EFFECTS OF INPUTS OF STORMWATER RUNOFF ON THE STABILITY OF METAL-SEDIMENT ASSOCIATIONS IN A HARDWOOD WETLAND[1]

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ABSTRACT

The movement and fate of heavy metal inputs (Cd, Zn, Mn, Cu, Al, Fe, Pb, Ni, and Cr) from stormwater runoff were investigated in a hardwood wetland near Sanford, Florida. Both quantity and quality of stormwater inputs were monitored over a one-year period. Core samples were collected to a depth of 20 cm in the flow path and in isolated control areas to characterize the accumulation and attenuation of heavy metals. Sediment samples were carried through a series of sequential extraction procedures to examine the type of chemical associations binding metals to the sediments. An apparatus was built which allowed sediments to be incubated under various conditions of redox potential and pH to investigate the importance of these factors on metal-sediment stability. Monitoring wells were installed in the flow path and in the control area for comparison of metal concentration in groundwaters.

Continual inputs of stormwater and base flow generally resulted in higher levels of both pH and redox potential in the path area. Sediment metal concentrations in both the flow path and control areas were highest near the surface and declined rapidly with increasing depth. Most metal species, except cadmium and lead, were found to be tightly bound to Fe/Mn oxides and organic matter in relatively stable associations. Both redox potential and pH were important in regulating the release of metals from sediments. Metal species such as Zn, Mn, Cu, Al, and Fe appeared to be retained more efficiently in the flow path area while Cd Pb, Ni, and Cr were retained to a larger degree in the control area.

Keywords: speciation, redox potential, sequential extraction, groundwater

FOOTNOTES

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INTRODUCTION

It has long been recognized that nonpoint sources of pollution contribute significantly to receiving water loadings of both nutrients and toxic elements such as heavy metals and oils and greases (Wanielista, 1982). As a means of protecting surface waters from further deterioration, many states have established regulations which require new developments to treat stormwater runoff before discharge from the property. In many cases this treatment involves retention or detention of specified amounts of runoff volume in shallow ponds. Recently, interest has risen in the use of natural treatment systems, such as wetland areas, for assimilation of stormwater pollutants in order to minimize the loss of valuable land in meeting these new regulations.

Although numerous studies have been conducted on the treatment efficiency of controlled inputs of secondary effluent in wetland systems, few detailed studies have been conducted on the feasibility of wetland systems in treating sporadic inputs of stormwater runoff in spite of the fact that numerous wetland areas are currently being used for this purpose. This research focused on the fate and movement of runoff related inputs of heavy metals in a hardwood wetland north of Orlando, Florida.

MATERIALS AND METHODS

Study Area

The natural wetland site investigated in this research was a 48.4 ha hardwood hammock located adjacent to Hidden Lake, north of Orlando, Florida (Figure 1). The dominant canopy vegetation is divided between sweetbay, red maple, an swamp ash with an understory of ferns, greenbriar, and

