EFFECTIVENESS OF DETENTION/RETENTION BASINS FOR REMOVAL OF HEAVY METALS IN HIGHWAY RUNOFF

by: Harvey H. Harper, Yousef A. Yousef, and Martin P. Wanielista
Department of Civil Engineering and Environmental Sciences, University of Central Florida
Orlando, Florida 32816

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. Stormwater characteristics were compared with average retention pond water quality to determine removal efficiencies for heavy metals within the pond. A total of 138 sediment 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. 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.

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 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.

SITE DESCRIPTION

The site selected for this investigation is the Maitland Interchange on Interstate 4. This interchange, located north of the city of Orlando, was constructed in 1976 (Figure 1). Three borrow pits dug to provide fill for constructing the overpass remain to serve as stormwater detention/retention facilities. The ponds are interconnected by large culverts and the northwestern (Pond B) has the capability to discharge to the southwestern (referred to hereafter as the West Pond) when design elevations are exceeded. However, under normal conditions, the only input into the West Pond is by way of a 45 cm concrete culvert that drains much of the Maitland Boulevard overpass. Discharge from the West Pond travels to Lake Lucien through a large culvert. A flashboard riser system regulates the water level in the West Pond, and a discharge rarely occurs to Lake Lucien.

The West Pond has an approximate surface area of 1.3 ha and an average depth of 1.5 m. The pond maintains a large standing crop of filamentous algae, particularly Chara, virtually year round. Because of the shallow water depth and large amount of algal production, the pond waters remain in a well oxygenated state. The sediment material is predominately sand which is covered by a 1 cm layer of organic matter.

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 and an exit lane, the other carrying two lanes of westbound traffic and another exit lane. Traffic volume on Maitland Boulevard is approximately 12,000 average daily traffic (ADT) eastbound and 11,000 westbound. Traffic volume on I-4 through the Maitland Interchange is approximately 42,000 ADT eastbound and westbound each.

