

INTERDISCIPLINARY APPROACHES  
TO  
FRESHWATER WETLANDS RESEARCH

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**EFFECTS OF COAL FLY-ASH DISPOSAL ON WATER CHEMISTRY  
IN AN INTRADUNAL WETLAND AT INDIANA DUNES**

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**ABSTRACT**

An intradunal wetland within the Indiana Dunes National Lakeshore on the south shore of Lake Michigan was flooded for 15 years by seepage from fly-ash settling ponds located adjacent to the park. Studies were undertaken to determine the effects of the seepage on water chemistry in the flooded wetlands. These water chemistry conditions have been correlated to ongoing studies of soil contamination and secondary succession in the wetland basin following cessation of seepage. The seepage increased the concentrations of calcium, potassium, sulfate, aluminum, boron, iron, manganese, molybdenum, nickel, strontium, and zinc in ground water and surface water downgradient from the settling ponds. Chemical interactions with aquifer materials, particularly organic matter, significantly limit the transport of aluminum, iron, nickel, and zinc in this system. The organic soils of the dewatered wetland basin now contain elevated concentrations of aluminum, boron, manganese, and zinc that are potentially phytotoxic under the low pH (<4) conditions that exist. Plant growth and secondary succession were affected by the soil chemistry of the dewatered wetlands.

**INTRODUCTION**

The use of coal as a fuel in electrical generating facilities has increased as a result of the recognized long-term limits on petroleum-based fuel supplies. The major waste product of coal combustion is fly ash, small (0.5 - 100 um diameter) inorganic particles that are entrained in the gas stream and carried up the stack following combustion. Fly ash is composed primarily of the oxides of silica, aluminum, iron, and calcium, with smaller amounts of magnesium, titanium, sulfur, sodium, and potassium. Trace elements are also found in fly ash, either on the surface of the particle or incorporated into its matrix (Campbell *et al.*, 1978). To prevent much of the fly ash from entering the atmosphere, electrostatic precipitators are used to collect the ash. The ash is normally transported to a landfill in dry form or sluiced to settling ponds in a water slurry. Leachates from fly ash are known to contain inorganic ions that can affect biota in aquatic receiving systems (see review by Cherry *et al.*, 1984).

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The purpose of this paper is to 1) describe the effects of fly-ash leachate on water resources, particularly wetlands, and 2) discuss the role of water chemistry studies in an interdisciplinary wetland research project.

## STUDY AREA

The study area (Figure 1) is located on the Calumet Lacustrine Plain in Porter County in northwest Indiana, partly within the boundaries of Indiana Dunes National Lakeshore. The area is within a large complex of dunes deposited during a level of ancestral Lake Michigan higher than the modern lake level. Many of the lowlands within the dune complex are wetlands. The largest wetland addressed in this study has historically been called Blag Slough (Cook and Jackson, 1978). It was probably a seasonally-flooded wetland prior to disturbance of the natural hydrologic regime (Wilcox *et al.*, 1985).

A coal-fired electrical generating station was constructed near the site in the mid-1960's, and fly-ash settling ponds were constructed adjacent to the southern edge of the wetland. The station burns coal mined primarily from Indiana and Illinois having medium to high sulfur contents (Magee *et al.*, 1973). Leachate from the fly-ash ponds seeped into Blag Slough through a sand dike at a rate of about 7.5 million liters/day (Meyer and Tucci, 1978), causing water levels to rise and become stabilized. As a result, Blag Slough and unnamed wetlands to the north had become perennially flooded by 1967.

Seepage from the fly-ash ponds was terminated in 1980 when the ponds were drained and sealed, and the wetland basins were dry by August of that year. Low-lying areas of the Blag Slough basin have flooded seasonally in subsequent years.

## METHODS

Sampling sites for water chemistry analyses were established along a transect beginning upgradient of the fly-ash settling ponds, including the settling ponds, and ending with downgradient ground and wetland surface-water sites (Figure 1). The transect is generally parallel to the direction of ground-water flow. Sites 1 and 3 were observation wells, screened in the surface aquifer, that were installed as part of the Meyer and Tucci (1978) study. The well casing at upgradient control site 1 was constructed of ABS plastic; the casing at site 3 in the sand dike was low carbon steel. Site 2 was a surface-water sampling site in the settling pond immediately adjacent to Blag Slough, and sites 4, 5, and 6 were surface-water sampling sites in the wetlands.