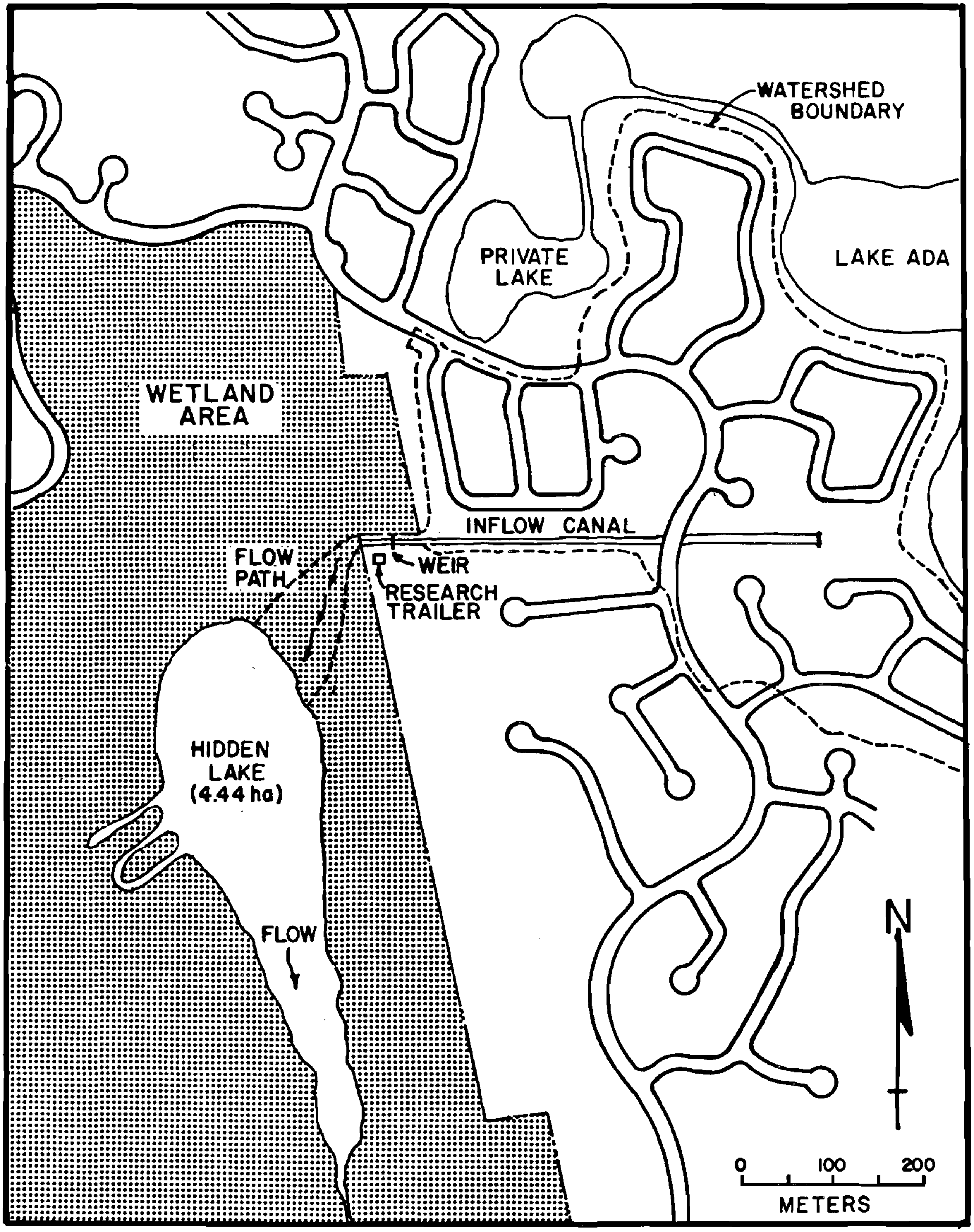

Figure 1. Study site at Hidden Lake.

blackberry. Soils within the wetland area are poorly drained organic soils characterized by a surface layer of dark reddish-brown muck approximately 10-20 cm thick over a loose peat layer approximately 1 meter thick, underlain by a dense sand or clay base.

The wetland has been receiving residential runoff since 1975 from a 22.4 ha drainage basin of single and multi-family residences. Both curb and gutter as well as grassed swales are used to convey the runoff waters to a single small vegetated canal which flows into the wetland as indicated in Figure 1, constituting the major input into the wetland. Stormwater inputs upon entering the wetland, generally observe the flow patterns indicated in Figure 2. Only approximately 1 ha of the total 48.4 ha wetland area comes into contact with runoff flow during most rain events.

During the winter and spring months (January-June), the water table is generally at or slightly beneath the wetland surface although the soil remains wet. Stormwater inputs during this period are usually infiltrated into shallow groundwaters. However, during the summer and fall months, standing water ranging from 1 to 20 cm is common, and occasionally the wetland becomes hydraulically connected to Hidden Lake following heavy rain events.

Field Methods

Surface water flow into the wetland was monitored continuously from January-December 1985 for both base flow and runoff flow at a weir installed across the input canal (Figure 2) using an ISCO flowmeter and flow totalizer. An ISCO sequential refrigerated sampler was also installed at the weir and used to collect flow weighted composite runoff samples over

