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

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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 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

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 HNO_3 – 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 ^{210}Pb 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 μ m 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

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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