

Contamination of Wetland Sediments Indiana Dunes National Lakeshore: Implications for Wetland Restoration Strategies

Project Account Number: R/PS-02-98

PRINCIPAL INVESTIGATOR: Catherine J. Souch

INITIATION DATE: March 1, 1998

COMPLETION DATE: August 1, 2000

AFFILIATION: Indiana University Purdue University Indianapolis

Catherine J. Souch
Department of Geography
#213 Cavanaugh Hall
Indiana University Purdue University Indianapolis
Indianapolis, IN 46202-5140
Phone: (317) 274-1103
Fax: (317) 274-2347
csouch@iupui.edu

Gabriel Filippelli
118 SL Building
Indiana University Purdue University Indianapolis
Indianapolis, IN 46202
Phone: (317) 274-3795
Fax: (317) 274-7966
gfilippe@iupui.edu

For more than 100 years, the wetland sediments at the Indiana Dunes National Lakeshore (IDNL) and adjacent Indiana Dunes State Park have received atmospheric input of trace metals from industrial sources located upwind and to the west. The objective of this study was to document the extent and magnitude of this trace metal pollution both aerially and with depth within the IDNL, and to identify trends in metal distribution and mobility associated with different hydroperiods/degrees of human disturbance. This information is of value in assessing the potential for heavy metal release associated with changes in hydrology, hydrochemistry and sediment chemistry that may occur during and following wetland restoration of the Great Marsh.

OBJECTIVES:

1. To quantify the current environmental quality, both in terms of metal concentrations and ambient conditions (pH, Eh temperature, groundwater flow directions and velocities), in different sub-environments (defined in terms of hydrologic, ecological and disturbance histories) of the Great Marsh, Indiana Dunes National Lakeshore.
2. To develop simple models/relationships to explain the spatial distribution of heavy metals across the Great Marsh and with depth within the sediments, and the environment conditions associated with enhanced mobility.

3. To use these models/relationships to determine the potential for heavy metal release associated with certain changes in hydrology, hydrochemistry and sediment chemistry that may occur during and following wetland restoration at the Great Marsh.

METHODOLOGY: Sediment cores will be collected from four subwetlands in the Great Marsh (undrained, drained, and the wet and dry portions of a proposed restoration site). Heavy metals concentrations will be taken from replicate cores at each site at multiple depths. Data will be collected on ambient environmental conditions (water levels, pH, and soil organic matter content). This will provide insight into the distribution and mobility of metals in the sediments of the Great Marsh. The WATQ4F, MINTEQA2, and NETPATH models will be used to explore the distribution of heavy metals across the marsh and to identify conditions associated with enhanced metal mobility. These models will then be used to make predictions about the effects of wetland restoration strategies on the potential release of sediments both at IDNL and more generally at other polluted wetlands in the region.

RATIONALE: Many heavy metals, even if present in minute quantities, are toxic to plants and animals. Thus their release to aquatic environments from either natural or anthropogenic sources can have an adverse effect upon ecosystem health. Perhaps no where are the accumulations of anthropogenically released heavy metals as apparent as in wetland environments. This results in part from the fact that wetlands are generally dominated by fine grained particles and organic matter which tend to be geochemically reactive. Depositional environments, like peat/wetland soils, thus have the potential to absorb and store heavy metals. This fact is being exploited in many instances as wetlands are constructed/restored with the explicit objective of trapping contaminants from influent ground and surface water, thereby improving water quality. However, once absorbed in wetland sediments these metals are not permanently "fixed". Changes in environmental conditions, which often occur in wetland environments from natural or human-induced processes, can easily release metals from their temporary storage on sediment particles and reintroduce them to the aquatic system, making them bio-toxic once again.

Many constructed/restored wetlands lie in or near urban areas, and many serve as important recreational sites. One example is the Great Marsh of the Indiana Dunes National Lakeshore (IDNL) located in close proximity to Lake Michigan. For the last century, the southern shore of Lake Michigan has been a major industrial center, as well an important transportation corridor for the Midwest. Thus IDNL receives atmospheric deposition of airborne pollutants from these industrial centers, and ground and surface water discharging into the wetlands are also loaded with an array of heavy metals like copper, zinc, and lead. Preliminary data show elevated concentrations of heavy elements (5-20 times background levels) and strong evidence for post-depositional diffusion/mobility.

