Long-term Nonpoint Pollution Abatement by a Lake Erie Marsh and its Implications for Wetland Restoration Policies

Final Report to the
Ohio Lake Erie Commission

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Lake Erie Protection Fund Contract: 97-49

December 1999

Abstract

Because of increasing anthropogenic pressure on freshwater resources, research on the ability of wetlands to mitigate pollution from nonpoint sources continues to receive high priority by scientific and regulatory communities. Wetlands may act in the short-term as a sink for nutrients and pesticides. They can remove these materials from farm runoff by microbial processing, sedimentation, or biomass production. This removal may diminish over time and appears dependent on soils, vegetation, and hydrology. Unfortunately, long-term (i.e., decades) studies on the potential of wetlands to trap nutrients and pesticides from runoff are lacking. We addressed this issue in a study of two marshes along the southwestern shore of Lake Erie (lat. 41°28'N, long. 82°59'W, Ohio), by analyzing accumulation records of sand-silt-clay, total phosphorus (TP), bioavailable phosphorus (BAP), total nitrogen (TN), total carbon (TC), organic matter (OM), metals, and pesticides preserved in four sediment cores from each marsh. The two marshes, North Marsh (260 ha) and West Marsh (220 ha), have been managed in the same fashion by the Winous Point Shooting Club for the past 150 years except that the West Marsh has been free from runoff since 1978. Their agricultural watersheds have poorly drained soils. Both marshes have been protected by dikes from the high-energy open-lake environment since ca.1920 and are situated between agricultural land to the north and Muddy Creek Bay to the south. This bay drains into Lake Erie. The sediment cores were sectioned in 1 cm intervals and dated with ^{210}Pb, ^{137}Cs, and *Ambrosia* pollen. Unsupported ^{210}Pb activities decreased down-core and approached background at depths up to 35 cm. Counting errors averaged ± 0.016 Bq g^{-1} with an average sample weight of 1.81 g and count times between 19 and 46 hours. Dating uncertainty increased with sediment age and made ^{210}Pb-dates older than 100 years unreliable (90% c.i of ± 30 years). The onset of ^{137}Cs activity corresponded with a ^{210}Pb-derived date of 1960.4 (±7.4 years). TP and BAP accumulation rates during the last 10 years in the North Marsh more than tripled compared with rates during 1920-1977 interval. These increases were considerable less in the West Marsh and were independent of the levels of aluminum, iron, and manganese in the sediments. The ratios of TP to TC and TP to TN accumulation in the North Marsh were higher during the most recent decade of deposition, whereas these ratios remained nearly constant in West Marsh sediments since 1920. The ratio of TC to TN accumulation did not change in either marsh since 1920 and the absence of a sedimentary signal of increased trapping of these elements in the North Marsh is likely due to the significance of atmospheric pathways of removal. Aldrin, endrin, HCHs, and DDT concentrations varied over depth in the cores following patterns related to the known onset and banning of their use. However, some pesticides continued to accumulate at lower rates after agricultural use was discontinued. High concentrations of HCHs and endrin in West Marsh sediments since mid-1960's point to a possible airborne source from adjacent agricultural lands. The continued assimilation of TP, BAP, and target pesticides suggests the long-term utility of these marshes to mitigate the effects of nonpoint-source pollution on downstream systems.

Acknowledgements

We wish to thank Nick Kusina, Brian Marlow, Corey Pacer, and Shelly Spera for their help in the laboratory. Michael Benedict, assisted by the University of Toledo's Department of Geography and Planning, was responsible for the analysis of land-use in the watersheds. Dr. Linda C.K. Shane of the University of Minnesota's Limnological Research Center, advised us on palynological techniques. CHN analysis was carried out by the University of Toledo's Instrumentation Center and the Water Quality Laboratory at Heidelberg College allowed us to use their particle-size analyzer for the grain-size analysis.

This work would not have been possible without the cooperation from the Winous Point Shooting Club. They provided us with unlimited access to field sites, boats, and vehicles. Support for this project came from the Lake Erie Protection Fund (contract 97-49), the Society of Wetland Scientists' Student Research Awards Program, and the University of Toledo's Lake Erie Center.

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1. Introduction

Wetlands may offer many environmental benefits. They may act as a sink for nutrients, suspended solids, and pesticides (Ewel and Odum 1978; Hey *et al.* 1994) and therefore may serve as a filter for agricultural drainage. Mechanisms for removal of chemicals include microbial processing, sedimentation and biomass production (Kadlec and Knight 1996). Short-term assimilation of constituents in agricultural drainage by wetlands is reasonably well documented (Ewel and Odum 1979, Klarer and Millie 1989, Mitsch *et al.* 1989, Hammer 1993, Kadlec and Hey 1994, Dortch 1996). Unfortunately, the relative importance of these mechanisms for long-term processing of agricultural runoff by Lake Erie marshes is untested and poorly understood. The ability of a wetland to remove these materials from influent waters may vary from year to year and diminish with time (Richardson 1985). Factors affecting such removal include flooding regime (Craft *et al.* 1988), composition and density of the plant community, water-retention time, and related processes (Mitsch and Gosselink 1993; Kadlek and Knight 1996). Programs of wetland acquisition and management designed to emphasize water-quality benefits of marshes, however, should not only consider short-term data but should be based on long-term information on contaminant assimilation by wetlands. Consequently, programs that do not consider such long-term information lack a complete scientific basis. The Winous Point marshes in the Lake Erie watershed serve as a natural laboratory where these long-term processes can be investigated. These marshes have been managed since the early 1900s and detailed records and maps exist as far back as 1856 (Gottgens *et al.* 1998).

1.1. Wetland Structure and Functions

1.1.1. Structure

Wetlands occupy low-lying areas in the landscape where they generally form ecotones between upland and open-water ecosystems. Wetlands have shallow water levels that facilitate germination and are dominated by vegetation that can tolerate waterlogged soils for long periods of time throughout the year. Furthermore, these water-logged sediments are usually anaerobic with the exception of oxygenated zones in the vicinity of the roots of some plant species (Horne and Goldman 1994). Many wetlands also have low water flow rates which promotes settling of particulate suspended matter from the water column.

The basic structure of a wetland includes underlying lithology, hydric soils, detritus, a seasonally flooded zone, and emergent vegetation (Kadlec and Knight 1996). Wetlands, such as those at the Winous Point Shooting Club (WPSC), are considered palustrine emergent marshes according to the United States Fish and Wildlife Service (Cowardin *et al.* 1979). These nontidal wetlands are dominated by persistent emergents, tress and shrubs and have salinities less than 0.5 ppt.

1.1.2. Functions

Wetlands are important at three different scales. At the population level they provide habitat for many species of animals and plants, including some species which are economically important (Mitsch and Gosselink 1993). Wetlands are important at the ecosystem level because they may mitigate the effects of floods and they may improve water quality. The potential for wetlands to mitigate the effects of flooding or water pollution has only recently been addressed. Because wetlands usually have shallow, slow-moving water, they can minimize the effects of flooding by acting as water detention systems (Kadlec and Knight 1996). In wetlands that have long water retention times water is lost to the atmosphere through transpiration and evaporation (Mitsch and Gosselink 1993). The ability of some wetlands to function as "kidneys" and accumulate or transform pollution present in inflowing surface-water has given rise, in part, to the new discipline of ecological engineering in which wetlands are designed, constructed and maintained for the improvement of water quality (Mitsch 1995; Kadlec and Knight 1996). Wetlands can accumulate or transform pollutants through abiotic and biotic pathways. Wetlands with low flow-rates may deposit their organic and inorganic material thereby sequestering their absorbed and adsorbed pollutant load. Pollutants can also be sequestered through the processes of bioaccumulation where nutrients, pesticides, and their breakdown products are assimilated by algae, macrophytes and the microbial community. Once assimilated, these pollutants may be removed from the system by burial in sediments, respiration, degassing, or exported or harvested as biomass. Although these processes have been studied in the short-term (from one to 10 years), the sustained ability of wetlands to remove pollutants during many decades is poorly documented.

On a global level wetlands play important roles in carbon (C), nitrogen (N), phosphorus (P), and other element cycles. Major nutrients can be transformed, sequestered and even exported from wetlands through a variety of organic and inorganic processes. N that enters a wetland can be released to the atmosphere as a product of denitrification which occurs in anaerobic sediments. Although C can be lost to the atmosphere from wetlands as carbon dioxide or methane (520-590 x 10^6 mtons yr^{-1}), large quantities of the world's C are sequestered in high latitude peatlands (76 x 10^6 mtons yr^{-1}) (Mitsch and Gosselink 1993). As wetlands are destroyed and peat is harvested, C is increasingly lost to the atmosphere (Mitsch and Gosselink 1993). P in wetlands can be stored in sediments, though some can be lost through the export of biomass.

1.2. Processes Affecting Nutrient and Pesticide Retention in Wetlands

Nutrient retention by wetland soils is regulated by several physical, chemical, and biological processes that take place at the sediment-water interface where litter and sediments appear to be the key components (Kadlec 1989). P dynamics are controlled, in part, by iron-aluminum (Fe-Al) bound soil fractions in acidic sediments (Gale *et al.* 1994) and redox values with sediments dominated by Fe-bound P are predicted to release P under anaerobic conditions (Wetzel 1983, Mitsch and Gosselink 1993). Nutrient release to overlying water may be promoted or repressed by physical and chemical activities of biota (Montague 1986). Sediment composition and texture may influence the rate of nutrient release from sediments to adjacent water. Fine-grained sediments are considered to be the most geochemically active and important in nutrient dynamics because of their ability to bind nutrients (Stone and English 1993). Assimilation by macro- and especially microphytic vegetation may remove nutrients from overlying water. Unless peat is formed and buried, vegetation is only a short-term, seasonal sink for nutrients in marsh water. Hydrological characteristics may also dominate nutrient retention by wetlands. For instance, Klarer and Millie (1989) documented that an undiked coastal Lake Erie marsh may act as a nutrient sink for agricultural runoff. Their data showed a significant positive correlation in PO_4^{3-}, NO_3, Fe, Cu and Zn concentrations with increasing turbidity (which was used as an indicator of storm water). Furthermore their data showed reductions in outfall concentrations for NO_3, PO_4^{3-}, and Si of 35 - 72% relative to inflow values. They felt that these values were greater than could be accounted for by sedimentation or geochemical processes.

Similarly, pesticide degradation depends on the environmental conditions during transport and burial. In the streams that entered the Great Lakes with a pH of 6.5- 8.5, atrazine remains in a non-ionic state and was dissolved in water rather than absorbed to suspended solids (Frank *et al.* 1979). Sheets (1970) noted that persistence of atrazine in soil depended on pH, temperature, and microbial activity. The highest rates of atrazine decomposition were found in acidic soils. The behavior of pesticide residues is strongly dependent on the adsorption and desorption properties of the sediments. Kalousková (1989) noted that atrazine is adsorbed onto humic acids at pH values below 5.5 and no adsorption occurred at pH values of 5.5 - 6.2. Organic compounds in solution can modify the adsorption and desorption of herbicides. Barriuso *et al.* (1992) found that atrazine adsorption was favored when soil was pretreated with dissolved organic matter (DOM). A reverse effect was noted for other herbicides. Locke (1992) noted that organic matter content may be the decisive factor in alachlor adsorption. In conservation tillage systems the increase in plant residue at the soil surface increased the water residence time at the surface, which, in turn, increased the potential for alachlor movement in water runoff. Guo *et al.* (1993) showed that different types of organic matter affected the leaching potential of alachlor from soil. These were all short-term studies covering a maximum of a few years.

Although the assimilative capacity of marsh sediments depends on their physico-chemical properties, and can vary from year to year, the long-term record of material transfer between water and sediment may be preserved in the sediment stratigraphy. Accumulation rates can be calculated for the past 100 years by dating the sediment column using activities of radionuclides such as lead-210 (^{210}Pb) and cesium-137 (^{137}Cs) (Goldberg 1963; Gottgens and Crisman 1993). Reddy *et al.* (1993) successfully applied the ^{137}Cs dating technique to a series of sediment cores taken from the Florida Everglades. The use of additional radioisotopes enhances the confidence associated with the chronologies (Gottgens 1996).

1.3. Sediment Cores as Potential Records for Long-Term Material Transfer Between Water and Sediments

In depositional environments such as wetlands, lakes, reservoirs, and oceans a fraction of the material in the water column continually settles on the bottom. Over time, the composition of these deposits may change in response to changes in the drainage basin, the redox potential at the sediment-water interface, and other factors. If the sediments are buried and remain undisturbed they may form a stratigraphic record of physical, chemical and biological changes that occurred in such an aquatic ecosystem.

This sedimentary record may be sampled in the form of a core, collected with a sampling device (e.g., a stainless steel, or polycarbonate tube) which is inserted into the sediments and successfully withdrawn. Alternate methods of coring include box coring and freeze coring. The primary goal of coring is to obtain an undisturbed, representative sample of the total depositional record of the system under study.

If the sediments have not been disturbed since they were deposited, the core represents a subset of the total history of the drainage basin. Using the proper analytical techniques, the history of the drainage basin can be characterized. Parameters of interest include radioisotopes for absolute age-dating of the sediments for chronologies, physical parameters such as grain-size distribution, biological indicators of past environmental conditions, and chemicals such as major nutrients or pesticides. If a core produces a reliable chronology, then analyses for other environmental parameters of interest can generate trends in accumulation of those parameters over time.

Because of the aforementioned aspects of sediments and coring, cores can be used to reconstruct a depositional history and secure pre-European baseline data for comparison with current marsh conditions. An additional benefit of using data from sediment cores is that annual, and perhaps spurious, fluctuations are integrated as a product of the sampling processes. Consequently, long-term trends and major changes become more obvious than in traditional real-time studies.

1.4. History of Wetlands in the Western Basin of Lake Erie

Soils of the Lake Erie region are composed of lacustrine and glacial sediments that were deposited on folded sedimentary formations of the Paleozoic Era. The composition of the glacial sediments is due to the underlying source-rock such as the Delaware Limestone and Columbus Limestone as well as clastic formations such as the Ohio Shale and Berea sandstone (Muller 1992) and igneous and metamorphic material from the Canadian shield.

Lake Erie was formed 3500 years BP, almost 10,000 years after the close of the Wisconsinan ice age. From 125,000 to 12,000 BP northern Ohio was covered by a continental ice sheet up to 1.5 kilometer thick. As the Wisconsinan ice age subsided and the continental glaciers receded northward, periglacial lakes, the precursors to Lake Erie, formed against the glacial lobes to the north. It was these bodies of water, such as lakes Maumee, Arkona, Whittlesley, Warren, and Wayne, some with elevations 230 feet higher than current lake levels (Hansen 1999), that created the deposits that form the silty/clayey soils and sediments found in the marshes of southwestern shore of Lake Erie.

Coastal wetlands in the Great Lakes' basin are important transitional ecosystems connecting terrestrial upland with open water. Prior to 1850, some 4,000 km^2 of diverse wetlands ("The Black Swamp") covered the watershed of the western basin of Lake Erie (Herdendorf 1987). These coastal marshes and forested swamps served as habitat for wetland species, and changed the chemical and biological make-up of water flowing into the lakes (Langlois 1954). The inland boundaries of these wetlands have moved landward and lakeward with changes in water level (Mitsch 1992). However, starting in the middle to late 1800s, most of the marshes along the western basin of Lake Erie were drained and converted for agricultural and urban development (Herdendorf 1987). Dikes and other structures were built along the shore to protect developed areas from the effects of high lake levels such as erosion and siltation. As a result of these measures, the remaining natural marshes became trapped between dikes and rising water levels and their plant communities were, for the most part, destroyed (Mitsch 1992). Starting in the early part of this century, additional dikes were installed between most of the remaining wetlands and the open lake water. This was done to shield the marshes from wave erosion, control water levels, and allow for the maintenance of aquatic vegetation (Bookhout *et al.* 1989). At present, less than 5% of the original western Lake Erie marshes remain (Herdendorf 1992), most of which are protected and maintained behind dikes.

The remaining marshes are not managed for the purpose of contaminant removal from agricultural, industrial, or urban runoff. This runoff enters drainage ditches that bypass the remaining marshes and flow unimpeded into Lake Erie. As such, the lake is directly exposed to sediment, pesticides, and nutrients from fertilizers. Without scientific evidence of the long-term water quality benefits of Lake Erie wetlands, political mechanisms (e.g., zoning, land-use planning, economic incentives, etc.) and criteria for enhancing Ohio's coastal resources cannot be developed. This is particularly significant at the State level because, under provisions of the Clean Water Act and Coastal Zone Management Act, the Ohio Environmental Protection Agency (OEPA) is responsible for managing wetlands in coordination with the United States Army Corps of Engineers (USACE), United States Department of Agriculture's (USDA) Natural Resources Conservation Service, and county and township officials.

1.5. Rationale for the Study

A decade to century-long study could determine the long-term effect of agricultural runoff on the assimilative capacity of Lake Erie marshes. Studies of this kind, though valuable, have two distinct problems. First, this type of research is time-consuming and expensive. Second, this type of study cannot provide pre-European baseline data for comparison with current values. An alternative to the aforementioned approach is to utilize the record of target-analytes accumulated in marsh sediments over the time-span of interest. Cores are taken from the study site and analyzed for a chronology as well as signals of interest. This approach, utilized by paleoecologists and paleolimnologists, is relatively inexpensive, quick, and can provide the necessary baseline data (Gottgens and Liptak 1998).

Using a paleolimnological approach, a study of the long-term effects of agricultural runoff on the accumulation capacity of two Lake Erie marshes was undertaken. Both marshes have drainage basins dominated by agricultural activity initiated by European settlers during the middle of the 19th century. These two Winous Point marshes were managed by the Winous Point Shooting Club (WPSC) in the same fashion with the exception that in 1978 the upland dike of one marsh was closed, thereby effectively separating that marsh from its watershed. Because the other marsh continued to receive agricultural runoff from its drainage basin, these two marshes provided a system whereby a comparison between the accumulation rates of target analytes of a marsh which received agricultural runoff could be made with a similar and adjacent marsh that did not. Additionally, this system could provide a long-term record of target analyte accumulation to determine the effect, if any, of European agricultural practices on the marshes' capacity to accumulate contaminants from that source.

2. Objectives

Building on the results of a pilot study (Gottgens and Liptak 1998), we studied two Lake Erie marshes at the WPSC to quantify long-term contaminant assimilation-rates. Our goal was to quantify the long-term rate of contaminant assimilation from nonpoint-source agricultural runoff by comparing a time-series of target analyte accumulation from a marsh subjected to agricultural runoff with a time-series from an adjacent, similar system, free from this impact since 1978. Such an experimental arrangement with two adjacent marshes was not available at any other Ohio coastal marsh. We tested the hypothesis that the marsh subjected to continued agricultural runoff has maintained consistently higher accumulation rates for target analytes since 1978 than the reference marsh. By comparing recent accumulation rates with pre-1978, we also tested whether the impacted marsh continued to filter agricultural runoff or whether assimilative saturation had occurred. Target analytes were those that have a negative impact on water quality in the littoral and open water zones of Lake Erie. The contaminants include sediment (turbidity), carbon, organic matter, nitrogen, phosphorus (total and bio-available), selected pesticides and their breakdown products. The social science portion of this work intended to set this natural experiment in its 120-year government, economic, and social context.

3. Study Site and Methods

3.1. Study Site

The project was carried out in the Winous Point marshes (lat. 41°28'N, long. 82°59'W, Ohio, USA), situated between areas of agricultural land to the north and Muddy Creek Bay to the south (Figure 1 and Figure 2). The bay drains via Sandusky Bay into the central basin of Lake Erie. These marshes are privately owned by WPSC, established in 1856, and have been managed by professional wildlife biologists since 1946. Original survey maps (Bourne 1820; WPSC unpubl. surveys) indicate that farms have defined the marshes' upland boundary since their establishment prior to 1850. Water flows into the wetland from the Sandusky River, several small creeks and agricultural ditches, and then drains first into Sandusky Bay and then into Lake Erie. By 1920, "lakeward" dikes were completed to protect some of these marshes from wind and wave action from the open lake and bay (Gottgens *et al.* 1998). Growth of emergent aquatic macrophytes is stimulated by periodic lowering of the water level in the impoundments from mid-May through early August (Sherman *et al.* 1996). The diked marshes contain a combination of shallow water, emergent vegetation, and some woody plants on higher elevations. Dominant emergent plants include narrow-leaved cattail (*Typha angustifolia*), several millet and barnyard grasses (*Echinochloa* spp.), smartweeds (*Polygonum pensylvanicum* and *P. lapathifolium*), pickerelweed (*Pontederia cordata*), nutsedge (*Cyperus esculentus*), and switchgrass (*Panicum virgatum*) which grows on the dikes (Sherman *et al.* 1996). Water milfoil (*Myriophyllum spicatum*) and several pondweed species (*Potamogeton pectinatus* and *P. crispus*) are common submerged species interspersed with American lotus (*Nelumbo lutea*).

The field sites for this project have been protected from physical disturbance from waves with the use of dikes since the early 1900s. The property includes a 260 ha marsh (North Marsh) subject to non-channelized runoff from approximately 200 ha of farmland, primarily used for the production of corn and soybeans. Runoff from similar farmland has been diverted from an adjacent 220 ha marsh (West Marsh) since 1978 (Figure 2).

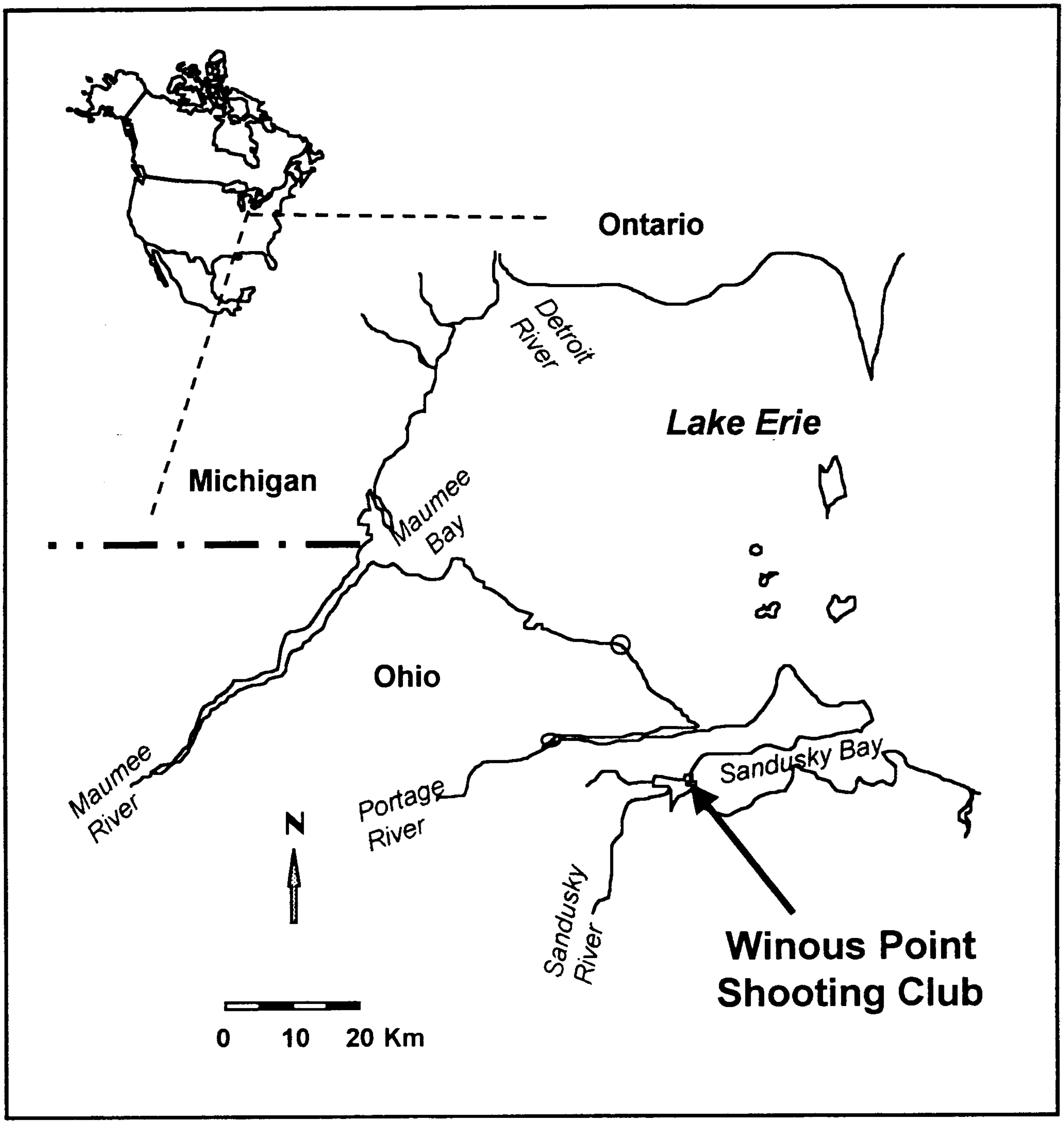


Figure 1. Location of the Winous Point Shooting Club Marshes.

