retention or detention designs which intend to optimize heavy metal removal should provide conditions which encourage a low flow velocity to aid in sedimentation of particles and maximize the distance from the inlet to the discharge point. Also, design features which minimize the possibility of short circuiting are recommended.

Vertical Distributions of Heavy Metals in the Sediments of the Maitland Pond

In general, measured concentrations of total heavy metals in the sediments of the Maitland retention pond exhibit highest concentrations in the surface layer with a rapid decline in concentration with increasing depth. The same general trend was observed for moisture and organic content as well. The rapid decline in concentrations was found to observe an exponential decay relationship with values of R-square in most cases in excess of 0.90 when fitted to the model: $\ln (C/C_0) = K \times (\text{depth})$.

The mobility of heavy metals predicted by the model above is similar to that reported by Nightingale (1975) in studies on concentrations of lead, zinc, and copper in the sediments of retention ponds in Fresno, California, ranging in age from 3 to 13 years and in control basins which do not receive stormwater runoff. A summary of his findings is given in Table 5-5. Although the surface layer concentrations of lead and zinc are somewhat higher than those reported in Table 4-10 for the Maitland sediments, the same rapid attenuation was observed with increasing depth.

TABLE 5-5

SUMMARY OF MEAN CONCENTRATIONS OF LEAD, ZINC, AND COPPER IN
STORMWATER RETENTION BASINS AS REPORTED BY NIGHTINGALE (1975)

DEPTH (cm)	MEAN CONCENTRATION ($\mu\text{g/g}$ DRY WT)*		
	LEAD	ZINC	COPPER
0-5	224.8	107.9	19.9
5-15	25.4	38.6	10.7
15-30	17.0	35.5	10.8
Control basin 0-30	16.5	36.2	17.5

* based on 12 observations

All of the heavy metals tested in this research are present in unpolluted soils as common ions in varying concentration. Since the chemical and physical associations which bond heavy metals to natural soil particles may be different from those formed within retention ponds as metals settle and accumulate into the sediments, it was desired to separate the runoff related accumulations of metals in the upper sediment layers from those concentrations which may have been present naturally. To evaluate the extent of the vertical migration of the runoff associated heavy metal concentrations, an estimate of runoff related accumulations was made. This estimate was achieved by subtraction of the mean background soil metal concentrations from the mean total metal

concentrations in each of the five core sections analyzed. It was assumed that background metal concentrations in the retention pond soil could be estimated from mean soil concentrations in the split-spoon soil core samples collected at 1.5 m intervals during drilling of monitoring wells 2 and 3 which are located on the edges of the Maitland pond. These concentrations were presented in Table 4-24. Concentrations at depths of 3 m or greater were assumed to be free of the influence of the retention pond and the lower three core sections at wells 2 and 3 were combined and averaged to estimate the background soil concentrations for each metal.

The subtraction of background soil concentrations from the pond sediment concentrations revealed the added accumulations as a result of highway runoff. Two separate data sets of runoff related metal accumulations were created. One data set was based upon the mean sediment metal concentrations at each of the five depths in all of the core samples collected on the three collection dates. This represents a total of 46 samples x 3 collection dates = 138 samples at each depth. Background concentrations were subtracted from these mean values to provide an estimate of runoff related metal migrations. These values are listed in Table 5-6. The other data set of runoff related concentrations was created by subtraction of background concentrations from mean concentrations for each depth on each sample date. Each heavy metal concentration in this data set represented an average of 46 values for each of the three sample

TABLE 5-6
SUMMARY OF BACKGROUND AND RUNOFF RELATED METAL
CONCENTRATIONS IN THE SEDIMENTS OF THE MAITLAND POND

SEDIMENT DEPTH	MEAN SEDIMENT METAL CONCENTRATION ($\mu\text{g/g}$ DRY WT.)										NO. OF OBS.	
	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	Mn			
<u>0 - 1 cm:</u>												
Mean Conc.	2.20	45.4	19.1	49760	4554	112.7	16.5	44.7	43.9		138	
Background	0.40	1.5	2.0	12058	654	7.9	1.98	7.63	1.65		6	
Added Conc.	1.80	43.9	17.1	37702	3900	104.8	14.5	37.1	42.3			
<u>1 - 3.5 cm:</u>												
Mean Conc.	0.89	10.7	9.44	24574	1761	37.6	6.49	19.3	12.4		138	
Background	0.40	1.5	2.00	12058	654	7.9	1.98	7.63	1.65		6	
Added Conc.	0.49	9.2	7.44	12516	1107	29.7	4.51	11.7	10.8			
<u>3.5 - 6 cm:</u>												
Mean Conc.	0.56	6.49	7.50	18256	1303	24.5	4.15	15.4	6.86		138	
Background	0.40	1.50	2.00	12058	654	7.9	1.98	7.63	1.65		6	
Added Conc.	0.16	4.99	5.50	6198	649	16.6	2.17	7.77	5.21			
<u>6 - 8.5 cm:</u>												
Mean Conc.	0.45	4.64	5.07	17205	874	17.0	4.03	10.8	5.55		138	
Background	0.40	1.50	2.00	12058	654	7.9	1.98	7.63	1.65		6	
Added Conc.	0.05	3.14	3.07	5147	220	9.1	2.05	3.17	3.90			
<u>8.5 - 13 cm:</u>												
Mean Conc.	0.66	3.16	4.16	12485	482	13.5	3.31	4.01	4.96		138	
Background	0.40	1.50	2.00	12058	654	7.9	1.98	7.63	1.65		6	
Added Conc.	0.26	1.66	2.16	427	0	5.6	1.33	0	3.31			

dates. This data set was used in a regression procedure described below.

The attenuation of runoff related accumulations of heavy metals was examined by regression of the mean runoff related metal accumulation for each of the three sample dates against the sediment depth in a semi-log relationship, as described previously, using the PROC REG routine of SAS. A summary of the regression statistics for this model is given in Table 5-7.

In general, the same rapid attenuation rate observed for total metal concentrations was observed for runoff related metal concentrations as well. According to the calculated values of the attenuation slope, K, for the semi-log relationship, the mobility of runoff related heavy metals in the sediment phase was found to be:

Least		Most
Mobile:	Fe < Zn < Cd < Pb < Cr < Mn < Al < Ni < Cu:	Mobile

This order is somewhat different from the order of attenuation found for total sediment concentrations. Runoff associated sediment concentrations of lead and nickel were found to increase in mobility when compared with total sediment lead concentrations. Aluminum, iron, and cadmium in runoff associated accumulations were found to decrease in mobility.

The calculated regression equations for runoff related metal accumulations can be used to estimate the extent of metal migration from runoff related sources by estimation of the depth at which

TABLE 5-7

SUMMARY OF REGRESSION STATISTICS FOR ATTENUATION OF
 RUNOFF RELATED HEAVY METALS IN THE TOP 13 CM OF
 THE MAITLAND POND FOR A SEMI-LOG RELATIONSHIP
 FOR ALL THREE SAMPLE DATES COMBINED

HEAVY METAL	NO. OF OBS.	VALUE OF K FOR "BEST-FIT" EQUATION OF THE FORM: * $\ln(C/C_0) = -KZ$	VALUE OF R-SQUARE
Cd	9	$\ln(Cd) = -0.374 (Z)$	0.821
Zn	11	$\ln(Zn) = -0.398 (Z)$	0.898
Cu	12	$\ln(Cu) = -0.286 (Z)$	0.877
Al	11	$\ln(Al) = -0.311 (Z)$	0.902
Fe	10	$\ln(Fe) = -0.549 (Z)$	0.821
Pb	12	$\ln(Pb) = -0.368 (Z)$	0.926
Ni	12	$\ln(Ni) = -0.304 (Z)$	0.898
Cr	9	$\ln(Cr) = -0.346 (Z)$	0.913
Mn	9	$\ln(Mn) = -0.327 (Z)$	0.895
Organic Content	12	$\ln(Org.) = -0.241 (Z)$	0.850

* Metal concentrations in units of $\mu\text{g/g}$; organic content in percent; and depth (Z) in units of cm.

normal background levels resume. It was assumed for purposes of calculations that the limit of runoff related migration could be estimated by examination of the depths to which soil concentrations declined by 90 percent and 99 percent to values which were 10 percent and 1 percent above estimated background levels. The calculated depths are listed in Table 5-8.

TABLE 5-8
ESTIMATED VERTICAL MIGRATIONS OF RUNOFF RELATED SOIL
ACCUMULATIONS OF HEAVY METALS IN THE MAITLAND POND

HEAVY METAL	VERTICAL DEPTH (cm) TO:	
	10% OF SURFACE RUNOFF CONC.	1% OF SURFACE RUNOFF CONC.
Cd	6.2	12.4
Zn	5.8	11.6
Cu	8.1	16.2
Al	7.4	14.8
Fe	4.2	8.4
Pb	6.3	12.6
Ni	7.6	15.2
Cr	6.7	13.4

The depths at which runoff related accumulations of heavy metals were attenuated to only 10 percent of the surface runoff related concentrations were quite shallow. All metal species tested were reduced in concentration by 90 percent in the first 10 cm or less. These results are similar to those reported by Nightingale (1975) in Table 5-5. He reached the conclusion that sediment concentrations of lead, zinc, and copper approached natural background levels in the 15-30 cm soil depth layer.

Although the substantial majority of metal species were attenuated in the first 10 cm of sediments, the depths necessary to achieve 99 percent reductions in runoff accumulations suggest that certain metals may be slowly migrating to lower depths. However, the vertical extent of this sediment-associated migration appears to be limited since all metal species were reduced in concentration by 99 percent within 20 cm or less. These calculations provide further proof of the stability of metal-sediment associations since, after eight years of metal accumulations in the Maitland pond, 99 percent of most metals associated with sediments have remained in the top 0.20 m of the sediment layer.

Another method of evaluating the mobility of sediment associated migration of heavy metals is by calculating a diffusion coefficient of the metal species through the sediments. This diffusion coefficient (units of cm^2/yr) could be compared to the diffusion coefficients of other major groundwater ions, water, and a relative retention factor could be calculated.

From a material balance, the accumulation of heavy metals can be represented by the following differential equation:

$$dC/dT = D(d^2C/dz^2) + W(dC/dz)$$

where:

dC/dT = change in metal concentration of sediments with time

D = diffusion coefficient of the metal through the sediments (cm^2/year)

z = sediment depth, cm

W = deposition rate of sediments (cm/year)

Under steady-state conditions, $dC/dT = 0$, and

$$D(d^2C/dz^2) = -W(dC/dz) \quad (5-1)$$

A model previously used to model the attenuation of runoff related sediment metal concentrations was given as:

$$C = C_0 e^{-Kz} \quad (5-2)$$

where:

C = runoff related sediment metal concentration at depth z ($\mu\text{g}/\text{g}$ dry wt)

C_0 = runoff related sediment metal concentration in the surface 0-1 cm layer ($\mu\text{g}/\text{g}$ dry wt)

z = the sediment depth (cm)

K = metal attenuation constant ($1/\text{cm}$)

From equation (5-2):

$$dC/dz = - KC_0 e^{-Kz} \quad (5-3)$$

and

$$d^2C/dz^2 = K^2 C_0 e^{-Kz} \quad (5-4)$$

From equations (5-1), (5-3), and (5-4), it is possible to derive an expression for D:

$$D(K^2 C_0 e^{-Kz}) = -W(-KC_0 e^{-Kz})$$

or

$$D = W/K$$

From visual observations of sediment cores, the accumulation of organic sediments in the surface layer appears to be 1-2 cm, depending on location in the pond. Assuming an average accumulation of 1.5 cm over the 8 year life of the pond, the accumulation rate, W, can be estimated as 0.2 cm/year. Using the metal attenuation constants, K, listed for the semi-log relationships given in Table 5-7, the diffusion coefficient for migration of each metal species through the sediments can be calculated. These values are listed in Table 5-9.

In general, the diffusion of runoff related metal species was estimated to be less than 1 cm²/year. These values indicate a very slow rate of diffusion through the sediments when compared with

TABLE 5-9

ESTIMATED DIFFUSION COEFFICIENTS, D, FOR
MIGRATION OF RUNOFF RELATED HEAVY METALS THROUGH
THE SEDIMENTS OF THE MAITLAND POND.

HEAVY METAL	DIFFUSION COEFFICIENT, D (cm ² /YEAR)
Cd	0.53
Zn	0.50
Mn	0.61
Cu	0.70
Al	0.64
Fe	0.36
Pb	0.74
Ni	0.66
Cr	0.58

diffusion coefficients for movement of major ions in groundwater. The major ions in groundwater (Na⁺, K⁺, Mg⁺², Ca⁺², Cl⁻, HCO₃⁻, SO₄⁻²) have diffusion coefficients in the range of 1 x 10⁻⁹ to 2 x 10⁻⁹ m²/sec at 25°C (Freeze and Cherry 1979) which corresponds to 315 to 730 cm²/year. Calculated diffusion coefficients for heavy metals in the sediments of the Maitland pond suggest diffusion rates which are 300 to 2000 times less than those observed for major ions in groundwater flow.