A wetland restoration program has been proposed by the National Park Service for a portion of the Great Marsh. Hydrologic and ecologic data have been collected to formulate target levels for the restoration (i.e. what the wetland is to be restored to). However, one aspect so far neglected is the geochemistry of the wetland sediments and the possible impacts of restoration: specifically, the concentrations of heavy metals in sediments and ground and surface waters and the likely implications of different management strategies on the potential for mobilizing these metals. Of particular interest are the effects of changing water level and changes in plant structure/rooting depth, which have the potential to change groundwater flow patterns, the nature of organic material/organic carbon content and redox conditions. It is hoped that this research will refine current understanding of heavy metal behavior in freshwater wetland sediments, such that findings of this study can be extrapolated and tested in other similarly polluted wetlands in this region.

BENEFITS:

This research will refine current understanding of heavy metal behavior in freshwater wetland sediments, and provide a sounder basis for management and restoration of wetlands both at IDNL and other similar sites.

Major goals and objectives:

1. To quantify heavy metal concentrations in different sub-environments (defined in terms of hydrologic, ecologic

and disturbance histories) of the Great Marsh, Indiana Dunes National Lakeshore (IDNL).

2. To develop simple relationships to explain the spatial distribution of heavy metals across the Great Marsh and with depth within the sediments, to identify the environmental conditions associated with enhanced mobility.
3. To measure heavy metal speciation by sequential extraction procedures, to gain further insight into potential mobility and to determine the potential for heavy metal release associated with changes in hydrology, hydrochemistry and sediment chemistry that may occur during and following restoration of the Great Marsh.

Summary

To quantify the magnitude of heavy metal contamination of the wetlands of the IDNL, twenty-five sediment cores were taken at varying distances from the principal industrial sources, and from environments with different disturbance histories (and thus different hydroperiods). For each core, sub-samples of sediments were taken at multiple depths and analyzed for strong-acid extractable concentrations of Cd, Cr, Cu, Mn, Ni, Pb, Se, and Zn (Perkins et al., 2000). Petrographic analyses of the organic matter in four cores were used to document the concentration, type and size of anthropogenic organic material within the sediments (Mastalerz et al., 2000), to provide a chronology of anthropogenic inputs and sediment accumulation rates. Results show that metal concentrations in near-surface sediments are comparable to those found in other soils and sediments in the region, with surficial enrichment over background levels. Zn concentrations are as high as 1,700 ppm, Pb as high as 280 ppm, and Mn as high as 2,700 ppm. The data suggest that surficial sediment concentrations of Pb, Zn, Cr, and Cu are elevated at sites in close proximity to anthropogenic sources, while the other metals do not exhibit a trend in concentration with distance from sources (Perkins et al., 2000). Based on the results of bulk geochemistry and the metal profiles with depth, Pb, Cr, and Cu appear to be relatively immobile after deposition, while Cd, Ni, and Se appear to have some mobility. The duration and/or frequency of flooding at a site appear to be important in determining the mobility of Zn and Mn.

To gain greater insight into potential mobility and geochemical sensitivity of metals during restoration, sediment cores from three different sites at IDNL were subjected to a sequential extraction procedure following the method of Tessier *et al.*, (1979). The sites were selected to reflect variations in organic matter content and hydroperiod. Results show metal fractionation to be both site specific and metal specific (Dollar, 2000; Dollar *et al.*, in preparation). For example, in surface sediments the exchangeable fraction in periodically submerged sites ranged from 39-50% non-residual Zn and up to 33% non-residual Cd, but was absent in a permanently flooded site. The fraction of metals bound to Fe/Mn oxides varied for Cd, Mn, Pb and Zn by site. By contrast, the elements Cr and Cu are predominantly affiliated with organic matter/sulfide bound fractions and show little difference between sites. Analysis of sulfur fractionation found it sequestered predominantly along with the organic bound fraction. This “oxidizable” fraction dominates the geochemistry for Cr, Cu and Fe. Given the stability of metals in all fractions may be affected by changes in pH and oxidation reduction potential, the results of this study suggest that Cr, Cu and Fe exist in forms not likely to be mobilized, whereas Cd, Mn, Pb and Zn are potentially mobile if the depth and/or duration of standing water at a sites is increased. These findings have important implications for predicting remobilization of previously stored heavy metals associated with wetland restoration activities that may involve flooding previously drained sites.