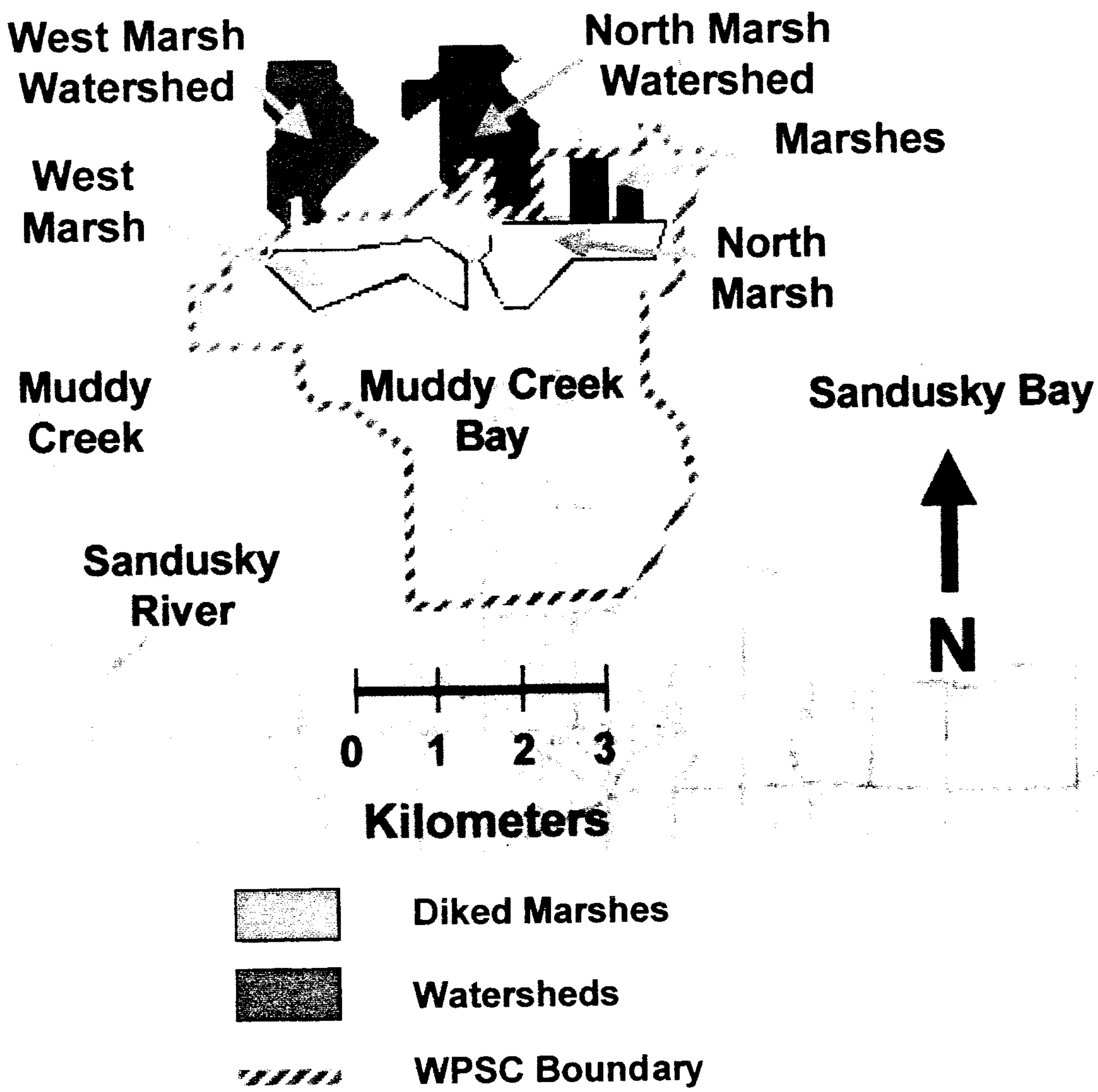


Figure 2. Winous Point Shooting Club site map showing the the North and West marshes with their respective watersheds. The two smaller marshes to the NNE of the North Marsh are non-agricultural units. Both North and West marshes drain into Muddy Creek Bay.

3.2. Analysis of Soils and Landuse

Two Ottawa County United States Geologic Survey quadrangle maps (Vickery; Wightman's Grove) were digitized with ARC/INFO™ (ESRI), a Geographic Information System (GIS), to produce three geo-referenced layers. These layers included boundaries of the watersheds for the North and West marshes, main roads, and 21 control points (within and outside of the watersheds). These layers were geo-referenced to four known UTM coordinates. The layers were imported into ArcView™ 3.1 (ESRI) to perform spatial analyses, which included the calculation of perimeters (m) and total area (m^2) for each watershed, and the overlay of watershed boundaries on the soils map.

Soils data for the area of study were obtained from a GIS coverage of soil mapping units for Ottawa County. This coverage was obtained from the Ohio Department of Natural Resources (ODNR) web-page containing original soil survey data (USDA-NRCS 1980) in an ARC/INFO export vector format. The soil coverage was projected to UTM coordinates using ArcView 3.1 to allow an overlay with the watershed boundaries. With these two coverages superimposed, we could identify the soil units that occurred within the areas of the two watersheds. The legend utilized for the soil types was the original classification for the soil mapping units provided by the ODNR file.

Photocopies of aerial photos of the area (Ottawa County Natural Resource Conservation Service, Oak Harbor, Ohio) covering both watersheds were scanned into digital format (uncompressed TIFF files). Photocopies for the following years were obtained for each of the watersheds: North marsh: 1939, 1950, 1957, 1970, 1988; West marsh: 1950, 1957, 1970, 1988. The aerial photo TIFF files were imported into an image-editing software (Adobe Photoshop 5.0; Adobe Systems Inc.) and land cover was reclassified according to four categories of land use: Row Crops; Orchards; Forest, Marsh or Old Field; and Roads and Residential. Forest, marsh or old field land covers grouped together as the image quality and resolution available with the photocopies was not sufficient to accurately separate these landscape units. The TIFF file for North Marsh 1939, had an additional category, "No-coverage", for part (4.3 %) of the watershed area not obtained with the photocopy of the aerial photo.

Relative percentages of area for each land use category were obtained for both watersheds for each year, using a histogram function in Photoshop™. This function generated a pixel count for each land use category in each watershed. These pixel counts were then converted to hectares by computing the area covered by one pixel based on the total area value for each watershed.

3.3. Field Methods

3.3.1. Core Locations

Two factors were considered in locating the coring sites in the marshes. First, the core locations were selected in areas with the greatest water depth and a high probability of inundation throughout the year. Second, we selected sites with a history of minimal disturbance. Using these considerations, five coring locations were picked from each of the studied marshes.

3.3.2. Coring

At each site, two cores were taken. One core from each location was used by investigators from the Biology Department to determine sediment chronology, nutrient concentrations, grain size distribution, and pollen composition. The second core was used by investigators from the Geology Department for metals and pesticide analyses.

We used 7.5 cm internal diameter, clear polycarbonate core barrels to collect marsh sediments. Cores were taken from a small boat by inserting a core barrel into the marsh sediments until refusal. Because of the high water content and fine-grained sediment in the core, we covered the bottom of the core barrel with a cap to prevent the sediments from sliding out upon retrieval. Any headspace in the core barrel was filled with marsh water to limit disturbance of the sediment/water interface during transport. The top of the core barrel was also capped and secured with duct tape. Aluminum foil was then wrapped around the core barrel as insulation and to limit the autotrophic activity caused by light exposure to the sediments. Cores were then carefully transported back to the laboratory in a vertical position and stored up to 14 days at 4°C in a coldroom pending sectioning.

3.4. Laboratory Methods

3.4.1. Core Sectioning

Each core was sectioned at one-centimeter intervals. Special tools for this process include a core-barrel holder and a piston. The core-barrel holder is welded together from steel L-bar and square tube stock and mounted to a wall. The core barrel is fastened to the holder using pipe clamps. The piston is a rubber stopper with a diameter slightly smaller than the internal diameter of the core barrels. This piston is affixed to the top of a wooden rod marked at 1 cm intervals. The core barrel was lowered at 1 cm intervals and samples were taken and transferred to a plastic jar which was labeled with the core ID, sample ID and the sampled interval (e.g., 10-11 cm). Because smearing of sediments may occur in the sediments in contact with the inside of the core barrel, the outer 1cm of each section was discarded to minimize cross contamination. The procedure was repeated to include all but the deepest 2 cm of the core, which were discarded because of possible disturbance and contamination due to contact with the piston. Following sectioning, samples were frozen pending further analyses.

3.4.2. Core Chronologies

To calculate age/depth relationships in the sediment cores, the activity of unsupported ^{210}Pb (half-life 22.26 years) was measured by determining the total and supported ^{210}Pb activity. Supported 210Pb results from, and is maintained by, radioactive decay of radium-226 (^{226}Ra, half-life 1622 years) in the sediments. Unsupported ^{210}Pb is formed by the decay of ^{226}Ra to radon-222 (^{222}Rn, half-life 3.82 days), that escapes into the atmosphere, eventually decays to ^{210}Pb which is washed out of the atmosphere by dry deposition or wet precipitation and enters the marsh via direct deposit or surface water inflow. Subtracting supported ^{210}Pb from total ^{210}Pb in sediment samples yields unsupported ^{210}Pb.

The age of a sediment layer was calculated from the activity of unsupported ^{210}Pb. Because of ^{210}Pb's short half-life, this dating technique is restricted to sediments deposited in the last 100-120 years. The activity of cesium-137 (^{137}Cs, half-life 30 years) served as an independent time marker in the sediment profile (Robbins and Edgington 1975; Krishnaswami and Lal 1978), because maximum activities coincide with a period of widespread atmospheric nuclear testing in the early 1960s. In the eastern woodlands of North America, the increased abundance of *Ambrosia* sp. (ragweed) pollen, known as the "*Ambrosia* horizon", following the advent of widespread European agricultural practices in the middle 19th century (Anderson 1974), was used to corroborate and extend the earliest ^{210}Pb dates.

Activities of total ^{210}Pb, supported ^{210}Pb and ^{137}Cs were measured independently and simultaneously by direct-assay using an intrinsic-germanium well-detector following techniques described by Gäggeler *et al.* (1976), Appleby *et al.* (1986), and Gottgens *et al.* (1999). The activity of unsupported ^{210}Pb is used for generating chronologies. However, unsupported ^{210}Pb cannot be directly measured, it must be calculated by subtracting supported ^{210}Pb, which is estimated from the activities of two of its parents (^{214}Pb, ^{210}Bi), from total ^{210}Pb.

The samples were dried at 100°C for 24 hours, pulverized, placed in low-density polypropylene vials (4mL), sealed with "Seal All"™ cement (Allen Products Corp.) and stored for a minimum of 21 days to allow secular equilibrium to establish between ^{222}Rn and ^{210}Pb. Counts for regions of interest were obtained with a high-resolution multi-channel analyzer calibrated at 0.186 keV/channel. Counting times were as long as 46 hours depending on the weight of the samples and the activity of ^{210}Pb; small samples with low activities require longer count times to reduce error. Blanks and standards were run to determine background values, to track efficiency and to calculate the ^{226}Ra conversion factor (Bq cps^{-1}). Counts were corrected for Compton scattering by subtracting the below-the-peak area from the total counts. Counting efficiency as a function of sample density was determined from a series of uranium-238 standards (^{238}U, half-life 4.5 billion years) with a range of densities. A regression of efficiency versus density was performed and the resulting function was used to adjust each sample's efficiency based on its density.

Calculation of ^{210}Pb dates followed the Constant Rate of Supply (CRS) model (Goldberg 1963). Chronologies were calculated using IRC_3A.SQL, a collection of SQL*Plus™ and PL/SQL™ (Oracle Corp.) programs coded for this project. Accumulation rates (g m^{-2} yr^{-1}) were calculated by determining the target analyte's concentration per volume (g cm^{-3}), integrating this concentration over depth (cm), and dividing that by the ^{210}Pb-determined time (yr) that it took to deposit that material. Uncertainty analysis was based on both the random variation of counting errors associated with radioactive decay and the nature of the CRS model (Binford 1990). Counting errors (± 1standard deviation) in the calculation of net isotope-activities were propagated using first-order analysis. Monte Carlo simulations (1,000 iterations) were used to estimate error (90% confidence interval) associated with the calculation of age following the CRS model.

3.4.3. Pollen Analysis

Pollen analysis was performed to provide an independent age marker in the middle 19th century to extend the ^{210}Pb chronologies. For this purpose, samples were analyzed to determine the *Ambrosia*-horizon (*Ambrosia sp.*), a well-known indicator in the eastern United States of the advent of widespread European agricultural practices (Anderson 1974). Samples were prepared for pollen analysis following Shane (1992), but modified to exclude hydrofluoric acid (HF) treatment of the samples. Because of the low silica concentrations in our samples and the acute hazard associated with the use and disposal of HF, we eliminated this treatment and added an extra 8 µm nylon mesh-screening step. Samples were spiked with a calibrated *Eucalyptus globulus* pollen spike (spike 01APR98). Spiking the samples allowed for absolute pollen concentration calculation (Davis and Deevey 1964, Shane 1992).

Processed samples were dehydrated and suspended in silicone oil (Brookfield Engineering Laboratories). A sub-sample was placed on a slide, covered with a 9mm X 9mm coverslip and sealed with fingernail polish. Five pollen-counting transects were run per slide and all *Eucalyptus* and *Ambrosia* pollen were counted. The ratio of *Ambrosia* pollen to total pollen (*Eucalyptus* plus *Ambrosia*) was used to determine the approximate depth in the core dated to 1860. A Leica DM-LB compound microscope (Leica Mikroskopie und Systeme GmbH) was used for all pollen analysis. Scans were performed at 200X using brightfield illumination with L-plan widefield 10 X 25 eyepieces and N-plan 20X/0.40 objectives.

3.4.4. Physical Parameters

3.4.4.1. Bulk Density

Bulk density values were determined for each section of each core. These values were generated as part of the ^{210}Pb assay sample preparation process. For bulk density, a sub-sample of known volume was taken from the core section. This sub-sample was placed in a tared crucible or aluminum drying-pan, placed in an oven and dried at 100°C for 24 hours. The crucible or drying pan was then transferred to a dessicator for cooling. After cooling, the sample was reweighed and the gross weight recorded. Sub-sample volume, crucible/drying pan tare-weight and gross weight were loaded into LEED and then the bulk density was calculated using INSERT-DBD.SQL.

3.4.4.2. Percent Organic Matter

Percent OM was determined using the loss-on-ignition method (Dean 1974). Analysis was performed as part of the total phosphorus (section 4.3.5.1) sample preparation procedure. Samples of known dry weight in tared crucibles were placed in a muffle furnace and heated at 500°C for one hour. After the oven had cooled, deionized water was added and the samples were put in an oven and heated at 100°C for an hour. This last part of the procedure was done to replace the hydroscopic moisture that the clays may have lost when the sample was ignited at 500°C. After heating the samples at 100°C the samples were placed in dessicators to cool and reweighed. Dry weights, ash weights and tare weights were loaded into the project database and OM percent was calculated using INSERT_OM.SQL..

3.4.4.3. Particle Size Analysis (PSA)

PSA was performed with a Malvern Mastersizer Laser Analyzer (MMLA) (Malvern Instruments Inc.) at the Water Quality Laboratory at Heidelberg College, Tiffin, Ohio. This method of analysis was used instead of the hydrometer method because MMLA permits very small sample sizes (less than one gram) common in core studies. This procedure allowed analysis of individual 1 cm thick samples, whereas with the hydrometer method required combined samples from adjacent horizons to achieve the minimum required sample size, thereby integrating the particle size distribution over many years, and diluting the resolution of the analysis. Because we were only interested in the proportions of biogeochemically active sediments only particle sizes less than 0.5 mm were analyzed.

A fresh, thawed sub-sample was washed through a 2mm sieve with deionized water into a 125 ml polypropylene jar. Fifty ml of sodium hexametaphosphate (40 g l^{-1} solution) was added to the jar that was closed and mixed by shaking for one minute. For analysis in the MMLA, the samples were diluted in deionized water in a one liter polypropylene beaker. Prior to adding part of the sample to the beaker, it was vigorously shaken to insure a well-mixed representative subsample. Prior to sampling with the MMLA, background values were taken using a deionized blank. The sample was then placed in the instrument and the obscuration ratio (OR) measured. Malvern recommends ORs between 10 and 30 %. If the OR was less than 10%, the sample was discarded and another subsample prepared. If the OS was greater than 30%, then additional deionized water was added until the OS fell below 30%. After the sample was run the report was printed and the MMLA system rinsed with deionized water to eliminate any contamination from the previous sample.

MMLA reports values of particle sizes in percent of counts per total counts in the sample. Values of percent clay (percent sample less than 2 μm), percent silt (percent sample between 2 μm and 62 μm) and percent sand (percent sample between 62 μm and 500 μm) were calculated from the report and entered into the project database. This protocol excluded grains larger than 500μm.

3.4.5. Chemical Parameters

Chemical analyses of a core were only performed after a ^{210}Pb chronology was generated and the chronology core was deemed reliable. Sections for chemical analysis from these cores were chosen based on ^{210}Pb ages and represented the same time intervals in each core.

3.4.5.1. Total Phosphorus (TP)

TP was measured using Andersen's ignition method (1976). After OM percentage had been determined (section 4.4.4.2), the ashed sample was transferred to a 50 ml Erlenmeyer flask with 25 ml HCl solution. The samples were heated to 100°C, digested for 15 minutes, and filtered through a 0.45 μm filter (Millipore P15-047-00) using a mild vacuum. Samples were diluted to 100 ml with deionized water, placed in 100 ml beakers, and covered with parafilm pending analysis.

The concentration of liberated PO_4^{3-} in the filtrate was determined colorimetrically with the ascorbic acid method (A.P.H.A. 1992: Method 4500P). A Spectronic 21D (Model 332278, Milton Roy) was used to quantify the concentration of PO_4^{3-} at 880 nm. Five PO_4^{3-} standards (500, 250, 100, 50, 25 μg l^{-1}) were used to generate a standard curve linking the concentration of PO_4^{3-} with their absorbance. We performed the colorometric analysis within a 30 minute window to insure that color variance associated with reagent age was kept to a minimum. For quality control, we ran two controls and two replicates for each sample series.

Values for sample absorption and the slope and intercept of the standard curve were loaded into the database and the TP concentrations were calculated using the program INSERT-P.SQL.

3.4.5.2. Bio-Available Phosphorus (BAP)

BAP, approximated by non-apatite inorganic phosphorus, was measured using a method developed by Williams *et al.* (1976) and modified by Schelske and Hodell (1995). Dried and pulverized samples were subjected to a mild, 1N HCl digestion in 125 ml Erlenmeyer flasks. The flasks were placed on a shaker plate for 17 hours to provide sufficient mixing of the sample with the reagent. At the conclusion of the digestion, the supernatant was filtered through a 0.45 µm glass-fiber filter (Millipore, see section 4.4.5.1). The filtrate was analyzed for PO_4^{3-} with the ascorbic acid method described in section 4.4.5.1. Values for absorption and the slope and intercept of the standard curve were loaded into the database and the BAP concentrations were calculated using the program INSERT-BAP.SQL.

3.4.5.3. Total Carbon and Total Nitrogen

TC and TN percentages were determined using a Perkin-Elmer 2400 CHN analyzer located in The University of Toledo's Instrumentation Center (IC). The Perkin-Elmer 2400 CHN analyzer uses combustion in a pure O_2 environment to release CO_2, H_2O, and N_2 gases. These gases are separated under exact conditions of pressure, temperature, and volume. The C, H, and N concentrations are then quantified as a function of thermal conductivity (Perkin-Elmer 1988). For this analysis, fresh thawed material was dried at 30°C for several days and pulverized using a mortar and pestle. CHN values for TC and TN from the IC were reported in percent (mass/mass) and these values were loaded into the project database.

3.4.5.4. Heavy Metal Analysis

USEPA Method 3050, "Acid Digestion of Sediments, Sludges, and Soils" (U.S. Environmental Protection Agency, 1986) was used for sample preparation for ICP analysis of metal concentrations. Metals chosen for analysis include zinc, manganese, nickel, lead, chromium, copper, cadmium, aluminum, vanadium, and iron. Ten milliliters of 1:1 HNO_3 was added to one gram portions of homogenized air-dried sediment, mixed, and covered with a watch glass. The sample was heated to 95°C and refluxed for 15 min without boiling. The sample was allowed to cool, 5ml of concentrated HNO_3 were added, and the sample was refluxed for 30 min. This last step was repeated to ensure complete oxidation. The solution was then allowed to evaporate to approximately 5ml without boiling. The sample was cooled, and 2ml of distilled, de-ionized water and 3ml of 30% H_2O_2 were added. A total of 10 ml of H_2O_2 was added in 1-ml aliquots. Five milliliters of concentrated HCl were added, along with 10 ml of distilled, de-ionized water. The beaker was covered and returned to the hot plate for an additional 15 minutes refluxing. After cooling, the digestate was filtered through Whatman No. 41 filter paper and diluted to 100 ml using distilled, de-ionized water. Standards and blanks for all metals were also prepared in the same fashion. Buffalo River sediment from the National Institute of Standards and Technology was also analyzed to determine accuracy of the technique. The samples were analyzed for adsorbed metal concentration on the Perkin-Elmer Plasma 1000/2000 Emission Spectrometer.

3.4.5.5. Pesticide Analysis

Preparation of sediment samples for pesticide analysis requires column chromatographic separation of the organic extracts contained in the sediment. Initially, the organic fraction was extracted from a known quantity of sediment using methylene chloride solvent in the Tecator Soxtec Extraction System HT 1043. Sulfur removal was accomplished during this step using solvent cleaned copper strips. A two step column chromatographic separation segregated co-eluting compounds within these extracts. The first step used 0.5% diethyl ether in hexane and 40% diethyl ether in hexane solvents in a florisil column. The second step used 0.5% toluene in hexane and 25% diethyl ether in hexane in an acidized silica gel column. Duplicate samples were extracted and analyzed for confirmation. Supelco pesticide and PCB standards were used to quantify the data and determine recovery efficiencies. Blanks and spiked samples were also included in the protocol.

Gas chromatographic analysis of these extracts was performed on a Hewlett Packard 5890 II gas chromatograph equipped with an HP-5 MN crosslinked 5% PH ME Siloxane capillary column and an electron capture detector. Inlet and detector temperatures were 205°C and 250°C, respectively. Helium carrier gas was set to 6ml min-1 flow. Splitless injection was used. The oven was set to 100°C for two minutes, ramped at 15°C min-1 to 160°C, ramped at 5°C min-1 to a final temperature of 250°C, that was held for 10 minutes. Analytical integration of the resulting peaks was limited to a minimum area count of 1000 using an RTE integrator that approximated the minimum detection limits for most compounds.

Confirmation of standard and many sample peaks was accomplished using a Hewlett Packard 6890 gas chromatograph equipped with an identical column and mass selective detector. The gas chromatographic method was identical to the previously described method.

3.5. Data Management

A Personal Oracle™ 7.1 relational database (MacOS – PowerPC™) was used to manage data resulting from this research. The Lake Erie Environmental Database (LEED) resides on an Apple Macintosh™ 233 MHz PowerBook™ with 32 MB RAM and 2 GB hard drive. LEED was created for this research and all data loading, maintenance, backups and coding were done in-house. All codes for data management and calculations were written in SQL*Plus™ or PL/SQL™. Descriptions of tables used, as well as the number of records in each table, are listed in Appendices section 8.1.1.

4. Results and Discussion

4.1. Watershed Soils and Land-Use

4.1.1. Soils

Based on maps provided by the Ottawa County Natural Resources Conservation Service (USDA Oak Harbor, Ohio), the soil type distribution of the North and West marshes are considerably different although both are dominated by Toledo Silty Clay (To) (Table 1, Figure 3). Other soils represented in the watersheds are: Latty silty clay (Lc), Bono silty clay (Bo), Toledo silty clay ponded (Tp), and Nappanee silty clay loam (NpA). With the exception of the NpA, which is formed from glacial till and is only somewhat poorly drained, all other soils are glacial sediments that have been reworked by lake water and are poorly to very poorly drained. Soil types Tp, To, and NpA are common to both watersheds whereas Lc and Bo are only found in the North Marsh's watershed (Figure 3). The areal

Table 1. Description of soils types in the watersheds of the North Marsh and West Marsh at Winous Point, Ohio.