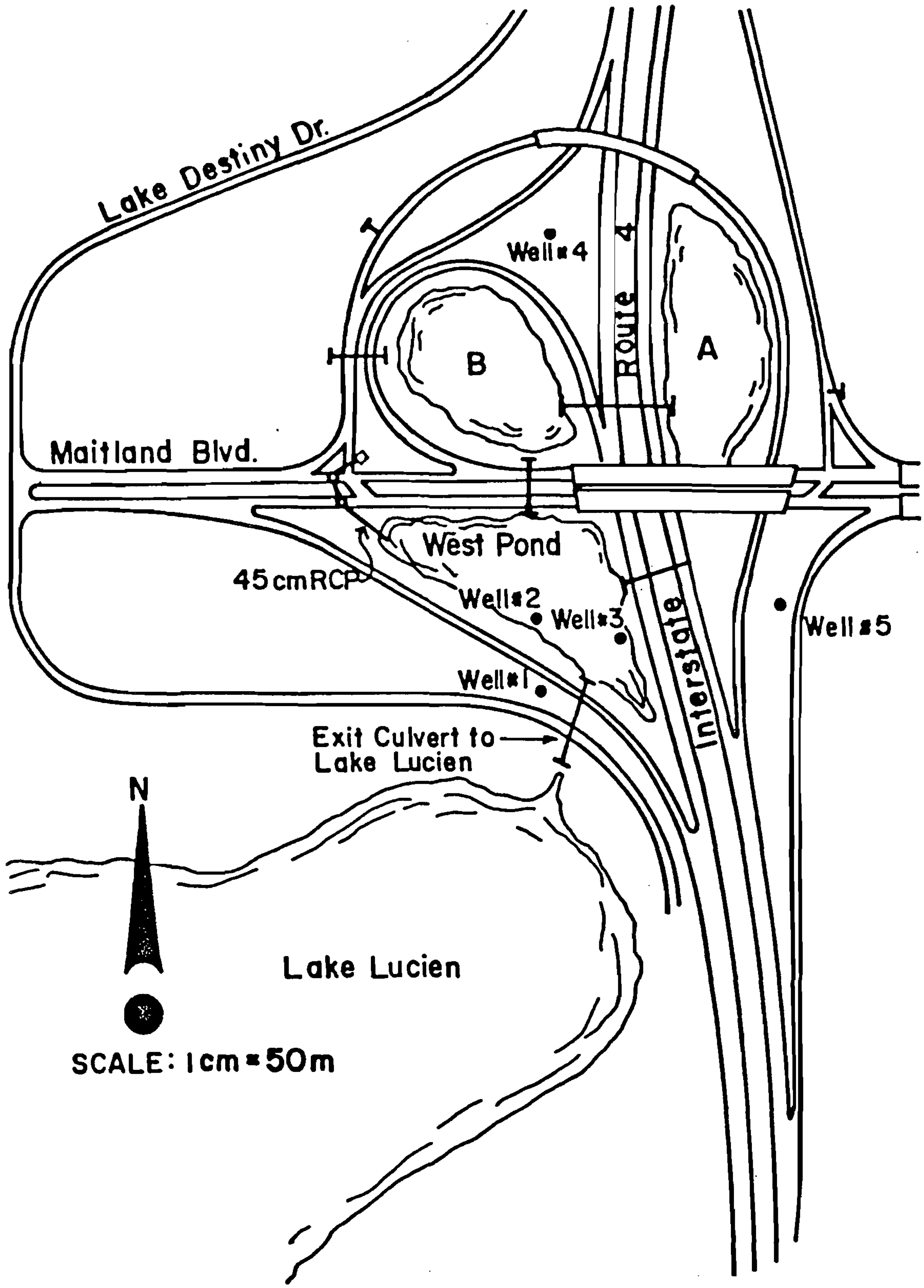

Figure 1. Study Site at Maitland Interchange.

FIELD INVESTIGATIONS

Field investigations conducted during 1982 and 1983 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 accumulation of heavy metals in the sediments of the pond; and (4) monitoring of heavy metal concentrations in ground waters beneath the retention basin. To determine the quantity of heavy metals entering the West Pond by way of stormwater runoff, an Isco automatic sampler was installed on the 45 cm stormsewer line. Flow-weighted composite samples were collected over a 1 year period for 16 separate storm events representing a wide range of rainfall intensities and antecedent dry periods. Samples were analyzed for heavy metals using argon plasma emission spectroscopy.

Water samples were collected on a biweekly basis for 1 year in the West Pond to document average retention pond water quality. Each of the five samples was analyzed separately for the heavy metals listed, and an average value was calculated for each metal on each sampling date.

The accumulation and vertical distribution of heavy metals in the sediments was examined by collection of a series of 2.5 cm diameter core samples to a depth of 15 cm. Forty-three separate core samples were collected in the 1.3 ha West Pond, and metal concentrations in sediment layers 0-1 cm, 1-3.5 cm, 3.5-6.0 cm, 6.0-8.5 cm and 8.5-13.0 were measured for each core sample. Metal concentrations in the 0-1 cm layer were used to investigate horizontal movement of heavy metals from the point of discharge into the pond. Average metal concentrations in each of the sediment layers were used to determine the extent of vertical migration.

Multiport monitoring wells were installed at the locations indicated in Figure 1 to investigate the possibility of groundwater contamination by leaching of heavy metals from the stormwater management system. Two of the monitoring wells were installed at the edges of the West Pond with the remaining three installed at various locations surrounding the stormwater management system. The wells were designed so that all of the sample ports were housed in a single casing to minimize soil disturbance and reduce recovery time for obtaining representative groundwater samples compared to other monitoring well designs such as cluster wells.

All wells were installed to a depth of 6 meters with sample ports at 0.1 m, 0.5 m, 1.0 m, 3.0 m, and 6.0 m below the average water table depth in the area of the well. Groundwater samples were collected from each sample port on a monthly basis using a peristaltic pump. Approximately 10 liters of groundwater were pumped and discarded from each port before a sample was collected. Collected groundwater samples were analyzed for heavy metals as described previously.

CHARACTERISTICS OF HIGHWAY RUNOFF AT THE MAITLAND SITE

A total of 16 storm events, including a total of 150 separate runoff samples were collected and analyzed over this period for 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.

A summary of mean flow-weighted heavy metal concentrations measured at the Maitland site is given in Table 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. Average dissolved concentrations of all heavy metals, with the exceptions of iron and aluminum, were less than 70 ug/l, with nickel, chromium, manganese, and cadmium less than 3 ug/l. Measured mean concentrations of total metal species were in excess of 100 ug/l for lead, aluminum and iron, while nickel, chromium, manganese, and cadmium were all present in average total metal concentrations of 10 ug/l or less. In general, the variability of mean flow-weighted dissolved metal concentrations appears to be much less than that observed for mean total concentrations, with most dissolved species exhibiting a five-fold difference in range of concentrations, while total concentrations exhibited over a ten-fold range in most cases.

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 constitutents 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. Therefore, 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.

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.

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

HEAVY METAL	METAL SPECIES	NUMBER OF SAMPLES	MEAN (ug/l)	STANDARD DEVIATION	RANGE OF VALUES (ug/l)	PERCENT DISSOLVED (%)
LEAD	Dissolved	150	33.0	40.2	7.0 - 413	
	Total	150	181	331	11.0 - 3,596	18.2
ZINC	Dissolved	150	40.0	42.6	1.0 - 324	
	Total	150	73.9	71.2	5.0 - 372	54.1
COPPER	Dissolved	150	28.6	24.7	6.0 - 175	
	Total	150	38.6	28.8	6.0 - 176	74.1
NICKEL	Dissolved	150	2.5	2.4	0.5 - 15	
	Total	150	3.4	2.8	0.5 - 18	73.5
CHROMIUM	Dissolved	150	2.5	2.2	0.5 - 16	
	Total	150	4.2	3.2	0.5 - 18	59.5
IRON	Dissolved	150	77.9	59.7	11.0 - 466	
	Total	150	378	354	44.0 - 2,172	20.6
ALUMINUM	Dissolved	150	125	124	19.0 - 832	
	Total	150	561	563	53.0 - 3,499	22.3
MANGANESE	Dissolved	150	2.70	6.7	<1 - 59	
	Total	150	9.53	10.8	<1 - 62	28.3
CADMIUM	Dissolved	150	1.7	2.0	<1 - 12	
	Total	150	2.2	2.4	<1 - 12	77.3
pH		101	6.30	0.88	4.95 - 8.49	---