Accomplishments: *Characterization of metal concentrations across the Great Marsh*

1. Twenty-five wetland sediment cores have been taken across IDNL, at varying distances from the principal industrial sources, and from environments with different disturbance histories (and thus different hydroperiods).
2. Samples from multiple depth increments in each of these cores have been subjected to strong-acid extractions, and concentrations of the trace elements Cd, Cr, Cu, Mn, Ni, Pb, Se, and Zn have been determined.
3. Petrographic analyses of sediment samples from multiple depth increments in four cores have been conducted to document the concentration, type and size of anthropogenic organic material within the sediments. The results provide information on anthropogenic inputs for approximately the last century and allow sediment accumulation rates to be quantified.
4. Results show that metal concentrations in near-surface sediments are comparable to those found in other soils and sediments in the region, with surficial enrichment over background levels.

5. Analysis of all bulk geochemical data has been completed. One MS thesis has been written, one paper has been published, and a second is submitted. Six conference papers have been presented on this portion of the work.

Characterization of trace metal partitioning

1. Three sediment cores were taken at wetland sites with contrasting (but representative) variations in organic matter content and hydroperiod. Tessier-type sequential analyses have conducted on sub-samples from multiple depth increments for each of these cores.
2. Results show metal fractionation to be both site specific and metal specific. Cr, Cu and Fe exist in forms not likely to be mobilized, whereas Cd, Mn, Pb and Zn are potentially mobile if the depth and/or duration of standing water at a sites is increased.
3. Sequential extraction analyses have been completed and interpreted. One MS thesis has been written, and one paper, based on this, is in preparation. Two conference papers have been presented.

Keywords: Wetlands; Heavy Metal Contamination; Indiana Dunes National Lakeshore

Narrative report:

Objective: For more than 100 years, the wetland sediments at the Indiana Dunes National Lakeshore (IDNL) and adjacent Indiana Dunes State Park have received atmospheric input of trace metals from industrial sources located upwind and to the west. The objective of this study was to document the extent and magnitude of this trace metal pollution both areally and with depth within the IDNL, and to identify trends in metal distribution and mobility associated with different hydroperiods/degrees of human disturbance. This information is of value in assessing the potential for heavy metal release associated with changes in hydrology, hydrochemistry and sediment chemistry that may occur during and following wetland restoration of the Great Marsh.

Activities: We collected and analyzed a total of 28 sediment cores from different wetland sub-environments in and around IDNL. Twenty five coring sites were selected initially to document the areal extent of trace metal pollution. A sub-set of three sites were then re-cored and subjected to further analyses to gain insight into trace metal partitioning. Sampling sites were selected to document along-lake trends in metal concentrations (away from primary sources), and across wetlands with varying disturbance histories (and thus varying hydrologic conditions, from permanently to seasonally flooded). Nine cores were taken along a T-shaped transect from a site within the Great Marsh. The majority of samples were taken from sites far away from roadsides, and no samples were taken within 300 m of U.S. Highway 12, the major highway running through the study area.