Most sites were sampled 12-16 times during the period September 1976 to May 1978. All surface water samples were grab samples collected 2-3 m from shore in waters that were not vertically stratified. Ground water samples were collected from the wells. Sample pH was measured in the field at the time of

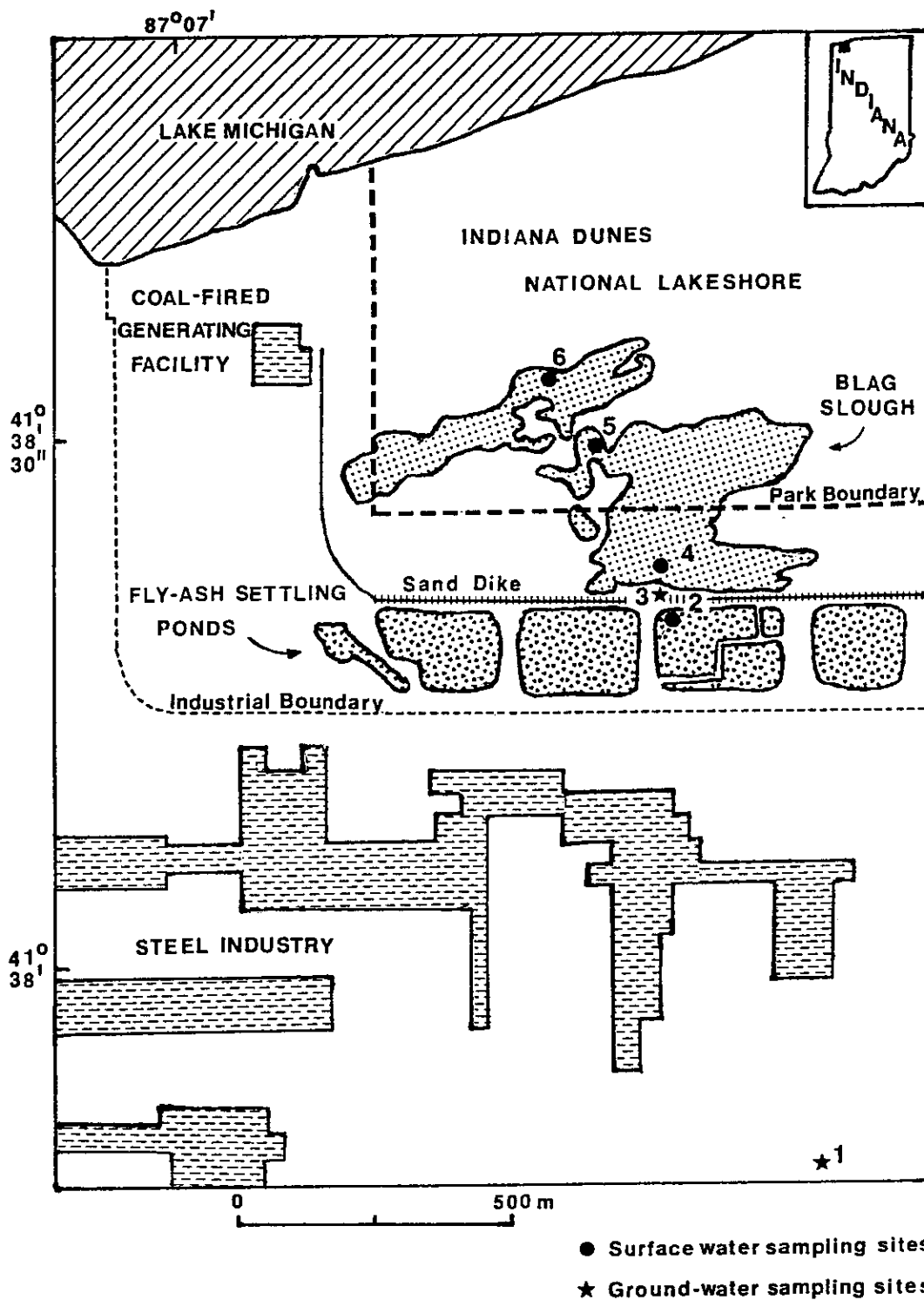


Figure 1. Site location map of Blag Slough, adjacent wetlands, coal-fired generating facility, and fly-ash settling ponds. Sampling sites and National Park Service boundaries are also shown.