As a final technique to examine the mobility of soil associated heavy metals, metal/zinc ratios were examined for each sediment layer. Assuming that zinc is attenuated to the greatest degree, examination of metal/zinc ratios can be useful in quantifying the various migration rates in comparison with the slowest. This technique was used successfully by Pita and Hyne (1975) to examine accumulation of runoff related metals in a receiving stream. In their study, zinc was assumed to be relatively immobile in sediments. Differences in the zinc/metal ratio for various metals in stormwater and that found in the sediments were used to estimate the remobilization and loss of other metals from the sediments over time.

A summary of sediment metal/zinc ratios for runoff related mean sediment metal concentrations for all three sample collection dates is given in Table 5-10. Ratios which remain relatively constant over the five sediment layers indicate a mobility similar to that of zinc. Ratios which increase or decrease substantially, particularly in the lower layers, indicate a rapid increase or decrease in sediment accumulation when compared with the accumulation of zinc.

Three general trends appear to be present in the accumulation patterns of various metal species. One trend which is readily apparent is a gradual increase in the rate of accumulation with increasing depth. This type of behavior was exhibited by copper, nickel, and to a smaller degree, lead. This trend indicates that

TABLE 5-10
 METAL/ZINC RATIOS FOR RUNOFF RELATED MEAN SEDIMENT METAL
 CONCENTRATIONS USING ALL THREE SAMPLE DATES COMBINED
 (Fractions of the surface layer ratio are listed in parentheses)

HEAVY METAL	RATIO OF METAL/Zn IN SEDIMENT LAYER				RATIO OF METAL/Zn IN RUNOFF
	0-1 cm	1-3.5 cm	3.5-6 cm	6-8.5 cm	
Cd	0.041 (1.00)	0.053 (1.29)	0.032 (0.78)	0.016 (0.39)	0.16 (3.90)
Cu	0.39 (1.00)	0.81 (2.08)	1.10 (2.28)	0.98 (2.51)	1.30 (3.33)
Al	859 (1.00)	1360 (1.58)	1242 (1.45)	1639 (1.91)	257 (0.30)
Fe	88.8 (1.00)	120 (1.35)	130 (1.46)	70.1 (0.79)	-----
Pb	2.39 (1.00)	3.23 (1.35)	3.33 (1.39)	2.90 (1.21)	3.37 (1.41)
Ni	0.33 (1.00)	0.49 (1.48)	0.43 (1.30)	0.65 (1.97)	0.80 (2.42)
Cr	0.85 (1.00)	1.27 (1.49)	1.56 (1.84)	1.01 (1.19)	-----
Mn	0.96 (1.00)	1.17 (1.22)	1.04 (1.08)	1.24 (1.29)	1.99 (2.07)

copper, nickel, and lead are accumulating at a faster rate than zinc in sediment layers beneath the 0-1 cm layer. This behavior supports previous data presented that zinc is almost totally retained in the top sediment layer. The fact that copper and nickel are accumulating in the lower layers faster than zinc is indicative of their increased mobility over zinc in the sediments.

Another accumulation pattern was observed for elements which exhibited substantial increases in the accumulation rate in the 8.5-13 cm layer. This type of behavior was observed by cadmium and manganese. This trend suggests that cadmium and manganese may be released from the upper 8 cm and are either migrating in a concentration front that has reached the 8.5-13 cm layer, or are becoming immobilized by conditions present in this lower layer and accumulating at this depth.

The third accumulation pattern, observed mainly by aluminum, was typified by a substantial reduction in the accumulation in the 8.5-13 cm layer compared with the upper layers. The rather rapid reduction in metal/zinc ratio observed for aluminum in the 8.5-13 cm layer suggests that conditions present in this layer may be causing aluminum to become mobilized and leave this layer.

A mass balance was attempted between the existing sediment metal mass and the calculated mass input due to runoff using estimates of runoff concentrations listed in Table 4-1. For these calculations, it was assumed that the retention pond had a mean age of eight years during the sediment core collection period of

1982-1984. The watershed which discharges into the 45 cm RCP inlet was assumed to have an area of 1.6 ha with a runoff coefficient of 0.80 based on field measurements as well as observations of runoff produced for various rainfall amounts. The theoretical potential watershed into the pond was assumed to be 18.0 ha, based on DOT drainage plans with a weighted runoff coefficient of 0.20.

For the purposes of calculations, runoff entering the pond from these areas was assumed to have characteristics similar to those measured at the 45 cm RCP inlet. Average annual rainfall at the Maitland site was assumed to be 127 cm/year. A pond basin surface area of 1.2 ha was used, and the following sediment layer dry densities measured in laboratory tests were used: 1.81 g/cm³ for the 0-1 cm layer, 2.07 g/cm³ for the 1-3.5 cm layer, 2.12 g/cm³ for the 3.5-6.0 cm layer, 2.17 g/cm³ for the 6.0-8.5 cm layer, and 2.11 g/cm³ for the 8.5-13 cm layer. Only the sediment concentrations which are runoff related, listed in Table 5-6, were used in this mass balance.

Four of the measured heavy metals (cadmium, zinc, copper, and lead) were found to have ratios of total runoff related sediment metal mass to estimated runoff mass inputs which were near a value of 1.0. The remaining five metals (aluminum, iron, nickel, chromium, and manganese) were all found to have sediment runoff related concentrations from 10 to 100 times that predicted by runoff inputs in the entire 18.0 ha watershed since 1976. Calculated sediment concentrations of iron, nickel and chromium were in excess

of 100 times the predicted value. This same trend was apparent in the metal/zinc ratios listed in Table 5-10.

The results described above are somewhat unexpected. One of the objectives of this research was to be able to predict both the rate of accumulation of metal species in the sediments as well as the rate of loss of metal species from the sediments if it was found that sediment concentrations were not accumulating as rapidly as expected. However, it appears from the experimental results that natural variability in the hydrology of the watershed and the complexity of the dynamic nature of the metal inputs are masking any trends which may be present.

The mean sediment concentrations for each metal at each sample depth on each of the three collection dates listed in Table 4-10 were intended to be used for an estimation of accumulation rates over the 18 month collection period. A considerable amount of effort was involved in the collection of the 46 core samples on each date at the fixed locations indicated in Figure 3-7, sectioning each of the samples, analyzing for organic and moisture contents, and finally metals analyses. In spite of this effort, sediment metal concentrations were found to fluctuate between the three sample collection dates with no obvious pattern. Comparisons of the mean metal concentrations on the three dates using PROC ANOVA of SAS indicated no significant differences at the 0.05 level in any metal concentrations on any of the three sample dates.

In summary, examinations of the horizontal migrations of sediment associated heavy metals indicate that the substantial portions of all metal species appear to have accumulated in the top centimeter of the retention pond. Sediment concentrations below this depth were found to decrease in an exponential fashion with increasing depth and were found to fit a semi-log relationship between metal concentrations and depth.

The depths to which 90 percent reductions in runoff-related concentrations were achieved were less than 10 cm with 99 percent reductions in runoff-related concentrations within the first 0.20 m. Estimated diffusion coefficients for the runoff-related metal accumulations were, in general, less than $1 \text{ cm}^2/\text{year}$. This diffusion is much slower than diffusion coefficients for the movement of major groundwater ions such as K^+ and Na^+ .

Both metal/zinc ratios and a mass balance were examined to determine if substantial portions of a particular metal species may be releasing into groundwater and leaving the pond sediments. However, difficulties were encountered in that aluminum, iron, nickel, chromium, and manganese were all present in sediment quantities which were in excess of the amounts that could be explained by runoff inputs. It is possible that additional unmeasured inputs of runoff, presumably with elevated concentrations of these elements, may be responsible for these discrepancies.

Mechanisms of Immobilization of Heavy Metals
in the Pond Sediments

The discussion presented in the previous section on the attenuation of heavy metals in the sediments of the Maitland pond presents strong evidence to suggest that a substantial portion of the heavy metals have remained within the top few centimeters of the sediments. For this phenomenon to have occurred, the mechanisms which bind metals to the sediments and retard heavy metal movement must be strong and substantial. These mechanisms are discussed in this section.

The summary of the speciation of heavy metals in the sediments of the Maitland pond presented in Table 4-13 indicates that fractions of total extracted metal concentrations bound to Fe/Mn oxides were in excess of 50 percent for all metals except cadmium. Organic bound associations were found to make up the majority of the remaining fractions. The combination of Fe/Mn bound species and organic bound species accounted for approximately 90 percent or more of the total speciation for all metal except cadmium and lead.

The large exchangeable fractions for cadmium and lead of near 50 percent are measured in this study and are of particular note since they represent a potentially mobilized quantity of toxic metal species. Similar exchangeable fractions for cadmium were reported by Harrison et al. (1981) in the sediments of a stream receiving highway runoff. Although it was concluded that a portion of the exchangeable fraction of cadmium was due to partial dissociation of

the carbonate phase with the acetate solution used to extract the exchangeable phase, it still appears that a substantial portion of the cadmium in the sediments may be in a potentially easily released form. The minor role for the organic phase in the speciation of cadmium noted in this research was observed by Harrison et al. (1981) as well. Cadmium was also found to exhibit the largest soluble and carbonate bound fractions of any metal species. On this basis, cadmium in the sediments of the Maitland pond can be considered to have a significant component which is either immediately available (soluble portion), easily available (exchangeable portion), or moderately available (carbonate portion) for transport into groundwater in an ionic form.

The relative ease of the release of cadmium from the sediment phase into the liquid phase was apparent in the release experiments conducted under various conditions of redox potential and pH. During experiments conducted with no pH control, cadmium was found to be released to the greatest degree of any metal species tested. Percentage release rates ranged from 9.7 percent of the total sediment concentrations under oxidized conditions to 5.3 percent under reduced conditions. This apparently provides supporting evidence that cadmium is being released from the sediments of the pond into groundwaters under both oxidized and reduced environments. This movement was also apparent in the metal/zinc ratios given in Table 5-10.

Although lead did not exhibit a significant soluble or carbonate bound fraction, it was found to exhibit a large exchangeable fraction. Although lead may be bound in an exchangeable form, it is one of the strongest associations by virtue of the +2 oxidation number (Weber 1972), the high selectivity by organic compounds for lead (Weber 1972), and the affinity of clay particles for lead (Mitchel 1964). Since the available information suggests that few other ions are capable of displacing lead ions into solution, lead associations in exchangeable fractions may be relatively stable, and little lead would be expected to be lost from the sediments into solution. This conclusion is supported by the low release rates of lead in the redox experiments with no pH control (Table 4-17). As a result, lead appears to be fairly stable in the retention pond sediments under current conditions.

With the exceptions discussed previously of lead and cadmium, the remaining species appear to be associated virtually totally with either Fe/Mn oxides or organic compounds. The predictive relationships between runoff associated sediment concentrations of heavy metals and concentrations of iron, manganese, Fe/Mn (iron concentration plus manganese concentration), and organic content of the sediments in the Maitland pond were investigated in a series of regression analyses. The results of these analyses are presented in Table 5-11. Each of the measured heavy metal species was found to exhibit strong predictive relationships with either Fe, Mn, Fe/Mn, or organic content with values of R-square in excess of 0.91 for all metals except cadmium and copper.

TABLE 5-11

SUMMARY OF PREDICTIVE RELATIONSHIPS BETWEEN SEDIMENT CONCENTRATIONS OF HEAVY METALS AND CONCENTRATIONS OF IRON, MANGANESE, AND ORGANIC CONTENT

HEAVY METAL (y)	"BEST FIT" EQUATION*	VALUE OF R-SQUARE	MEAN VALUE OF y, (μ)	UNIT LENGTH STANDARDIZED "BEST FIT" EQUATION	NO. OF OBS. IN MODEL
Cd	$Cd = 0.010 + 0.058 (Mn)$	0.840	0.775	$Cd = \mu + 0.917 (Mn)$	10
	$Cd = 0.122 + 0.00059 (Fe/Mn)$	0.818	0.775	$Cd = \mu + 0.905 (Fe/Mn)$	10
Zn	$Zn = -1.18 + 0.911 (Mn)$	0.984	10.74	$Zn = \mu + 0.992 (Mn)$	10
Cu	$Cu = 4.05 + 0.0038 (Fe/Mn)$	0.633	8.24	$Cu = \mu + 0.796 (Fe/Mn)$	10
	$Cu = 3.33 + 1.207 (Organic)$	0.450	7.40	$Cu = \mu + 0.671 (Organic)$	14
Al	$Al = 2027 + 9.09 (Fe)$	0.981	13253	$Al = \mu + 0.990 (Fe)$	14
	$Al = 2697 + 8.89 (Fe/Mn)$	0.988	12488	$Al = \mu + 0.994 (Fe/Mn)$	10
Pb	$Pb = 0.13 + 2.40 (Mn)$	0.975	31.5	$Pb = \mu + 0.987 (Mn)$	10
	$Pb = 4.45 + 0.025 (Fe/Mn)$	0.970	31.5	$Pb = \mu + 0.985 (Fe/Mn)$	10
	$Pb = 1.60 + 9.96 (Organic)$	0.930	35.2	$Pb = \mu + 0.964 (Organic)$	14

TABLE 5-11 -- CONTINUED

HEAVY METAL (y)	"BEST FIT" EQUATION*	VALUE OF R-SQUARE	MEAN VALUE OF y, (μ)	UNIT LENGTH STANDARDIZED "BEST FIT" EQUATION	NO. OF OBS. IN MODEL
Ni	Ni = 0.704 + 0.330 (Mn)	0.985	5.02	Ni = μ + 0.992 (Mn)	10
	Ni = 1.323 + 0.00336 (Fe/Mn)	0.967	5.02	Ni = μ + 0.983 (Fe/Mn)	10
	Ni = 0.738 + 1.316 (Organic)	0.911	5.16	Ni = μ + 0.954 (Organic)	14
Cr	Cr = 0.521 + 0.0095 (Fe)	0.986	12.25	Cr = μ + 0.993 (Fe)	14
	Cr = 0.143 + 0.0094 (Fe/Mn)	0.983	10.50	Cr = μ + 0.991 (Fe/Mn)	10
	Cr = -1.11 + 0.887 (Mn)	0.923	10.50	Cr = μ + 0.961 (Mn)	10
Mn	Mn = -0.434 + 4.74 (Organic)	0.982	13.08	Mn = μ + 0.991 (Organic)	10
	Mn = 1.95 + 0.010 (Fe)	0.973	13.08	Mn = μ + 0.986 (Fe)	10
Fe	Fe = -155.5 + 95.02 (Mn)	0.973	1088	Fe = μ + 0.986 (Mn)	10

* all metal concentrations in units of $\mu\text{g/g}$ dry sediment and organic content as %.