Probability distributions of mean flow-weighted heavy metal concentrations in the 16 measured storm events were examined by plotting flow-weighted mean metal concentrations for each measured event on probability paper. Total concentrations of heavy metals appeared to best approximate a straight line relationship with a log-normal distribution of concentrations for the events measured. Dissolved concentrations of heavy metals also seem to approximate a log-normal distribution. However, cadmium appears to exhibit a convex curvilinear relationship.

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.

FATE OF HEAVY METALS ENTERING THE MAITLAND POND

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 ug/l with dissolved concentrations of cadmium, zinc, manganese, nickel, and chromium rarely exceeding 10 ug/l. Total metal concentrations followed a similar pattern with only manganese, aluminum, iron, and on one occasion lead, exceeding 100 ug/l on any given sample day at any of the five sampling stations within the retention pond. The mean pH value of the retention pond water was 7.46 with a range of 6.62-8.46. Measurements of dissolved oxygen indicated an aerobic water column on all sample dates. The mean value for dissolved oxygen was 5.6 mg/l with measurements of ORP generally in excess of 500 mv.

The Maitland pond was found to be very effective in removal of heavy metal inputs from highway runoff. A comparison of summary statistics for highway runoff and Maitland pond water is given in Table 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. The order for reduction of particulate metal species upon entering the West Pond is:

TABLE 2. COMPARISON OF SUMMARY STATISTICS FOR HIGHWAY RUNOFF AND MAITLAND RETENTION POND WATER

HEAVY METAL	METAL SPECIES	STORMWATER RUNOFF[1]		RETENTION POND WATER[2]		PERCENT REMOVAL IN POND	STATE OF FLA. CLASS III WATERS CRITERIA (2/1/83)
		MEAN (ug/l)	PERCENT OF TOTAL	MEAN (ug/l)	PERCENT OF TOTAL		
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
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

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

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. The order for reduction of dissolved runoff species upon entering the West Pond is:

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

Studies by Yousef et al. (1985) 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. In the research by Yousef, et al., isolation chambers were placed in a newly constructed retention pond near Epcot Center. The isolation chambers were constructed of inverted polyethylene 200-liter barrels placed on the sediments - which isolated a 0.25 m^2 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 collected and analyzed for metal content. A summary of their work is presented in Table 3.

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. By 4/18/83 (the next sample collection date) concentrations in the closed chamber 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.

ACCUMULATION OF HEAVY METALS IN THE SEDIMENTS

HORIZONTAL DISTRIBUTION OF HEAVY METALS

Distributions of heavy metals in the top 1 cm of 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. The distributions of selected heavy metals as a function of distance from the 45 cm RCP inlet are shown in Figure 2. 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 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

TABLE 3. 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* AFTER	4-4	4-18	4-21	4-25	5-5	5-9	5-12	5-19	5-24
Sediment Contact-Control(no metals added)	Cu	23	-	15	17	27	8	11	9	13	15	22
	Zn	7	-	9	5	6	4	4	3	4	4	4
	Fe	596	-	614	455	596	743	781	916	904	1118	1267
	Pb	23	-	32	26	23	27	24	28	26	23	23
Sediment Contact (metals added)	Cu	21	683	71	17	19	24	24	26	20	19	46
	Zn	14	857	82	10	10	11	10	5	12	5	10
	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 Contact (metals added)	Cu	23	590	61	19	17	22	14	64	28	28	41
	Zn	13	749	50	3	10	4	5	7	7	7	10
	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-----> was Supplied			<--------------Diffused Air was Shut-off------------>							

* After addition of nutrient and heavy metal solution.