sampling. All other analyses were conducted by the U.S. Geological Survey's Central Laboratory in Doraville, Georgia according to the methods of Brown et al. (1970). One dry fly-ash sample was also collected and chemically analyzed.

Log-transformed water chemistry data (except pH) from the six sampling sites were compared by one-way analysis of variance (ANOVA) and Scheffe multiple range tests. The latter procedure was selected because it is valid when sample sizes are unequal. For pH, the ANOVA was performed using actual values, which were more normally distributed than hydrogen ion concentrations. All means reported are geometric means.

## RESULTS

The fly-ash sample contained high levels of leachable, sorbed calcium, silica, sodium, sulfur, aluminum and iron (Table 1). Moderate concentrations of potassium, magnesium, and boron were also present. The pH of 4.9 represents the free hydrogen concentration of the ash slurry but not the reserve (buffered) concentration.

Table 1. Chemical analysis of fly-ash sample from electrical generating station. Concentrations are in mg/kg, except for pH, and represent leachable rather than total concentrations.

<u>Parameter</u>	<u>Concentration</u>
pH	4.9
Calcium	12,000
Chloride	11
Fluoride	92
Magnesium	770
Potassium	990
Silica	150,000
Sodium	2,000
Sulfur	10,000
Aluminum	5,000
Arsenic	100
Barium	50
Beryllium	3
Boron	490
Cadmium	3
Chromium	2
Cobalt	10
Copper	30
Iron	4,600
Lead	60
Manganese	60
Mercury	0.2
Molybdenum	22
Nickel	10
Selenium	0.2
Strontium	70
Zinc	90

Site 1 upgradient of the fly-ash ponds had calcium bicarbonate waters, and all downgradient waters were calcium sulfate types. Compared to the upgradient site, calcium, potassium, sulfate, and hydrogen (pH) were significantly enriched ( $\alpha = 0.05$ ) in and/or downgradient of the settling ponds (Table 2). Alkalinity and chloride were significantly lower in the settling pond and downgradient sites than in the upgradient control site. No statistical differences were found for fluoride, magnesium, silica, or sodium.

Table 2. Mean concentrations of major ions at sampling sites along transect. Concentrations are in mg/l, except for pH.

Indicator	Sampling Site					
	1	2	3	4	5	6
pH (units)	7.5	5.7	5.9	6.7	7.6	7.5
Alkalinity as CaCO <sub>3</sub>	210	2	5	22	44	35
Calcium	80	94	123	98	110	100
Magnesium	30	27	28	23	24	22
Sodium	32 <sup>1</sup>	19	18	16	16	16
Potassium	2.0	18.1	22.2	16.3	18.9	14.8
Silica	12	6	8	6	3	2
Chloride	70 <sup>1</sup>	10	10	11	11	10
Fluoride	0.1	0.3	0.4	0.3	0.2	0.2
Sulfate	65	398	458	342	357	338

<sup>1</sup>Site 1 is probably affected by road salting.

The pH of waters in the settling pond (site 2) varied widely (3.2-7.7). However, the mean values at site 2 (5.7) and site 3 (5.9) were both significantly lower than upgradient at site 1 (7.5). Although the pH in Blag Slough downgradient from settling ponds was not significantly different from site 1, alkalinity data indicate that ash-pond seepage significantly reduced the buffering capacity of water at all downgradient sites. Significant enrichment of calcium over the upgradient concentration was found only for sites 3 and 5. Potassium and sulfate, however, were enriched at all downgradient sites. Values for fluoride were greater at downgradient sites, but the differences were not significant.