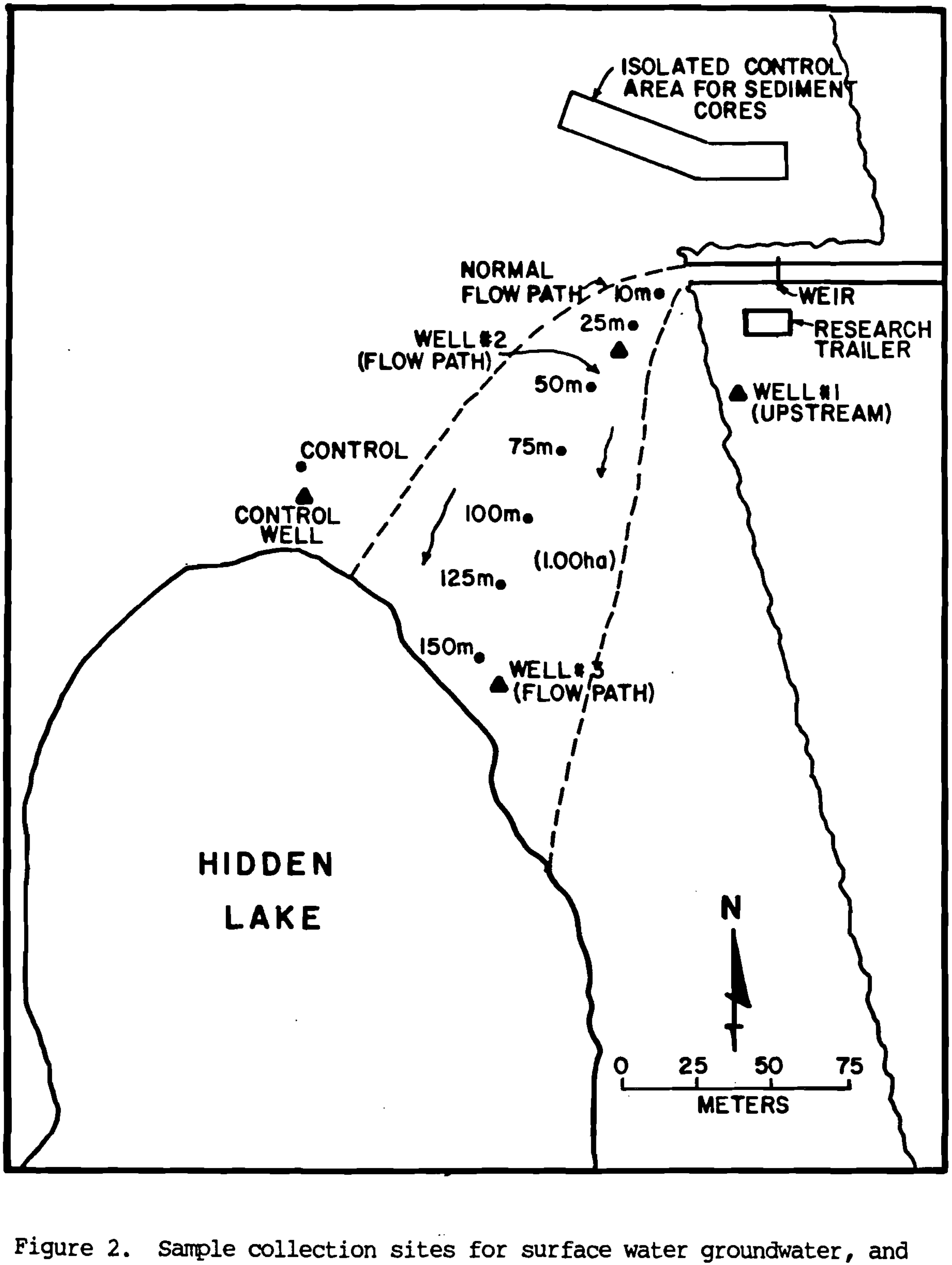

Figure 2. Sample collection sites for surface water groundwater, and sediments in the Hidden Lake.

the hydrographs of selected storm events to provide an estimation of the water quality characteristics of inputs to the system.

Surface water samples were collected on a bi-weekly basis from January-December, 1985 at seven fixed stations within the wetland at 25 m intervals along the dominant flow path to a distance of 150 m. This distance was observed to be the extent of runoff movement into the wetland during most storm events. A fixed control station was also established in an area of the wetland removed from runoff influence. Field measurements of pH, specfic conductivity, water temperature, dissolved oxygen, and ORP were collected by pumping surface water samples into a flow-through cell attached to a Hydrolab model 8000 water quality monitor.

Multi-port groundwater sampling devices were constructed and installed with sample ports 0.1 m, 0.5 m, 1.0 m beneath the soil surface at locations indicated in Figure 2. A total of four monitoring wells were installed with one upstream of the weland, two in the major flow path, and one in the control area. Water samples and measurements of piezometric surface were collected on a monthly basis.

Sediment analyses were conducted on core samples collected near the sample stations in the flow path and control areas to characterize the deposition and attenuation of heavy metals. Each core sample was divided into the following layers: (1) 0-1 cm, (2) 1-5 cm, (3) 5-10 cm, (4) 10-15 cm, and (5) 15-20 cm. Three 5 cm diameter samples were collected at each fixed station and combined to form a single sample for each station. Each layer was analyzed for acid extractable heavy metals, moisture content, and organic content. Each sediment core was also carried through a series of sequential extraction procedures to examine the type of chemical associations and stability of metal species in the sediments. Details of this procedure are given by Harper (1985). This procedure allowed metal-sediment associations to be divided into fractions of soluble, exchangeable, bound to carbonates, bound to Fe/Mn oxides, and bound to organic matter. It is generally believed that the stability of metal sediment associations increases in the same order.