The sediment cores were taken using 5-cm inside-diameter PVC and butyrate tubes, cut into 0.6 and 0.9 m lengths. Compaction of the sediment cores was measured, and ranged from 12% up to 215%. The cores were capped and sealed in the field. On return to the lab, the cores were refrigerated and stored upright until ready for sampling and analysis. All laboratory analyses were conducted at Indiana University/Purdue University at Indianapolis (IUPUI). The stratigraphy and sedimentology of the cores was described (in terms of criteria such as depth units, presence of root/stem/leaf fibers, color, grain size of mineral matter if present, degree of decomposition). Sediments were then sampled at 2-cm intervals along the vertical profile of one half of each of the cores for bulk geochemical analyses, and at 1 cm intervals for the more detailed sequential analyses. Initial preparation involved oven-drying at 60° C for 2-3 days to remove moisture. The dried samples were then ashed in a muffle furnace at 550° C for 3 hours to determine Loss-On-Ignition (LOI) organic matter content of each sample.

For the bulk concentrations, the samples then underwent a strong-acid digestion (see details in Perkins *et al.*, 2000). This releases into solution all but the refractory fraction of trace metals (associated with strong-acid resistant silicates). The strong acid digestion is used to assess the amount of trace metals that are potentially available to plants and soil microorganisms (“*bioavailable*”), as opposed to complete digestion, which is used to determine the *total* amount of trace metals in sediments. To examine how the results of these two techniques differ, complete acid digestion of

samples from a core taken from the Great Marsh (G1) also was conducted. Microwave-assisted complete digestion of each sediment sample, in a HNO₃ – HCl – HF acid mixture, was carried out using EPA SW-846 Method 3051.

Microwave digestion was accomplished in acid-cleaned Advanced Composite Vessels, using a CEM corp. MDS 2000 microwave digestion oven.

The sequential extractions followed the standard procedures of Tessier *et al.* (1979), with small modifications to account for the high organic content of the samples (Dollar, 2000). The metals selected for study were Cd, Cr, Cu, Mn, Ni, Pb, Se, and Zn, all of which are emitted to the air principally by activities associated with steel production and/or coal-burning (Winchester and Nifong, 1971; USEPA, 1995; Moore, 1998). Sediment sample solutions were analyzed by ICP-AES). Sample introduction was by ultrasonic nebulization (CETAC Corp. AT-5000+), providing low detection limits

A ²¹⁰Pb chronology was determined for one of the cores at Teledyne Brown Engineering. Sedimentation rates and age/depth relationships were calculated based on the Constant Flux Constant Sedimentation (CFCS) model. This information was supplemented by optical counts of anthropogenic fragments (coal, metallurgical coke, petroleum coke, char, solid bitumen and fly ash) within the sediments. The analyses were conducted in white reflected light as well as fluorescence mode using a Leitz MPV-2 microscope. Samples from the cores were dried, ground and made into polished blocks according to standard organic petrography procedures. For each sample, all anthropogenic particles within a zone of 50 μm around the scale of the ocular and perpendicular to the direction of the drive of the microscope stage were counted and classified.

Results

Initial results show that metal concentrations in near-surface sediments are comparable to those found in other soils and sediments in the region, and show surficial enrichment over background levels. Zn concentrations are as high as 1,700 ppm, Pb as high as 280 ppm, and Mn as high as 2,700 ppm (Table 1).

Table 1. Metal concentrations reported in soils and sediments from the Northwest Indiana region.

Surficial Trace Metal Concentration (ppm)								
Location:	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
IDNL Wetlands ^a	2 - 8	15 – 100	17 - 150	100 - 2700	14 - 42	65 - 280	35 - 160	95 - 1700
Cowles Bog ^b	4	9	36	150	15	196	--	438
East Chicago Wetlands ^c	16	--	184	--	--	628	--	2919
East Chicago Urban Soils ^d	1 - 12	--	10 - 150	--	--	64 - 401	--	142 - 2300

Grand Calumet River / Indiana Harbor Canal Bottom Sediments ^e	7- 37	24 – 602	36 - 380	996 - 4230	30 - 350	153 - 4700	--	930 - 9900
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a – This study ; b – Cole et al., 1990; c – Parker et al., 1978; d – Miller and McFee, 1983; e – USACE, Chicago District, 1979; USEPA, Region 5, Water Division, 1985; Polls, 1988.