Symbol	Name	Description	Permeability	Slope (%)
Bo	Bono Silty Clay	Deep, very poorly drained soils that formed in depressions on lake plains. These soils formed in lacustrine sediments	Low or very low	0 - 2
Lc	Latty Silty Clay	Deep very poorly drained soils that formed in clayey lacustrine sediment on lake plains.	Low	0 - 2
NpA	Nappanee Silty Clay Loam	Deep, somewhat poorly drained soils on till plains in areas of former lake beds. Nappanee soils formed in calcareous glacial till that was modified in the upper part by water action.	Very low	0 - 3
To	Toledo Silty Clay	Deep, very poorly drained soils that formed in clayey lake-laid sediment on lake plains and deltas.	Low	0 - 2
Tp	Toledo Silty Clay Ponded	Deep, very poorly drained soils that formed in clayey lake-laid sediment on lake plains and deltas.	Low	0 - 2

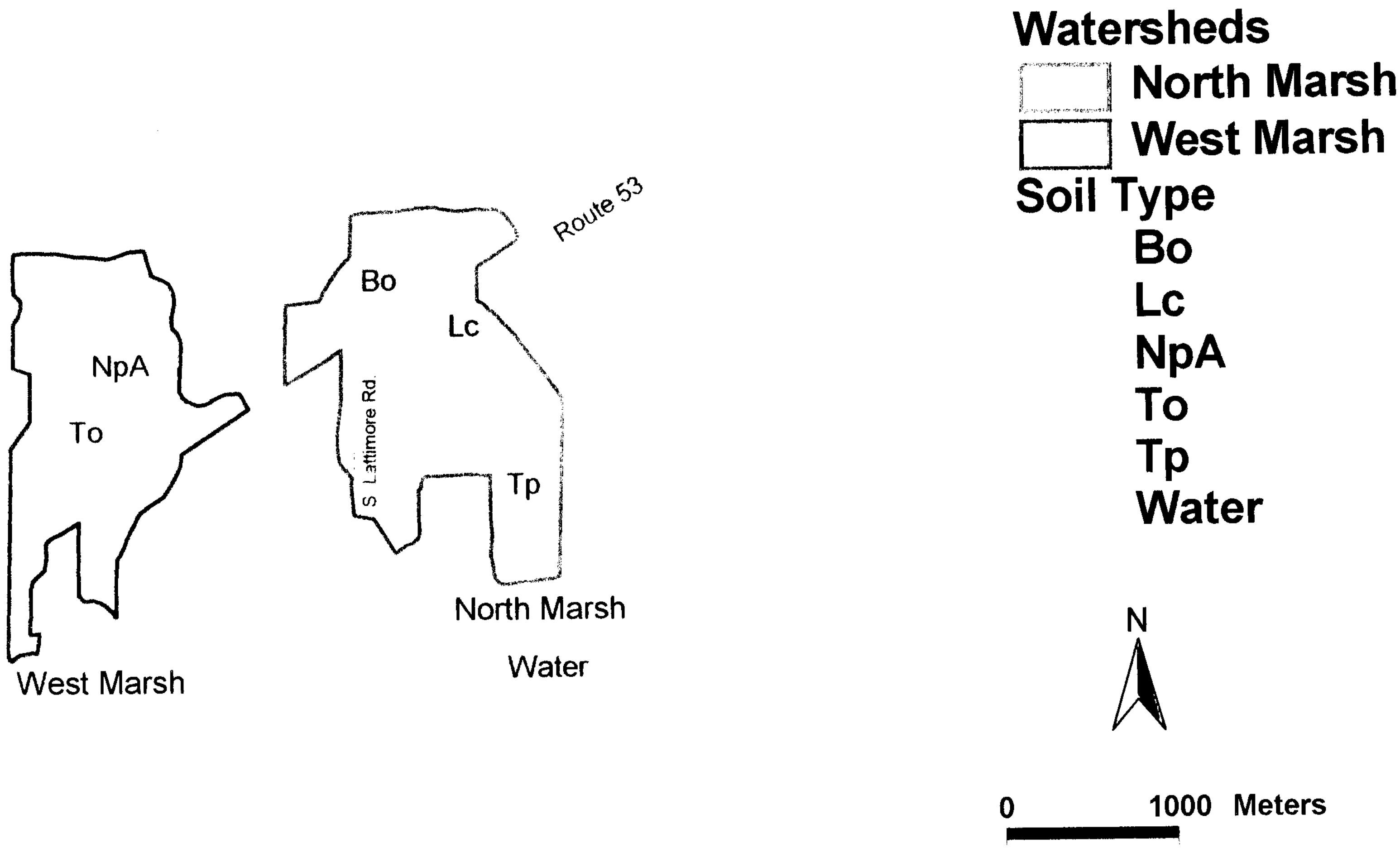


Figure 3. Surface soils of the Winous Point marshes' watersheds. Southern boundary of map shows extent of the soil survey. Data provided by the Ottawa County Natural Resources Conservation Service (USDA Oak Harbor, Ohio).

extent of the soils types in each marsh are listed in Table 2. A grain size analysis of the To soil (Paschall *et al.* 1928), the soil type with the greatest areal extent in both watersheds, revealed an average clay content of 63% and an average silt content of 35%.

Table 2. Distribution of soils types in the watersheds of the North Marsh and West Marsh at Winous Point, Ohio

Type	North Marsh (ha)	West Marsh (ha)
Bo	53	-
Lc	1	-
NpA	31	27
To	96	137
Tp	31	7

4.1.2. Land-Use

We were able to distinguish four land-use categories in the analysis of the North and West marshes: "Roads and residential", "Forest, marsh or old field", "Orchard", and "Row crops". The North Marsh watershed comprised 212 hectares and the West Marsh watershed was slightly smaller: 171 hectares. Analyses of land-use in the North Marsh watershed were based on aerial photograph of the study site taken in 1939, 1950, 1957, 1970, and 1988 (Table 3) and coverage for the West Marsh watershed included 1950, 1957, 1970, and 1988 (Table 4).

Land-use in the watersheds of both the North Marsh and West Marsh have changed somewhat since 1950 (Figures 4 and 5). During that time, the area of land in either watershed that was dedicated to orchards was halved. The amount of area taken by "Roads and residential" in the watersheds doubled since 1950.

Table 3. Land use (ha) in the North Marsh watershed, Winous Point, Ohio. Ten hectares of land were not covered by the 1939 aerial survey.

	1939	1950	1957	1970	1988
Row Crops	128	149	155	153	149
Orchard	25	16	8	8	9
Forest, Marsh or Old Field	46	42	44	44	44
Roads and Residential	4	6	6	6	11

Table 4. Land use (ha) in the West Marsh watershed, Winous Point, Ohio.

	1950	1957	1970	1988
Row Crops	152	154	154	144
Orchard	5	3	2	2
Forest, Marsh or Old Field	7	6	6	5
Roads and Residential	7	8	9	21

However, there is a greater difference in land-use between the North Marsh and West Marsh watersheds than in the change in land use within either watershed since 1950. Since 1950, 88% (average) of the West Marsh's watershed has been covered by "Row crops" whereas "Row crops" only comprise 71% (average) of the North Marsh's watershed. The second largest land-use type in the North Marsh's watershed was " Forest, marsh or old field" which covered 21% (average) of the total area, whereas those lands only comprised 4% of the West Marsh's watershed. "Roads and residential" comprised 3 - 6% of the North Marsh's watershed and 4 - 15% of the West Marsh's watershed. "Orchards" covered 4-8% of the North Marsh's watershed and only 1-3% of the West Marsh's watershed.

4.1.3. Ramifications of Soils and Land-use on Nutrient Accumulation Rates

The soil series represented in the watersheds of both marshes are characterized by their high clay-content, low to very low permeabilities, resulting in low percolation and high runoff rates. Both watersheds had large areas used for row crops that received significant quantities of fertilizer (Paschall *et al.* 1928). The combination of soils with low permeabilities and the application of fertilizer created a situation where significant quantities of nutrients may have been present in runoff from these fields. Although both watersheds have approximately 150 ha of land in row crops, row crops only comprise 71% (average) of the North Marsh watershed. Twenty-one percent of the North Marsh watershed's area was "Forest, marsh or old field" which was not fertilized and may have diluted the nutrient concentration in runoff from crop land. Alternatively, this forested and marshy area may have provided a filter for runoff from farmland prior to the inflow into the North Marsh.

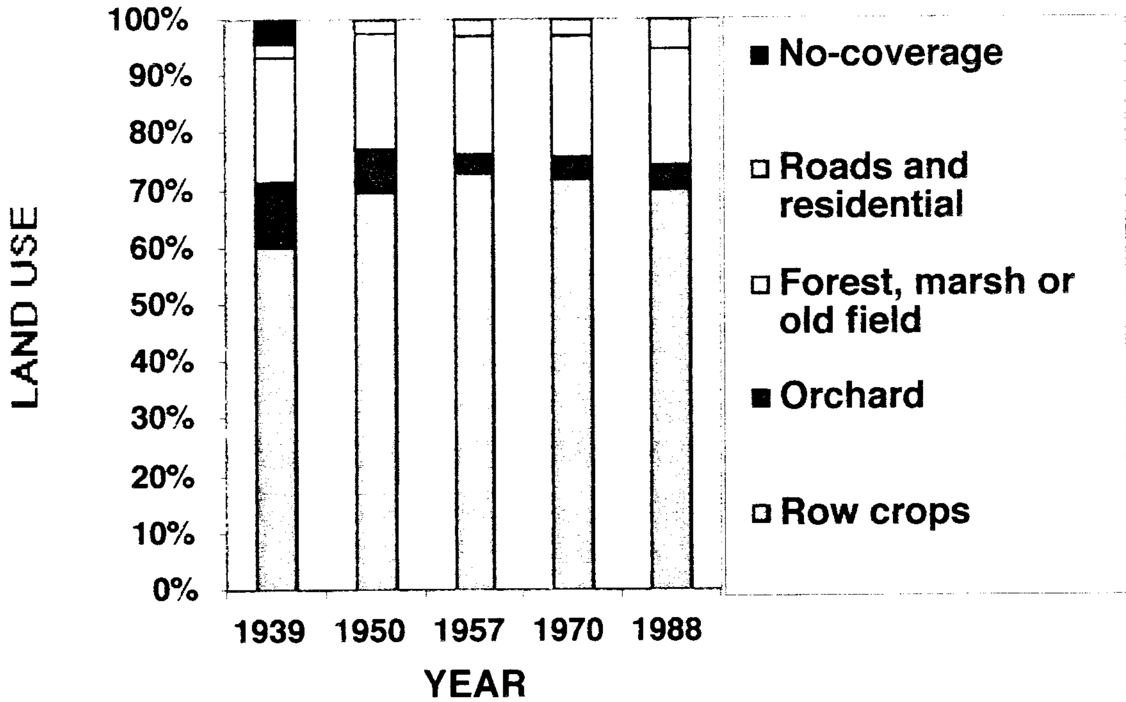


Figure 4. North Marsh watershed land-use distribution, Winous Point, Ohio

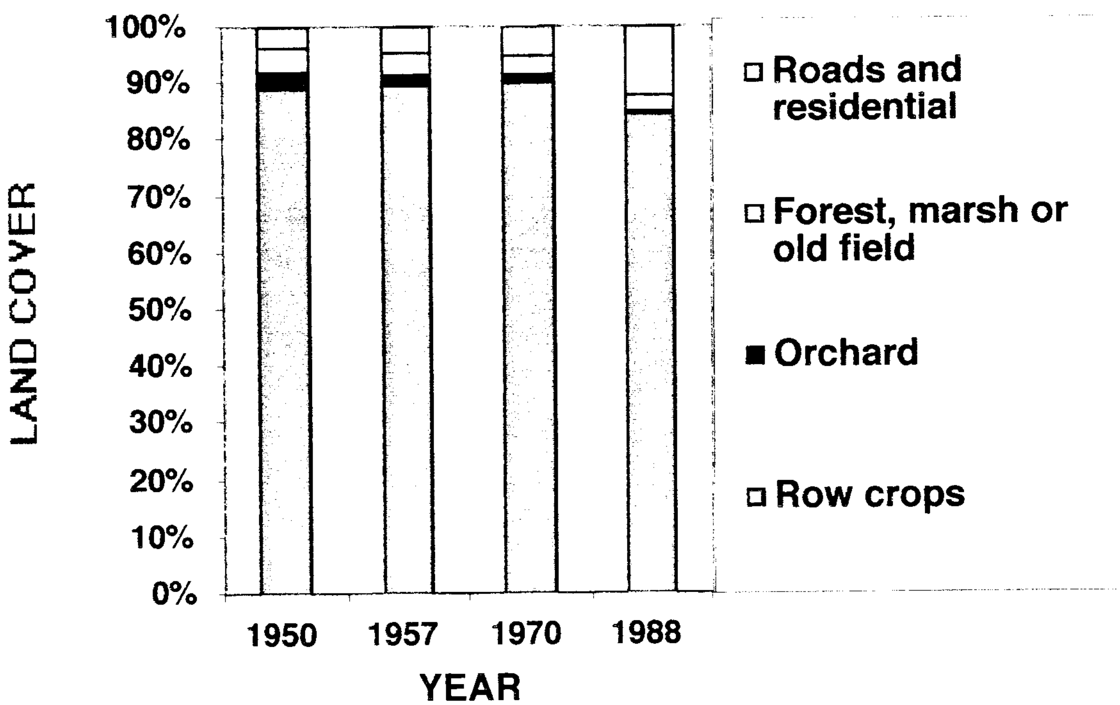


Figure 5. West Marsh watershed land-use distribution, Winous Point, Ohio

4.2. Core Chronologies

The time intervals of relevance to the study of the long-term accumulation of chemicals in the marsh sediments were 1920-1977, 1978-1987, and 1988-1997. The years 1920 and 1978 were significant in the study because 1920 was the approximate date for the completion of the dikes surrounding the marshes and 1978 was the year that the West Marsh's upland dike was closed. Consequently, after 1978 runoff from the West Marsh's watershed was directed around the marsh and released directly into Muddy Creek Bay. The most recent 10-year interval was used to evaluate sustained accumulation of target nutrients. Target analytes were: bulk sediment, particle size distribution, TC, TN, TP, BAP, OM, and selected trace metals and pesticides.

4.2.1. ^{210}Pb Chronologies

^{210}Pb activities were measured for all sections of all ten cores taken for this study. Reliable core chronologies had unsupported ^{210}Pb profiles that decreased with depth, similar cumulative residuals within the accepted range for this region, and ^{210}Pb dates that matched well with known ^{137}Cs fallout (Appleby and Oldfield 1983). Only two cores (WPB-3B and WPB-8B) indicated significantly disturbed chronologies and were deemed unreliable for this study. The cores with reliable chronologies revealed unsupported ^{210}Pb approaching background levels between 14 and 35 cm (Figures 7 - 15). Counting errors for unsupported ^{210}Pb averaged ± 0.016 Bq g^{-1} with an average sample weight of 1.81 g and count times between 19 and 46 hours. Confidence intervals from a Monte Carlo analysis of all ^{210}Pb dates revealed increasing uncertainty with age (Table 5). The large dating errors that occurred toward the bottom of the cores made ^{210}Pb-dates unreliable for sediments older than 100 years before present.

Table 5. Average 90% confidence intervals based on ^{210}Pb chronologies of eight cores taken from the North Marsh and West Marsh at Winous Point, Ohio.

Years before present	**Average 90% C.I. (± Years)**
10	2
25	5
50	10
100	30

Figures 6-13 Radioisotope activities (unsupported ^{210}Pb and ^{137}Cs), *Ambrosia* percentages, and age-depth data for all cores taken from the North and West marshes, Winous Point, Ohio.

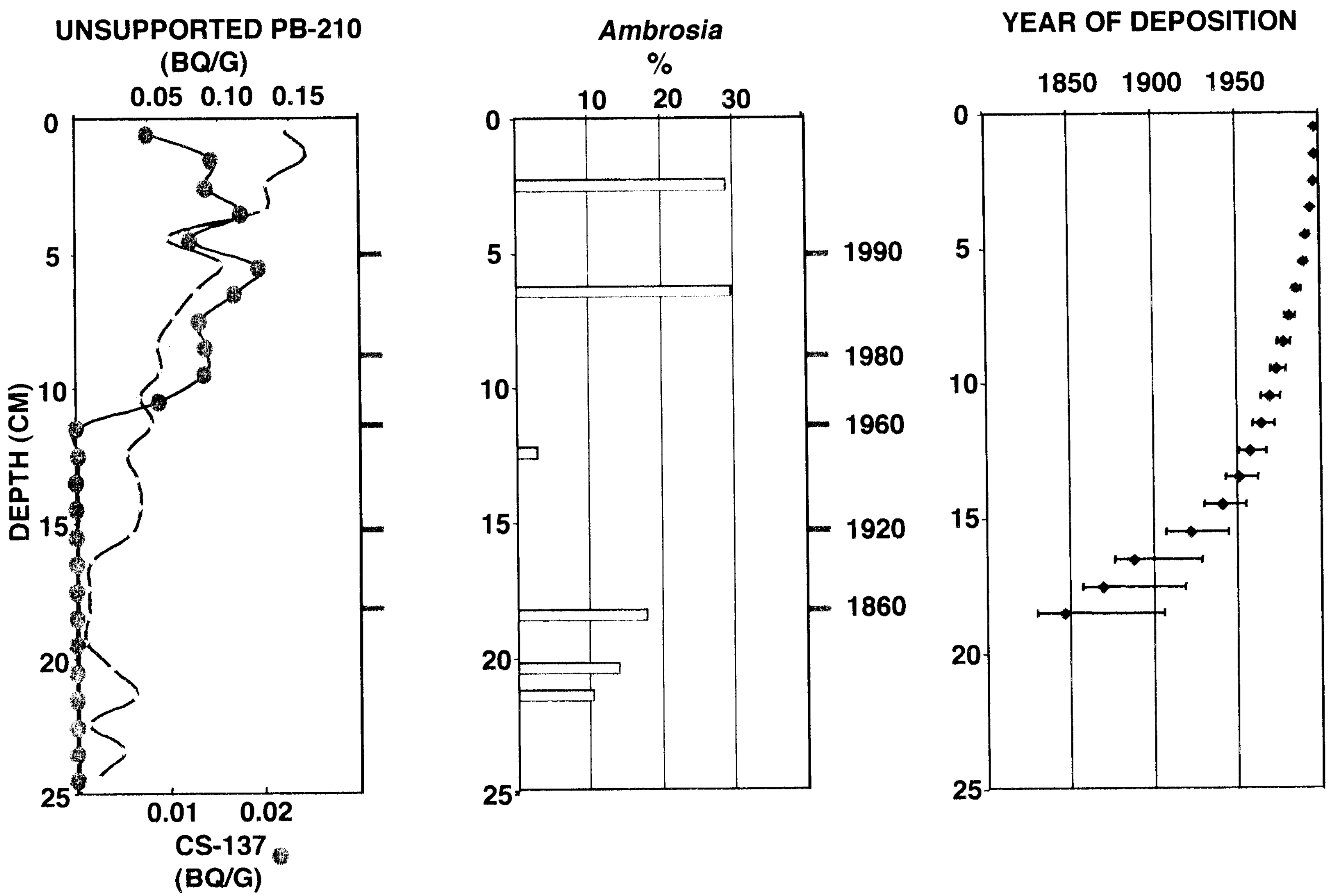


Figure 6: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-1B (North Marsh).

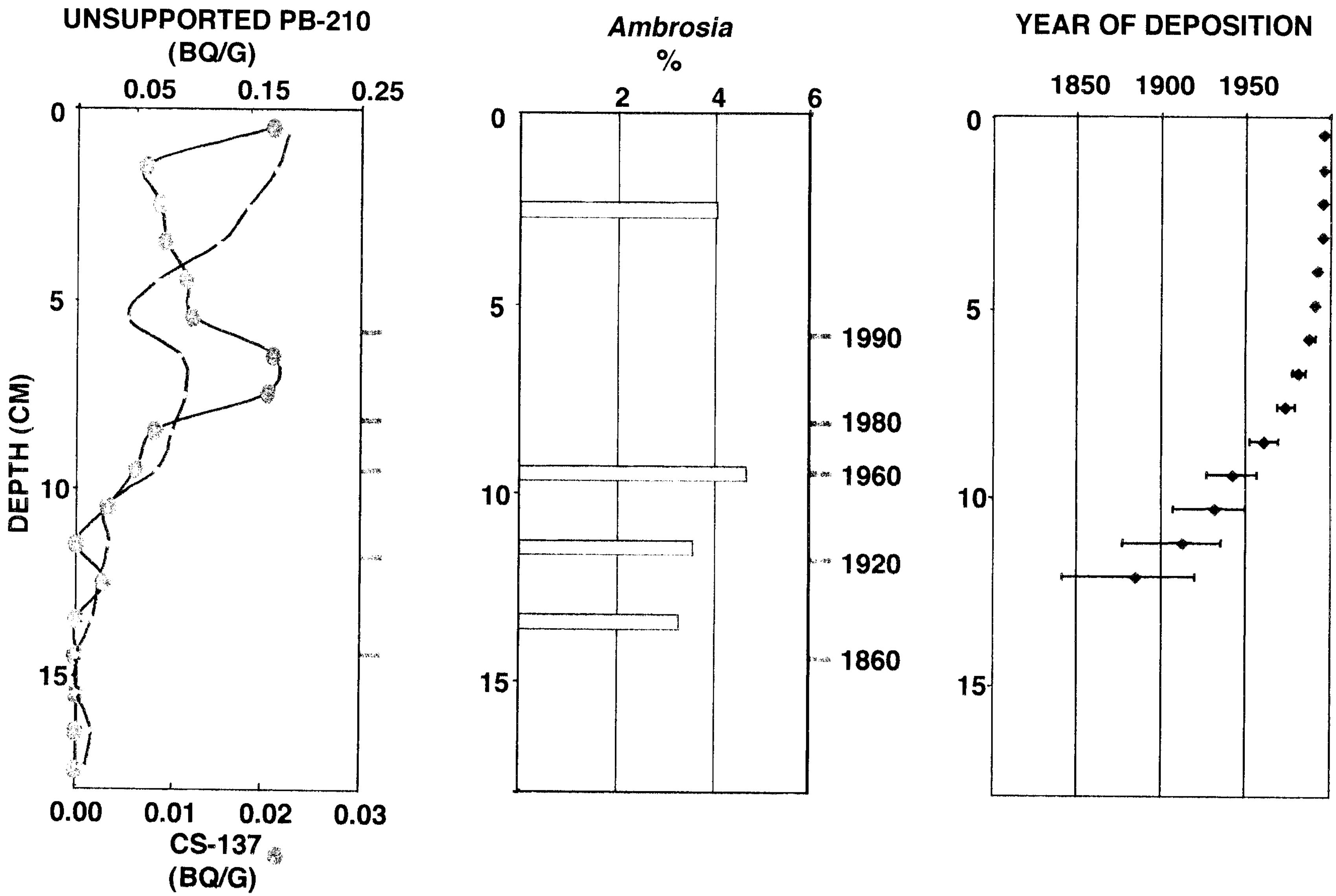


Figure 7: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-2A (North Marsh).