It appears certain that iron, manganese, and organic content play dominant roles in regulating the mobility of metal species in the sediments of the Maitland pond. Jenne (1976) reported that the hydrous oxides of iron and manganese constitute significant sinks of heavy metals in aquatic systems under oxidizing conditions. These hydroxides and oxides are capable of readily sorbing or coprecipitating cations and anions, and even a low percentage of $\text{Fe}(\text{OH})_3$ and MnO_2 was shown to have a controlling influence on distribution of heavy metals. The common occurrence of these oxides as coatings on larger particles allows them to exert chemical activity far out of proportion to their total concentration.

The controlling influence of Fe/Mn oxides is apparent in the release rates listed in Table 4-17 for the redox experiments without pH control. With the exceptions of cadmium that were discussed previously, the percentage of metals released from the sediments under both oxidized and reduced conditions were one percent or less. However, Jenne (1976) indicated that under reducing conditions, the sorbed heavy metals are readily mobilized and hydrous Fe/Mn oxides can act as a significant source of heavy metals under certain conditions.

The chemistry of manganese in the pond sediments can explain to a large degree the measured increases of manganese in the retention pond waters over that measured in highway runoff. A conceptual model for the transport of manganese and iron at a redox boundary was presented by Davidson (1985). Davidson indicated that

particulate manganese which is supplied to the sediments is usually more readily reduced than iron. Consequently, most of the manganese which is supplied to a highly reducing sediment is solubilized and re-released to the water column, whereas only a small fraction of the iron is solubilized. He concluded that very little manganese is permanently retained in such a sediment. In contrast, most of the iron which reaches the sediment surface becomes incorporated. Although the release of iron can be measured under anoxic conditions, the majority of iron will be retained in the sediments while manganese will be released.

The affinity of heavy metals for organic substances and degradation products was apparent for at least several metal species. The most important products formed during the decomposition of organic substances are humic and fulvic acids which can be found in sediments as well as in the corresponding aqueous solutions. According to Welte (1969), about 60 percent to 80 percent of the dissolved organic carbon and particulate organic carbon in fresh waters consists of humic substances. The attractive forces between metal ions and soluble, colloidal, or particulate organic material have been shown to range from weak (physical adsorption) to strong (undistinguishable from chemical bonds). As a result, the stability of chemical organic associations may be difficult to predict. However, since the organic fractions measured during the extraction experiments were measured after removal of the soluble, exchangeable carbonate, and Fe/Mn bound fractions, it seems

reasonable to assume that the organic fractions listed in Table 4-13 represent tightly bound associations.

The results from the speciation and redox experiments combined with the analyses of the sediment metal concentrations presents evidence that, under the current conditions within the sediments of the Maitland pond, metal species, with the exceptions of cadmium and manganese, are relatively stable and exist in immobile associations with Fe/Mn oxides and organic matter. However, cadmium and manganese appear to exhibit at least limited mobility and may be released into the pond water and groundwaters even under current conditions.

The extent of metal release under current or future conditions within the sediments of the Maitland pond must be qualified by examination of the fractions of total metal concentrations which are potentially available for release. A comparison of the total acid extracted sediment concentrations with the cumulative total of metals released during the speciation investigations was presented in Table 4-14. In this table the total acid-extracted metal concentrations are compared with the cumulative extracted amounts corresponding to the soluble, exchangeable carbonate, Fe/Mn, and organic bound fractions. The differences between the total acid-extracted metal concentrations and the sequentially extracted concentrations represent the portions which were not released by even the rigorous organic extraction techniques. These residual

metals are presumably incorporated into crystalline structures and are unavailable for release even under the most rigorous sediment conditions.

With the exception of manganese, the potentially available fractions of most heavy metals in the 0-1 cm layer were equal to 60 percent of the total metal concentration or less with cadmium, aluminum, and chromium present in available fractions of less than 20 percent. As a result, even if cadmium is being released from the sediments, the fraction of potentially available ions is relatively small.

A trend which is somewhat apparent in Table 4-14 is the increase in the available fractions with increasing sediment depth. Cadmium, for example, has an available fraction of only 16.8 percent at the surface, but at depths of 8.5-13 cm this fraction increases to 91 percent. Apparently, the available fractions of metals in sediments increase with increasing depth.

In summary, it was concluded that all heavy metal species examined in this research with the exception of cadmium are bound into strong sediment associations upon entering the sediments. For all metals except lead, this association involves dominant combinations with Fe/Mn oxides and organic matter. Lead is apparently held to a large degree in an exchangeable fraction which seems to be very tightly bound. No evidence of substantial release of heavy metals, except cadmium, was found under oxidized or reduced conditions under natural pH. Metal associations in the upper

sediment layer appear to be largely residual in nature and unavaivable for release under any natural conditions. The extractable fraction was found to increase with increasing depth.

Potential for Future Mobilization of Heavy Metals from the Maitland Pond Sediments

Natural aging processes within retention ponds as well as lakes result in the increased deposition of organic matter to the bottom sediments derived primarily from the death and decay of both plant and animal matter. As the decomposition of organic matter increases, organic acids as well as CO_2 are released into the sediment layers, affecting pH. Occurring simultaneously are other redox processes such as nitrification, denitrifiaction, or sulfate reduction which also affect pH, as well as redox potential. Processes such as nitrification, oxidation of H_2S , pyrite oxidation, and production of organic acids result in a reduction in alkalinity and pH, while processes such as denitrification and sulfate reduction result in increases in alkalinity and pH.

Although reduction of sediments was found to cause an increase in pH in these investigations, a decrease in pH is commonly noted for reduced sediments. Wetzel (1975) stated that often sediments with large accumulations of organic matter are dominated by production of CO_2 and organic acids which produce a net decrease in pH. A similar conclusion was reached by Mortimer (1971) in studies on the Great Lakes. Although incubation studies currently indicate

an increase in pH within the Maitland sediments, as they became more reduced future accumulations of organic matter may reverse this trend. As a result, both the current conditions of pH as well as more acidic conditions were investigated.

The stability of metal sediment associations was investigated in pH and redox controlled incubations which are summarized in Figures 4-8 to 4-10. Although all of the heavy metals examined were found to be influenced by redox potential to varying degrees (especially aluminum and iron), pH was the dominant factor in regulating the magnitude of the release of each metal.

With the exception of manganese, cadmium was released by decreases in pH to a larger degree than any of the other metals. In general, approximately 5 percent of the total sediment cadmium concentrations were released in sediment suspensions with pH values in the range of 7.5-8.5, 15 percent at a pH of 6.5, and 20-30 percent at a pH of 5.0. As seen in Figure 2-9, the solubility of cadmium increases substantially as the pH increases from 7.5. This behavior could explain in part the increased release of cadmium. However, most of the other heavy metals tested also exhibit increases in solubility in this range, but were not released to a substantial degree.

The large release of cadmium from sediments under acidic conditions may be related to its predominant association with exchangeable species. Apparently, the stability of the sorption processes which bind cadmium to the sediments are reduced

significantly by decreases in pH causing cadmium to be released. Once cadmium is released, it is unlikely that it will readsorb onto soil particles as long as the acidic pH is maintained. This suggests that, once mobilized, cadmium may be capable of transport by groundwater flow in an ionic form. Cadmium also appeared to be more mobile under oxidized conditions at a pH of 5.0. As indicated in Figure 2-17, cadmium is considerably more soluble under oxidized conditions since CdS forms in a reduced environment.

The pattern of release of lead was similar to that of cadmium, although to a substantially reduced degree. The release of lead increased, in general, from 1 percent under current pH conditions, 3 percent at a pH of 6.5, and 6-8 percent at a pH of 5.0. Lead was also present in the sediments in a large exchangeable fraction. However, for reasons discussed previously, lead is apparently held very tightly by these associations and does not exhibit the magnitude of release exhibited by cadmium. Lead was also found to exhibit increased release under oxidized conditions where ionic forms of lead are more likely.

The large release rates of manganese under acidic conditions were unexpected. Apparently, the solubility of manganese increases rapidly as pH decreases to the extent where at a pH value of 5.0 manganese is almost totally solubilized from the sediments. A 50-fold increase in solubility was found from the current sediment conditions at a pH of 7.5-8.5 to a pH of 6.5. The fact that this large release of manganese did not result in corresponding increases

in solubility of other metals suggests that the iron associations in the sediments may be more important in determining stability or that metals released from manganese oxides as they solubilize are quickly taken up by ferrous oxides. Therefore, it appears that manganese is released from sediment associations at all pH values tested in the range of 5-8.5.

The stability of zinc, nickel, and chromium in the sediments appears to be somewhat similar since each metal exhibited similar release relationships with changes in redox potential and pH. Each of these metals increased in solubility as the pH was decreased to 6.5 and 5.0. The magnitude of release at these lower pH values was approximately two to three times that observed under current sediment conditions. As indicated in Figures 2-6 and 2-10, both zinc and nickel exhibit increased solubilities as pH decreases. It also appears that zinc and nickel are more soluble under oxidized conditions at a pH of 5.0 than under reduced conditions. Both nickel and zinc form insoluble sulfides under reducing environments at pH values greater than two.

As reported by numerous other researchers, the release of iron from the sediments was found to be largely regulated by redox potential. As seen in Table 4-17, the release of iron increased by a factor of approximately seven from oxidized conditions to reduced conditions under current pH conditions. A similar release was observed under a pH of 6.5. However, at a pH of 5.0, the solubility increased by a factor of 32 from oxidized to reduced conditions.

This large increase in solubility is presumably related to the fact that iron exhibits its maximum solubility at a pH of 5.0, as indicated in Figure 2-5. Solubilities at pH values of 6.5 and 7.5 are substantially lower. The release of iron under reduced conditions at higher pH values is probably limited by the solubility of iron in the soluble phase.

The release of iron under reduced acidic environments did not result in noticeable increases in the solubility of the other metals in spite of the fact that iron appears to be a dominant element in regulating the solubility and mobility of other elements. As redox potential decreases and metals are released from iron oxides, metal sulfides are formed. In addition, organically bound metals would not be affected by solubilization of iron.

Although aluminum appeared to be relatively insoluble under most conditions of redox potential and pH, a slight increase in solubility was observed for the sediments suspension incubated at pH values of 7.5-8.5 under reduced conditions. The release of aluminum under these conditions was approximately 10 times that measured for the same pH range under oxidized conditions. Since this pH range is near the range of minimum solubility for aluminum, and it is generally recognized that aluminum compounds are inert to changes in redox potential (Cooke and Kennedy 1981), this behavior is not fully understood.

In summary, it was found that pH is more dominant in regulating the solubility of heavy metals in the sediments of the Maitland pond

than redox potential. Decreases in pH were found to increase the solubility of all heavy metals tested. However, these increases were only a small fraction of the total metal mass present in the sediment. The solubility of all heavy metals tested, with the exceptions of iron, aluminum, and manganese, was found to decrease, presumably by formation of metal sulfides, under reduced and acidic environments. Manganese and cadmium were found to increase in solubility substantially as sediment pH decreases with almost total release of manganese and 25-35 percent release of cadmium at a pH of 5.0. A similar but substantially reduced release pattern was observed for lead. The similarities in the release patterns of cadmium and lead was linked to their dominant associations with exchangeable fractions in the sediments. The lower release rate for lead was attributed to its strong association as an exchangeable ion.

The results previously presented suggest that as the Maitland pond ages and accumulations of organic matter in the sediments begin to cause sediment pH values to decrease, mobilization of all metal species tested will increase. Although all metals were found to increase in solubility by a fraction of at least two at pH values of 6.5 and 5.0, the release is only a small fraction of the total sediment metals present. It appears that under the most extreme natural conditions of pH, most heavy metals remain held tightly in the sediment layers.

The release of cadmium and manganese can be expected to increase substantially as the sediments become more acidic. Releases of this magnitude may produce measurable increases in groundwater concentrations beneath the pond. In the case of cadmium, a health hazard may be present under these extreme conditions.

The results presented above suggest that maintenance procedures may be necessary after a period of time to remove the accumulated sediment deposits which may cause conditions of low pH and release of metals. However, it is beyond the scope of this research to evaluate this possibility to the extent at which specific maintenance procedures or frequencies could be recommended.