SOURCE: Yousef et al. (1985)

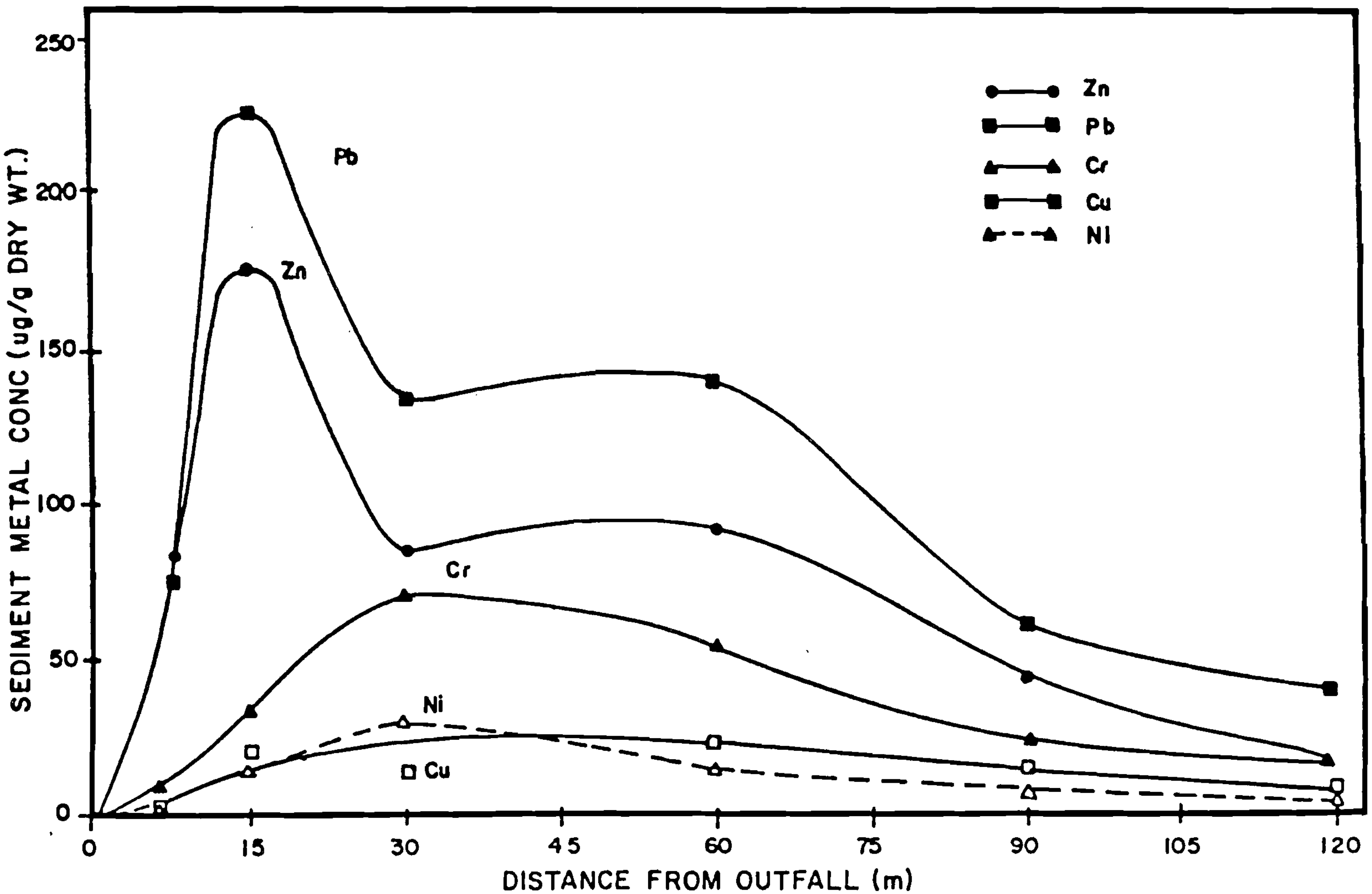

Figure 2. Sediment Concentrations of Selected Heavy Metals in the Top 1 cm of the Maitland West Pond as a Function of Distance from the Outfall.