An apparatus was constructed 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. Details of this system are also given by Harper (1985). Sediments were incubated at a pH characteristic of the control area (5.0) as well as a higher value of 6.5 which was characteristic of the flow path area. At each pH value the sediments were incubated at four redox potentials, ranging from highly reduced to well oxidized: -250 mv, 0 mv, 250 mv, and 500 mv. Samples of supernatant were collected after 10 days at each combination of pH and redox potential and analyzed for soluble metal ions.

RESULTS AND DISCUSSION

During the "wet" season, which extends from June into December, hydrologic inputs into the wetland flow path through the canal were continuous although large variations were measured in flow rates. Flow rates into the wetland ranged from as low as 0.01 m^3/sec to as large as 10 m^3/sec, although inputs of this magnitude were rare. Mean flow rate into the wetland during this period was approximately 2.50 m^3/hour. This corresponds to a mean flow velocity of 0.33 m/hour.

Even though mean flow rates into the wetland were relatively low, the resulting circulation and flushing effects were sufficient to produce substantial increases in pH and redox potential in both surface waters and groundwaters in the flow path when compared to a stagnant control area. A comparison of mean values of pH and redox potential in the flow path and control areas is given in Figure 3.

Mean values of pH in surface waters along the flow path were approximately 1.5 units greater than the control area. These differences in pH were found to extend into groundwaters as well with the flow path area higher by 1 pH unit at 0.1 m and 0.5 pH unit at 0.5 m. At a depth of 1 m the pH values began to be similar although the flow path area remained slightly higher. Apparently, the low pH values in the isolated control area are a result of decomposition processes in the sediments which consume alkalinity and release organic acids under stagnant conditions.

Continuous inputs and circulation in the flow path area were also sufficient to raise redox potentials in surface and groundwaters. Redox potential in the flow path area was more than 200 mv greater than the stagnant control area. This difference decreased to 80 mv at 0.1 m and only 20 mv at 0.5 m and 1.0 m. Mean concentration of dissolved oxygen in the flow path area was 3.4 mg/L compared with 0.9 mg/L in the stagnant control area. Increased dissolved oxygen concentrations in the flow path are presumably a result of circulation which promotes gas transfer in addition to the well oxygenated nature of the canal inputs.

Comparisons of Surface Waters and Groundwaters

The effects of the differences in redox potential and pH on the solubility of metal ions is apparent by comparison of average metal