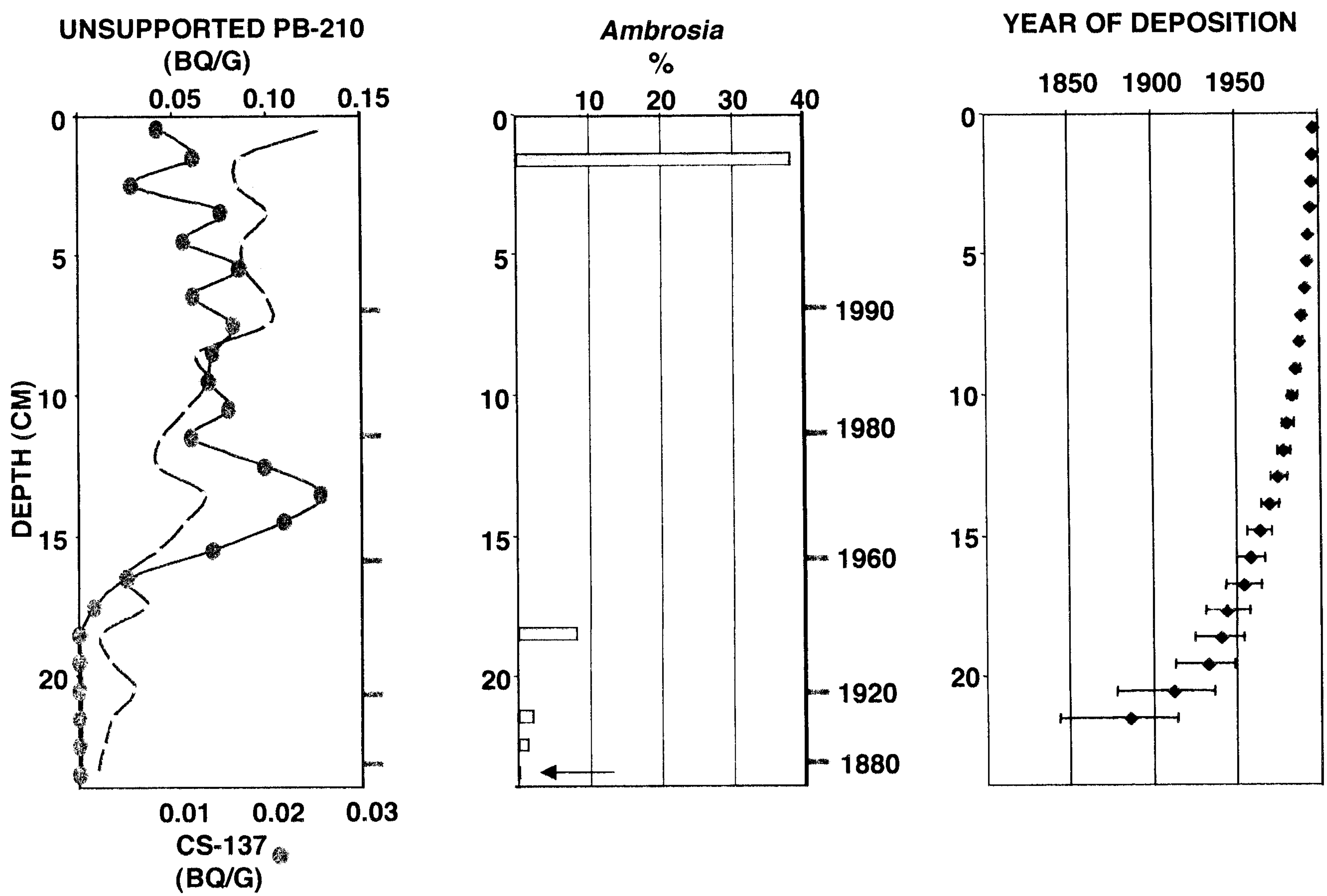


Figure 8: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-4B (West Marsh).

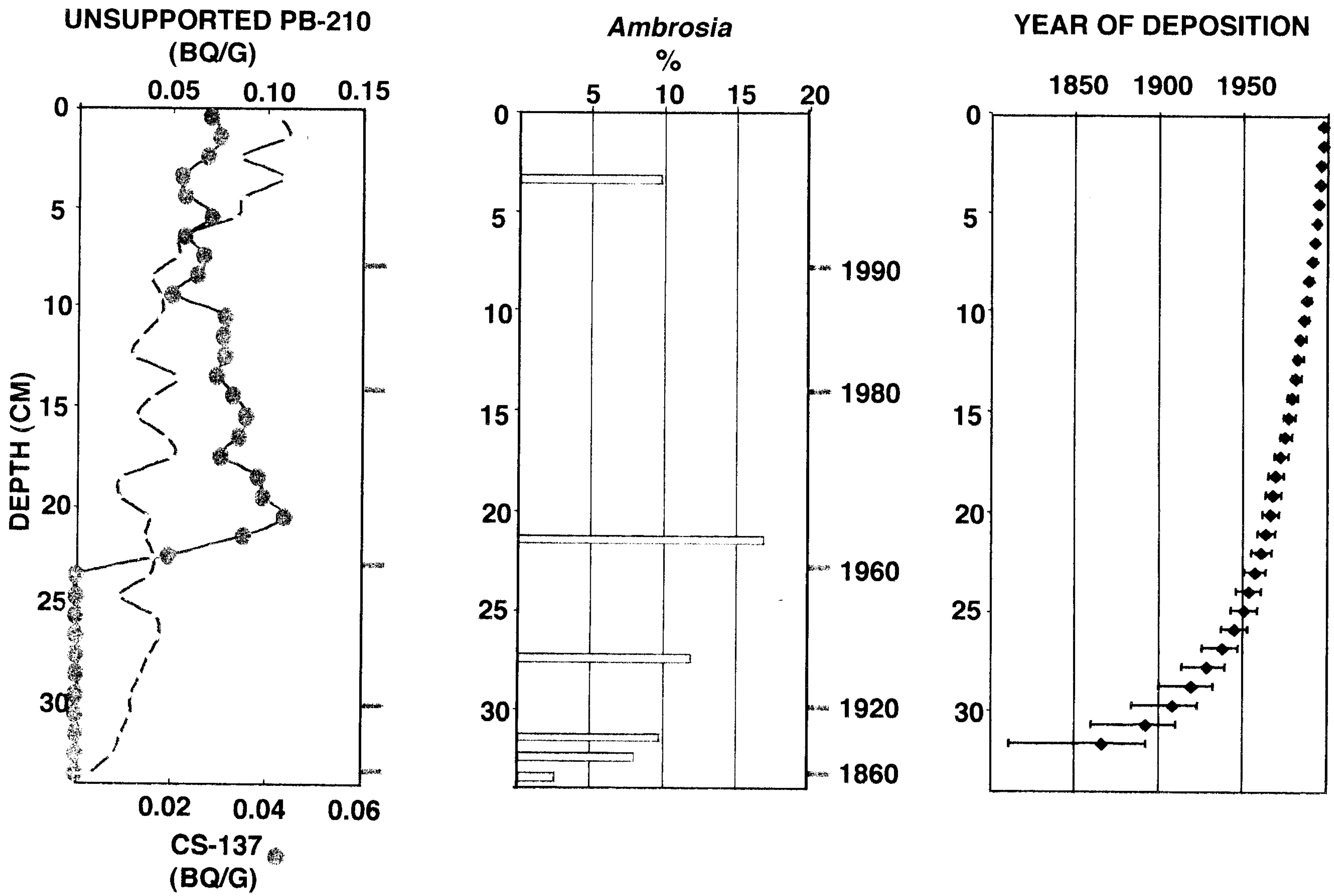


Figure 9: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-5B (West Marsh).

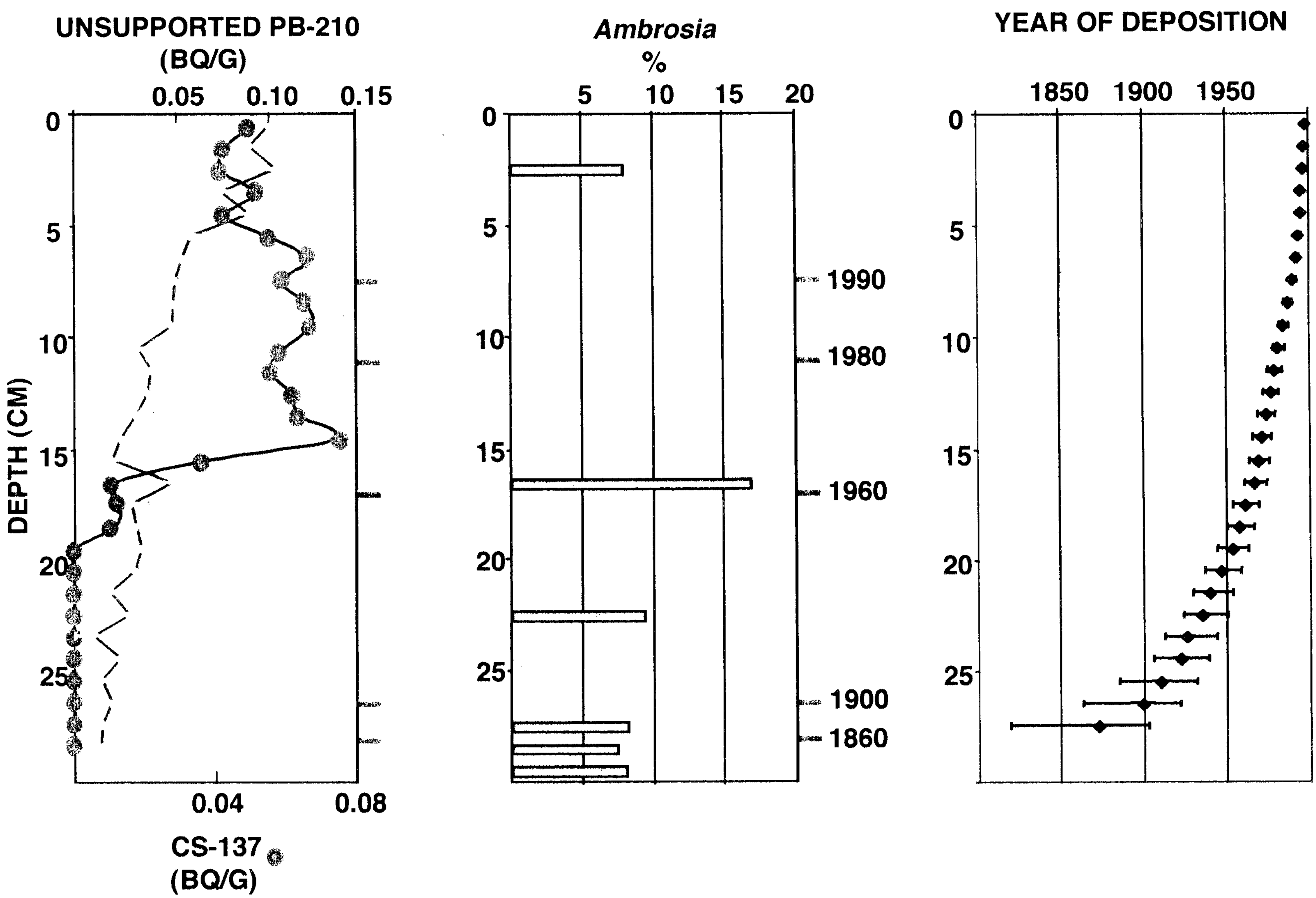


Figure 10: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-6A (North Marsh).

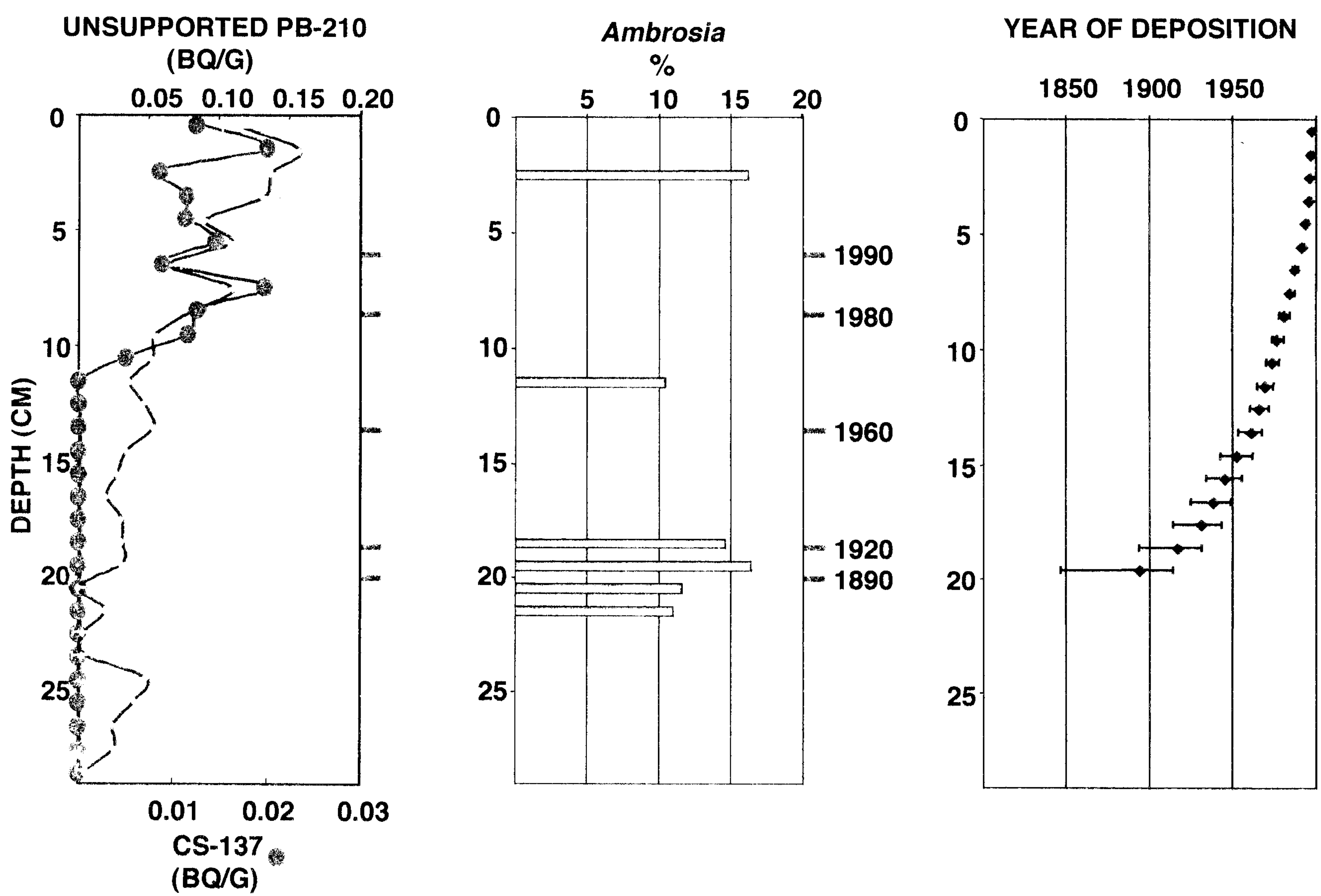


Figure 11: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-7B (North Marsh).

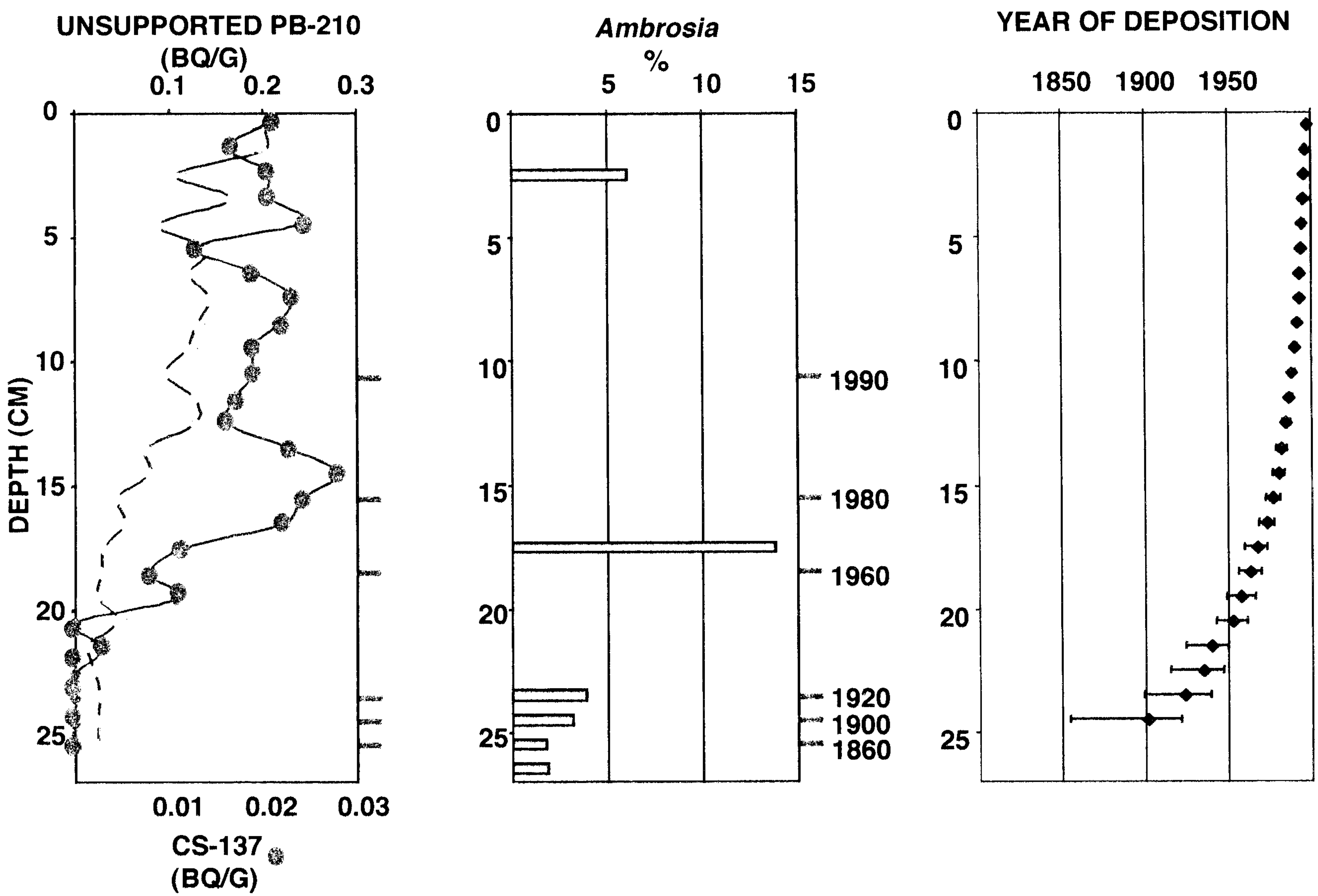


Figure 12: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-9B (West Marsh).

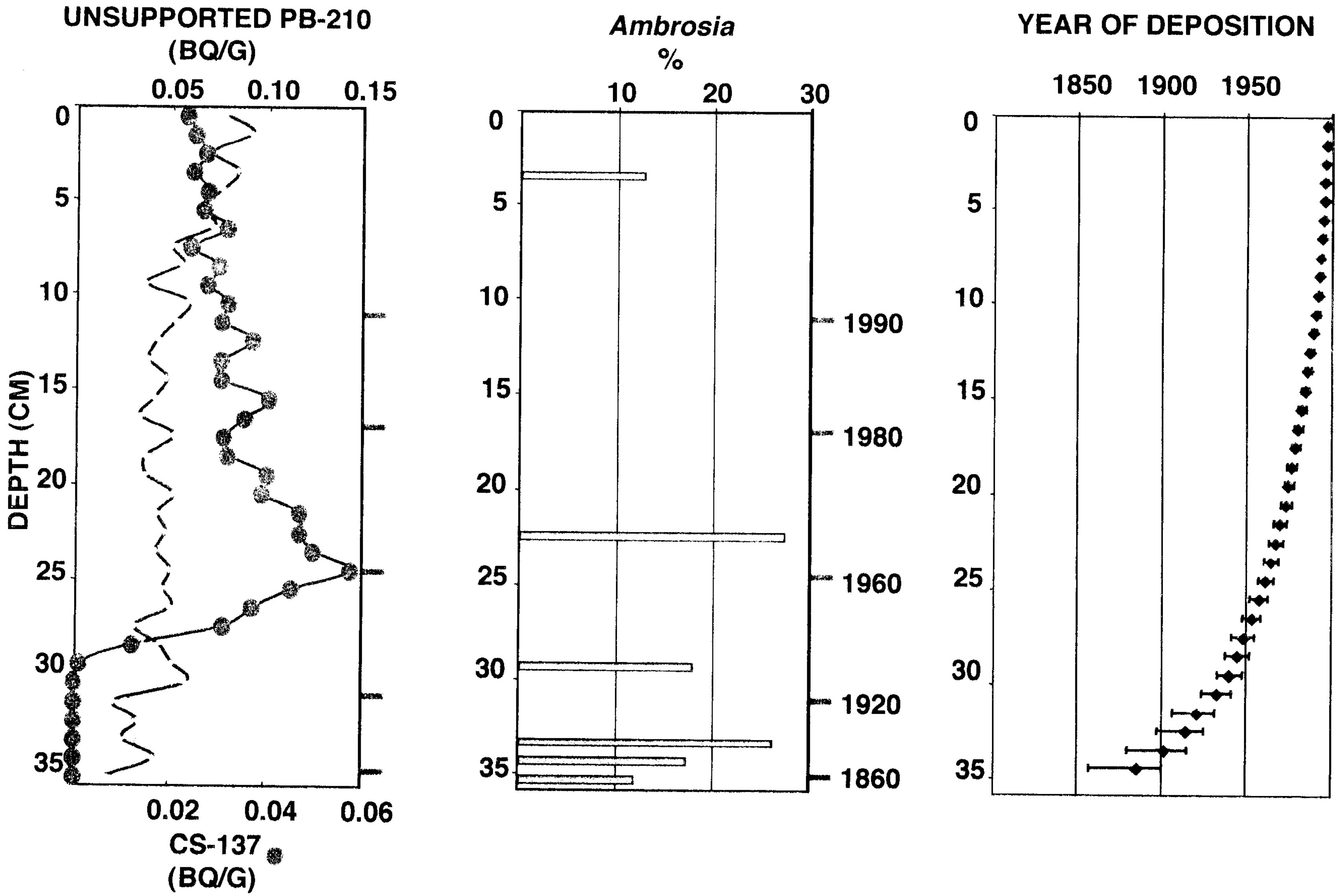


Figure 13: Radioisotope activities, Ambrosia percentages and age-depth data for Winous Point Shooting Club core WPB-10A (West Marsh).

Fallout rates of unsupported ^{210}Pb were calculated for all cores and ranged from 0.011 - 0.025 Bq cm^{-2} yr^{-1} (Table 6). These values fall within the 0.007 to 0.033 Bq cm^{-2} yr^{-1} global range reported by Appleby and Oldfield (1983), but are higher than the unsupported ^{210}Pb fallout range for Lake Michigan of 0.004 - 0.009 Bq cm^{-2} yr^{-1} reported by Robbins and Edgington (1975).

Table 6. Summary of chronology data for all cores from the North and West marshes Winous Point, Ohio. Values in parentheses below ^{137}Cs onset are 90% CI in years.

Core ID	Cumulative Residual ^{210}Pb (Bq cm^{-2})	Fallout Rate ^{210}Pb (Bq cm^{-2} yr^{1})	Onset ^{137}Cs (^{210}Pb-year)	Ambrosia ratio (post-1860 / pre-1860)
WPB-1B	0.57	0.018	1969 (6)	1.5
WPB-2A	0.50	0.015	1962 (9)	-
WPB-3B	0.34	0.011	-	-
WPB-4B	0.58	0.018	1958 (10)	21.4 (6.7)
WPB-5B	0.80	0.025	1960 (6)	4.5
WPB-6A	0.41	0.013	1957 (8)	1.4
WPB-7B	0.52	0.016	1974 (4)	1.3
WPB-8A	0.80	0.025	-	-
WPB-9B	0.46	0.014	1958 (9)	3.7
WPB-10A	0.75	0.023	1945 (7)	1.7

4.2.2. ^{137}Cs Data

The onset of ^{137}Cs activity (≥ 0.005 Bq cm^{-2}) corresponded well (± 6 years) with an average ^{210}Pb-derived date of ca 1963 in all cores except WPB-7B and WPB-10A (Table 6). In core WPB-7B the onset of ^{137}Cs activity corresponded with a ^{210}Pb date of 1974 which was three centimeters above the 1960 horizon. Core WPB-10A exhibited four centimeters of downward migration of ^{137}Cs. Cores WPB-3B and WPB-8B revealed ^{137}Cs through out most of the cored intervals and were not used in the study.

4.2.3. Pollen Analysis Data

We used pollen analysis to determine the *Ambrosia* horizon to assist in separating the deeper, pre-European agricultural deposits from sediments that are more recent. The ratio of post-1860 *Ambrosia* pollen percentages to pre-1860 was calculated to determine the increase in post-1860 *Ambrosia* (Table 6).

Data from cores WPB-1B, WPB-6A, WPB-7B, and WPB-10A revealed relatively modest increases in *Ambrosia* over the 1860 boundary (1.3 - 1.7 fold increase) and the *Ambrosia* horizon in these cores was difficult to distinguish. By comparison, cores WPB-2A, WPB-4B, WPB-5B, and WPB-9B showed much larger increases of 3.7 to 21.4 fold in post-1860 sediments, increases that pointed to a distinguishable *Ambrosia* horizon. The 38% *Ambrosia* reported from the 1996 section in core WPB-4B may be spurious. If that section is omitted from the analysis, the post-1860 increase fell to 6.7 fold.