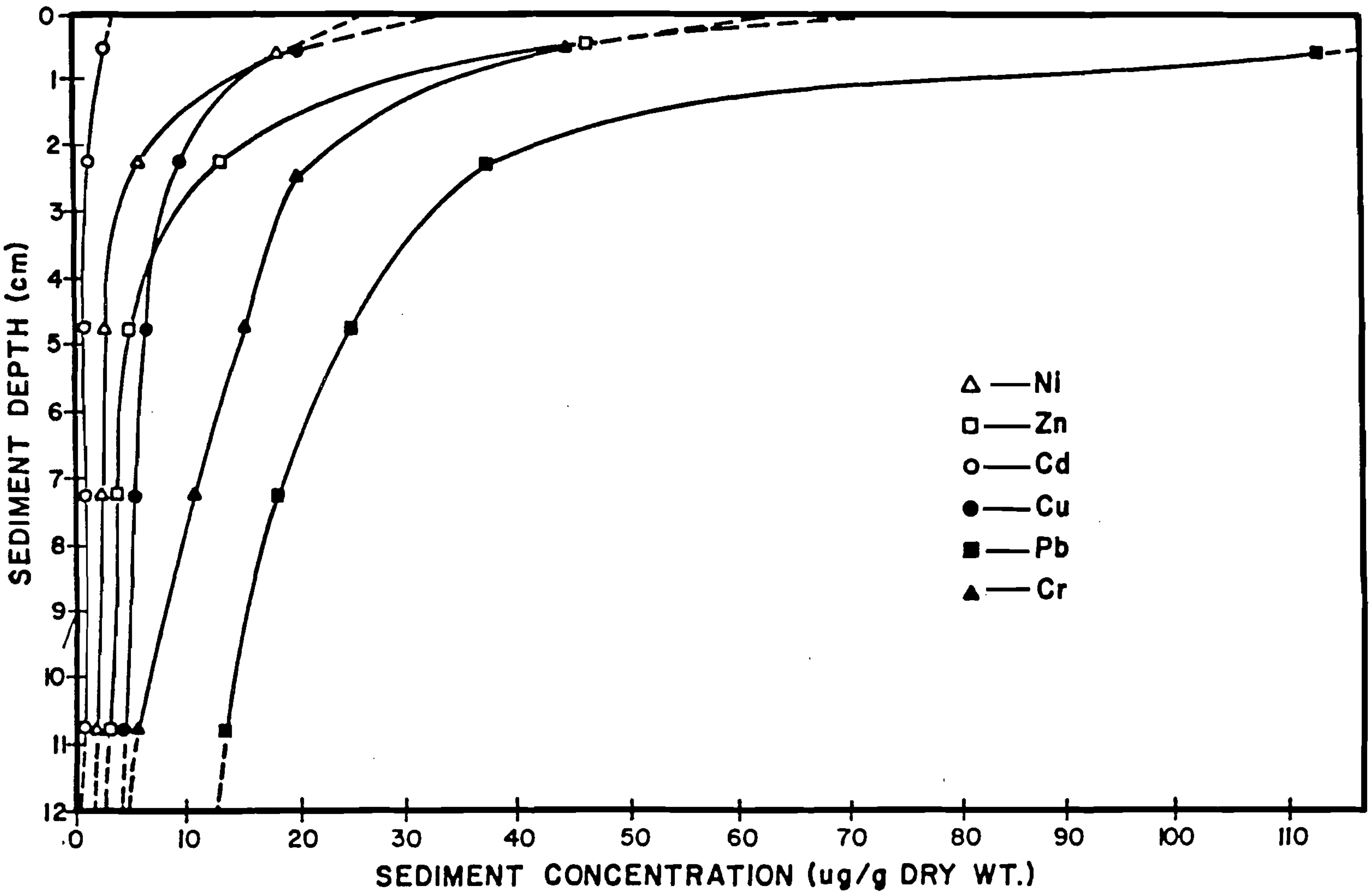

Figure 3. Attenuation of Heavy Metals in the Bottom Sediments of the Maitland Pond for Samples Collected 10/15/82.

TABLE 4. SUMMARY OF BACKGROUND AND RUNOFF RELATED METAL CONCENTRATIONS IN THE SEDIMENTS OF THE MAITLAND POND

SEDIMENT DEPTH	MEAN SEDIMENT METAL CONCENTRATION (µg/g DRY WT.)									NO. OF OBS.
	Cd	Zn	Cu	Al	Fe	Pb	Ni	Cr	Mn	
0 - 1 cm:										
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	
1 - 3.5 cm:										
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	
3.5 - 6 cm:										
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	
6 - 8.5 cm:										
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	
8.5 - 13 cm:										
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	

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

The vertical distribution of heavy metals in the sediments of the Maitland West Pond was characterized by analysis of average sediment metal concentrations by layer on each of the three sample dates. The vertical distributions of selected heavy metals in the sediments of the Maitland pond are given in Figure 3. Aluminum was the most abundant metal present in the Maitland pond sediments at all depths, followed by iron. 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. 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.

Background soil concentrations of heavy metals in the retention pond area were estimated from mean soil metal concentrations in core samples collected at depths of 3 m or greater during drilling of monitoring wells beneath the pond. These background concentrations were subtracted from the total sediment metal concentrations to provide an estimate of the added accumulations as a result of inputs of highway runoff. A summary of background and runoff related metal concentrations in the sediments of the Maitland pond is given in Table 4.

Sediment concentrations of runoff related heavy metals were also observed to decline rapidly 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: $\ln(C/C_o) = -K \times (\text{depth})$. A summary of the regression of statistics for the semi-log model is given in Table 5. 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:

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

The calculated regression equations for runoff related metal accumulations were used to estimate the extent of metal migration from runoff related sources by estimation of the depths necessary to reduce runoff accumulations by 90 percent and 99 percent to values which are 10 percent and 1 percent above estimated background levels. All runoff related accumulations were reduced in concentration by 90 percent in the first 10 cm or less.

Although the substantial majority of metal species were attenuated in the first 5.0 cm of sediments, the depths necessary 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.

CURRENT STABILITY OF METAL-SEDIMENT ASSOCIATIONS

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 following order: soluble < exchangeable < bound to carbonates < bound to iron and manganese oxides < bound to organic matter.