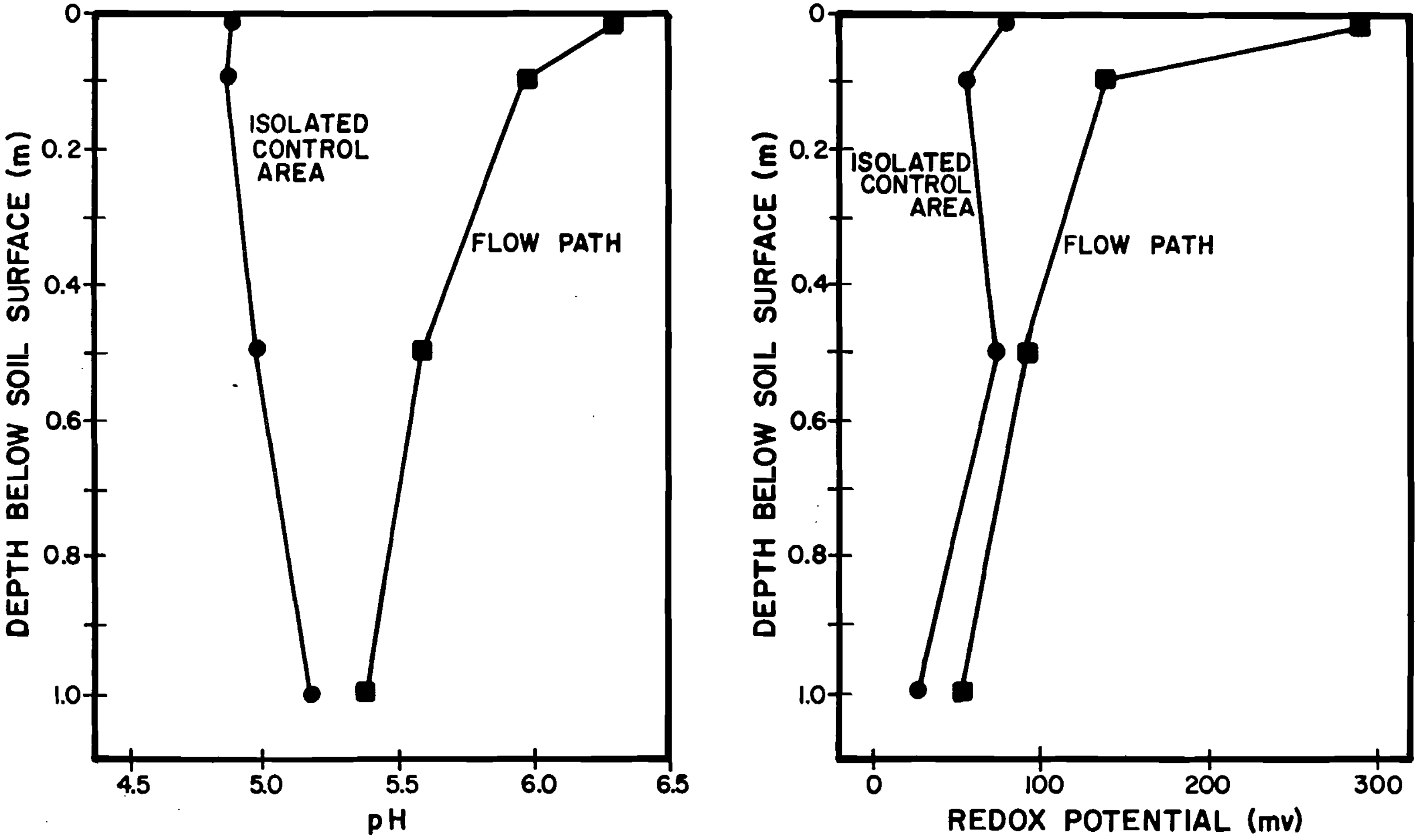

Figure 3. Comparison of mean values of pH and Redox potential in flow path and control areas.

concentrations in the flow path and control areas as given in Table 1. Two different patterns appear to exist for metal ion behavior in the flow path and control areas. Soluble concentrations of certain metal species, such as Zn, Mn, Cu, Al, and Fe, were 40-73% less in the flow path area than in the isolated stagnant control area. This trend for lower concentrations extended into groundwaters as well for all metals except Mn, with lessening differences at the 0.5 and 1.0 m depths.

However, soluble concentrations of the remaining metal species Pb, Ni, and Cr were found to be larger in the flow path area than in the isolated control area. Increases in concentrations in surface waters ranged from 1.4 to 1.7 times those measured in the control area. Solubility diagrams for each of these metals indicate that solubility increases at pH values less than 6.5 under oxidized conditions (Harper, 1985). As seen previously, the elevated concentrations in the flow path area extended into groundwaters as well, with concentrations in flow path and control areas becoming similar after a depth of 0.5 - 1.0 m.

Comparative Speciation of Metals

A summary of metal speciation in the top 20 cm of the wetland is given in Tables 2 and 3. Metals such as Cu, Al, Cr, and to a lesser extent Fe, were found to be primarily bound to sediments in association with organic matter such as peat. These associations are considered to be relatively stable and immune to the effects of pH and redox potential. Metals bound in these associations should be retained well in the wetland soils under most conditions. However, Cu, Al, and especially Fe also were found to have significant associations with Fe/Mn oxides, which can potentially solubilize under reduced conditons. This trend is apparent in Table 2

TABLE 1

COMPARISON OF HEAVY METAL CONCENTRATIONS IN SURFACE WATERS AND GROUNDWATERS IN FLOW PATH AND CONTROL AREAS AT HIDDEN LAKE

	FLOW PATH AREA				ISOLATED CONTROL AREA			
HEAVY METAL	SURFACE WATER CONC. (μg/1)	GROUNDWATER CONC. (μg/1)			SURFACE WATER (μg/1)	GROUNDWATER CONC. (μg/1)		
		0.1 m	0.5 m	1.0 m		0.1 m	0.5 m	1.0 m
Cd	3.92	5.93	5.18	4.87	2.30	3.88	4.52	5.75
Zn	3.90	20.9	16.3	21.0	6.57	37.3	42.6	26.4
Mn	3.10	18.0	8.09	7.92	7.57	9.80	12.5	28.7
Cu	19.9	30.3	42.2	29.7	28.7	28.0	54.8	28.7
Al	176	290	262	310	296	710	976	744
Fe	105	868	724	1102	389	1172	1586	2285
Pb	24.7	35.8	27.2	21.2	15.9	21.6	26.4	31.3
Ni	2.71	5.84	3.12	2.73	1.91	3.24	4.32	5.02
Cr	2.78	3.69	3.34	2.74	1.89	2.80	3.03	3.39