The depth at which the first anthropogenic material appears, which likely marks the onset of industrialization (ca 1890's), varies from 16.5 cm at the western-most sites, to approximately 20 cm in the center of the Great Marsh. Concentrations of anthropogenic organic matter vary between locations. They are higher for those cores closest to the industrial sources (up to 15% of the organic material by volume). In all locations, the highest concentration is noted for the horizon around 10 cm depth (7 cm for the western most site). This depth likely marks the time around 1955 when steel production in the region reached its peak (Colton, 1985) or the early 1960's with the development of the Bethlehem Steel site, close to the IDNL. A decrease in the uppermost sediments (0-2 cm) reflects decreases in steel production since the 1980's, as well as more restrictive legislation controlling emissions.

Based on the results of the bulk geochemistry, Pb, Cr, and Cu appear to be relatively immobile after deposition; metal concentrations are highest near the surface and decline rapidly below ~ 16 cm (the depth representing the onset of anthropogenic inputs). Cadmium, Ni, and Se appear to have some mobility. The duration and/or frequency of flooding at a site appear to be important in determining the mobility of Zn and Mn.

Results from the sequential extractions show metal fractionation to be both site specific and metal specific (Dollar, 2000; Dollar *et al.*, *in preparation*). For example, in surface sediments the exchangeable fraction in periodically submerged sites ranged from 39-50% non-residual Zn and up to 33% non-residual Cd, but was absent in a permanently flooded site. The fraction of metals bound to Fe/Mn oxides varied for Cd, Mn, Pb and Zn by site. By contrast, the elements Cr and Cu are predominantly affiliated with organic matter/sulfide bound fractions and show little difference between sites. Analysis of sulfur fractionation found it predominantly sequestered along with the organic bound fraction. This "oxidizable" fraction dominates the geochemistry for Cr, Cu and Fe. Given the stability of metals in all fractions may be affected by changes in pH and oxidation reduction potential, the results of this study suggest that Cr, Cu and Fe exist in forms not likely to be mobilized, whereas Cd, Mn, Pb and Zn are potentially mobile if sites are flooded (*i.e.*, associated with wetland restoration).

Conclusions

The data collected reveals several important factors and processes controlling trace metal accumulation in these wetland environments.

1. Concentrations of trace metals are enriched in surficial sediments, and are comparable to metal concentrations in soils and sediments from other parts of the region.
2. Metal concentrations show spatial variability and variability with depth that cannot be accounted for by organic matter content alone.
3. Anthropogenic contribution of metals is substantial and verifiable across IDNL
4. Pb, Zn, Cr, and Cu concentrations in surficial wetland sediments all show increases with increasing proximity to anthropogenic sources.
5. Based on trends in metal concentration with distance from sources as well as surficial enrichment factors, Pb, Cr, and Cu appear relatively immobile after deposition, while Cd, Ni, and Se appear to have elevated mobility.
6. There is evidence that hydroperiod (duration and/or frequency of flooding) may be important in determining metal mobility in wetland sediments, especially for Zn and Mn.
7. Some of the drier wetland sites may have experienced greater metal mobility, likely due to the unbuffered

effects of acidic rainfall, although this is not true for all sites.

8. Results from the sequential extraction analyses show metal fractionation to be both site specific and metal specific. For example, the elements Cr and Cu are predominantly affiliated with fraction 4 (the organic matter/sulfide bound fraction) for all sites. However, the dominant fractions for the elements Cd, Mn, and Zn vary according to site and are seemingly influenced by differences in hydroperiod.

9. A considerable portion of Cd, Ni, Pb, and Zn exist in forms potentially predisposed to mobilization. Flooding previously drained sites may result in the rapid release of such metals.

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Undergraduate/graduate students supported by project:

Steven Perkins, MS student, Department of Geology, IUPUI (completed September 1998). Thesis title: *Trace metal contamination of wetland sediments at Indiana Dunes National Lakeshore.*

Nancy Dollar MS student, Department of Geology, IUPUI. Thesis title: *Chemical Fractionation of Metals in Wetland Sediments: Indiana Dunes National Lakeshore, Indiana (completed March 2000)*

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