Trace elements that were significantly enriched ( $\alpha = 0.05$ ) in and/or downgradient of the fly-ash settling ponds were aluminum, boron, iron, manganese, molybdenum, nickel, strontium, and zinc (Table 3). Although enriched in the settling pond (site 2), concentrations of arsenic, barium, cadmium, cobalt, copper, and lead were not significantly enriched downgradient of the pond. No statistical differences were found for beryllium, chromium, mercury, or selenium.

Table 3. Mean concentrations of enriched trace elements at sampling sites along transect. Concentrations are in  $\mu\text{g/l}$ .

Indicator	Sampling Site					
	1	2	3	4	5	6
Aluminum	22	556	431	107	59	--
Boron	104	2106	2896	2236	2248	1851
Iron	16	378	1676	355	122	111
Manganese	6	169	307	391	224	95
Molybdenum	3	53	33	87	214	--
Nickel	3	135	47	44	26	--
Strontium	123	490	478	424	483	--
Zinc	30	644	638	113	38	--

Of the trace elements enriched downgradient of the settling ponds, aluminum, iron, nickel, and zinc showed direct gradient declines in concentration from site 3 to site 6. Boron, manganese, molybdenum, and strontium did not display as clear a pattern.

## DISCUSSION

### Water Chemistry

The acidic nature of the fly-ash leachate from mid-west coal (Kopsick and Angino, 1981; Peffer, 1982) is of special concern in this study because the biological availability of many trace elements is generally higher at low pH values. Dissolution of trace elements from fly-ash particles is also generally greater at lower pH values (Andren *et al.*, 1980; Mejstrik and Pospisil, 1983). Although the total quantity of boron leached from fly ash is independent of pH, the leaching is greater into acid solution (Cox *et al.*, 1978). A major cause of acid formation is the dissolution of the sulfur oxides from fly-ash particles (Guthrie *et al.*, 1982). Chu *et al.* (1978), Andren *et al.* (1980), and Pagenkopf and Connolly (1982) suggest that the pH of ash-sludging water is primarily determined by the relative quantities of sulfate and alkaline earth metal oxides dissolved from the ash. The raw data from the fly-ash ponds show that low pH values were generally found in samples with lower ratios of alkaline earth metals (primarily calcium) to sulfate (Hardy, 1981). The effects of the acidic leachates at the study site are shown by the predominance of low pH and/or alkalinity data from sites downgradient of the settling ponds. Variations in pH from 3.2 - 7.7 in the ash pond are probably the result of ashes from a variety of sources having different sulfur contents. Higher pH levels at sites 4, 5, and 6 may be the result of reactions of the leachate with calcareous materials in the dune sands that comprise the surficial aquifer and dike.

Because water levels have receded and the wetlands of Blag Slough no longer support true aquatic fauna such as fish, the trace elements of major concern are those that are available for

plant uptake and are known to exhibit toxic effects. The trace elements that were enriched in the leachates analyzed in this study are among those commonly reported to leach from fly ash (Cherry and Guthrie, 1977; Kopsick and Angino, 1981; Dodd, 1983; Humenick et al., 1983; Mika et al., 1985). Of these, uptake and concentration in the tissues of aquatic and wetland plants has been demonstrated for aluminum (Furr et al., 1979; Guthrie and Cherry, 1979a, 1979b), boron (Kovacs et al., 1984), manganese (Hutchinson and Czyrska, 1975; Guthrie and Cherry, 1979a, 1979b; Aulio and Salin, 1982), nickel (Aulio and Salin, 1982; Kovacs et al., 1984), and zinc (Folsom and Lee, 1981; Schierup and Larsen, 1981; Aulio and Salin, 1982).

Although aluminum, boron, manganese, nickel, and zinc are all reported to cause toxic effects in certain agricultural plants (U.S. Environmental Protection Agency, 1976; Foy et al., 1978), documentation of toxic effects of these elements on aquatic/wetland plants is scarce. Hutchinson and Czyrska (1975) found a synergistic toxic effect of cadmium and zinc and also of copper and nickel in studies with Lemna (duckweed) and Salvinia (floating fern). However, van der Werff and Pruyt (1982) found no clear evidence of zinc toxicity in four aquatic plant species, despite considerable tissue accumulations. Similar results were reported by Cherry et al. (1984) and Mika et al. (1985).