Heavy Metal Concentrations in Groundwaters Beneath the Maitland Interchange

Suitability of the Multi-Port Sampling Technique

As indicated in the previous chapter, examinations of heavy metal concentrations in samples collected from each of the five monitoring wells indicated that disruption of soil and groundwaters during the installation process appeared to be minimal. Concentrations of heavy metals measured in each of the wells at each sample port (see Appendix IV) indicate that this disturbance lasted for approximately 60-90 days before relatively constant groundwater concentrations were obtained.

As a further analysis of this sample technique, plots were constructed of field measurements of specific conductivity versus time for each monitoring well at each sample port. These plots are given in Figure 5-3. Specific conductivity is an indirect measure of the amount of dissolved charged ions in water. This measurement includes the effects of not only heavy metals but other major groundwater ions such as K^+ , Na^+ , Mg^{+2} , Ca^{+2} , etc. As a result, specific conductivity can be used as a measure of general groundwater disturbance, and can be used as an estimate of the time necessary for an initial disturbance to subside.

Not all of the well installations at the Maitland Interchange resulted in a groundwater disturbance sufficient to be detected by increases in specific conductivity. Wells constructed in dry areas at the control site (well 4) and in the dry swale area (well 1) did not exhibit elevated measurements of specific conductivity at any time. However, elevated values were measured in wells constructed along the pond edges (wells 2 and 3) as well as in the wet swale area (well 5). These disturbances were more apparent for the upper sample ports above 1 m than for those below this depth. In some cases these initial elevated values were several times greater than the relatively constant values measured after 30-60 days.

It appears, therefore, that wells constructed in areas where the surface is dry and does not have standing water are subjected to much less groundwater disturbance than wells constructed in wet areas. Presumably the standing water and surface mud in wet areas

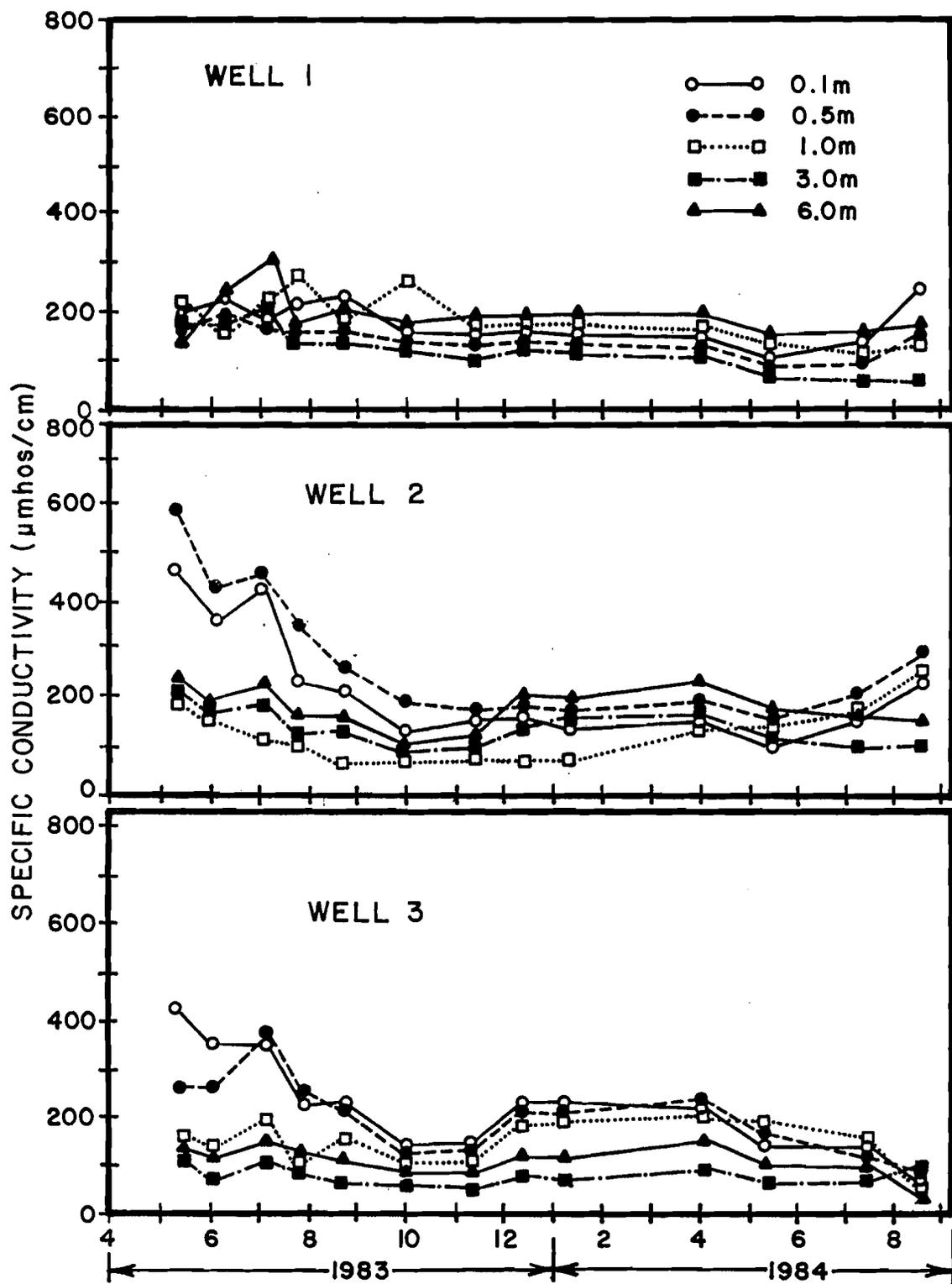


Figure 5-3. Field Measurements of Specific Conductivity at Various Depths in Monitoring Wells at the Maitland Interchange.

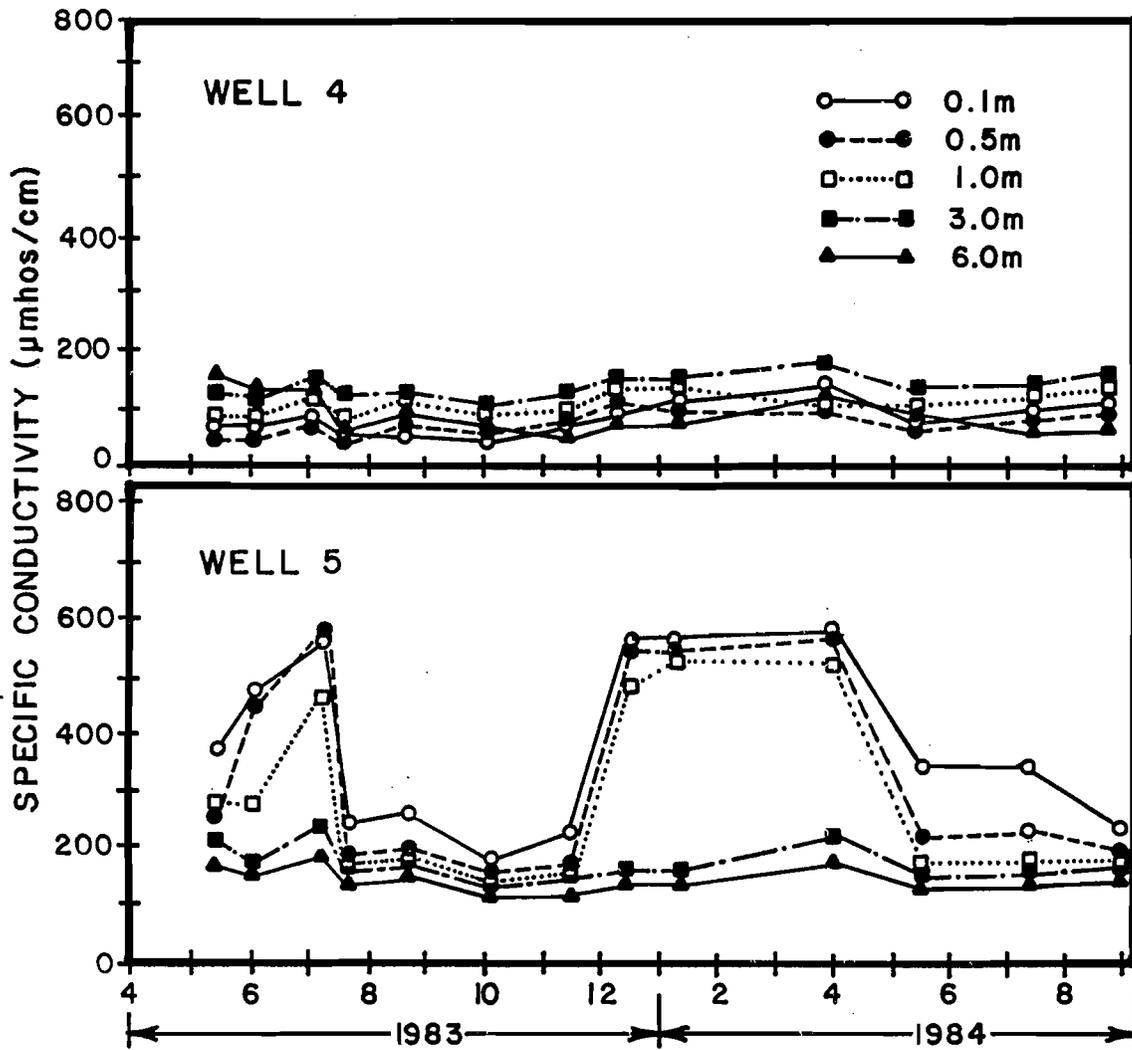


Figure 5-3 (continued). Field Measurements of Specific Conductivity at Various Depths in Monitoring Wells at the Maitland Interchange.

fills up the initial bore hole during drilling before the first casing section is inserted. This water and mud is then transported to soils at lower depths by the drilling process where it slowly migrates away with the groundwater flow. Bore holes constructed in areas with a dry surface layer are affected only by groundwater seepage into the hole, and are able to recover to undisturbed groundwater quality relatively quickly. However, in spite of the fact that monitoring wells constructed in wet areas were subjected to an initial disturbance, dissipation of this disturbance was relatively rapid, with constant values measured after 60-90 days.

In general, the multi-port monitoring wells used in this research appear to be very well suited for applications involving monitoring of heavy metals. The sample collection technique of slowly pumping the samples through inert teflon tubing is clearly superior to techniques such as bailing or submersible well pumps since both contamination and de-gassing of the samples are eliminated. The sample collection technique used in this research also allowed the possibility of pumping the samples through a monitoring cell for instantaneous measurements of parameters such as pH, redox potential, and dissolved oxygen which are subject to almost instant change when exposed to air. The sample collection technique also allows for sample collection from exactly the same locations on each sample date which minimize sources of variability in the data.

Predictive Relationships for Heavy Metal Concentrations in Groundwaters

Regression analyses were conducted as described previously to investigate predictive relationships between concentrations of dissolved heavy metals in groundwater and other common ions. For these analyses, concentrations of heavy metals measured in each of the five wells and at each of the five sample ports were combined into one data set along with simultaneous field measurements of parameters such as specific conductivity, temperature, pH, and redox potential, as well as laboratory analyses of alkalinity, NH_3^+ , NO_2^- , NO_3^- , dissolved orthophosphorus, Ca^{+2} , Mg^{+2} , Na^+ , SiO_2 , O_2^{+2} , K^+ , Cl^- , SO_4^{-2} , and humic acids. Characteristics of this data set with all monitoring wells and sample ports combined are given in Table 5-12. The purpose of these regression analyses was to examine general predictive relationships between dissolved concentrations of metals in groundwater and concentrations of other groundwater constituents to aid in prediction of conditions or ions which may affect the solubility of certain metal species. The results of these analyses are summarized in Table 5-13.