* n = 12 samples

TABLE 2

SUMMARY OF MEAN METAL SPECIATION IN THE TOP 20 CM OF THE WETLAND AT HIDDEN LAKE

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

* All values given as percent

TABLE 3

SUMMARY OF MEAN METAL SPECIATION IN THE TOP 20 CM OF THE WETLAND AT HIDDEN LAKE

METAL SPECIATION	Fe		Pb		Ni		Cr	
	FLOW PATH	CONTROL AREA	FLOW PATH	CONTROL AREA	FLOW PATH	CONTROL AREA	FLOW PATH	CONTROL AREA
Soluble	0.2*	0.2	0.9	1.6	2.1	5.6	1.3	1.9
Exchange	1.1	0.9	73.0	45.5	45.5	36.4	13.2	9.5
Bound to Carbonates	0.6	0.5	12.6	21.5	2.1	0.1	0.9	0.01
Fe/Mn Oxides	39.6	31.5	5.7	11.0	8.5	8.3	4.1	3.0
Organic Bound	58.5	66.9	7.8	20.4	41.8	49.6	80.5	85.5
Total Metal Released	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* All values given as percent

where concentrations of Cu, Al, and Fe increase substantially in groundwaters where reduced environments prevail.

Another group of metals, Cd, Mn, and Pb, were found to be predominately present in rather weak exchangeable fractions which were more dominant in the flow path area than in the control area. These metals are not considered to be tightly bound in the sediments and appear to be less tightly bound in the flow path area than in the control area. It is expected that these metals would accumulate and be retained in the soil to a lesser degree, particularly within the flow path. As seen in Table 1, concentrations of Cd and Pb in surface and groundwater were greater in the flow path area than in the control area.

The remaining two metals, Zn and Ni, exhibited relatively large exchange portions but also more stable fractions such as Fe/Mn oxides or organic bounds. These metals would be expected to acculmulate in the soils to some degree but also maintain a large potentially soluble pool as well.

Comparative Accumulation of Metals in Sediments

A comparison of mean metal concentrations in the top 20 cm of the wetland soils in flow path and control areas is given in Figure 3. It is apparent that soils in both flow path and control areas are retaining and accumulating heavy metals within the first few centimeters since concentrations are greatest near the surface and decrease rapidly with increasing depth.

With the exception of copper, differences in accumulation patterns between flow path and control areas can be explained to a large extent by the sediment speciations discussed previously. Metals such as Al, Cr, and Fe are bound to sediments primarily by strong organic associations which