Fractional distributions of the total extracted heavy metals for each of the five extracted species are presented in Table 6. 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. Alminum 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 soluble or carbonate form although cadmium, zinc and nickel had soluble fractions of approximately 10 percent. It appears certain that iron, manganese, and

TABLE 5. SUMMARY OF REGRESSION STATISTICS FOR ATTENUATION OF RUNOFF RELATED HEAVY METALS IN THE TOP 13 CM OF THE 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/Co) = -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 μg/g; organic content in percent; and depth (Z) in units of cm.

TABLE 6. SPECIATION OF TOTAL HEAVY METAL CONCENTRATIONS IN THE SEDIMENTS OF THE MAITLAND WEST POND AS A FRACTION OF THE TOTAL METAL PRESENT

	PERCENT OF TOTAL EXTRACTED METAL CONCENTRATION					
HEAVY METAL	SOLUBLE	EXCHANGABLE	CARBONATE	BOUND TO Fe/Mn OX.	BOUND TO ORGANICS	TOTAL
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

organic content play dominant roles in regulating the mobility of metal species in the sediments of the Maitland pond.

In addition to the speciation analyses, 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. Sediment suspensions were incubated at pH values of 5.0, 6.5, and 7.5-8.0 which simulated current conditions of sediment pH in the pond, and at redox potentials of -250 mv, 0.0 mv, 250 mv and 500 mv, ranging from highly reduced to highly oxidized. A summary of metal release under these conditions for selected heavy metals is given in Figures 4 through 6. In general, release of most heavy metals was less than a few percent of the total sediment content under current conditions of pH (7.5-8.0). The influence of pH was found to be much more important than redox potential in regulating metal release for most metal species.

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, lead, and manganese, are stable and exist in relatively immobile associations with Fe/Mn oxides and organic matter. Lead and cadmium are apparently held to a large degree in strong exchangeable associations. 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 is equal to approximately 5% of the total metal present.

EFFECTS OF THE MAITLAND 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 7. 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.

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 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