The predictive variables listed in the "best fit" equations were able to explain approximately 90 percent of the variability in concentrations of dissolved lead, approximately 60 percent of the variability for iron, 50 percent of the variability for cadmium, zinc, copper, aluminum, nickel, and chromium, and about 30 percent of the variability for manganese. As a result, the predictor variables tested in these regression analyses appear to be important

TABLE 5-12

CHARACTERISTICS OF THE COMBINED DATA SET FOR
ALL MONITORING WELLS USED IN REGRESSION ANALYSES

PARAMETER	MEAN VALUE	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	NO. OF OBS.
<u>Dissolved Metals ($\mu\text{g/l}$)</u>					
Cadmium	1.96	2.17	0.5	12	92
Zinc	31.8	26.1	0.5	92	92
Manganese	49.5	42.0	1.0	196	92
Copper	15.3	19.0	0.5	85	92
Aluminum	275	335	3.0	1768	91
Iron	783	1143	8.0	5605	92
Lead	26.1	22.2	0.5	110	92
Nickel	2.56	2.13	0.5	12	92
Chromium	2.90	2.66	0.5	12	92
Conductivity ($\mu\text{mho/cm}$)	169	109	35	546	92
Temperature ($^{\circ}\text{C}$)	23.2	2.9	17.5	27.9	92
pH	4.89	-	4.12	6.58	92
ORP (mv)	386	95	195	656	92
Alkalinity (mg/l)	43.9	63.5	0.0	289	92
$\text{NH}_3\text{-N}$ ($\mu\text{g/l}$)	196	277	5	1804	92
$\text{NO}_3\text{-N}$ ($\mu\text{g/l}$)	320	576	5	2403	92
Dissolved P ($\mu\text{g/l}$)	27	22	1	110	92
Cl (mg/l)	7.1	4.8	0.9	22.3	92
$\text{SO}_4\text{-S}$ (mg/l)	18.0	27.0	0.6	248	92
Humic Acids (mg/l)	6.4	7.7	0.3	40.0	92

TABLE 5-13

SUMMARY OF REGRESSION STATISTICS FOR RELATIONSHIPS BETWEEN DISSOLVED METAL CONCENTRATIONS IN GROUNDWATERS AND OTHER CHEMICAL PARAMETERS

METAL (Y)	"BEST FIT" EQUATION	R ²	MEAN VALUE OF (μ)	UNIT LENGTH STANDARDIZED "BEST FIT" EQUATION	NUMBER OF OBS. IN MODEL
Cd	Y = -5.95 + 0.00271 (COND) + 0.265 (TEMP) + 0.00110 (NO ₃) + 0.0288 (PO ₄)	0.539	1.77	Y = μ + 0.165 (COND) + 0.430 (TEMP) + 0.352 (NO ₃) + 0.374 (PO ₄)	95
Zn	Y = 24.39 - 0.133 (COND) + 0.0879 (ORP) + 0.138 (ALK) + 0.026 (NH ₃) - 0.755 (PO ₄) + 0.821 (HUMIC)	0.445	31.8	Y = μ - 0.556 (COND) + 0.321 (ORP) + 0.337 (ALK) + 0.276 (NH ₃) - 0.647 (PO ₄) + 0.243 (HUMIC)	95
Cu	Y = 131.2 - 3.66 (TEMP) + 0.00415 (NO ₃) - 0.521 (X1) - 5.79 (pH)	0.450	12.9	Y = μ - 0.657 (TEMP) + 0.149 (NO ₃) - 0.156 (Cl) - 0.208 (pH)	95
Al	Y = 869 + 0.722 (COND) - 195.2 (pH) + 11.2 (SO ₄) + 22.8 (HUMIC)	0.518	301	Y = μ + 0.209 (COND) - 0.298 (pH) + 0.334 (SO ₄) + 0.716 (HUMIC)	93
Fe	Y = 3973 + 1.96 (COND) - 754.0 (pH) - 0.567 (NO ₃) + 103.7 (HUMIC)	0.636	925	Y = μ + 0.146 (COND) - 0.303 (pH) - 0.224 (NO ₃) + 0.833 (HUMIC)	97
Pb	Y = -4.22 + 0.0486 (COND) + 0.017 (ORP) + 0.285 (ALK) + 0.00623 (NO ₃)	0.895	22.9	Y = μ + 0.235 (COND) + 0.078 (ORP) + 0.741 (ALK) + 0.164 (NO ₃)	90

TABLE 5-13 -- CONTINUED

METAL (y)	"BEST FIT" EQUATION	R ²	MEAN VALUE OF (μ)	UNIT LENGTH STANDARDIZED "BEST FIT" EQUATION	NUMBER OF OBS. IN MODEL
Ni	Y = 9.06 - 1.21 (pH) - 0.005 (ORP) + 0.0182 (ALK) + 0.000765 (NO ₃)	0.442	2.28	Y = μ - 0.416 (pH) - 0.279 (ORP) + 0.673 (ALK) + 0.257 (NO ₃) +	95
Cr	Y = 4.12 - 0.655 (pH) + 0.032 (ALK) + 0.0202 (PO ₄)	0.503	2.37	Y = μ - 0.176 (pH) + 0.763 (ALK) + 0.218 (PO ₄)	89
Mn	Y = 32.4 + 0.127 (COND) - 0.0527 (ORP) + 0.370 (SO ₄) + 0.557 (HUMIC)	0.287	44.9	Y = μ + 0.428 (COND) - 0.156 (ORP) + 0.313 (SO ₄) + 0.200 (HUMIC)	94

in predicting concentrations of dissolved lead in groundwaters, while the same predictor variables play a much smaller role in regulating groundwater concentrations of the other metals.

Concentrations of heavy metals in groundwaters were found to be predominantly influenced by a relatively small number of other parameters. Decreases in pH values were found to increase concentrations of aluminum, copper, iron, nickel, and chromium. However, pH was not found to be an important predictor variable for groundwater concentrations of cadmium and manganese even though these two metals were affected by pH to the largest degree of all metals tested in the incubation experiments. Presumably, groundwater concentrations of these metals are regulated by sediment or soil pH before entering groundwaters. Increases in alkalinity were important in predicting increases in zinc, lead, nickel, and chromium. Humic acid was found to increase concentrations of zinc, aluminum, iron, and manganese, while increases in phosphate were found to increase concentrations of cadmium, zinc, nickel, and chromium. The presence of other ions such as chlorides, nitrates, or sulfates which have the potential of forming soluble metal complexes were found to increase solubilities of heavy metals, especially cadmium, zinc, copper, aluminum, iron, lead, nickel, chromium, and manganese.

Effects of the West Pond on Underlying Groundwaters

A comparison of dissolved concentrations of heavy metals in the Maitland pond water with groundwater collected beneath the pond, represented by wells 2 and 3 combined, is given in Table 5-14. In general, concentrations of all heavy metals measured, except copper, were greater beneath the pond than within the pond. For certain heavy metals such as zinc, manganese, aluminum, and iron, measured concentrations in groundwaters were from 5 to 75 times as great as measured concentrations in the pond water. However, in spite of increased metal concentrations beneath the pond, the sediments are clearly the primary sink for heavy metals.

As indicated in Table 4-17, all heavy metals tested were released as soluble ions from the pond sediments under current simulated conditions of pH in the incubation experiments to at least a small degree. This release is also apparent in Table 5-14, since most metals appear to have larger concentrations in the groundwater phase than in the pond water. However, even though all metals were found to be released in the incubation experiments to some degree, nickel, chromium, and copper were found to be released in substantially lower quantities than the other metals. This tendency is also apparent in Table 5-14 where nickel, chromium, and copper are shown to have similar concentrations in the groundwater phase and in the pond water.

The release of cadmium, zinc, manganese, iron, and aluminum from the sediment phase to the groundwater phase under current

TABLE 5-14
 COMPARISON OF DISSOLVED CONCENTRATIONS OF HEAVY METALS IN THE POND WATER
 WITH GROUNDWATER COLLECTED BENEATH THE POND IN WELLS 2 AND 3

HEAVY METAL	AVERAGE DISSOLVED CONCENTRATION IN POND ($\mu\text{g/l}$)	AVG. CONC. IN 0-1 cm SEDIMENT LAYER ($\mu\text{g/l}$)*	AVERAGE CONC. IN GROUNDWATER BENEATH THE POND					RATIO OF G.W. CONC. AT 0.1 m TO AVG. POND WATER
			0.1 m	0.5 m	1.0 m	3.0 m	6.0 m	
Cd	0.73	1,015	1.48	2.06	1.50	1.17	1.00	2.03
Zn	4.82	20,938	22.9	18.5	18.8	19.1	19.5	4.75
Mn	4.47	20,246	53.3	44.2	23.3	78.9	70.2	11.92
Cu	14.4	8,809	9.40	10.3	9.12	11.7	13.1	0.65
Al	57.9	22,949,100	709	742	192	89.2	543	12.25
Fe	18.4	2,100,285	1354	834	766	797	1912	73.6
Pb	15.0	51,977	24.4	24.8	20.5	11.2	10.9	1.63
Ni	1.62	7,610	2.88	2.63	1.98	1.94	2.13	1.78
Cr	2.18	20,615	3.02	4.15	2.60	1.29	1.54	1.39
pH	7.46		5.75	5.92	5.17	4.86	4.56	

* Average sediment concentration per liter of sediment.

conditions of sediment pH as measured in the incubation experiments is apparent also in Table 5-14. The largest measured releases in the incubation experiments under conditions of no pH control were noted for aluminum and iron which have the highest concentrations in groundwater of any metals. Manganese, which was also found to be released under current pH conditions, has a calculated concentration ratio similar to that of aluminum. As indicated in Table 4-17, zinc was released in amounts approximately twice that of cadmium under current conditions. This tendency is readily apparent in Table 5-14 where the concentration ratios for cadmium is approximately twice that of zinc.

According to the calculated concentration ratios of the groundwater to the pond water, the following order can be suggested for the relative release potential under current sediment conditions of heavy metals from the pond sediments:

Least		Most
Mobile:	Cu < Cr < Pb < Ni < Cd < Zn < Mn = Al < Fe:	Mobile

This order is very similar to the absolute order of release predicted by the incubation investigations with no pH control summarized in Table 4-17.

As indicated in Figure 2-11, the sediments of the Maitland pond are generally aerobic in the top few centimeters and anaerobic, or reduced, below this depth. The three metal species which exhibited the greatest release potential (manganese, aluminum, and iron) were

all less soluble in the incubation experiments under oxidized conditions and considerably more soluble under reduced conditions. As the metal species migrate downward and reach reduced sediments, they become solubilized and large sediment accumulation cannot develop. This in turn causes the rapid attenuation in sediment concentrations reported previously. Concentrations of copper, chromium, and lead (which had less attenuation in the sediment phase) were also found to have the least potential for release into the aqueous phase since they apparently remain stable at lower reduced depths and accumulate rather than release into groundwater. Therefore, it appears that metal species which exhibit the greatest attenuation in the sediment phase may do so because metals are being released at the lower depths.

The effects of heavy metals on groundwater concentrations were further investigated by examination of ratios of average pond concentrations of heavy metals to groundwater concentrations at various depths beneath the pond in wells 2 and 3. These ratios are summarized in Figure 5-4. Ratios greater than one indicate groundwater concentrations which are greater than pond concentrations, while ratios less than one indicate pond concentrations which are less than groundwater concentrations.

As indicated previously, mean concentrations of copper were lower within the pond than in groundwaters beneath the pond. Ratios of groundwater concentrations of copper to pond concentrations were

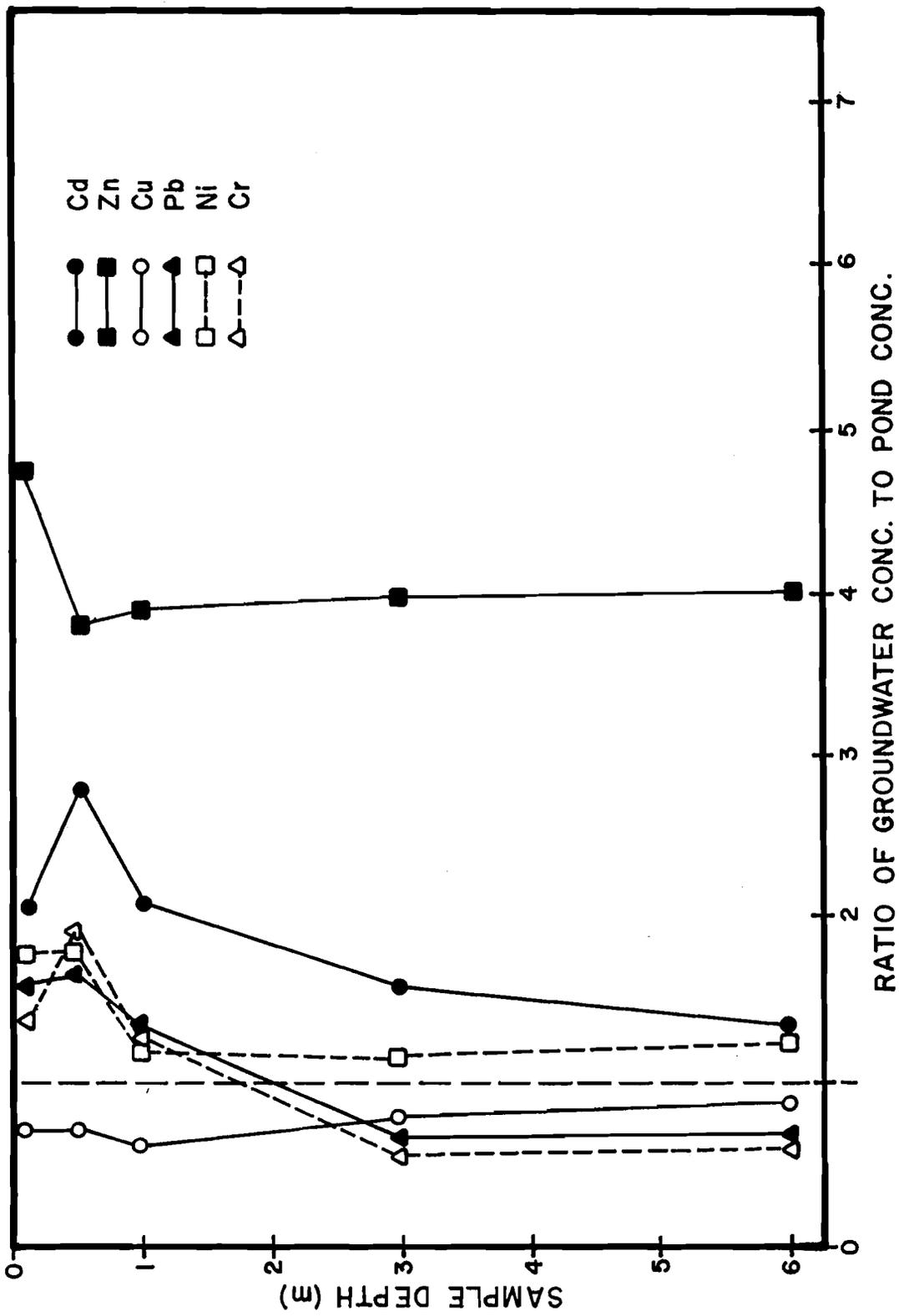


Figure 5-4. Ratios of Groundwater Concentrations of Heavy Metals Beneath the Pond Water Concentrations.

less than one at all sample depths. Concentrations of cadmium, lead, nickel, and chromium were all found to be higher in groundwaters than in the pond, up to a depth of approximately 1 m. Concentrations of each of these metals reached a peak at a depth of approximately 0.5 m beneath the pond, then exhibited a slow decline with increasing depth. Groundwater concentrations of lead and chromium reached levels less than the pond concentrations at depths below 1 m. Nickel was found to also reach a minimum value at a depth of one meter, although it remained slightly higher in concentration than the pond water. Cadmium, after reaching a peak concentration at a depth of 0.5 m, began a gradual decline with increasing depth and appeared to still be declining at the lowest sample depth of 6 m.