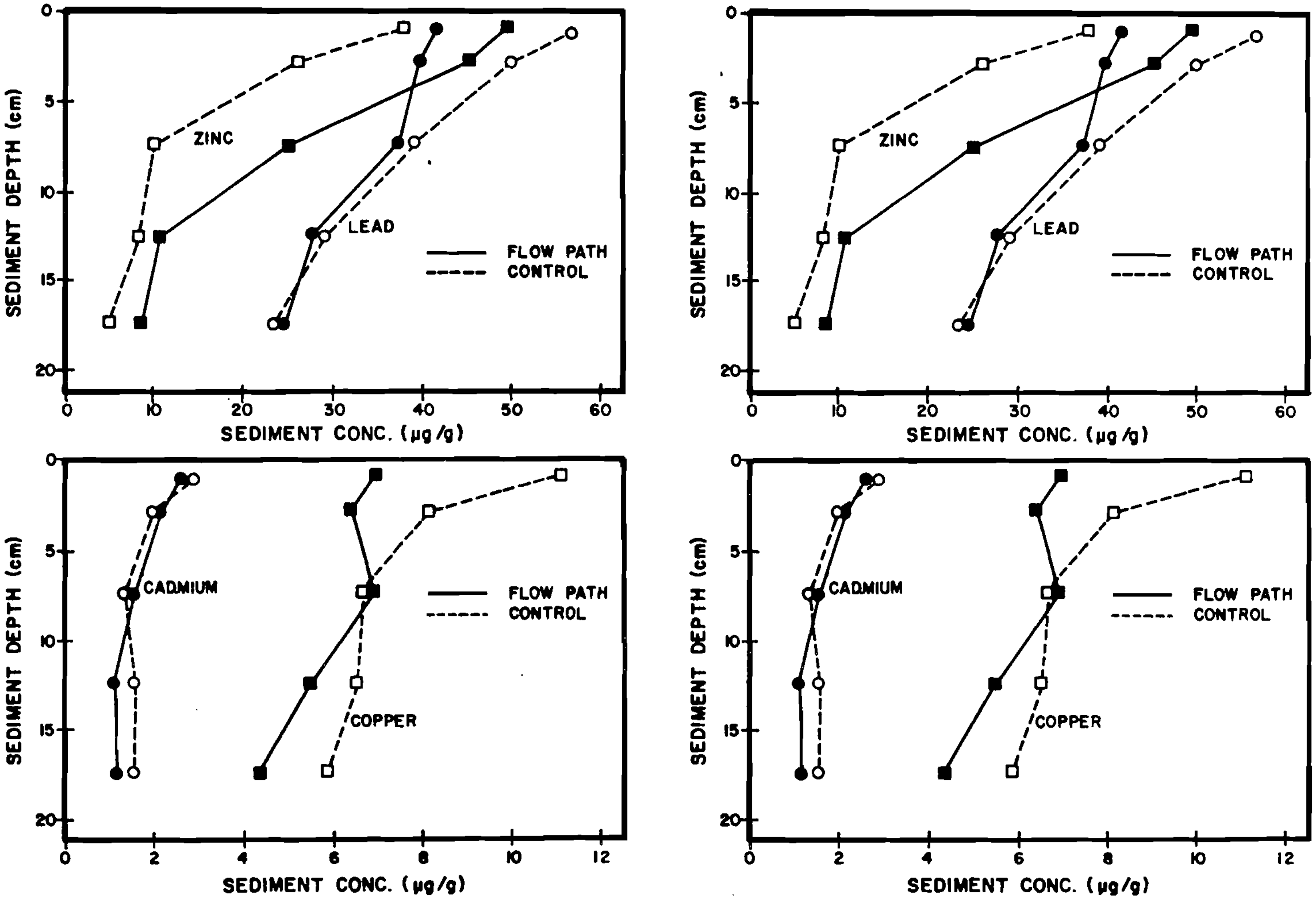

Figure 4. Sediment concentrations of heavy metals in flow path and control areas.

should be very stable. As seen in Figure 4, each of these metals are present in elevated concentrations near the surface with a rapid attenuation with increasing depth. Curves of this nature are characteristic of metals with strong bonding mechanisms that immobolize new ions rapidly upon contact with the sediment surface. Concentrations of metal ions in the flow path area were larger than in the control area as would be expected as a result of the larger mass loadings.

In contrast to the behavior of Al, Fe, and Cr, other metals such as Cd and Pb are bound into soils by weak exchange forces which were more dominant in the flow path area. These metals would be expected to be retained, in general, to a lesser degree than Al, Fe, or Cr and should exhibit much less pronounced attenuation in sediment concentrations. In addition, since the weak exchange fractions are more prevalent in the flow path area, this area would be expected to retain metals less readily than the control area. These predicted behaviors agree closely with the measured data in Figure 4 where concentrations of Cd and Pb are seen to exhibit a much less pronounced attenuation pattern and are often higher in control areas than in the flow path.

In spite of the strong organic association, copper does not appear to be accumulating in any sediments to a large degree. The ability of copper to form organic complexes is well known. These complexes would not be available for uptake onto soil particles and could explain the lack of copper accumulation.

Effects of Changes in Redox Potential and pH on Metal Solubility

The results of the incubations carried out at various combinations of pH and redox potential, summarized in Figure 5, agree, in general, with the