Increased accuracy in determining the *Ambrosia* horizon may be achieved by using more sections of the core for analysis. Furthermore, historical data on the watersheds of the North and West marshes showed that Bay Township in Ottawa County was "... predominantly prairie, interspersed with groves of timber. The prairie must have been largely of the wet land type." (Paschall *et al.* 1928). Given this information on the pre-European agriculture state of the surrounding land, an *Ambrosia* horizon may be difficult to find as open lands, as described by Paschall *et al.*, may have had *Ambrosia* species prior to European agricultural development.

4.3. Grain-size Distribution Over Time

Grain-size distribution profiles of cores from both marshes show a coarsening upward indicated by the higher percentage of sand-sized clasts in sediments deposited from 1987-1997 (Figure 14). Sixty per cent or more of the West Marsh sediments consisted of silt and clay-sized particles during the last 80 years of deposition. With the exception of the last 30 years of deposits, the North Marsh sediments contained a higher percentage of silt and clay-sized particles. Since non-apatite inorganic P and organic P concentrations increase with decreasing grain sizes (Stone and English 1993), we expect the somewhat larger particle sizes in the North Marsh during the last three decades of sedimentation to depress the P content of these deposits. On the other hand, because particulate organic matter (POM) in the sediment matrix may register in the sand-sized range during laser analysis, the coarsening upward noted in the North Marsh profile may simply reflect increased POM. To minimize this impact, we excluded the top two years (i.e., growing seasons) of organic deposits from the particle size analysis.

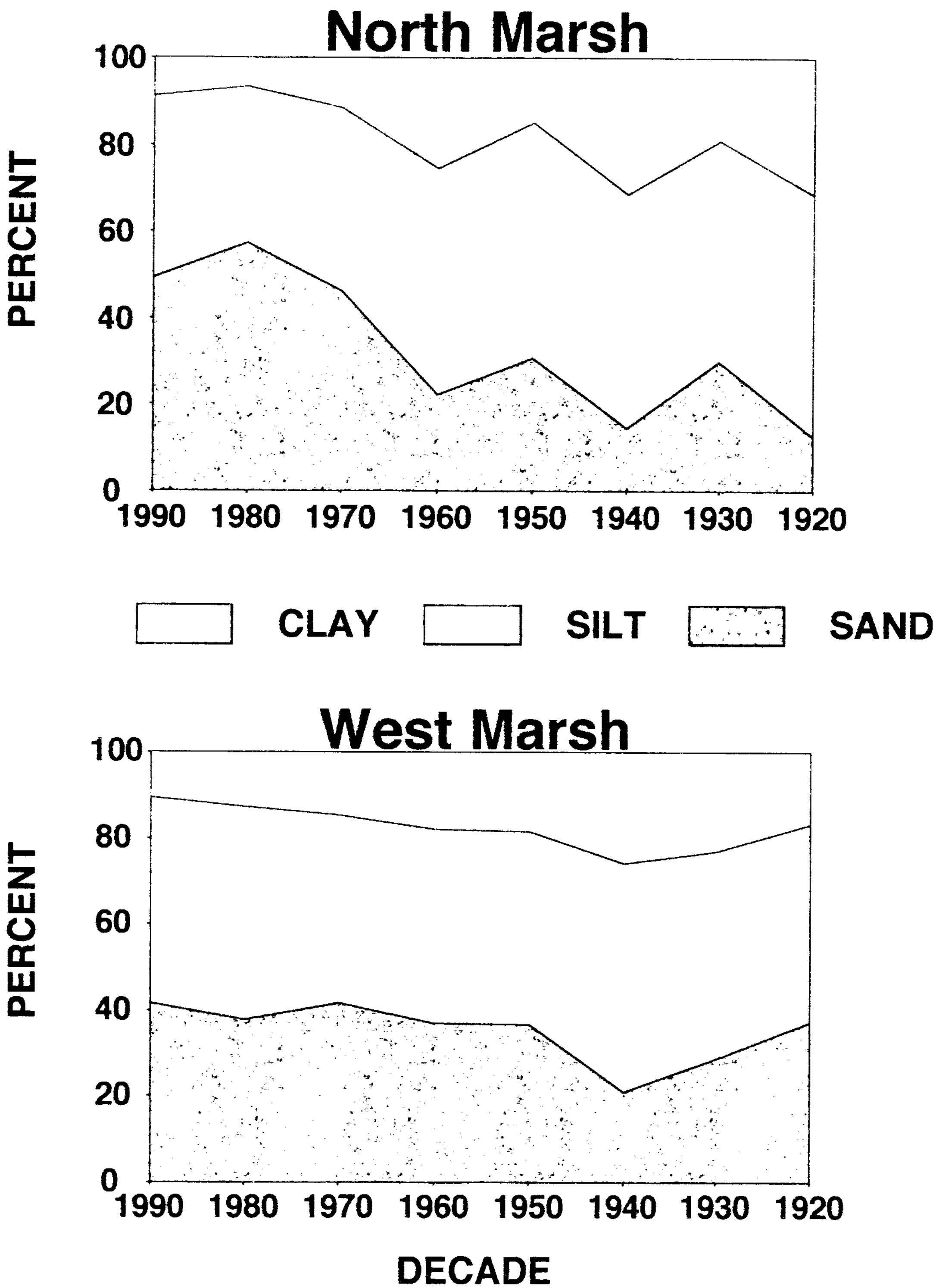


Figure 14: Grain size distribution of sediments North and West marshes, Winous Point Ohio. Average values for each marsh per decade. Range of grain sizes analyzed is 0.05 μm to 500 μm.

The 1970 data point in the North Marsh, representing the average grain-size distribution from 1965 to 1974, marked the onset of a period of relatively high percentage of sand-sized clasts. This time period coincided with the beginning of a high water period in the lake and may reflect increased erosional influx of coarse particles from the North Marsh's watershed. The West Marsh, isolated from its watershed during that time interval, did not show such an increase. Particularly in the North Marsh, low concentrations in sand-sized particles coincided with relatively dry periods as reflected in the 1940 data point (1935-1944) and the 1960 data point (1955-1964).

4.4. Major Nutrient, Organic Matter, and Sediment Accumulation Rates

Accumulation rates for bulk sediment, TC, TN, TP, BAP, organic matter, and sediment were calculated for each marsh for the following time intervals: 1920-1977, 1978-1987, and 1988-1997 (Table 7). Post-1978 accumulation rates were consistently higher than pre-diversion levels. Since 1920 the West Marsh has always had higher accumulation rates than the North Marsh. This may be related to the higher percentage area in row crops in the West Marsh's.

Table 7. Average accumulation rates (g m^{-2} yr^{-1}) for total carbon, total nitrogen, total phosphorus, bio-available phosphorus, organic matter, and sediments from the North Marsh and West Marsh, Winous Point, Ohio. Values are pooled from four cores per marsh. Values in parentheses are one standard deviation.

Marsh	Interval	TC	TN	TP	BAP	OM	Seds.
N	1988-1997	119.31 (33.06)	11.72 (2.54)	0.79 (0.08)	0.19 (0.04)	251.0 (78.9)	1478.6 (198.5)
N	1978-1987	105.64 (49.67)	10.00 (3.70)	0.54 (0.17)	0.13 (0.04)	220.9 (127.9)	1344.7 (375.5)
N	1920-1977	47.63 (23.25)	4.66 (1.35)	0.27 (0.08)	0.06 (0.01)	104.5 (47.3)	811.2 (144.7)
W	1988-1997	161.93 (60.72)	20.88 (14.36)	1.57 (0.62)	0.22 (0.04)	312.7 (92.3)	2370.8 (1222.6)
W	1978-1987	130.44 (60.12)	19.67 (15.44)	1.40 (0.71)	0.17 (0.06)	264.0 (100.3)	2585.6 (1399.5)
W	1920-1977	60.11 (29.68)	8.57 (6.37)	0.73 (0.22)	0.08 (0.03)	130.8 (44.5)	1301.9 (316.3)

Consequently, the pattern of material accumulation in the West Marsh was a poor reference for the North Marsh and we focused our analysis on quantifying the change within each marsh (normalized to the 1920-1977 rates), rather than evaluating the differences between both marshes. Normalizing accumulation rates to each marsh's pre-diversion rates reduced the variability associated with differences in each marsh's respective watershed. The average and standard deviation for the ratios of the accumulation rate for a target analyte from 1978-1987 (or from 1988-1997) and the corresponding rate for 1920-1977 are shown in Figure 15.

Sediment accumulation rates in the North Marsh from 1978-1987 were 1.7 times higher than those calculated for the 1920-1978 period. In the West Marsh, this rate nearly doubled compared to pre-diversion levels (1920-1977). From 1988 to 1997, sediment accumulation in both the West and the North Marsh was 1.9- and 1.8-fold higher than pre-diversion levels. Therefore, the rate at which the North Marsh is trapping sediment has continued to increase during the last two decades, whereas this rate remained the same in the West Marsh.

TC accumulation rates from 1978-1987 were 2.2 and 2.3 times higher compared to pre-diversion levels in the West and North Marsh, respectively. From 1988 to 1997, the TC accumulation in the West Marsh and North Marsh increased 2.9-fold over pre-diversion rates. Therefore, the rate of TC accumulation relative to pre-diversion rates has increased at similar rates in both marshes.

From 1978-1987, TN accumulation rates were 2.3 and 2.2 times the pre-diversion levels in the West and the North Marsh, respectively. The 1988-1997 TN accumulation in both the West and the North Marsh was 2.7 times the level of the pre-diversion period. Therefore, the increase in TN accumulation relative to pre-diversion rates was similar in both marshes.

The similarity between the pattern of TC and TN accumulation increases in both marshes is probably related to the similarity in the biotic and abiotic pathways leading to carbon and nitrogen sequestering in, or loss from, the sediments. Both carbon and nitrogen cycles have a gaseous phase component that is mediated, in part, by microbial processes in sediments. For TC, losses to the atmosphere occur as a consequence of methanogenesis and respiration; whereas TN losses can occur as a result of denitrification in anaerobic sediments (Wetzel 1983). The absence of a sedimentary signal of increased trapping of these elements in the North Marsh may be related to the fact that both elements have a significant atmospheric sink in addition to sediment storage.

TP accumulation rates from 1978-1987 nearly doubled in the West Marsh and more than doubled in the North Marsh compared to pre-diversion levels. Compared to pre-diversion rates, the TP accumulation in the West Marsh only increased by a factor of 2.2 from 1988 to 1997. TP trapping in the North Marsh more than tripled for these same time periods. Paired one-tailed t-tests were performed to evaluate whether or not the observed differences in the increase of TC, TN, TP, BAP and sediment accumulation over pre-diversion rates between marshes were significant. Only the TP accumulation from 1988-1997 versus

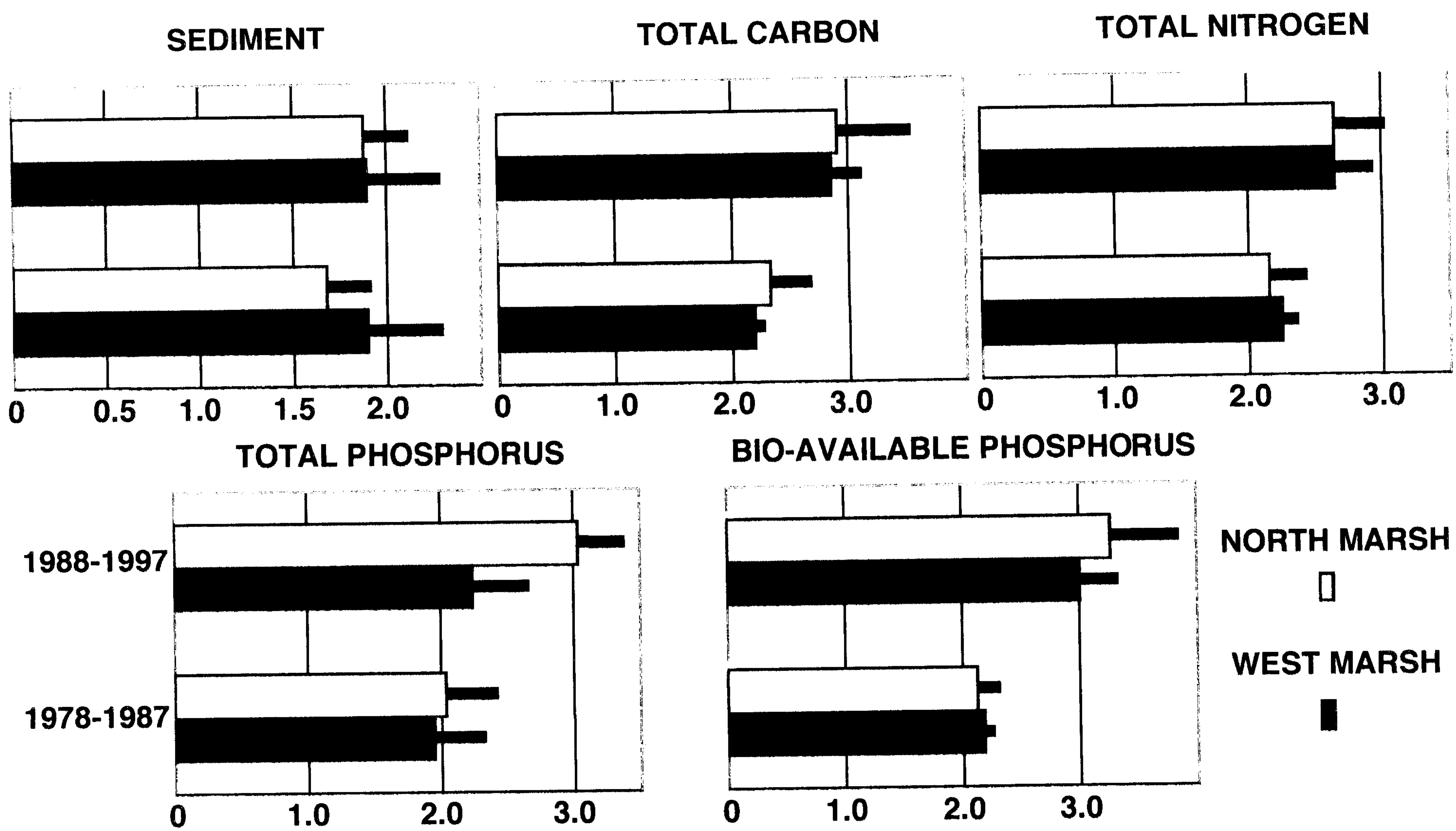


Figure 15. Change in target analyte accumulation rates relative to 1920-1977 accumulation rates for the North and West marshes, Winous Point, Ohio. Error bars equal 1 standard deviation.

1920-1978 was significantly different (p = 0.03, alpha 0.05) between the North and West marshes. Therefore, during the last decade, the North marsh trapped significantly more TP relative to pre-1978 rates than the West Marsh.

The pattern of BAP accumulation rates was similar to TP, albeit less pronounced. BAP accumulation rates from 1978-1987 more than doubled in the West and North Marsh compared to pre-diversion levels. Compared to pre-diversion rates, the trapping of BAP in the West Marsh tripled from 1988 to 1997. Comparing these same time periods, BAP accumulation increased by a factor of 3.3 in the North Marsh. Therefore, during the last decade, the North marsh accumulated more BAP relative to pre-1978 rates than the West Marsh.

Pronounced differences in TP and BAP accumulation rates between the North Marsh and West Marsh developed during the second decade after the West Marsh diversion of runoff. Prior to that time, increases in phosphorus trapping appeared similar between both marshes. This apparent delay in the sedimentary signal of increased phosphorus retention may be an artifact of upward migration of phosphorus in response to low redox potential in the sediment matrix (Engstrom and Wright 1984). Low redox-potential in sediments could create forms of phosphorus that were more soluble and could move with interstitial water until they precipitated back out in an oxidized zone (Engstrom and Wright 1984).

In addition, phosphorus deposition in these marshes may be dominated by internal recycling between sediments and the water column. Therefore, a sedimentary signal of the diversion of phosphorus runoff from the watershed would initially be dwarfed by internal recycling. We assumed that the phosphorus input into each marsh due to back-flooding from Muddy Creek Bay and the processes regulating the movement of phosphorus in and out of sediments were similar between both marshes over time.

As illustrated by the increase in the most recent decade, sediments in the North Marsh do not appear to be saturated with phosphorus in spite of receiving additional nutrients since the advent of European agricultural practices in its watershed. Although this finding points toward the marsh's resilience to long-term nonpoint-source agricultural runoff, it is not surprising because, in an absolute sense, the accumulation rates of phosphorus are still below those of the West Marsh.

4.5. Sediment Composition

4.5.1. Nutrient Accumulation Correlations

In addition to contrasting time series of accumulation rates for different sedimentary constituents between the two marshes, a comparison of the composition of the sediments may reveal the effects of long-term nonpoint-source agricultural runoff on the West and North marshes at Winous Point. Sediment composition was evaluated by comparing nutrient ratios over time in the cores from both marshes and by analyzing a series of correlations between TC and TP, TN and TP, TP and BAP, and TC and TN (Figures 16-19).

During the most recent decade, the North Marsh ratio of TP to TC accumulation was higher than during previous time intervals (Figure 16). This was not the case in the West Marsh. Generally, the ranges of accumulation rates for TP and TC were larger in the West Marsh for all time periods. Increasing TC accumulation correlated well with higher TP accumulation rates in the West Marsh with similar slopes over time. This phenomenon was less notable in the North Marsh, where only the correlation for the 1920-1977 time period was significant.

The ratio of TP accumulation relative to TN was higher in the North Marsh sediments for the interval 1988-1997 (Figure 17). This was not the case in the West Marsh where the correlations between TN and TP accumulation rates remained similar among time periods. All correlations in the West Marsh, as well as the 1920-1977 trend in the North Marsh were statistically significant. The TP to TN correlations in the North Marsh sediments from 1920-1977 and 1978-1987 were similar, albeit non-significant. Overall, TP and TN accumulation in West Marsh sediments was higher than in North Marsh sediments for all time periods. Some of the scatter in the trends for the West Marsh resulted from the large difference in TP accumulation rate among different cores from this marsh.

During the last decade (1988-1997), the North Marsh accumulated more TP and BAP than during prior periods (Figure 18). Furthermore, BAP accumulation seemed to have increased relative to TP in North Marsh sediments from 1988-1997. The ratio of accumulation rates of TP vs. BAP in the West Marsh showed statistically significant trends with slopes that remained fairly constant during all three time-intervals.

The correlations between TN and TC accumulation rates were similar and highly significant in both marshes over all time periods (Figure 19), suggesting either a direct causal link between the two rates or, more likely, a common process guiding both TN and TC trapping in these marshes. TN, and to a lesser extent, TC accumulation was higher in the West Marsh.

Figures 16-19 — Correlations of TC-TP, TN-TP, TP-BAP, and TN-TC in sediments of the North and West marshes, Winous Point, Ohio. Time periods of interest were 1920-1977 (Pre-diversion of runoff to the West Marsh), 1978-1987 (first decade post-diversion), and 1988-1997 (second decade post-diversion). Statistics included in tables with each graph.