The trends for lead and cadmium presented above can be explained easily by the discussions given previously for the speciation of cadmium and lead in sediments. Both of these metals exhibited exchangeable fractions near 50 percent. It was concluded by many researchers that lead was very reactive in exchange reactions and was capable of forming very strong associations with soils and sediments while cadmium was not. The strong affinity of lead for the sediment phase is apparently why aqueous lead concentrations decrease rapidly with increasing depths, and cadmium concentrations, which are attracted to soils by weaker exchange reactions, are capable of traveling further through the soil.

Concentrations of zinc ions were approximately four times higher in the groundwater than in the pond. Maximum concentrations were found at the surface with a constant concentration below 1 m. No apparent uptake of zinc ions was observed over the entire measured distance of 6 m. This behavior is explained well by the relatively good mobility of zinc in the aqueous phase.

Ratios of groundwater concentrations of aluminum, manganese, and iron to pond concentrations are examined in Figure 5-5. Since each of these elements are abundant in natural soils, it is difficult to associate elevated concentrations in groundwaters solely to leaching of metals from the pond sediments. However, elevated concentrations of these metals were observed beneath the pond, followed by a decline between 0.5 and 1.0 m. Concentrations appear to increase again after the 3.0 m depth. However, it is unreasonable to assume that this increase is related to the retention pond.

As a final comparison of pond concentrations with groundwater concentrations, a series of analysis of variance procedures were conducted. These analyses compared concentrations of heavy metals in the pond with concentrations in wells 2 and 3 combined. The analysis of variance procedure was conducted for each sample depth separately to determine the extent of the vertical differences between the pond and groundwaters.

Concentrations of all heavy metals measured (except copper and chromium) were significantly higher in groundwater collected at the

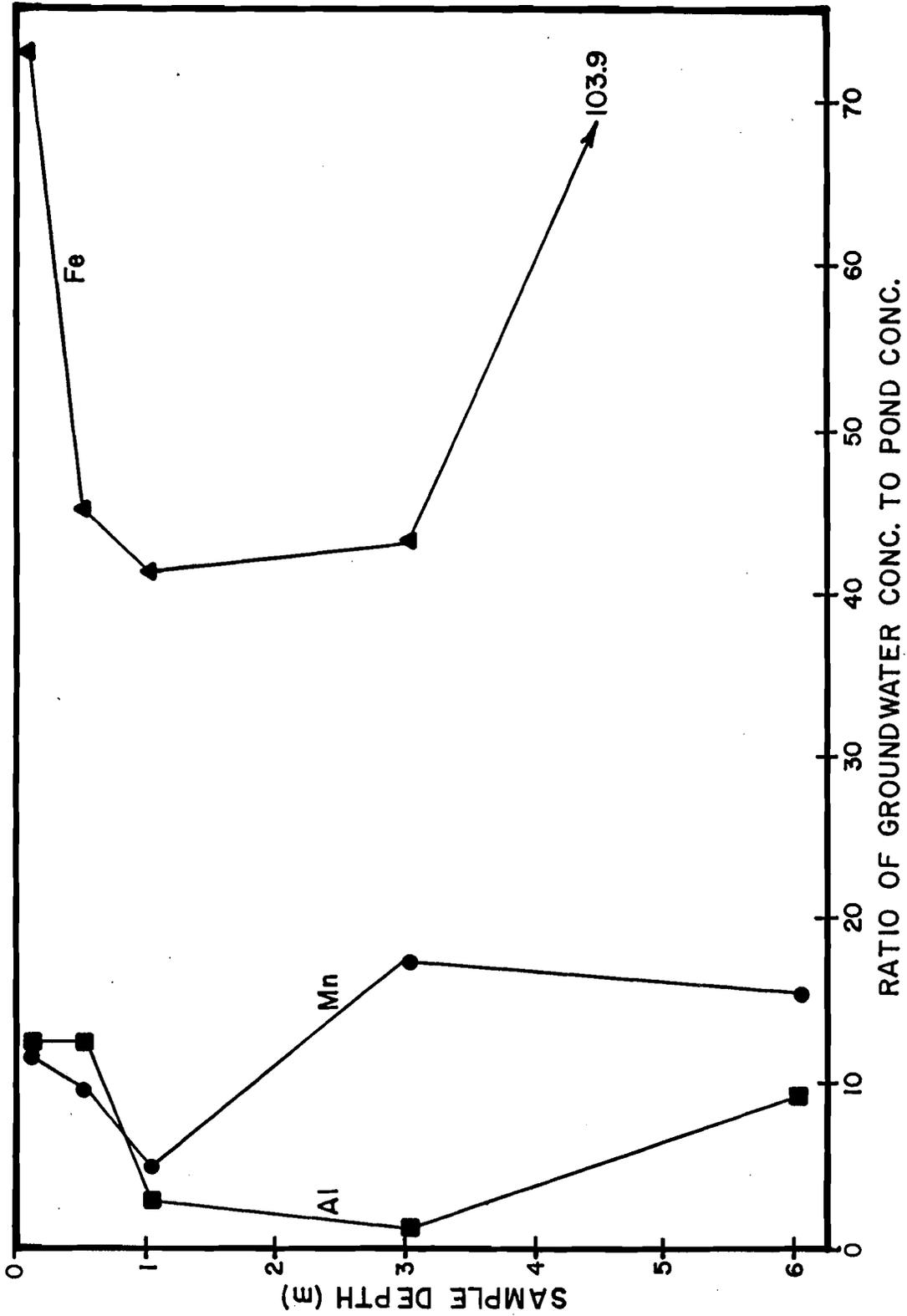


Figure 5-5. Ratios of Groundwater Concentrations of Aluminum, Manganese, and Iron Beneath the Pond to Pond Water Concentrations.

0.1 m depth than in the pond. Most of these differences were significant at the 0.001 level or better. A significant difference was also noted for copper except that pond concentrations were found to be significantly larger than well concentrations at 0.1 m.

Comparisons of pond concentrations with groundwater concentrations for samples collected at the 0.5 m sample depth indicated significant differences for all of the metals tested except copper. In each case where significant differences occurred, groundwater concentrations were greater than pond concentrations with a significance level for most metals of 0.01 or better with many in excess of 0.001.

When comparisons were conducted using groundwater concentrations at the 1.0 m level, nickel and chromium were no longer found to be significantly different. Apparently, the extent of groundwater leaching of these two metals does not extend to this level. However, all of the other heavy metals were found to be significantly different from the pond concentrations, with groundwater concentrations generally several times greater than pond concentrations. Copper was again found to be significantly greater in the pond than in groundwater.

Comparisons of pond water and groundwater collected at the 3.0 m level were somewhat different than those observed at the upper sample ports. Significant differences were observed between pond water and groundwater for all metals except copper and nickel.

However, lead and chromium were found to be higher in the pond than in groundwater. Apparently, the vertical extent of the migration of lead ions in the aqueous phase was reached at this depth.

The final comparison was conducted between pond water concentrations and groundwater concentrations at the 6.0 m level. At this depth only zinc, manganese, aluminum, iron, and lead were found to have significant differences with zinc, manganese, aluminum, and iron higher in groundwater and lead higher in the pond water. The vertical extent of the migration of cadmium appears to have been reached by this depth.

In summary, comparisons of concentration ratios between pond water and groundwater were combined with a series of analysis of variance procedures comparing pond concentrations with groundwater concentrations to evaluate the effects of the West Pond on underlying groundwaters. The calculated concentration ratios indicate that all metal species tested (except copper) have a greater affinity for the groundwater phase than the pond phase and are leaching into groundwaters to some degree. Analysis of variance procedures were used to estimate the vertical extent of the migration of heavy metals in the aqueous phase. Zinc, manganese, aluminum, and iron were significantly higher in groundwaters than in the pond at all depths tested. The extent of significantly higher concentrations of lead extended to the 1-3 m depth while nickel, cadmium, and chromium extended to the 0.5-1.0 m range. Copper was found to be significantly higher in the pond water than in

groundwater in all analyses. Average concentrations of zinc, manganese, aluminum, and iron were found to be 4, 12, 8, and 50 times greater, respectively, in groundwater than in the pond water.

Comparisons of Groundwater Concentrations
Beneath Pond, Swale, and Control Areas

A comparison of heavy metal concentrations in swale, pond, and control areas was conducted by grouping wells 1 and 5 into a general category of "swale" areas, wells 2 and 3 into a "pond" category, and Well 4 as the "control". An analysis of variance procedure was conducted with all sample ports combined. The results of these analyses were presented in Table 4-21.

All heavy metals tested exhibited significant differences at the 0.05 level between the three well types except nickel and copper. For each metal that exhibited a significant difference, groundwater concentrations beneath swale areas were the highest. Concentrations of aluminum, iron, lead, and chromium beneath swale areas were found to be approximately twice the measured concentrations beneath the pond and approximately 3 to 10 times higher than concentrations in the control well. For all metals, except zinc, the pond groundwater concentrations were second in magnitude behind the swale areas. The control areas were generally lower in concentration and statistically different from the other well types.

The data presented in Table 4-21 indicates that for most metals (with the exceptions of nickel and copper), swale areas are less

efficient in retaining heavy metals in the upper soil layers than the retention pond, and as a result, metals tend to enter groundwaters beneath these areas in greater concentrations. Manganese, aluminum, iron, lead, and chromium appeared to accumulate in groundwaters beneath swale areas to a larger degree than the other metals. This data suggests that copper may be held more tightly in the swale soils than manganese, aluminum, iron, lead, or chromium.

The order of suggested attenuation or release potential is very similar to the relative release potential of heavy metals from the pond sediments observed in the incubation experiments. In these experiments, copper was found to be released to the least degree while manganese, aluminum, and iron were released to the greatest degrees. A possible explanation for the apparent lower affinity of swale soils for heavy metals may involve the retention time of metals in the system. Runoff water entering swale areas generally infiltrates relatively rapidly. This type of movement does not allow adequate time for processes such as the formation of iron or manganese oxides, or organic complexation to occur to a large degree. In addition, metals infiltrating through a retention pond sediment generally travel very slowly through the top sediment layer where the abundance of reactive species makes reaction more likely. As a result, removal of heavy metals in swale areas may be dominated by more rapid processes such as adsorption or ion exchange, rather than slower processes such as bonding to Fe/Mn oxides or organic

complexation. Rapid processes are apparently less efficient than those which occur over time in the sediments of a retention basin.

In summary, it appears that all heavy metals tested (with the exceptions of copper and nickel) are significantly higher in concentration beneath swale areas than beneath retention ponds. For manganese, aluminum, iron, lead, and chromium, the increases beneath swale areas are more significant than for the remaining metals. It is suggested that the relatively rapid infiltration rates through the swale areas and the resulting short contact time with soil particles combine to produce a lower removal efficiency into the solid phase in swale areas than in retention ponds where diffusion and transport are very slow.

Comparison of Heavy Metal Concentrations in Groundwaters Beneath Wet and Dry Swale Areas

The experimental design at the Maitland Interchange allowed comparison of heavy metal concentrations beneath both "wet" and "dry" swale areas. The dry swale area, located at Well 1, was an area which was observed to drain completely between rain events. The soil type was largely fine sand with a small surface silt layer. The wet swale area, located at Well 5, was in a low area which was observed to be continuously either wet or submerged with several inches of water. Soils in this area were very silty and loose.

Significant differences (see Table 4-22) were observed between the two wells for manganese, aluminum, iron, and lead. Manganese,

aluminum, and iron were all higher in groundwaters beneath the wet swale area, while lead was higher beneath the dry swale area.

These results appear to follow exactly the pattern of metal behavior predicted by the incubation experiments. The wet swale area was characterized by an accumulation of organic matter, and was most likely lower in both pH and redox potential in the surface soils than the drier swale area. As indicated in Figures 4-8 and 4-9, manganese, iron, and aluminum are all released in large amounts under reduced conditions at pH values in the neighborhood of 5.0. However, as indicated in Figure 4-10, lead is more soluble under oxidized conditions which were presumably present in the dry swale area. It should be noted that the wet swale area was located in an area which received highway runoff characterized by a much larger traffic volume than the dry swale area. This increase in traffic could be responsible for the elevated concentrations of manganese, aluminum, and iron measured in groundwaters beneath this site. However, lead is generally considered to be an indicator metal for runoff contamination, and lead was in groundwaters beneath the lower traffic dry swale area. The fact that lead is substantially lower in groundwaters beneath the wet area in spite of the increased traffic adds further support to the theory that the swale areas and surface soils are retaining lead to different degrees.