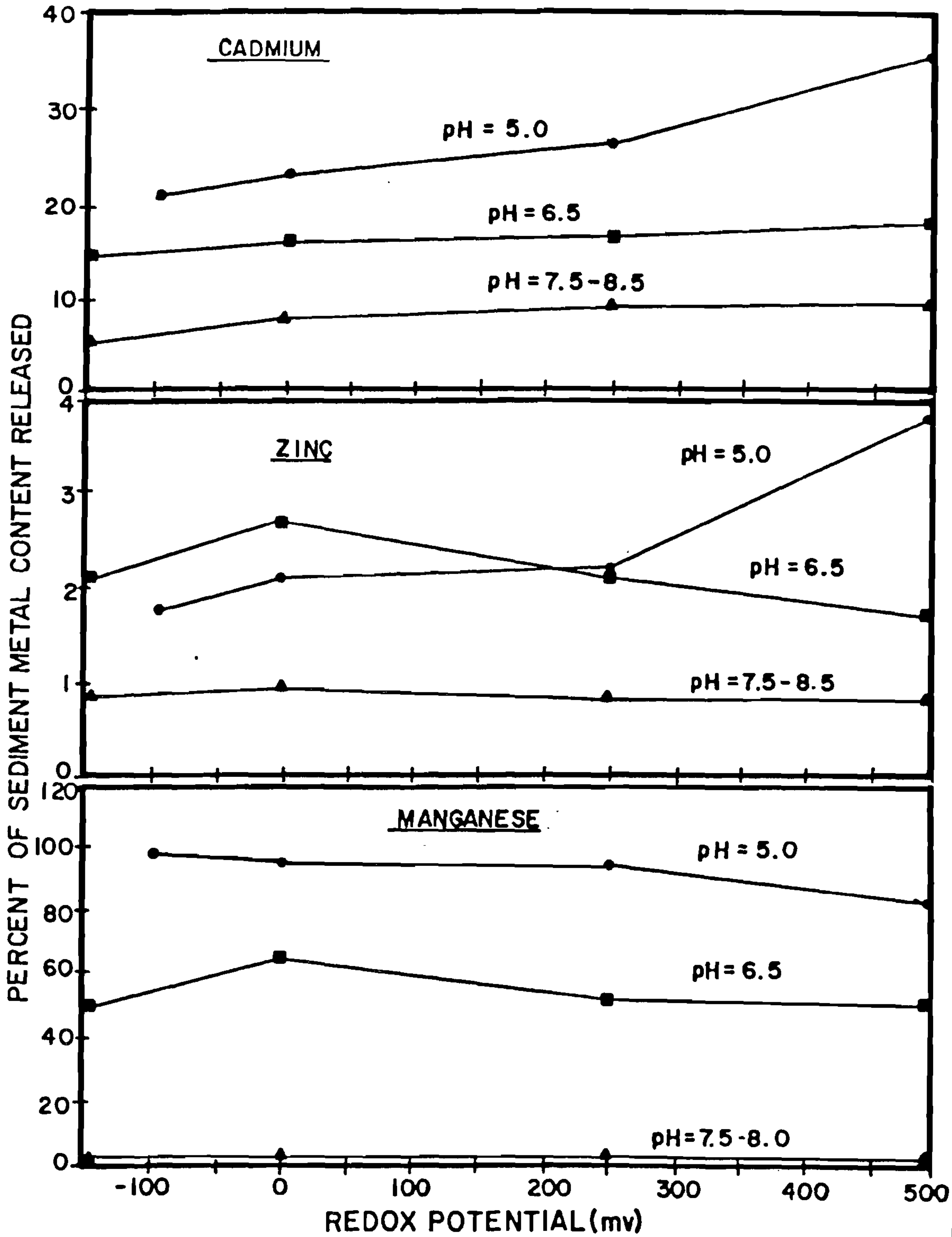

Figure 4. Fraction of Total Sediment Metal Concentrations of Cadmium, Zinc, and Manganese Released at Various Values of Redox Potential and pH.

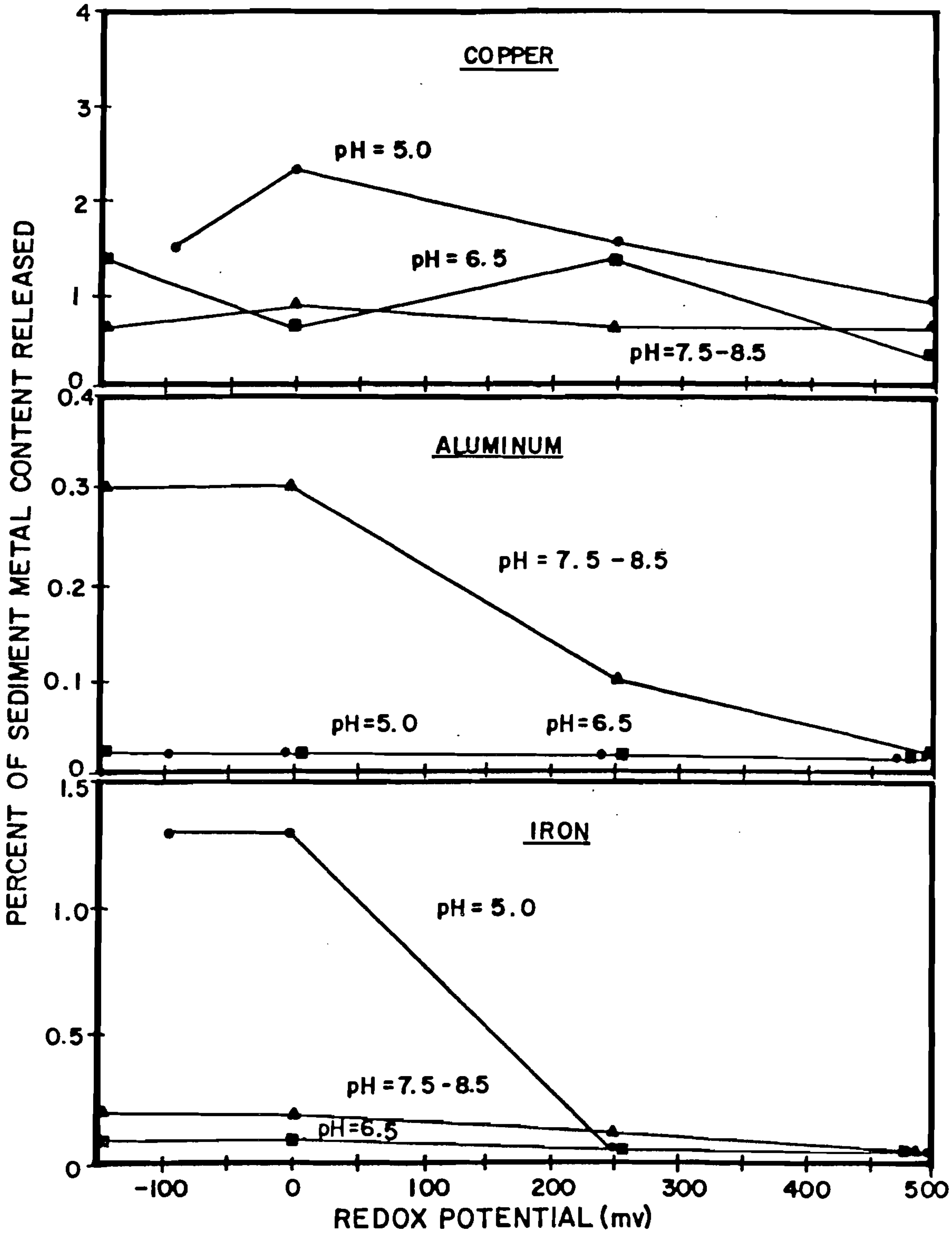

Figure 5. Fractions of Total Sediment Concentrations of Copper, Aluminum, and Iron Released at Various Values of Redox Potential and pH.