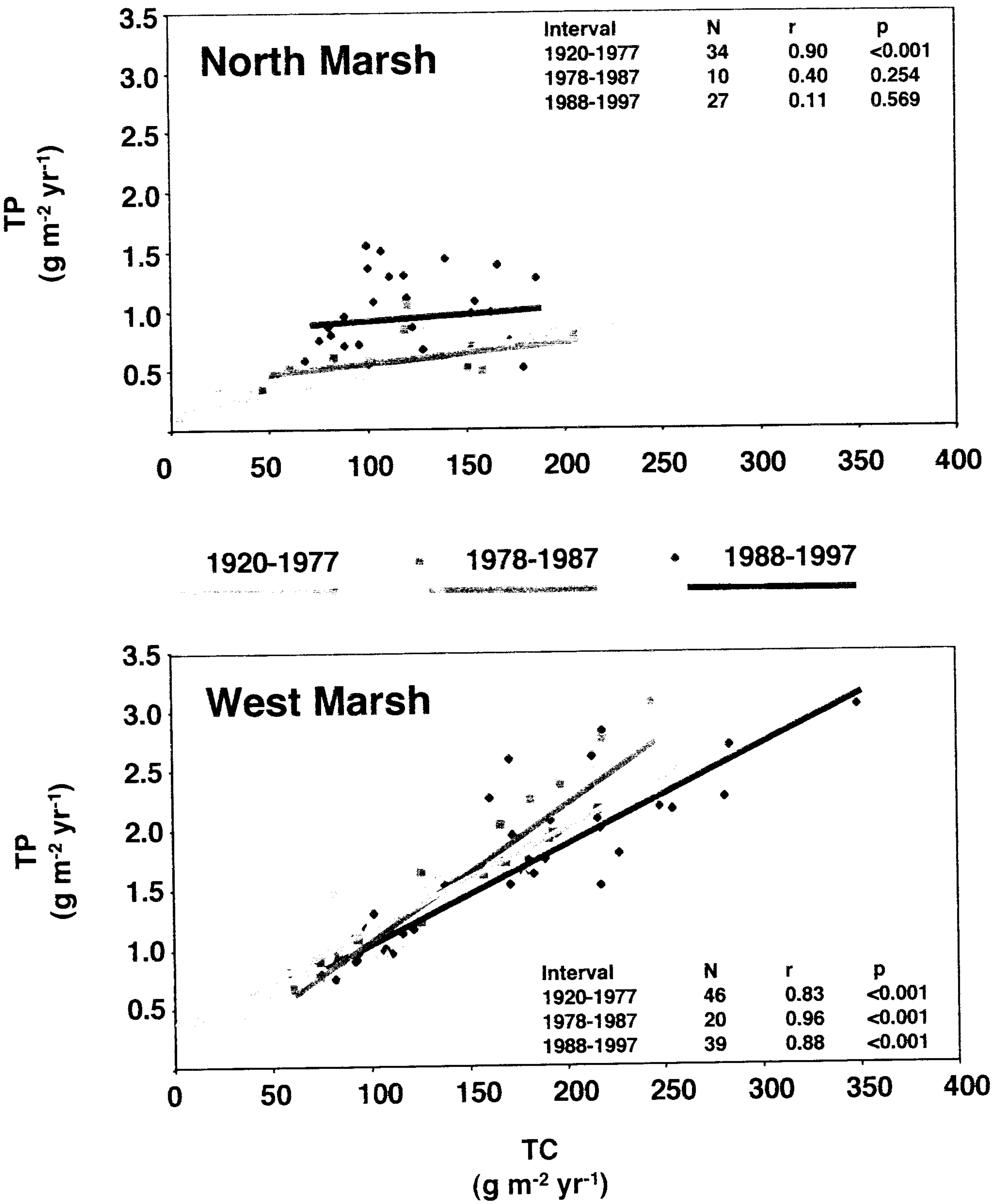


Figure 16. Total Carbon vs Total Phosphorus, Winous Point Marshes, Ohio

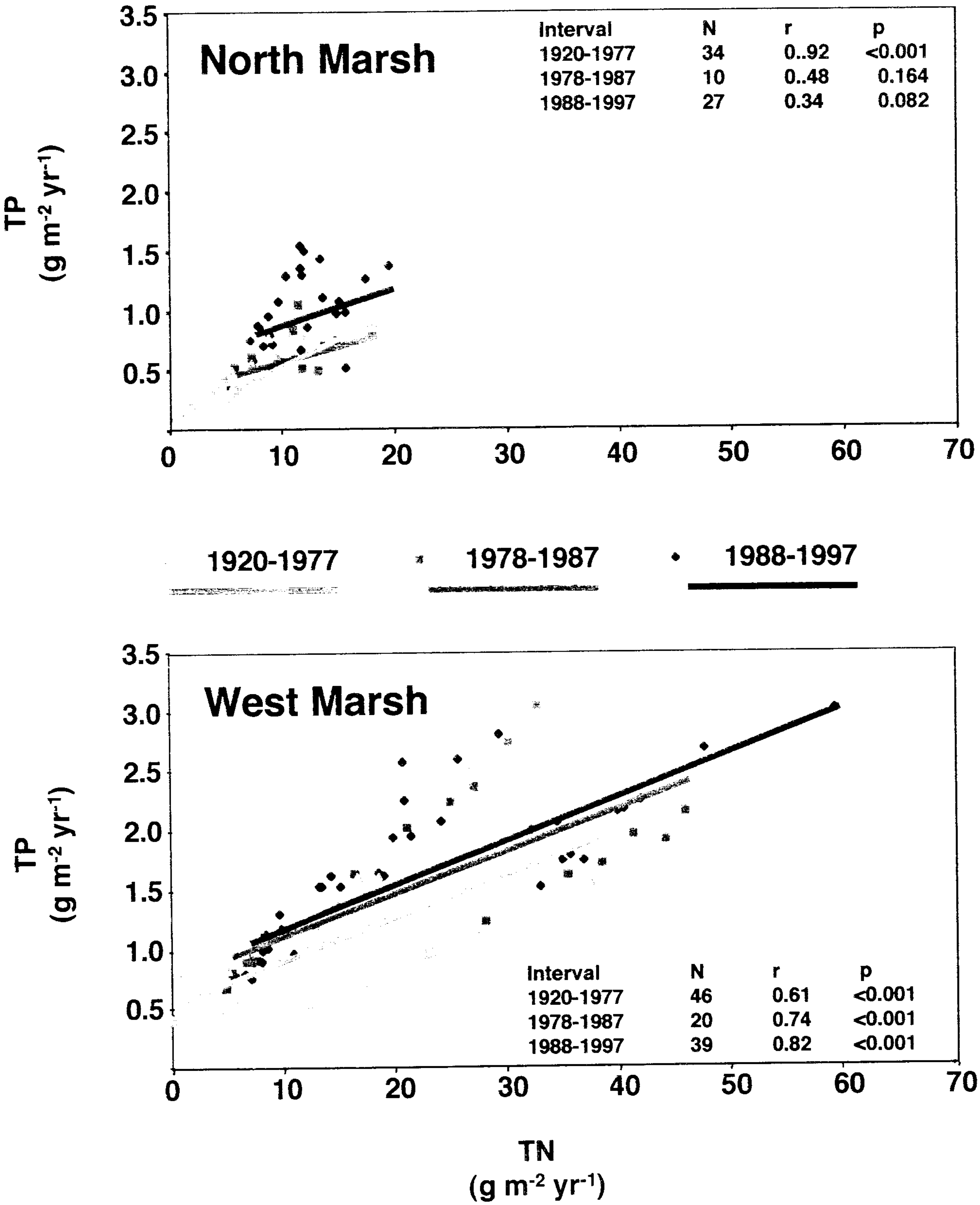


Figure 17 Total Nitrogen vs Total Phosphorus, Winous Point Marshes, Ohio

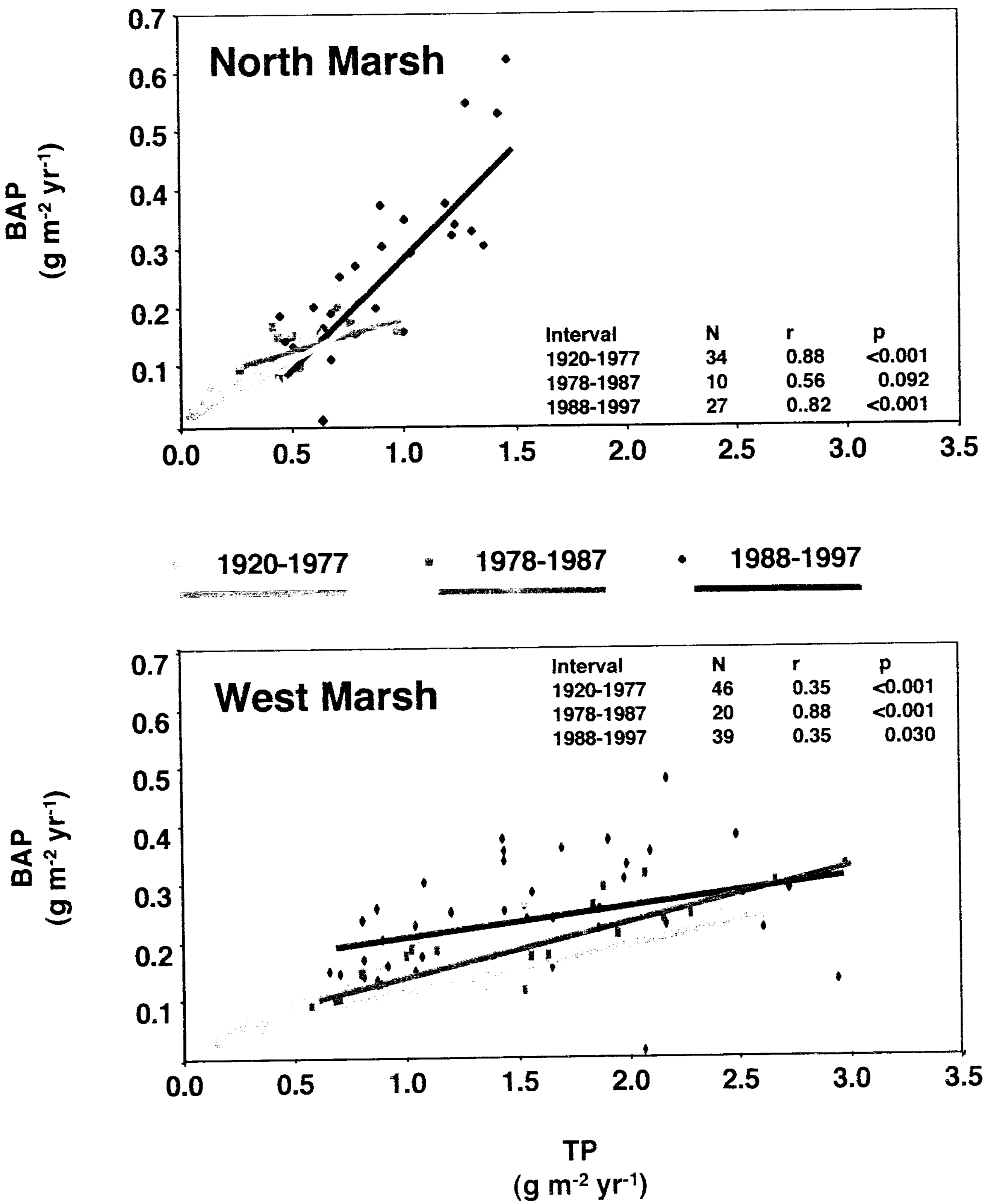


Figure 18. Total Phosphorus vs Bioavailable Phosphorus, Winous Point Marshes, Ohio

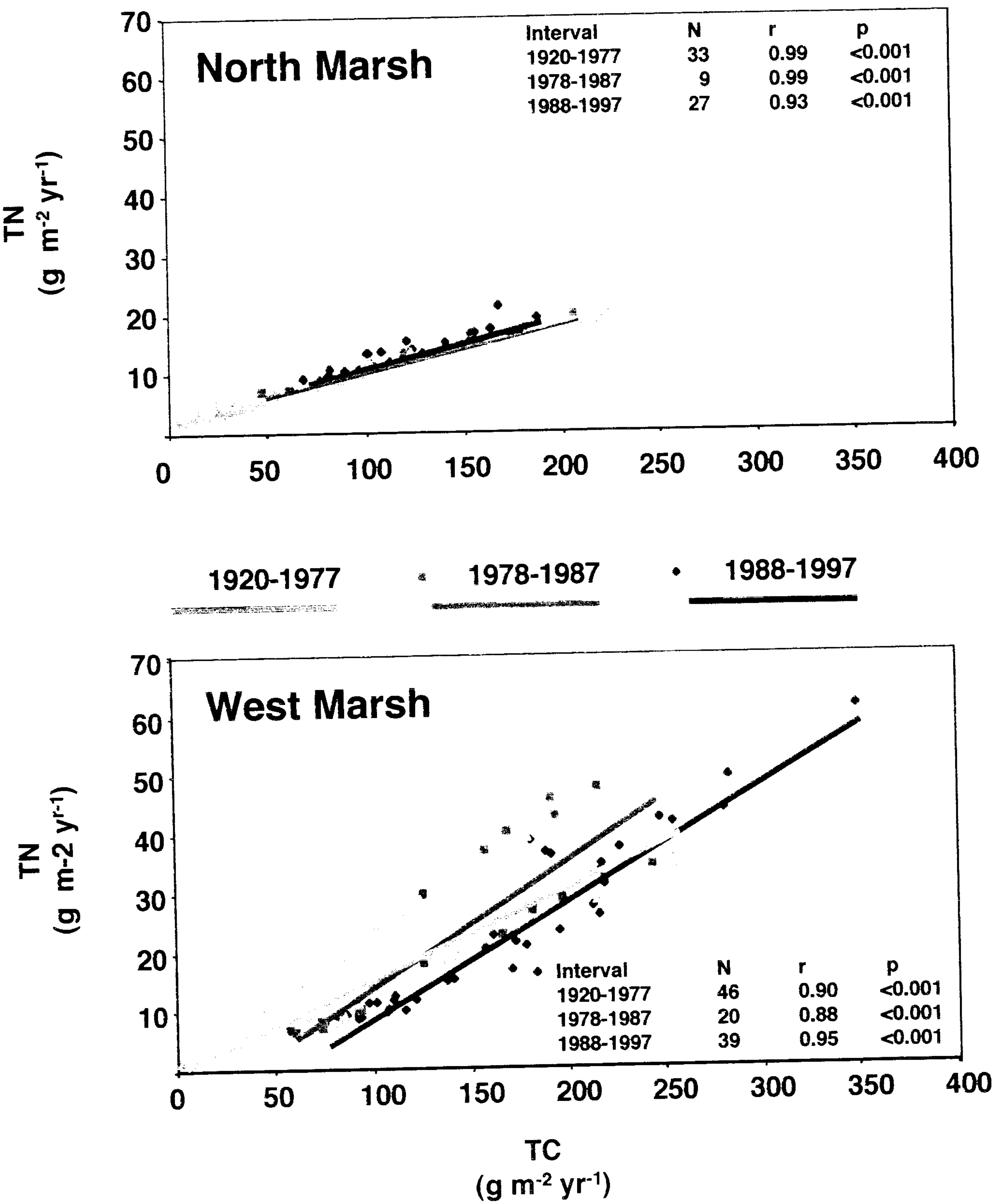


Figure 19. Total Carbon vs Total Nitrogen, Winous Point Marshes, Ohio

4.5.2. Nutrient-Metal Correlations

Certain metals (Al, Fe, Mn, and others) may function in regulating P sedimentation because they form chemical complexes with P or because they react differently when redox conditions change (Gale *et al.* 1994). In other words, P retention in wetland soils may depend on the availability of these trace metals in chemically-reduced state.

A comparison of Al and TP accumulation revealed that the North Marsh trapped more TP relative to Al in recent sediments than in pre-1978 deposits (i.e., the ratio of TP over Al accumulation was highest for the 1988-1997 period), although the correlations among these rates was only significant for the 1920-1977 time period (Figure 20). No obvious differences in the ratio of TP and Al existed among time periods in the West Marsh. Absolute rates of TP and Al accumulation were generally higher in the latter marsh.

The patterns of Fe and TP accumulation, as well as Mn and TP accumulation were very similar to the Al-TP correlations (Figures 21 and 22). Again, the ratio of TP vs Fe or Mn deposition in the North Marsh is highest during the last decade, a phenomenon not seen in the West Marsh. It appeared, therefore, that the increased retention of TP in the North Marsh since 1988 was not produced by increased Al, Fe or Mn. Alternatively, retention of TP did not seem limited by the availability of these metals that commonly bind with TP.

Finally, the correlations between Mn and TP deposition showed an increase in Mn relative to TP in sediments in the North Marsh since 1988 and in the West Marsh since 1978 (Figure 22). We suspect that, because Mn is mobilized in sediments at a somewhat higher redox potential than Fe, Mn would not only migrate more readily toward the top region of the core but apparently does so without moving TP along. Thus, elevated Mn in more recent sediments may reflect more its solubility response to redox profiles in the marsh sediments, rather than actual changes in its net accumulation.

Figures 20-22 Correlations of TP-Al, TP-Fe, and TP-Mn in sediment from the North and West marshes, Winous Point, Ohio. Time periods of interest were 1920-1977 (Pre-diversion of runoff to the West Marsh), 1978-1987 (first decade post-diversion), and 1988-1997 (second decade post-diversion). Statistics included in tables with each graph.

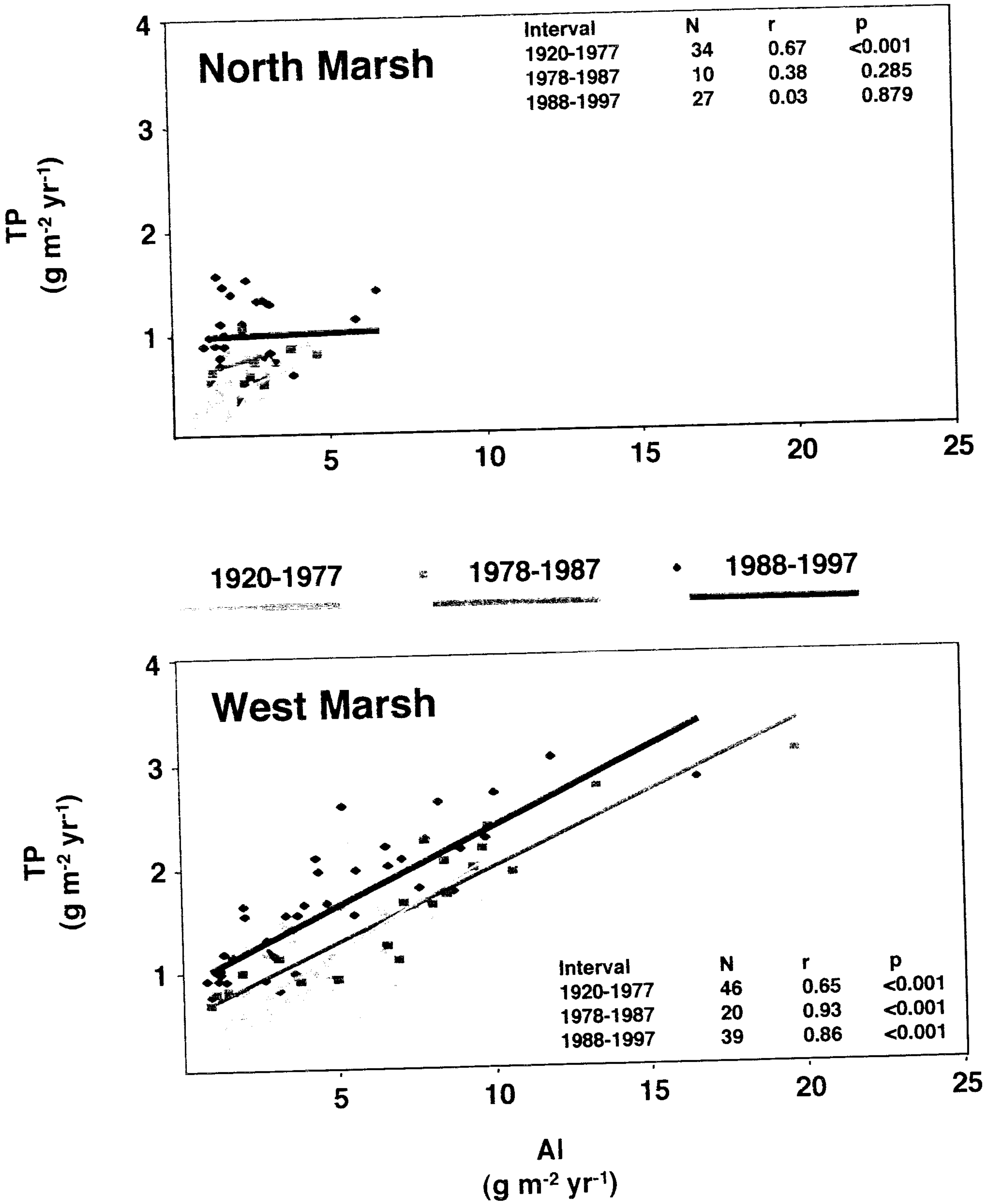


Figure 20. Total Phosphorus vs. Aluminum, Winous Point Marshes, Ohio

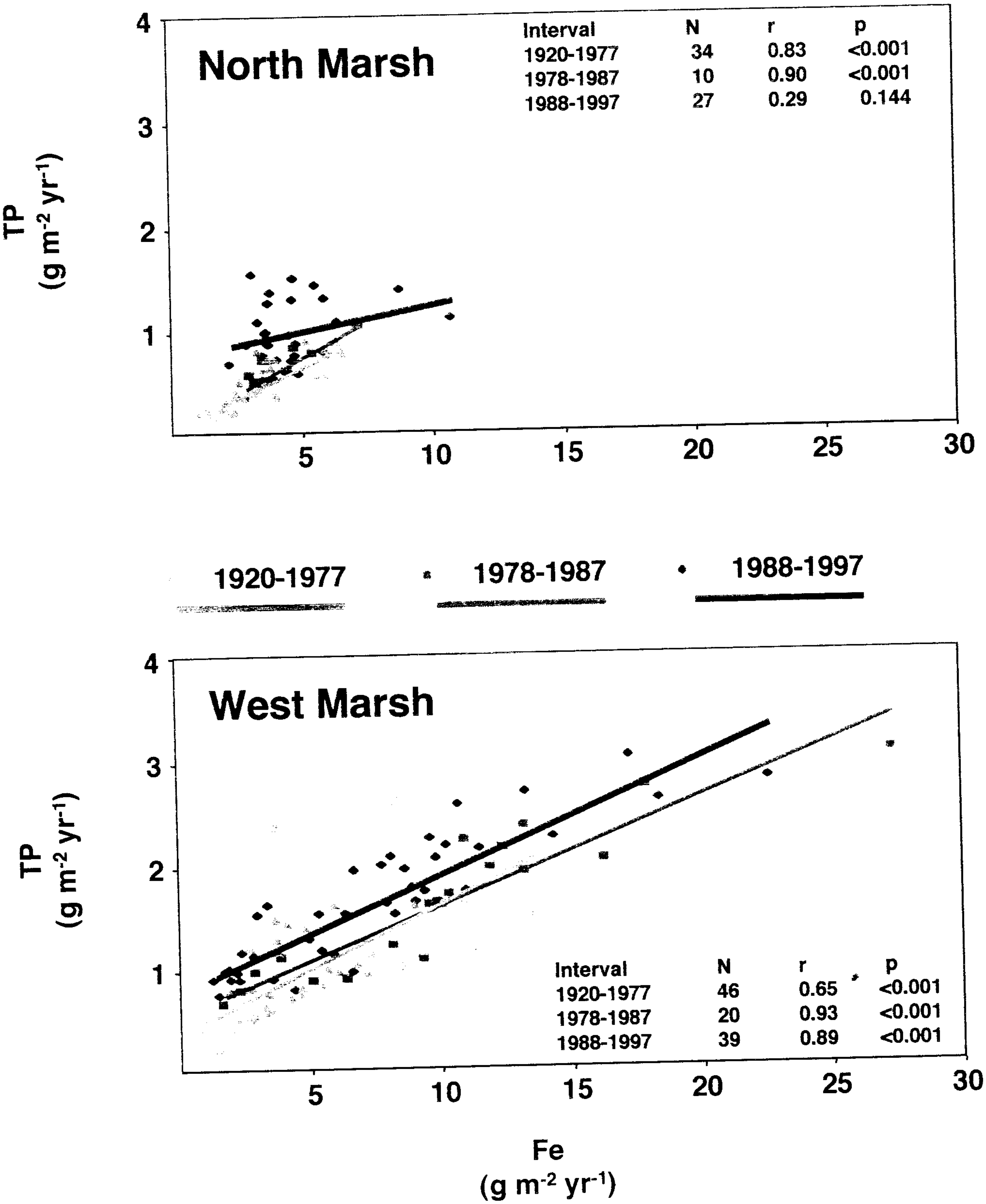


Figure 21. Total Phosphorus vs Iron, Winous Point Marshes, Ohio

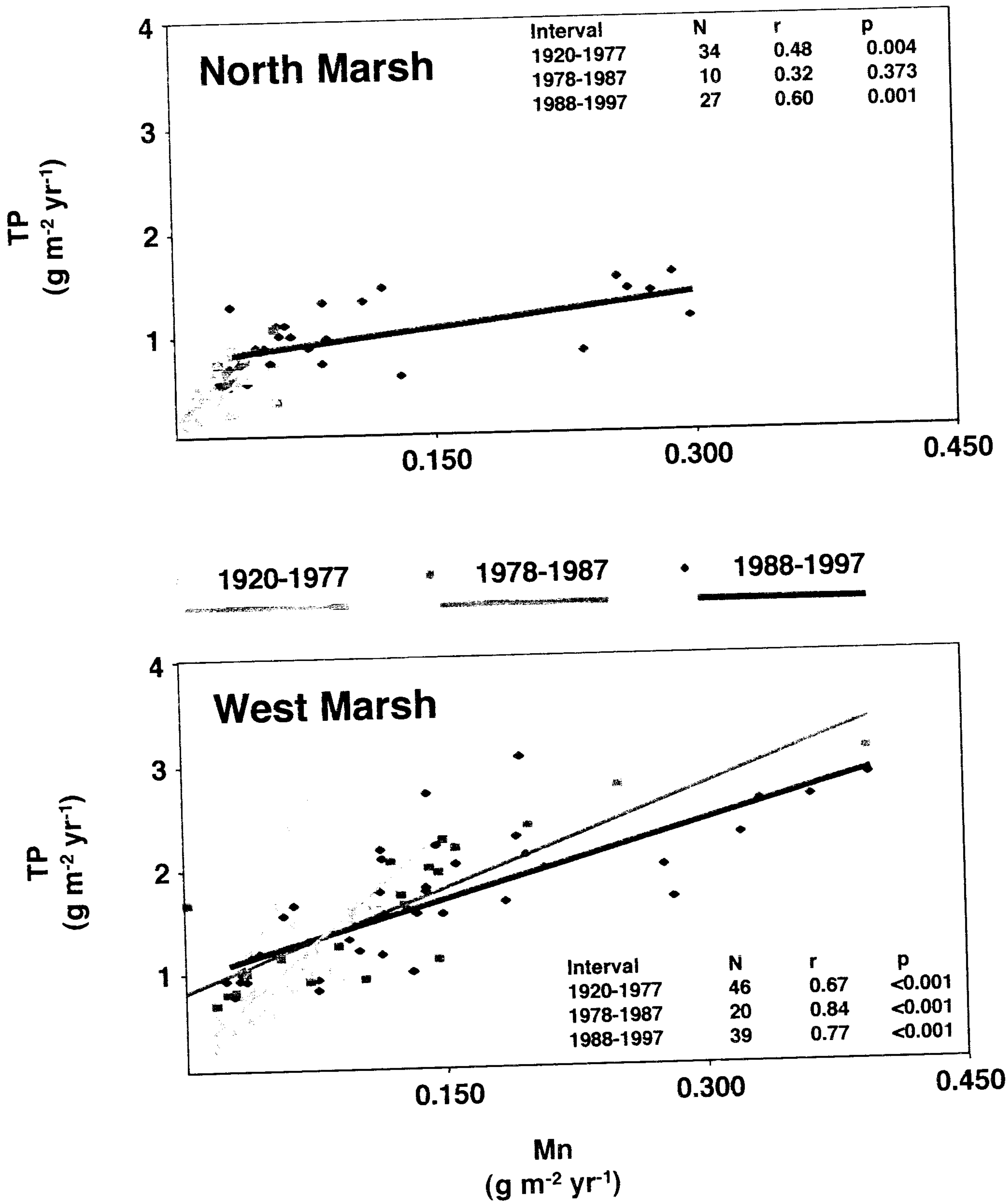


Figure 22. Total Phosphorus vs Manganese, Winous Point Marshes, Ohio

4.5.3. Nutrient Ratios

A series of TC:TN:TP ratios (based on accumulation rates) was calculated for both the North and West marshes for the time intervals 1920-1977, 1978-1987, and 1988-1997 (Table 8). The ratio of TC-TN-TP from North Marsh sediments showed an increase in TP relative to TC and TN since 1987. TC-TN-TP ratios from West Marsh sediments showed a decrease in TP relative to TC since 1978. The TC to TN ratio remained nearly the same over time in each marsh, although the West Marsh was richer in TN than the North Marsh.

Table 8 TC-TN-TP ratios from North and West Marsh sediments, Winous Point, Ohio. Ratios based on average accumulation rates (g m^{-2} yr^{-1}) for the time intervals 1920-1977, 1978-1987, and 1988-1997. Values in parentheses represent one standard deviation.

Marsh	Time	TC	TN	TP
N	1988-1997	155 (58)	15 (5)	1
N	1978-1987	197 (71)	19 (6)	1
N	1920-1977	173 (69)	17 (4)	1
W	1988-1997	107 (13)	13 (5)	1
W	1978-1987	95 (9)	13 (7)	1
W	1920-1977	84 (35)	12 (10)	1

In the West Marsh, BAP comprised a larger portion of the TP pool in sediments deposited since diversion than in pre-diversion sediments (1920-1977 9.7%, 1978-1987 12.5%, 1988-1997 14.4%). This difference was less pronounced in the North Marsh (1920-1977 21.9%, 1978-1987 23.6%, 1988-1997 23.1%), possibly influenced by watershed input of phosphorus with a high BAP:TP ratio. Overall, the North Marsh sediments contained twice as much BAP relative to TP as the West Marsh sediments.