Although lead was shown to be slightly more soluble under oxidized conditions, the increased concentrations of lead beneath the dry swale area are perhaps more than can be explained by this

small increase in solubility. The better retention of lead in wet swale areas may be related to the speciation of lead in highway runoff. It was suggested previously that lead exhibits a large exchangeable fraction in runoff as well as in sediments. Exchange reactions are favored in quiescent environments where contact opportunities between ions and soil particles are maximized. The slow infiltration characteristic of the wet area would provide much more contact time than a relatively rapidly infiltrating "dry" swale.

In summary, the release of heavy metals into underlying groundwaters appears to be different for certain metal species in dry swale areas than in wet swale areas. Under wet, reduced conditions, aluminum, manganese, and iron are released into groundwaters to a significantly greater degree than in a dry oxidized area. However, lead was found to be released into groundwaters to a greater degree in dry swale areas than in wet swale areas. It is believed that slower infiltration rates combined with increased opportunities for exchange reactions in the wet area favor retention of lead in the sediments. These results agree closely with the results of the incubation experiments.

Transport of Heavy Metals In Groundwater Flow

One of the objectives of this research was to monitor groundwater concentrations and flow patterns and to detect, if possible, the movement of heavy metals which leach into

groundwaters. To aid in this detection, piezometers were installed at each well and a record of piezometric surface was made approximately on a bi-weekly basis during 1983. The average measurements are given in Table 5-15.

TABLE 5-15
AVERAGE MEASUREMENTS OF PIEZOMETRIC SURFACE
AT MONITORING WELLS AT THE MAITLAND INTERCHANGE DURING 1983

LOCATION	PIEZOMETRIC SURFACE (m, MSL)
Well 1	27.35
Well 2	27.38
Well 3	27.37
Well 4	27.26
Well 5	26.87
Pond	27.38

As indicated in Table 5-15, the piezometric surface in wells 1, 2, and 3, as well as the retention pond were very close, with a mean value during 1983 of 27.37 m. The control well (Well 4) and Well 5 in the wet swale area were lower in piezometric surface, and presumably groundwater movement in the area was to the east-northeast (Figure 3-1). Heavy metals leaching into groundwaters in significant amounts at wells 1, 2, or 3 could then

be detected, assuming that adsorption or uptake on soil particles had not occurred at Well 5.

The velocity of groundwater flow can be estimated using Darcy's Law. The hydraulic gradient for the area can be calculated using the difference in piezometric surface between wells 1, 2, and 3, and Well 5, assuming an average distance between Well 5 and the other wells of 160 m. The hydraulic conductivity, K, can be estimated, assuming a silty sand soil, as approximately 5 m/day. The approximate velocity would then be:

$$v = K \frac{H}{L}$$
$$= \left(\frac{5 \text{ m}}{\text{day}} \right) \left(\frac{27.37 - 26.87 \text{ m}}{160 \text{ m}} \right) = 0.02 \text{ m/day}$$

At this relatively slow flow rate, the groundwater would move approximately 7.3 m/year, and a total of approximately 60 m in the eight-year history of the West Pond. As a result, the groundwater flow has probably not reached Well 5, and measurements of elevated concentrations, if they were present, are not possible at this time. The slow movement of groundwaters in this area provides a good environment for readsorption of released metals to occur, and probably decreases the potential for transport of these metals over longer distances.

Records of piezometric surfaces in the monitoring wells during 1983 indicate that the relative differences between the various

wells was fairly constant. This suggests that the velocity of horizontal groundwater movement does not change substantially during the year and probably remains near the calculated slow velocity. However, vertical fluctuations of piezometric surface were fairly large even though the different piezometers maintained their relative differences. Piezometric surfaces varied by as much as 0.8 m throughout the measurement period. Often these fluctuations would occur rapidly, particularly increases following long antecedent dry periods. It appears, therefore, that the predominant pattern of water movement in this area is an up and down vertical movement. Since very little horizontal movement is thought to occur, the elevated concentrations of heavy metals measured beneath the pond and swale areas could be a result of accumulations over a period of years, rather than representing the actual concentrations which leach continuously. Although groundwater concentrations of almost every metal measured in this study were shown to be substantially higher in groundwater, there is little evidence that the concentration plume is moving, and the contamination appears to be very localized.

The hydrologic conditions present at the Maitland site are similar to conditions at many other sites in the Central Florida area. It seems reasonable to assume that migration of metals into groundwaters at other sites would also remain relatively localized as long as the horizontal gradients remain small. As a result, it appears very unlikely that heavy metals from retention ponds along

highway systems in the Central Florida area will pose a pollution hazard. However, systems constructed in areas with a substantial horizontal groundwater gradient or in areas where direct contact with either shallow or deep aquifers can occur may allow transport of metals away from the site to other areas. Further research is needed in this area to define the extent and magnitude of the potential problem, if any.

CHAPTER 6

SUMMARY AND CONCLUSIONS

On a nationwide basis, the two most commonly used techniques for management of highway runoff are roadside swales and detention/retention facilities. As these facilities receive continual inputs of stormwater containing heavy metals, processes such as precipitation, coagulation, settling, and biological uptake will result in a large percentage of the input mass being deposited into the sediments. However, no previous definitive studies have been conducted to determine the fate of toxic species, especially heavy metals, in these stormwater management systems. In particular, no studies have been conducted to investigate if physical and chemical changes which may occur in these systems over time may mobilize certain species from the sediment phase back into the water phase.

The purpose of this research was to investigate the fate of heavy metals within stormwater management systems. The site selected for these investigations was a series of stormwater management facilities located at the Maitland Interchange on Interstate 4 north of the city of Orlando, Florida. A retention pond (West Pond) with relatively defined inputs and outputs was chosen as the primary study site. The West Pond originated as a borrow pit and has a triangular shape with an approximate surface area of 1.3 ha and an average depth of 1.5 m.

Characteristics of Highway Runoff

Automatic refrigerated sequential sampling equipment was used to collect highway runoff samples from the primary input into the pond. Flow weighted composite stormwater samples were collected with the automatic sampler over a 13-month period from 15 separate storm events, representing a wide range of rainfall intensities and antecedent dry periods. Depth composite surface water samples were also collected periodically at five stations within the West Pond. Both stormwater and pond samples were analyzed for dissolved and total forms of heavy metals.

Measured concentrations of heavy metals in highway runoff collected at the Maitland Interchange during 1983-84 showed considerable variability between storm events as well as during storm events. Average dissolved concentrations of all heavy metals, with the exceptions of iron and aluminum, were less than 70 $\mu\text{g/l}$, with nickel, chromium, manganese, and cadmium less than 3 $\mu\text{g/l}$. Measured mean concentrations of total metal species were in excess of 100 $\mu\text{g/l}$ for lead, aluminum and iron, while nickel, chromium, manganese, and cadmium were all present in average total metal concentrations of 10 $\mu\text{g/l}$ or less.

Of the heavy metals which were measured, the following orders were observed for mean concentrations of dissolved and total metal species:

Dissolved: Al > Fe > Zn > Pb > Cu > Mn > Ni = Cr > Cd

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

However, the metal species, aluminum, iron and manganese are common constituents of soils and may not be correlated with vehicle usage and highway operation, as would be expected for lead, nickel, chromium, copper, zinc, and cadmium. The most common vehicle related heavy metals found in highway runoff at the Maitland site were lead, zinc, and copper in ratios of 4.70:1.91:1.0, respectively, for total concentrations, and ratios of 0.85:1.04:1.0, respectively, for dissolved species. Together these three metals accounted for approximately 91 percent of the dissolved heavy metals present and 94 percent of the total metal concentrations, excluding aluminum, iron and manganese.

Concentrations of heavy metals measured in highway runoff at the Maitland site were found to be substantially lower than those measured by other researchers from northern urban highways with comparable average daily traffic and was similar to a rural Harrisburg highway location. It was suggested that the differences may be linked to the abundance of rainfall at the Maitland site which keep road surfaces relatively clean, the increased industrial activities and particulate emissions associated with the northern sites, and the use of salt to de-ice roadways in the northern locations during the winter months.

Another obvious characteristic of the highway runoff collected at the Maitland site is the large variation in the mean percentage

of dissolved species measured for the various metals. The heavy metals can be divided into three general groups according to the dissolved fractions present: metals with dissolved portions of less than 25 percent (including lead, iron, aluminum, and manganese), metals with dissolved portions of approximately 50 percent (including zinc and chromium), and metals with dissolved fractions near 75 percent (including copper and cadmium).

Although modeling of runoff characteristics was not intended during this research, it appears, for the limited number of storm events monitored, that average flow-weighted concentrations approximated a log-normal distribution. This suggests that the majority of events are represented by a relatively low concentration of dissolved and total species with more concentrated events making up a much smaller percentage of the total runoff events.

A "first flush" effect was observed for total concentrations of lead, zinc, iron, and aluminum. In general, approximately 50 percent of the total mass of these metals was found to be transported during the first quarter of a storm event, 25 percent during the second quarter, and the remaining 25 percent divided between the third and fourth quarters. This trend was not observed for total concentrations of the other metal species or for dissolved species of any measured metals.

Attempts to correlate the measured variabilities in heavy metal concentrations both within storm events and between storm events with other runoff related characteristics such as flowrate, antecedent dry period, cumulative rain event time, runoff pH,

rainfall duration and rainfall intensity showed little success. Runoff flowrate appeared to be somewhat important in regulating concentrations of virtually all metals, while cumulative time and antecedent dry period were important in regulating only a few metal species. These findings emphasize the poorly understood phenomena which regulate runoff characteristics and suggest that further research is necessary in this area.

Fate of Heavy Metals in Retention/Detention Systems

Although stormwater inputs into the pond were characterized by a considerable degree of variability, heavy metal concentrations measured in the pond were, in general, relatively consistent and low in value. Dissolved concentrations of all metal species in the pond with the general exception of aluminum, were never found to exceed 50 $\mu\text{g/l}$ with dissolved concentrations of cadmium, zinc, manganese, nickel, and chromium rarely exceeding 10 $\mu\text{g/l}$. Total metal concentrations followed a similar pattern with only manganese, aluminum, iron, and on one occasion lead, exceeding 100 $\mu\text{g/l}$ on any given sample day at any of the five sampling stations.

The Maitland pond was found to be very effective in removal of heavy metal inputs from highway runoff. Particulate species of heavy metals were found to be removed to a larger degree than dissolved species. Particulate species of lead and zinc are removed in excess of 95 percent, cadmium and iron near 85 percent, with copper and aluminum averaging near 75 percent. Reductions of

particulate nickel and chromium, however, were much less, with a removal of only 25-35 percent.

Dissolved forms of zinc were removed to the greatest degree with an average removal of almost 90 percent. Dissolved iron was removed at an efficiency of 75 percent, followed by lead, copper, aluminum, and cadmium with removals of dissolved species ranging 50-60 percent. Removal efficiencies for dissolved nickel and chromium were very poor, with removals of only 36 and 12 percent respectively. Those metals which were present with large fractions of reactive species (such as zinc, cadmium, and lead) were found to be removed efficiently. Other metal species which were not present as reactive species or were bound to organics were removed to a lesser degree. Although not specifically investigated in this research, uptake and concentration of heavy metals in aquatic plants and algae appears likely. Studies by other researchers as well as observations during this research suggest that the removal of dissolved metal species is rapid with as much as 90 percent removal occurring in four days.

Horizontal Distribution of Heavy Metals in the Maitland Pond Sediments

The horizontal and vertical distribution of heavy metals in the sediments of the West Pond were investigated by collection of a series of 2.5 cm diameter core samples to a depth of approximately 13 cm. Core samples were collected on 10/15/82, 10/15/83, and 4/15/84. On each date, 43 separate core samples were collected in

the West Pond at 7.5 m intervals along 10 transects, and analyzed for heavy metals in five layers: 0-1 cm, 1-3.5 cm, 3.5-6 cm, 6-8.5 cm, and 8.5-13 cm.

Distributions of heavy metals in the top 1 cm of the Maitland pond sediments suggest that upon entering the receiving water body, the majority of heavy metals associated with highway runoff settle out and are deposited near the point of input for the runoff. This tendency was most obvious for lead and zinc which peaked in sediment concentrations at a distance of only 15 m from the inlet followed by a rapid decline in concentrations with increasing distance. Deposition patterns of the other metals measured were much less pronounced than those observed for lead and zinc. Chromium, aluminum, and iron all appeared to reach peak sediment concentrations at a distance of 30 m from the inlet with increases and decreases much less rapid than those observed for lead and zinc. Copper, nickel, and manganese did not appear to exhibit pronounced peaks in sediment concentrations, but seemed to settle out over a longer flow path length. However, in spite of the differences in behavior most of the metals in the runoff water entering the Maitland pond were retained in the pond sediments within a distance of 60-90 m from the stormwater inlet.