Current research stresses the importance of nutrient uptake from the sediments by aquatic plants (see review by Spence, 1982) and also indicates that trace elements leached from fly ash may accumulate on sediments rather than remaining in the water column (Guthrie and Cherry, 1979b). In fact, the pattern of declines in dissolved concentrations of aluminum, iron, nickel, and zinc in Blag Slough downgradient of the settling ponds may reflect accumulation by the sediments. Folsom and Lee (1981) further indicate that trace metals accumulated in flooded sediments may become more available to plants when the sediments dry out due to organic decomposition. Therefore, the information obtained from the study of water chemistry in Blag Slough indicates that potentially toxic materials from the fly-ash leachate may be available for plant uptake from the soils of the now-dewatered wetland.

### **Coupling With Other Disciplines**

Work in other disciplinary fields has been conducted in conjunction with the water chemistry studies to provide a better understanding of the processes and effects of the seepage of fly-ash leachate into the Blag Slough wetlands. The hydrologic studies of Meyer and Tucci (1978) provided evidence that a ground-water mound from fly-ash pond seepage was actually responsible for the flooding of Blag Slough. Further hydrologic studies by Cohen and Shedlock (1986) documented the decay of the ground-water mound following cessation of seepage in 1980.

An interdisciplinary study of secondary succession in the Blag Slough wetlands was initiated in 1982 (Wilcox and Hiebert,



1984). The soils of the wetland basin were classified and mapped; shallow piezometers and land surveying were used to construct a water table map, a topographic map, and a contour map of the depth to the water table; major vegetation types were mapped and sampled quantitatively in successive years; and the wetland seed bank was assessed. In addition, a study of the fossil pollen record from a sediment core was undertaken (Futyma, 1986). This combination of studies assessed vegetative history and pointed out the importance of the moisture regime in contributing to the revegetation patterns observed. The extremely slow regeneration process was attributed partly to a lack of abundant viable seeds. Soil chemistry and contamination played a major role in determining which plant species were capable of surviving in the wetland following cessation of seepage. As stated previously, some of the contaminants should be present in the soil in plant-available forms. Soil chemistry data from the site were summarized by Wilcox *et al.* (1985) and are presented in Table 4. Zinc, manganese, boron, and aluminum were found in potentially phytotoxic concentrations in a low pH range where each is plant-available. In addition, the low soil pH may independently prevent the invasion of many common weedy species. Symptoms of boron phytotoxicity (vein-clearing) were observed in shrub species in the field and are being assessed by tissue analysis (Wilcox and Hiebert, unpublished). Bioassays utilizing soils from Blag Slough have shown reduced plant growth, morphological aberrations, and poor root development (a symptom of aluminum toxicity) (Wilcox and Hiebert, 1984).

Table 4. Maximum trace element concentrations ( $\mu\text{g/g}$ ) and pH (units) in soils from Scirpus cyperinus vegetation types, 1984<sup>1</sup>.

Vegetation Type	Zn	Mn	B	Al	pH
<u>Scirpus cyperinus</u>	34	24	2.2	500	3.7
<u>Scirpus/Polygonum</u>	26	42	2.0	600	3.8
<u>Scirpus/mixed forb mosaic</u>	13	14	3.2	190	4.0

<sup>1</sup>From Wilcox *et al.*, 1985.

The water chemistry study, which is the subject of this paper, is an integral part of the overall research project. There is an obvious relationship between the chemistry and hydrology of the seepage reaching the wetland. In addition, relationships between biological and environmental factors can be more easily explored because the water chemistry data provide the framework for understanding potential soil contamination and plant toxicity.

Clearly, correlations can be drawn between all aspects of the overall project, each discipline providing additional information to help understand the results of the others. Management impli-

cations and options, ranging from the Department of the Interior agreement with the power company to seal the fly-ash ponds to any possible amelioration attempts, must rely on as complete an understanding of all the wetland functions as is possible.

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