Elevated BAP toward the top of the core may be due to higher activity of decomposers in these biologically active layers as well as recycling by rooted aquatic macrophytes. Moreover, the near-constant ratio of TC:TP and TN:TP in West Marsh sediments since the diversion of agricultural runoff may be due to the conservative biological recycling of these nutrients in the upper sediments by rooted aquatic macrophytes. By comparison, increasing TP relative to TC and TN in the North Marsh sediments since 1988 may reflect the increasing TP accumulation in response to continued exposure to nonpoint-source agricultural runoff from its watershed.

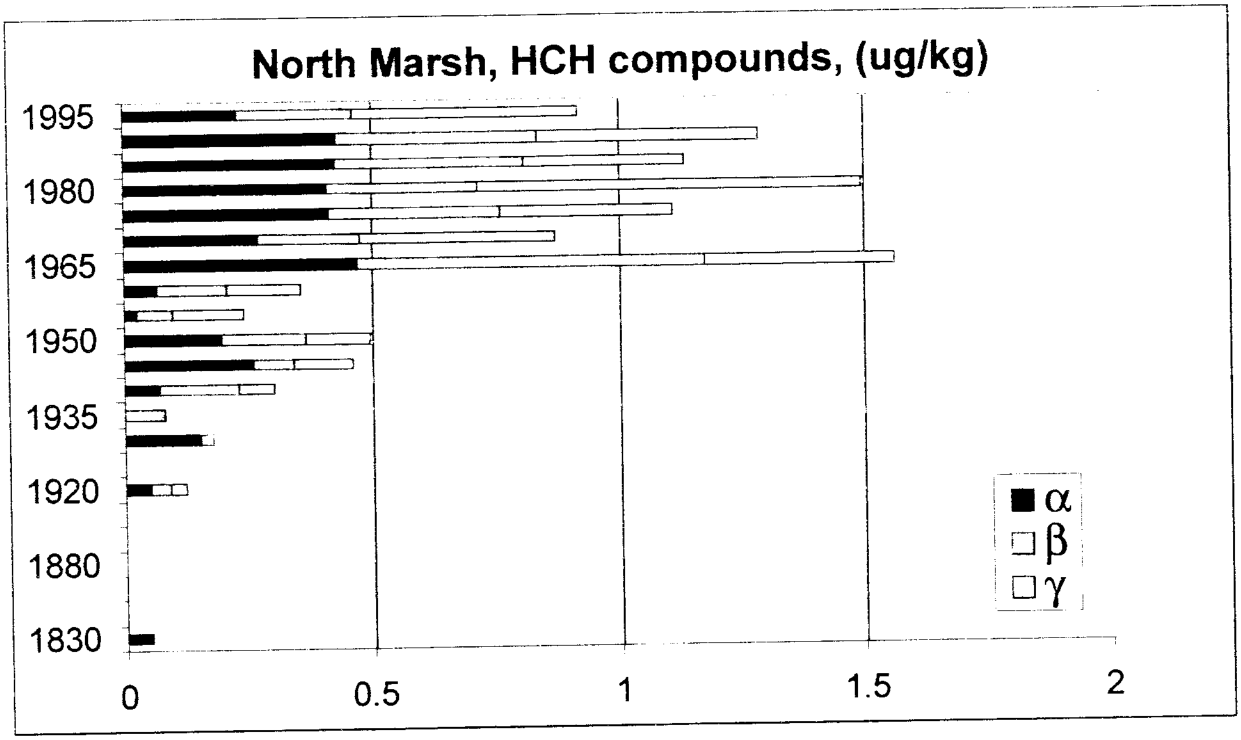
4.6. Pesticide Concentration Profiles

Whereas nutrients are required by biota within a particular range of concentrations, pesticides and many other xenobiotic compounds may be toxic even at very low concentrations. Many researchers have documented the occurrence of persistent organic pollutants (POPs) including polychlorinated biphenyls, polycyclic aromatic hydrocarbons and older organochlorine pesticides in lake and estuarine sediments (Gschwend and Hites, 1981; Jeremiason *et al.*, 1994). Loading of POPs may occur through atmospheric deposition, transport in solution or as adsorbed species. Many of these compounds are resistant to degradation. The hydrophobic character of POPs leads to preferential sorption on particulate matter where they can persist for decades in the sedimentary record. In the Great Lakes maximum levels of POPs in sediments correspond well to periods of peak use and manufacture of these chemicals in the USA (Eisenreich *et al.*, 1989).

The pesticides chosen for analysis in the Winous Point sediment cores include those highly persistent chlorinated compounds manufactured in the 1960-1980 era. These include aldrin and its metabolite dieldrin, endrin and its metabolite endrin aldehyde, DDT and metabolites DDE and DDD, and three hexachlorohexane pesticides α, β, and γ-HCH. γ-HCH is commonly known as lindane. These pesticides were designed to be persistent in the environment and have since proven to be highly detrimental to biota. All of these compounds have since been banned from use in the United States, except lindane which is currently highly restricted.

The data from Winous Point show variations with depth that can be attributed to anthropogenic activities. Figures 23-26 show concentrations of specific long-lived pesticides with time in both marshes. Even though these pesticides are banned from current use, the local people have mentioned illegal usage of some of these compounds. In general, the farms were settled along the wetland border prior to establishment of the Shooting Club in 1856. Common crops traditionally have been corn, wheat and soybeans, with the current usage being 10, 10, and 60%, respectively. The Brough farm, which drains into both marshes was established as an orchard pre-1950, followed by dairy farming until the mid-1970s, prior to crop farming. Former orchard operations included extensive use of pesticides such as DDT.

HCH compounds, which include the popular pesticide lindane, increase in both marshes in the mid-1960s (Figure 23). The North Marsh, which is still impacted by agricultural runoff shows an abrupt increase around 1965, followed by relatively stable concentrations until the past five years, when concentrations



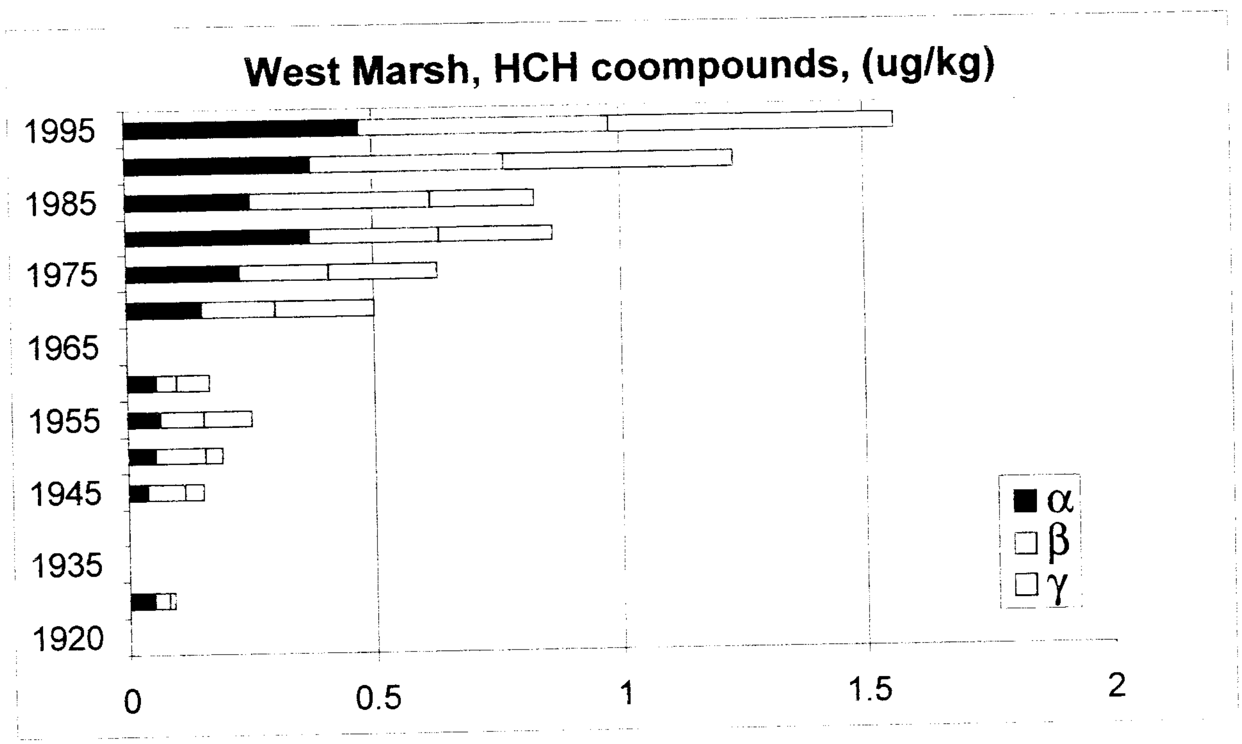
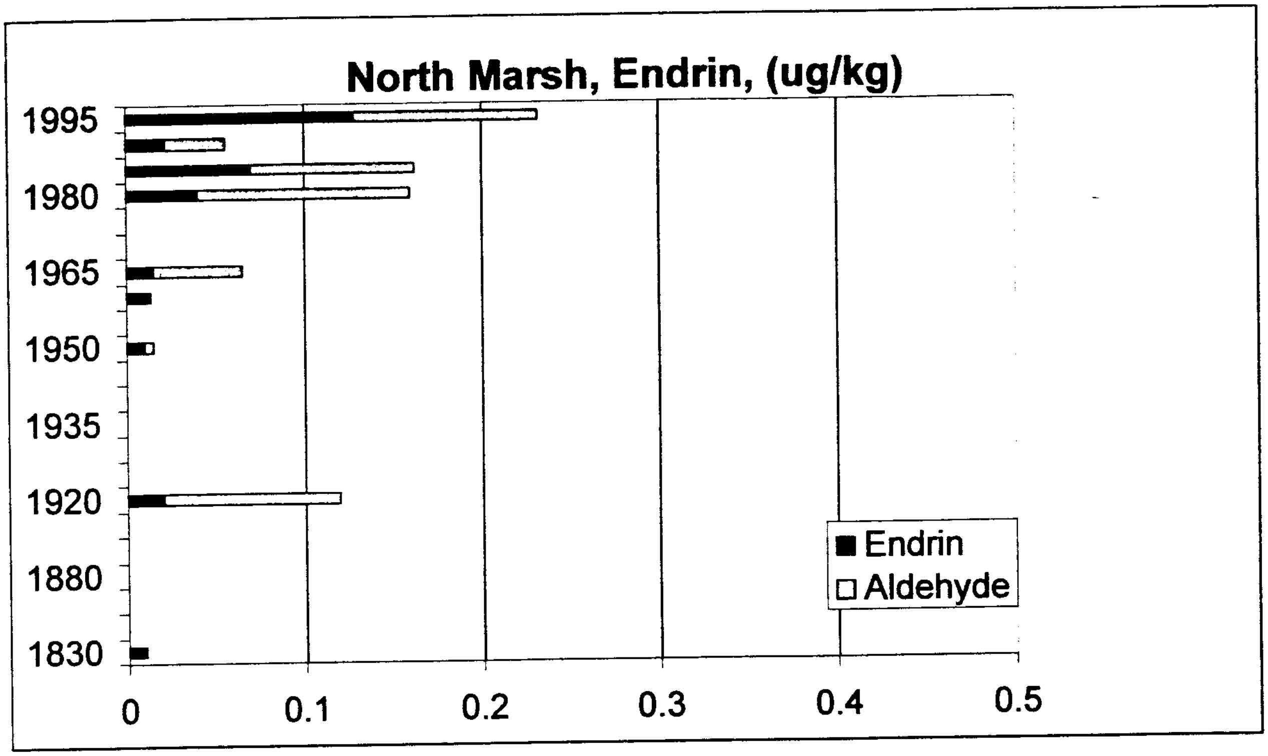


Figure 23: Concentrations of α, β, and γ (lindane) HCH pesticides at Winous Point marshes.



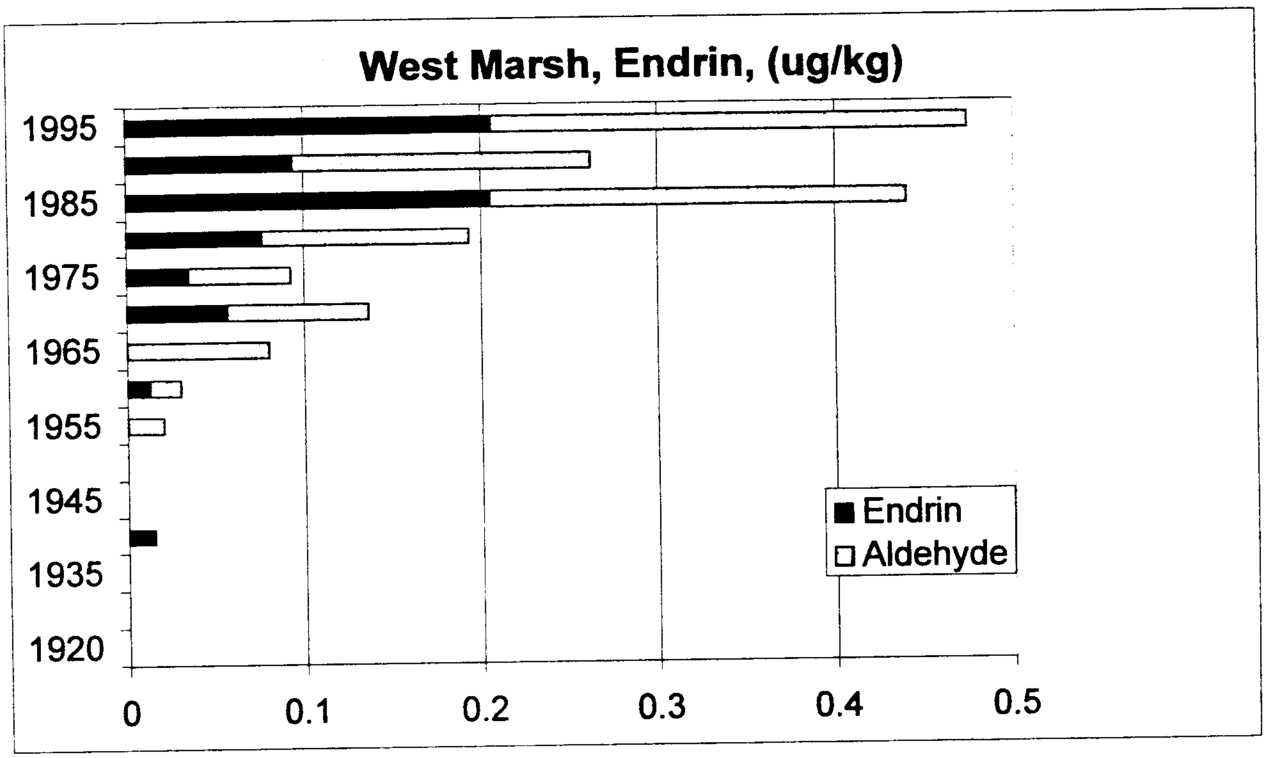
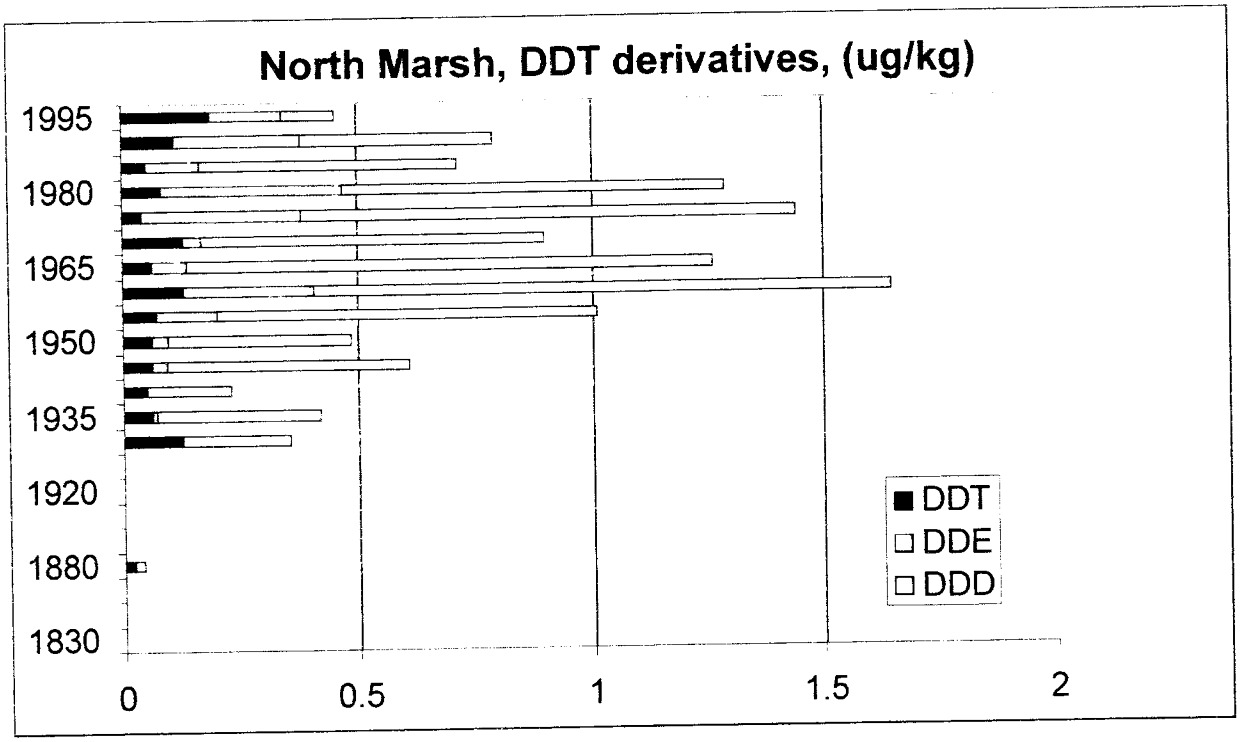


Figure 24: Concentrations of parent pesticide, endrin, and its metabolite endrin aldehyde at the Winous Point marshes.



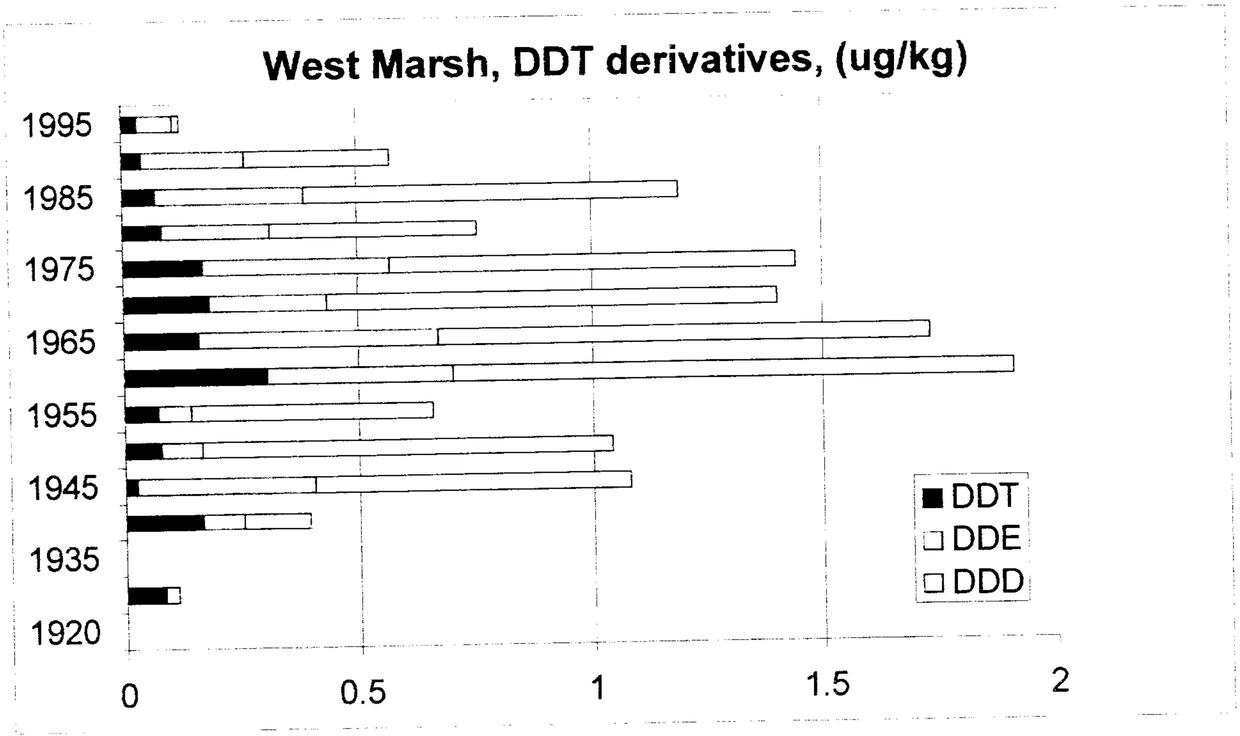
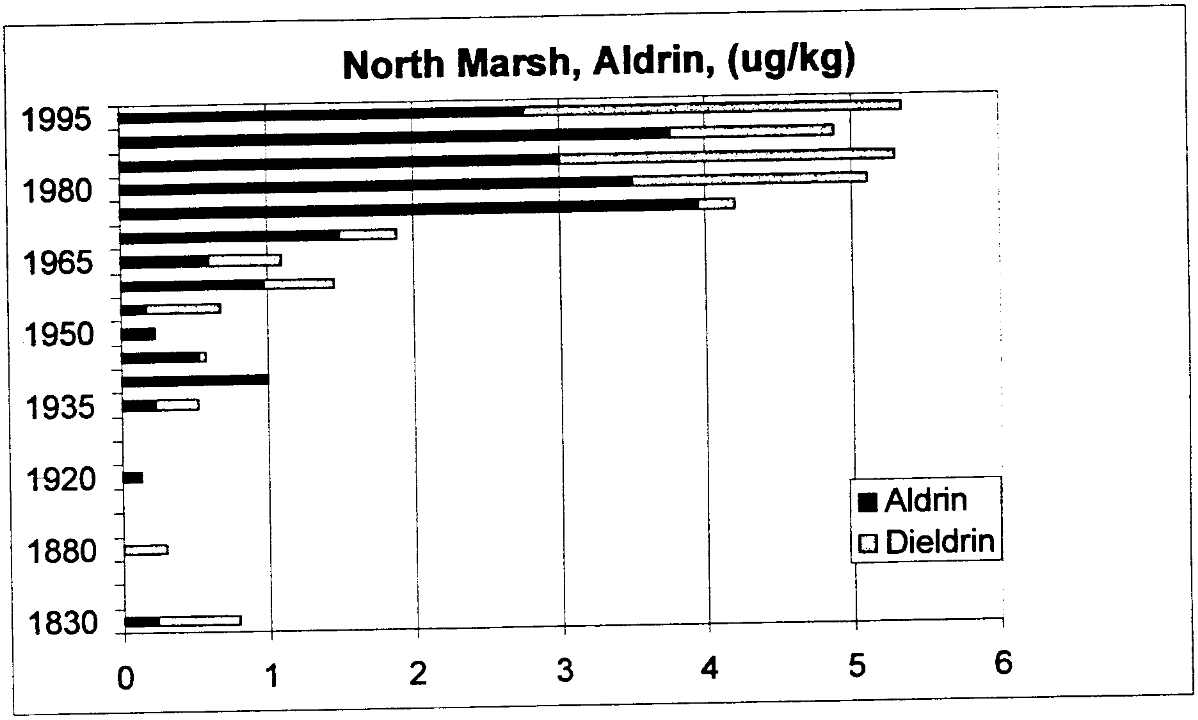


Figure 25: Concentrations of the parent pesticide DDT and metabolites DDE and DDD at Winous Point marshes.