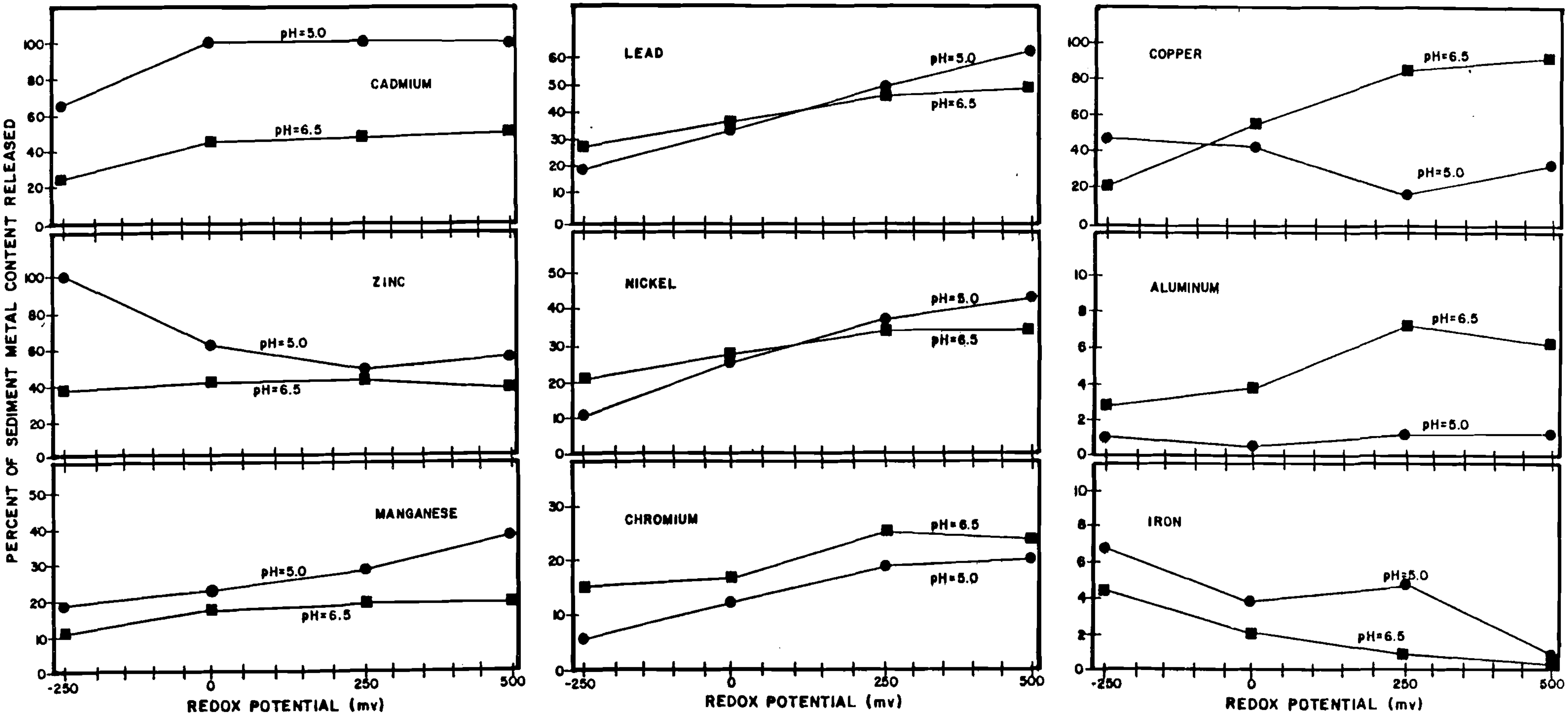

Figure 5. Release of heavy metals from wetland soils under various conditions of pH and Redox potential.

soluble metal concentrations measured in surface water and groundwater as presented in Table 1. Metals such as Pb, Ni, and Cr were found to be less soluble under even slightly reduced conditions at a pH value characteristic of the control area (5.0) than in the flow path (pH = 6.5). Each of these metals exhibited higher concentrations in surface and groundwaters in the flow path than in the control area (Table 1).

Cd, Zn, and Mn were all found to be less soluble under reduced conditions at a pH similar to that found in the flow path than at the lower pH of the control area. As seen in Table 1, measured concentrations of Zn and Mn were less in the flow path area. However, contrary to the trends presented in Figure 5, Cd was found in larger concentrations in the flow path than in the more acidic control area. Apparently the substantially larger degree of exchange bonding present in the flow path than in the control area allows more metal ions to escape into solution in spite of the reduction in solubility predicted by the higher pH.

Of the remaining metals, Al was found to be more soluble under oxidized conditions at a higher pH and less soluble under reduced conditions at a lower pH. This finding is in apparent contrast to concentrations listed in Table 1 where concentrations of Al are much lower in the higher pH flow path area. Iron was found to be more soluble in general at the low pH and under reduced conditions. These characteristics are consistent with concentrations listed in Table 1 in which iron is more concentrated in the lower pH control area and in reduced groundwaters.

CONCLUSIONS

Inputs of runoff into wetlands were found to produce a continuous but variable flow that resulted in an increase in pH and redox potential in surface and groundwater in areas along the flow path when compared to an isolated control area. These changes in water and sediment chemistry were found to affect the stability and retention of metal species in the wetland. Metals such as Zn, Al, Mn, and Fe are apparently more stable under these new conditions.

This stability is evident in the lower measured concentrations of these metals in the flow path area as well as the more favorable accumulation of these metals in the flow path soils. These metals also exhibited relatively strong organic or Fe/Mn bonding in sediments.

Solubility of the remaining metal species, Cd, Pb, N, and Cr, was incresed at the higher pH characteristic of the flow path area. Two of these metals, Cd and Pb, were found to be primarily bound into sediments by weak exchange bonds which are more dominant in the flow path area than in the control area. These two metals also appear to be accumulating in the flow path soils at a lesser rate than the control area soils.

The only metal which does not fit into the predicted trends is copper. Copper is known to form soluble organic complexes which may resist uptake into soil particles.

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