Of the four metal species which exhibited the most rapid settling characteristics (lead, zinc, iron, and aluminum), all but zinc had particulate fractions in runoff which were near 80 percent of the total metal measured. The remaining metal species (nickel,

chromium, and cadmium) which did not exhibit pronounced settling characteristics, were all present in highway runoff at the Maitland site predominately in a dissolved form with a small fraction of particulate species.

The results of the horizontal analyses of heavy metals suggest important design parameters for use in the design of retention basins to optimize removal of heavy metals. Designs should provide physical configurations where the flow velocity becomes very small to aid in sedimentation of particles. The distance from points of input to the discharge point from the pond should be maximized, and the design should minimize the possibility of short circuiting and avoid hydraulically dead zones.

Vertical Distributions of Heavy Metals in the Sediments of the Maitland Pond

Measured concentrations of total heavy metals in the sediments of the Maitland pond exhibited highest concentrations in the surface layer with a rapid decline in concentration with increasing depth. The rapid decline in concentrations was found to observe an exponential decay relationship with values of R-square in most cases in excess of 0.90 when fitted to the model: $\ln (C/C_0) = -Kx$ (depth). Values of K, which are a measure of the rate of attenuation in sediment metal concentrations, indicated the following order of attenuation of total heavy metal content in the sediment layers:

to achieve 99 percent reductions in runoff accumulations, based on the calculated regression equations, suggest that sediment concentrations of certain metals may be slowly migrating to lower depths. However, the vertical extent of this sediment-associated migration appears to be limited since all metal species were reduced in concentration by 99 percent within 20 cm or less. These calculations suggest a strong stability of the metal sediment associations since, after eight years of metal accumulations in the Maitland Pond, most metals associated with sediments have remained in top 10 cm of the sediment layer.

Diffusion coefficients were estimated for the runoff related metal sediment associations from a basic mass balance approach. Estimated diffusion coefficients for the movement of sediment associated concentrations were, in general, less than $1 \text{ cm}^2/\text{year}$. This diffusion is much slower than diffusion coefficients for the movement of major groundwater ions such as K^+ and Na^+ .

Current Stability of Metal-Sediment Associations in the Maitland Pond Sediments

The stability of metal-sediment associations was evaluated from the results of several different analyses. First, a sequential extraction procedure was used to determine metal speciation in composite samples of each of the five vertical core layers. Metal speciations were divided into soluble, exchangeable, carbonate bound, bound to Fe/Mn oxides, and organic bound fractions. It is generally believed that the stability of the metal-sediment

associations increases in the same order. Correlations between sediment metal concentrations and sediment concentrations of iron, manganese, and organic content were also examined to aid in describing these associations. In addition, an incubation apparatus was constructed which allowed simultaneous control of pH and redox potential in sediment suspensions to simulate metal adsorption or desorption under various environmental conditions.

The results from the speciation and redox experiments combined with the analyses of the sediment metal concentrations presents evidence that under the current conditions of redox potential and pH within the sediments of the Maitland pond, metal species, with the exceptions of cadmium and manganese, are stable and exist in relatively immobile associations with Fe/Mn oxides and organic matter. The only exception to this appeared to be with lead which is apparently held to a large degree in a strong exchangeable association. Changes in redox potential from strongly oxidized to strongly reduced conditions did not appear to affect the release of metals from the sediments under current pH values of 7.5-8.5. The release of most metals, except cadmium and manganese, from the sediment phase to the water phase was substantially less than 1% of the total metal present even after several weeks of incubation. However, cadmium and manganese appear to be less tightly bound to sediments than other metals. The release of both cadmium and manganese into solution from the sediment phase during incubation was equal to approximately 5% of the total metal present.

Metal associations in the upper sediment layer appear to be largely residual in nature indicating that they have become slowly incorporated into a stable crystal lattice over time. This makes much of the metal mass present in the upper sediments unavailable for release under any natural conditions. This residual fraction was found to decrease with increasing sediment depth. This suggests that metals bound to deeper sediments may be more susceptible to release mechanisms than metals in the surface layer.

Impacts of Stormwater Management Systems on Local Groundwater

Multiport groundwater monitoring wells were installed to depths of 6 m at five locations in the Maitland Interchange in retention pond, swale, and control areas. Groundwater samples were collected on a monthly basis for 16 months from five sample ports on each monitoring well. The multiport monitoring wells used in this research resulted in minimal groundwater disturbance and appear to be well suited for applications involving monitoring of heavy metals.

In general, mean concentrations of all heavy metals measured, except copper, were greater beneath the pond than within the pond. For certain heavy metals such as zinc, manganese, aluminum, and iron, measured concentrations in groundwaters were from 5 to 75 times as great as measured concentrations in the pond water.

Analysis of variance procedures were used to estimate the vertical extent of the migration of heavy metals in the aqueous

phase. Zinc, manganese, aluminum, and iron were significantly higher in groundwater beneath the pond than in the pond at all depths tested. The extent of significantly higher concentrations of lead extended to the 1-3 m depth while nickel, cadmium, and chromium extended to the 0.5-1.0 m range. Copper was found to be significantly higher in the pond water than in groundwater in all analyses. Average concentrations of zinc, manganese, aluminum, and iron were found to be 4, 12, 8, and 50 times greater respectively, in groundwater than in the pond water. Concentrations of cadmium and iron in groundwaters exceeded water quality criteria for Class III waters specified in Chapter 17-3 of the Florida Administrative Code.

However, in spite of the increased metal concentrations beneath the pond, the sediments are clearly the primary sink for heavy metals. Concentration ratios between the pond water and the groundwater indicate that all metal species, except copper, have a greater affinity for the groundwater phase than the pond phase and are leaching into groundwaters to some degree. The order of release potential of heavy metals into groundwater was estimated to be:

Least Mobile: Cu < Cr < Pb < Ni < Cd < Zn < Mn = Al < Fe: Most Mobile

and was found to be inversely related to the order of attenuation for metal species in the sediment phase. The magnitude of the release into groundwaters was found to closely correspond to the

order of release predicted by the incubation experiments conducted under natural conditions of no pH control.

Comparisons of Groundwater Concentrations
Beneath the Pond, Swale, and Control Areas

In general, it was found that all heavy metals tested, with the exceptions of copper and nickel, are significantly higher in concentration beneath swale areas than beneath the retention pond. For manganese, aluminum, iron, lead, and chromium, the increases beneath swale areas are more significant than for the remaining metals. It was suggested that the relatively rapid infiltration rates through the swale areas and the resulting short contact time with soil particles combine to produce a lower removal efficiency into the solid phase in swale areas than in retention ponds where diffusion and transport is very slow.

The release of heavy metals into underlying groundwaters appears to be different for certain metal species in dry swale areas than in wet swale areas. Under wet, reduced conditions, aluminum, manganese, and iron are released into groundwaters to a significantly greater degree than in a dry oxidized area. However, lead was found to be released into groundwaters to a greater degree in dry swale areas than in wet swale areas. It is believed that slower infiltration rates combined with increased opportunities for exchange reactions in the wet area favor retention of lead in the sediments. These results agree closely with the results of the incubation experiments.

Transport of Heavy Metals in Groundwater Flow

As a result of a very small hydraulic gradient, horizontal movement of groundwater in the Maitland area was calculated to be less than 10 m per year. It appears that vertical up and down movement with changes in seasonal water table may be more important than horizontal movement. As a result, the contamination appears to be very localized. Since the hydrologic conditions present at the Maitland site are similar to conditions at many other sites in Central Florida, it appears very unlikely that heavy metals from retention ponds along highway systems in the Central Florida area will pose a pollution hazard to nearby surface and groundwaters.

Potential for Future Mobilization of Heavy Metals from the Maitland Pond Sediments

Natural aging processes within retention ponds as well as lakes result in the increased deposition of organic matter to the bottom sediments primarily as a result of the death and decay of both plant and animal matter. As these processes occur it has often been observed that sediments become more reduced and decrease in pH. Although the incubation experiments indicated that most metal species are stable and tightly bound to sediments under current conditions of redox potential and pH, decreases in pH were found to increase the solubility of all heavy metals tested. Changes in redox potential produced no significant changes in release rates.

The results suggest that as the Maitland pond ages and accumulations of organic matter in the sediments begin to cause

sediment pH values to decrease, mobilization of all metal species tested will increase and release to groundwaters may occur. Although all metals were found to increase in solubility with decreases in pH, the release was in general, only a small fraction of the total sediment metals present. For zinc, iron, aluminum, copper, and chromium, the maximum release was less than 3 percent of the total acid-extracted metal in the sediments, even at the most extreme pH value tested of 5.0. For nickel and lead, the release extended as high as 6-7 percent at a pH of 5.0. However, the release of cadmium and manganese into groundwaters can be expected to increase substantially as the sediments become more acid. Manganese and cadmium were found to increase in solubility substantially as sediment pH decreases with almost total release of manganese and 25-35 percent release of cadmium at a pH of 5.0. Releases of this magnitude may produce measurable increases in groundwater concentrations beneath the pond. In the case of cadmium, a health hazard may be present under these extreme conditions.

The results suggest that maintenance procedures may be necessary after a period of time to remove the accumulated sediment deposits which may cause conditions of low pH and release of metals.

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

1. Measured concentrations of heavy metals in highway runoff collected at the Maitland Interchange during 1983-84 showed

considerable variability between storm events as well as during storm events.

2. With the exceptions of copper and cadmium, the majority of metal species were present in a particulate form. The most common vehicle related heavy metals found in highway runoff at the Maitland site were lead, zinc, and copper which together accounted for approximately 91 percent of the dissolved heavy metals and 94 percent of the total metal concentrations.

3. The Maitland pond was found to be very effective in removal of heavy metal inputs from highway runoff. Particulate species of most metals were removed in the range of 75-95 percent with most of this mass retained in the pond sediments within a distance of 60-90 m from the stormwater inlet. In general, dissolved forms of heavy metals were removed to a lesser degree than particulate inputs with efficiencies near 50 percent for most metals.

4. Mean concentrations of heavy metals within the pond were within water quality criteria established in Chapter 17-3 of the Florida Administrative Code (F.A.C.) for Class III (recreational) waters.

5. Measured concentrations of total heavy metals in the sediments of the Maitland pond exhibited highest concentrations in the surface layer with a rapid decline in concentration with increasing depth.

6. After eight years of accumulations in the Maitland pond, most metals associated with sediments have remained in the top 10 cm of the sediment layer.

7. Under current conditions of redox potential and pH within the sediments of the Maitland pond metal species, with the possible exceptions of cadmium and manganese, are stable and exist in relatively immobile associations with Fe/Mn oxides and organic matter.

8. In general, mean concentrations of all heavy metals measured, except copper, were greater in groundwaters beneath the pond than within the pond. Average concentrations of zinc, manganese, aluminum, and iron were found to be 4, 12, 8, and 50 times greater, respectively, in shallow groundwater than in the pond water. The extent of significantly higher groundwater concentrations of nickel, cadmium, and chromium extended to depths of 0.5-1.0 m, lead extended to the 1-3 m range, while zinc, aluminum, manganese, and iron were elevated in concentrations past the 6 m sample depth.

9. Violations of Class III water quality criteria were present for both cadmium and iron in groundwaters beneath the pond.

10. However, the horizontal movement of groundwaters in the study area was less than 10 m/year and as a result, the influence of the pond on groundwaters was extremely localized.

11. In general, it was found that all heavy metals tested, with the exceptions of copper and nickel, are significantly higher in concentration beneath swale areas than beneath the retention pond. Aluminum, manganese, and iron were found to be higher in concentrations in groundwaters beneath "wet" swale areas while lead was higher beneath "dry" swale areas.

12. As sediment accumulation occurs in retention ponds over time, the corresponding decreases in pH and ORP of the sediments will increase the release of metal ions into groundwaters. The effect of reductions in pH were found to be more important than reductions in ORP in regulating the release of metal species. For zinc, iron, aluminum, copper, and chromium, the maximum release was found to be less than 3 percent of the total metal present in the sediments, even at an extreme sediment pH of 5.0. For nickel and lead, the release extended as high as 6-7 percent while cadmium was released in quantities as great as 25-30 percent and manganese was almost totally released from the sediments. These releases may produce measurable increases in groundwater concentrations beneath the pond.

From the field and laboratory investigations conducted as part of this research, the following recommendations are made concerning design and management of stormwater management systems:

1. Retention or detention designs which intend to maximize heavy metal removal from highway inputs should provide physical configurations which encourage a gradual reduction in flow velocity inside the pond to aid in sedimentation of particles. The distance from the points of input to the discharge point from the pond should be maximized. The design should be carefully analyzed to avoid possible short circuiting of flows as well as hydraulically dead zones.

2. Maintenance procedures may be necessary in retention/detention systems after a period of operation to remove the accumulated sediment deposits which may cause conditions of low pH and release of metals. Since the growth and encroachment of vegetation into the pond will accelerate the accumulation of organic matter, it is recommended that vegetation be controlled as much as possible. Based on the estimated organic layer accumulation rate of 1 cm/yr in the Maitland pond, a maintenance or cleanout period of 10-15 years seems reasonable. However, it is beyond the scope of this research to evaluate the specific timing of maintenance procedures. Further research in this area is strongly recommended.

3. Research is recommended to develop guidelines for determination of optimum sizing retention/detention ponds based on water quality improvements. Pollutant loading parameters and hydraulic detention times may be utilized as design criteria.