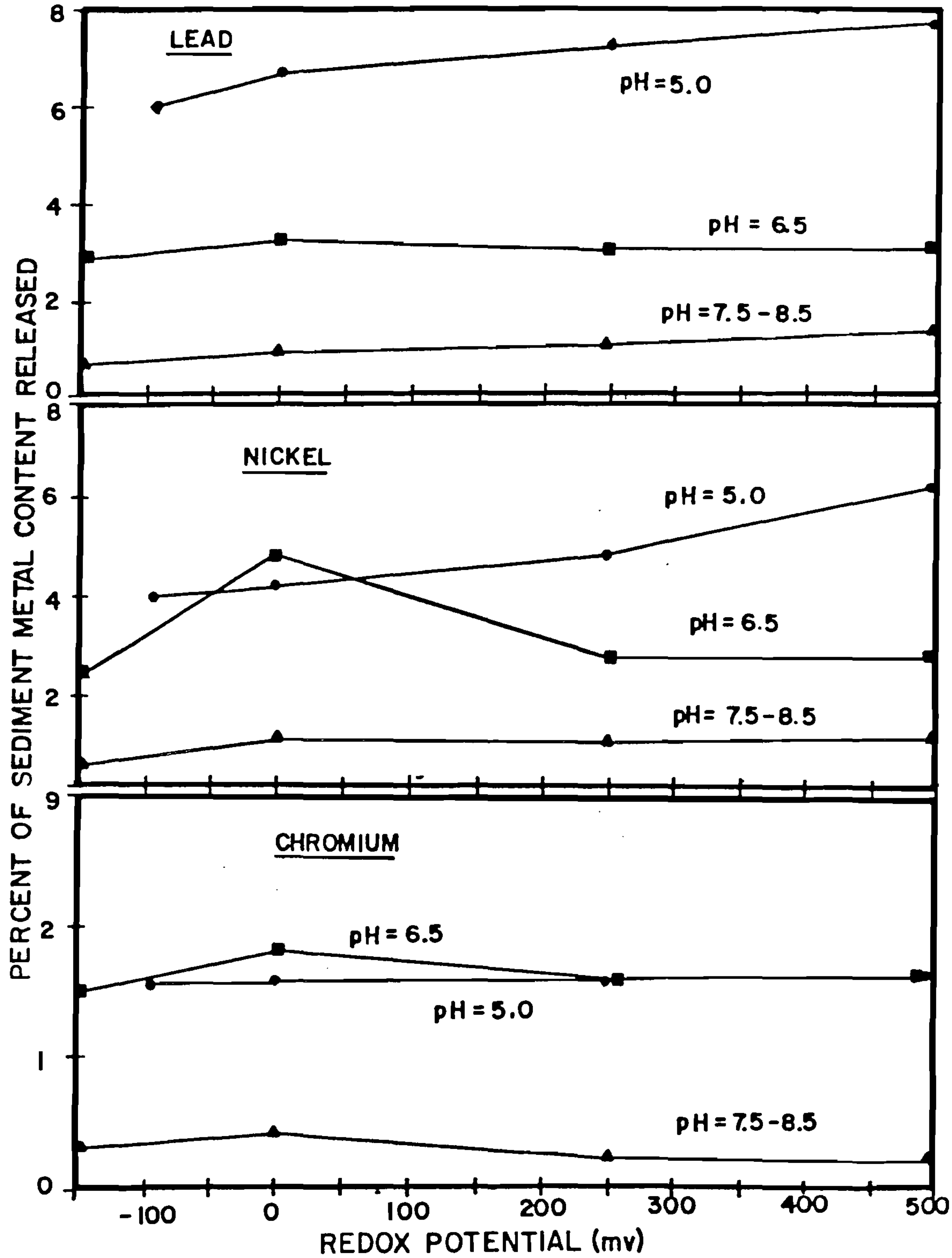

Figure 6. Fractions of Total Sediment Concentrations of Lead, Nickel, and Chromium Released at Various Values of Redox Potential and pH.

TABLE 7. 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 (μg/l)	AVG. CONC. IN 0-1 cm SEDIMENT LAYER (μg/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.

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.

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 pH (7.5-8.0). However, in spite of the increased metal concentrations beneath the pond, the sediments are clearly the primary sink for heavy metals.

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 8.

TABLE 8. 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	27.36
Well 5	26.87
Pond	27.38

As indicated in Table 8, little variation was measured in the piezometric surface between each well. As a result of this 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, metal contamination of groundwaters 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

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, as seen in Figure 4, the release of cadmium and manganese into groundwaters can be expected to increase 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 managanese 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.

CONCLUSIONS

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 grater, 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. 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 appears to be extremely localized.

11. 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.

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