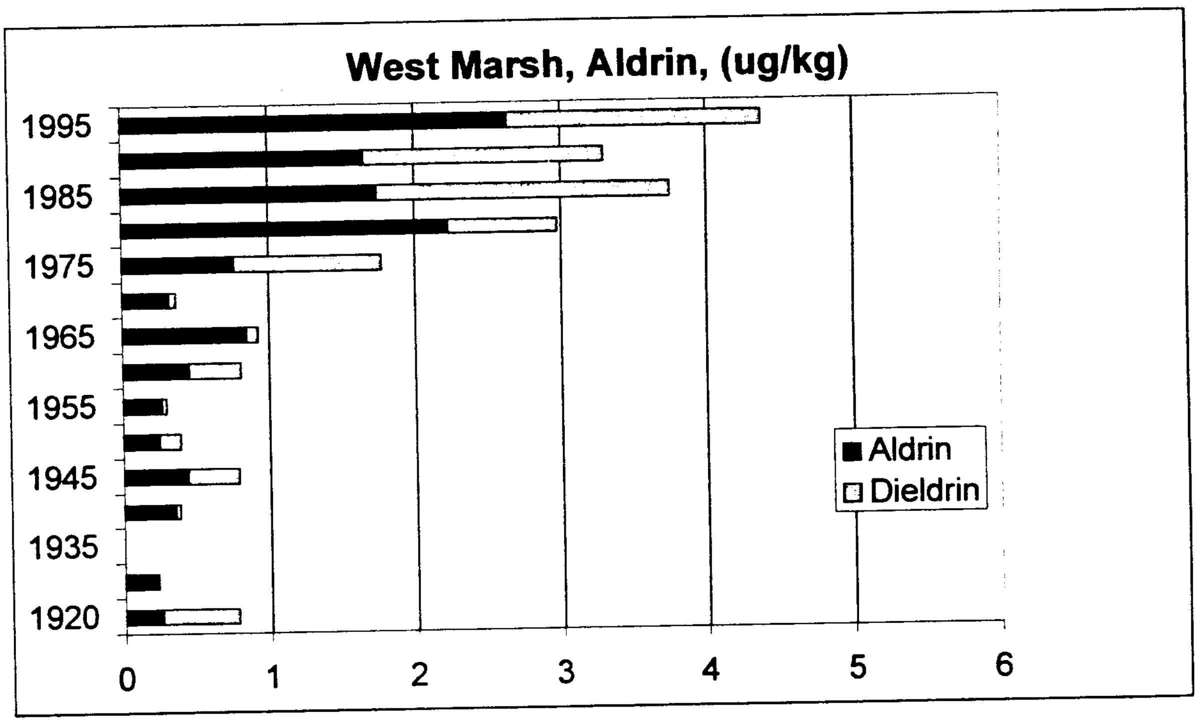


Figure 26: Concentrations of parent pesticide aldrin and metabolite, dieldrin, at Winous Point marshes.

seem to be decreasing. The West Marsh shows a steady increasing trend continuing to the present. Concentrations are similar in both marshes.

Endrin is present in very low concentrations in both marshes until the 1960s as well (Figure 24). However, the concentration in the West Marsh is roughly twice that in the North Marsh. The proportion of parent pesticide to its metabolite has remained stable up through the most recent samples despite its ban from usage in this country.

DDT and its metabolites show a very different pattern than the other pesticides (Figure 25). Concentrations of DDT, although still being detected in the most recent sediments, reached their maximum in the 1950s for both marshes. This correlates well with the presence of orchards in the drainage basin. Decreasing concentrations occur in the 1970s correlating with its ban from usage in this country. Concentrations are similar in both marshes. The major metabolite detected in both basins is the anaerobically generated compound, DDD. Degradation of DDT is therefore occurring in the reduced anoxic zone within the sediment, as opposed to degradation in oxidized surface sediments or degradation prior to transport and burial. Concentrations within the past five years have been very low to absent in the West Marsh, however, evidence of recent input is seen in the North Marsh. Source of this contamination is unknown. The continued, although decreasing, input of these compounds into the marshes after its ban indicates that either illegal usage is occurring to the present time, or that transport into the wetland is delayed by chemical or physical processes.

Aldrin and its metabolite, dieldrin, follow a trend similar to that of endrin (Figure 26). However, unlike the other pesticides, concentrations of aldrin in the North Marsh are higher than in the West Marsh. Increases in the North Marsh began around 1970, whereas the increase in the West Marsh is not apparent until 1975. Furthermore, concentrations of this banned compound in the most recent sediments indicate either illegal usage or delayed transport into the wetland.

Table 9 shows the pesticide data averaged over the following three time-intervals: 1920-1977, 1978-1987, and 1988-1997. The first interval represents the time period prior to diking the West Marsh. Many of the trends previously discussed are masked in these averaged data. However, data for all compounds except the DDT compounds show similar overall trends within each marsh. The HCH, endrin and aldrin compounds show similar averages in the two oldest intervals in the North Marsh, with a significant decrease in the most recent decade. The three compounds in the West Marsh, however, show a significant decrease in all three time-intervals. These trends are interesting in that no major management changes occurred in the wetland marshes in the late 1980s or 1990s. Therefore, the trends must be explained by agricultural practices during that time, with the most recent decrease representing the discontinued use of these compounds.

Interestingly, the North Marsh, which still receives agricultural runoff, does not always show the higher pesticide concentrations, possibly reflecting an airborne source for the pesticides into the West Marsh. There is a greater likelihood that the West Marsh would be impacted from an airborne source because of the prevailing westerly winds in this region. Furthermore the West Marsh is surrounded by a greater proportion of agricultural land, whereas the North Marsh and its watershed are surrounded by more marsh lands.

The periodic flushing of the North Marsh also does not seem to have an influence on the pesticide concentrations. The hydrophobic nature of all of these compounds would promote sorption of these compounds onto clay and organic particles. However, during flushing events suspended sediments can potentially transport significant quantities of sorbed pesticides. Evidently, either this removal process is insignificant in the North Marsh or the initial concentrations of pesticides were much greater than that represented in the sediment record.

Table 9. Winous Point averaged pesticide data (μg kg^{-1}) for the North and West marshes.

Marsh	**Time Interval**	**HCH α**	**HCH β**	**HCH γ**	**Endrin parent**	**Aldehyde**
North	1988-1997	0.355	0.343	0.439	0.070	0.071
North	1978-1987	0.408	0.314	0.474	0.040	0.076
North	1920-1977	0.145	0.149	0.147	0.005	0.010
West	1988-1997	0.404	0.443	0.483	0.161	0.224
West	1978-1988	0.294	0.249	0.226	0.109	0.144
West	1920-1978	0.070	0.079	0.073	0.011	0.020
Marsh	**Time Interval**	**DDT parent**	**DDT DDE**	**DDT DDD**	**Aldrin parent**	**Aldrin Dieldrin**
North	1988-1997	0.121	0.183	0.348	3.315	2.027
North	1978-1987	0.072	0.332	0.808	3.280	1.000
North	1920-1977	0.074	0.067	0.550	0.525	0.264
West	1988-1997	0.036	0.177	0.274	2.173	1.902
West	1978-1988	0.130	0.254	0.647	1.444	0.803
West	1920-1978	0.135	0.259	0.740	0.433	0.293

The ratio of parent pesticide to its metabolite does not change with time for any of the pesticides. Recent sediments contain about the same percent of parent molecule as do the sediments deposited during the assumed timeframe of maximum pesticide usage. Presence of parent molecule is usually interpreted to mean recent usage. However, the persistent ratio from current sediments to sediments >50 years old suggests that the compounds are of former application. The sediments may have been subjected to bioturbation or mixed to bring the older pesticides to the surface, or the transport of the pesticides into the sediment record may be inhibited by some chemical or physical process such as sorption. The isotopic data suggests that the sediments have not been extensively disturbed, therefore the latter interpretation of transport inhibition is most likely. Surprisingly, if this is indeed the case, the pesticides are still degrading at roughly the same rates as the pesticide buried within the anoxic sediment column.

4.7. Wetland Mitigation of Nonpoint Pollution: The Political Science Context

by David H. Davis, Department of Political Science and Public Administration, University of Toledo

Scientists have found that wetlands, such as the marshes along the shore of Lake Erie, are effective means of abating pollution from farm runoff. In this study, Gottgens and Muller documented long-term trapping of phosphorus in marsh sediments. Other research has found removal of carbon and nitrogen, likely into the atmosphere. Translating wetland abatement into effective government programs, however, presents difficulties due to lack of money and gaps in programs. The Winous Point Shooting Club, a duck hunting club on Sandusky Bay founded in 1856, has a long history of dedication to wildlife and environmental protection, but cannot always capitalize on its good intentions.

Programs under the 1972 Clean Water Act

Nonpoint sources of water pollution drew scant attention from Congress when it passed the original law in 1972. The term refers to drainage, primarily from agriculture, that does not come from a single point, such as a pipe from a sewage plant, a steel mill or a factory. Section 502 (14) specifically states that agricultural runoff is not a point source. Twenty seven years ago Congress concentrated on the more serious point pollution, but now the success of the law has greatly reduced point sources, and attention has turned to nonpoint sources. Today EPA estimates that "agriculture is the leading contributor to water quality impairments, degrading 60 percent of the impaired river miles and half the impaired lake acreage."[1]

Three factors led Congress to concentrate on point sources in 1972: (1) the immediate problem of raw sewage being dumped into rivers, (2) the experience of environmental groups with the 1899 Refuge Act, and (3) unsatisfactory attempts during the 1950s and 1960s trying to improve water quality by focusing on the receiving waters. As of 1972 many municipalities still did nothing to treat their sewage, and drained it directly into rivers and lakes. The Potomac suffered as much as many rivers, so Members of Congress had a daily reminder. One flagrant offender was Fairfax County in nearby Virginia, now an upscale suburb, but was then (in the words of a critic) "inhabited by a bunch of hillbillies." The 1899 Refuse Act was the second factor. The original purpose of the law was to protect navigation. After the Army Corps of Engineers dredged a river channel, it did not want anyone to dump spoil and impede shipping; therefore it required a

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[1] EPA, Office of Water, "Nonpoint Source Pollution: The Nation's Largest Water Quality Problem," EPA 841-F-96-004 A.

permit. In the 1960s environmental lawyers imaginatively seized on the Refuse Act and persuaded the courts that dumping pollution into a river was covered by the wording of the law, hence the polluter had to apply for and receive a permit. The third factor was the difficulty in achieving results from basing standards on the receiving waters. Finding out who was polluting a river or lake proved nearly impossible, so Congress decided the only way to control the ambient water was to control its sources.

The 1972 law provided generous grants of billions of dollars to solve the problem. This was continuing the tradition dating back to the New Deal of 1933-39, whereby the national government invested in water projects. In the early 1970s, Congress was quite explicit that it considered the grants to the states part of the bargain that was to encourage and compensate state and local governments to participate in national regulation. Over the next decade, the grant program worked quite successfully to accomplish its goal of controlling point sources of pollution. Thousands of municipalities built plants, and water quality improved markedly. Private industrial polluters, although they did not receive direct grants of money from the federal government, did receive indirect subsidies by being able to connect to municipal systems and by tax benefits on their investments in pollution control equipment.

EPA provided more than $60 billion for the construction of public wastewater treatment projects. These projects, which included sewage treatment plants, pumping stations, and collection and intercept sewers, greatly reduced the amount of pollution flowing into rivers and lakes. Although EPA terminated its construction grants program, it has continued to give the states grants for administering their functions under the Clean Water Act Section 106, such as permitting, pollution control activities, surveillance, monitoring, enforcement; advice and assistance to local agencies, training and public information.[2]

Due to a series of recessions from 1974 to 1982, and later opposition to government spending by the Reagan Administration, Congress abandoned the grants and replaced them with a far less generous loan program. With the 1987 amendments to the Clean Water Act, Congress set 1990 as the last year that grants funds would be appropriated. By phasing out the construction grants program, EPA shifted the method of municipal financial assistance to loans provided by state revolving funds. The total assets of the fund for all 50 states is currently $27 billion. As payments are made on loans, the money is recycled to fund additional water protection projects.

It was at this time that Congress and EPA began to address more seriously the problem of nonpoint sources. As long as point sources were contributing so much pollution, less attention was paid to nonpoint sources. Thus by the time

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[2] EPA, Office of Water, Office of Wastewater Management, "Financial Assistance" www. epa.gov/owm/

EPA got around to the nonpoint problem, federal money was no longer available. The original "contract" could not be duplicated. One can speculate that had Congress and EPA tackled the nonpoint pollution in 1972, the law would have provided a generous grant program to farmers, or would have provided for local governments to purchase wetlands to abate agricultural runoff. In contrast to the EPA command and control methods (sweetened by grants), the US Department of Agriculture has preferred to use technical and financial aid to farmers on a voluntary basis as its method of addressing control on nonpoint sources of pollution.

Attention Turns to Nonpoint Pollution Control

Section 319, added in 1987, established the Nonpoint Source Management Program that gives grants for technical assistance, financial assistance, education, training, technology transfer, demonstration projects, and monitoring for specific nonpoint source implementation projects. The amount was $100 million dollars annually, which Congress doubled in Fiscal Year 1999. A highlight is the monitoring program, which has 20-30 demonstration sites of watershed restoration, under the rubric of Remedial Action Plan (RAP).

The Maumee River is the largest tributary flowing into any of the five Great Lakes. Its Remedial Action Plan address problems on this river, which is the single largest contributor of phosphorus and sediment to Lake Erie. It contributes 46 percent of the phosphorus and 37 percent of the sediment entering Lake Erie, while providing only 3 percent of the inflow. Cropland covers about 80 percent of basin and the clay soil that erodes into the river is particularly prone to carry the phosphorus. The Maumee River RAP identified conservation tillage and winter cover residue as the best ways to reduce sediment and phosphorus. Consequently, the implementation strategy emphasized "buying down" or lowering the cost a farmer pays for farm equipment that leaves more plant residue on the soil surface. In 1991 EPA awarded the RAP a grant of $641,000 under Section 319. The plan included targeting critical areas. Five hundred farmers from 15 counties voluntarily participated, committing an average of $10,000 each in pollution control equipment. Farmers received approximately $641,000 in equipment cost-share payments, which generated over $5 million of matching funds. While this was an excellent program for Ohio, it was a single demonstration and funding is not available to solve nonpoint problems everywhere.[3]

The disadvantage of demonstration programs is, of course, that they are few in number. Aside from demonstration projects, some of the best opportunities are found in the US Department of Agriculture. Most are in the Natural Resources Conservation Service (NRCS). NRCS administers the Buffer program and the Wetland Reserves program. Buffers are small areas or strips of land in permanent vegetation designed to intercept pollutants, such as along streams.

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[3] Ohio EPA Northwest Office, "Maumee River Remedial Action Plan."

Benefits to the environment are reduced runoff of sediment, nutrients, pesticides and herbicides, cooler stream temperatures, and increased wildlife. Benefits to farmers are fewer: cleaner streams, increased wildlife, and scenic landscapes. The chief argument to persuade farmers is that the amount of acreage switched to buffer strips is small and the land is hard to cultivate anyway. Under the buffer program, farmers have three options. First is a permanent easement, for which the USDA pays 100 percent, second is a 30 year easement, paid at 75 percent and third is ten year restoration agreement paid at 75 percent for the cost of restoration only.[4]

The program made the news this past summer when Governor Bob Taft called a press conference at a farm near Tiffin to plant a tree in a buffer strip. The governor declared that "By leaving a grass filter strip, windbreak, restored wetland or forested buffer along stream banks, farmers can provide a number of important environmental benefits."[5] Unfortunately it made the news again two days later when reporters discovered that the farmer had dug up the tree and replanted it near his house.

The Wetlands Reserve Program is another USDA program, which gives farmers the opportunity to protect, restore, and enhance wetlands on their property. The NRCS provides technical and financial support. The farmer retains ownership and responsibility for the land, including any property taxes based on its re-assessed value as non-agricultural land. The farmer controls access to the land and the right to hunt, and fish. He may sell or lease land and may request compatible uses such as haying, grazing or timbering.

In the Department of the Interior, the Fish and Wildlife Service provides grants for states to purchase wetlands for restoration. The Federal contribution is 50 or 75 percent; but the typical purchase in only 100-200 acres. The NRCS coordinates financial incentives to farmers under this as well as the Environmental Quality Incentives, Wildlife Habitat Incentives, Emergency Watershed Protection, and the Stewardship Incentives programs.

A small, but desirable, related program is the North American Waterfowl Management Plan. This combined effort of Canada, the United States and Mexico seeks to reverse the decline in the population of water birds. In the United States, the Fish and Wildlife Service of the Department of the Interior gives grants of up to $1 million for joint projects with public, private and nonprofit organizations under provisions of the North American Wetland Conservation Act of 1989. The goal of this Plan, however, is not to protect the environment, but to provide habitat for waterfowl; mitigation of nonpoint sources is only incidental.

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[4] US Department of Agriculture, Natural Resources Conservation Service, "Wetlands Reserve Program" www. wf. fb-net.org.

[5] Fritz Wenzel "Taft Plants Tree. . ." *Toledo Blade* 20 July 1999.

Although funds for direct projects are scarce, the Federal government does have funding available for research on using marshes to abate pollution. Under Section 319 of the Clean Water Act, US EPA awards funds to state agencies. The National Oceanic and Atmospheric Administration (NOAA) administers Section 6217 of the 1990 Coastal Zone Act Reauthorization Amendments, a program that deals with nonpoint source pollution affecting coastal waters, and Section 306 of the Coastal Zone Management Act that provides funds for water pollution control projects, including nonpoint source management activities.

Congress could deal with the problem, of course, by tightening the standards for agricultural runoff, but this seems unlikely given the privileged position farmers occupy. Indeed the 1996 Agricultural Improvement and Reform Act was supposed to end crops subsidies, but they have been continued under the guise of "emergencies." Last year the four main farm aid packages cost $12 billion. A typical farmer in northwest Ohio with 1000 acres of soybeans, corn or wheat received $51,000. The buffer program, the smallest of the four, might have paid him a few thousand dollars.[6]

Agricultural economists have investigated the extent to which crop insurance may increase the amount of chemicals farmers use as fertilizer, pesticides and herbicides. Horowitz and Lichtenberg studied midwestern corn farmers who purchased crop insurance, finding that they spent 19 percent more on fertilizer and 21 percent more on pesticides.[7] Jun Jie Wu studied farmers in central Nebraska, finding that crop insurance was an incentive to plant corn rather than leave land for hay and pasture, and that corn requires more chemicals. He also found that farmers with higher erosion rates are more likely to purchase insurance. Wu concluded that the insurance may increase nonpoint pollution.[8] On the other hand, Smith and Goodwin found that insured wheat farms used fewer chemicals than uninsured farms[9]

Mitigation banking offers a new avenue to protect wetlands. The concept is that building roads, houses, and factories may destroy wetlands that are expensive or

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[6] Jane Schmucker, "Farm Subsidies" *The Toledo Blade* 29 Nov. 1998

[7] J. K. Horowitz and E. Lichtenberg, "Insurance, Moral Hazard and Chemical Use in Agriculture" *American Journal of Agricultural Economics* 75 (Nov. 1993): 926-935.

[8] Jun Jie Wu, "Crop Insurance, Acreage Decisions and Nonpoint Source Pollution" *American Journal of Agricultural Economics,* 81 (1999): 305-320.

[9] Vincent Smith, and Barry Goodwin, "Crop Insurance, Moral Hazard, and Agricultural Chemical Use" *American Journal of Agricultural Economics,* 78 (1996): 428-438.

difficult to replace at the original site and that a solution is to create new wetlands at a remote location, preferably in the same watershed. In 1995 the Corps, EPA, NRCS and the Fish and Wildlife Service issued regulations outlining how a business or nonprofit organization can establish a bank, under provisions of Section 404 of the Clean Water Act. The program is also applicable to the swamp buster provisions of the 1996 Farm Act. Advantages are that (1) the process is faster and more convenient, (2) larger sites are better for the environment than small, isolated, on-site projects and (3) professional management is better.

A number for profit companies have sprung up around the country such as the Mile High Wetland Bank near Denver, and the Katy-Cypress Mitigation Bank in Texas. In Utah the Kennecott Utah Copper Corporation runs a subsidiary called the Sea Shorebird Reserve Bank. US Wetlands Services, Critical Habitats, Inc. and Wetland Environmental Technologies seek to be nationwide in scope. The Ohio Wetlands Foundation, a non-profit organization, was formed in 1992 by the Ohio Home Builders Association. Its five sites are north of Fremont, in Lorain County, west of Marion, near Hebron, and near Columbus. The Finley Hancock Community Development Foundation has proposed establishing a bank so that when a new industry builds in the area, the company can solve any mitigation problems simply by writing a check.[10] A wetland mitigation bank first buys or gets control of a former wetland or property adjoining a wetland, and proceeds to flood it. Next it seeks clients such as builders. The builders pay the bank for the acreage they need. When the rights to all the acreage are used up, the bank continues to maintain the wetland, and seeks new acreage and new clients.

The Winous Point Shooting Club

This Club, located near Sandusky Bay of Lake Erie between Cleveland and Toledo, is a unique example of an environmental good citizenship. On the basis of scientific research showing how draining agricultural runoff through its marshes abates pollution, the duck hunting club has decided to breech its dikes to increase the amount of runoff that it abates. Runoff that used to flow around the marsh, now flows through it. The Club itself receives no benefit. Unfortunately, the public spirit of the Shooting Club may not be possible to transfer to other situations. Nevertheless, it offers lessons for protecting the environment. The situation has allowed a long-term scientific study, serves as an example for other hunting clubs, and benefits the water in Sandusky Bay. Under the sponsorship of the Ohio Lake Erie Protection fund, Johan Gottgens, Alison Spongberg and Barry Muller of the University of Toledo have measured more accurately than ever before the long-term effects. Prior research has been limited to only a few years. Taking sediment cores from the bottom of the marshes allows an evaluation for time periods up to a century. The natural archives of the sediments shows the long-term effects of the farm runoff. This

[10] Jennifer Feehan, "'Bank' Could Help Restore Wetlands" *The Toledo Blade* 1999

can be [augmented] by the Club's records of marsh management for the past century.

The Club dates to the period of pioneer settlement, having been founded in 1856 by Cleveland merchants to hunt ducks and geese. The marshes on the south shore of Lake Erie are rich in waterfowl and wildlife. In the Club's earliest years, only a few settlers farmed the adjoining land, and today the immediate region remains agricultural. During the nineteenth century other hunting clubs organized and purchased land along the entire Lake Erie shoreline, reaching a peak in the early twentieth century. At present, many clubs continue to exist, but none so old or large as Winous Point. The club takes pride in having restored and maintained more coastal wetland than any other private organization in the state. For the past 50 years, it has supported a full time biologist on site and sponsored research in cooperation with universities.

The drainage area has rich topsoil, devoted chiefly to soybeans. Other crops are corn, wheat and barley. The land is very low, some even below the level of Lake Erie, so farmers must dike their fields and drain excess water. Over the years, farmers have fertilized extensively, adding nitrogen and phosphorus. Much of this drains off, polluting the runoff. They also use herbicides extensively, especially with low tillage techniques. In the mid-nineteenth century farmers had built dikes around their fields to protect them from seasonal flooding from Sandusky Bay, and by the 1920s the Shooting Club had built lakeward dikes to protect their marshes from erosion. This created two large enclosed marshes of about 600 acres each that received runoff from nearby farms. In order to optimize plant growth to attract migrating ducks and geese, the Club controlled the water level in the marshes by pumping and backflow.

To improve hunting and prevent erosion, the Club in 1978 closed off the West Marsh from agricultural runoff, thus creating a natural laboratory with one marsh receiving farm runoff, and the other not receiving any. For the past three years Johan Gottgens and Barry Muller have been measuring the difference in how much carbon, nitrogen and phosphorus the two marshes have assimilated in their sediments, finding that the North Marsh has abated phosphorus runoff successfully and has done so for a long time. In a parallel fashion, Prof. Spongberg has been measuring DDT, which she has found to persist much longer. The marsh does trap the pesticide, and eventually degrades it, but it may take a long as ten years to reach the marsh from the farm.[11] The scientific conclusion appears clear that marshes can act as natural purifying places for agricultural runoff, but its practical application is much less clear. The Shooting Club receives no benefit from this diversion of runoff other than the satisfaction of helping the environment. The farmers receive no benefit because they are

[11] Alison Spongberg. 1999. University of Toledo, Department of Geology. Personal communication.

already complying with the weak environmental standards, and it makes no difference to them whether their runoff is abated or drains directly into Lake Erie.

The rapid decline of the water level of Lake Erie and the other Great Lakes in the past year has further complicated wetland management. The lake is now at its lowest level in 34 years and will go lower over the winter. This leaves many wetlands literally high and dry. For example, Metzger Marsh near Toledo had been touted as a great success for restoration, but with lower water levels, it is drying out. In fact, the water levels are not at the low range, but close to the historic average for the past 150 years. Shipping companies find that the channels are too shallow, and recreational boaters find their marinas are now mud flats. On the other hand, beaches have built up and new marshes are forming. These new wetlands are likely to enhance pollution abatement with new plant growth along the lake fringes.

With only a partial exception, none of the government programs appear directly applicable to Winous Point. For the NRCS buffer program, the land must be owned by the farmer, not by a third party. For the Fish and Wildlife Service program, the Shooting Club would have to sells its property to the State of Ohio or to Ottawa County, which would mean terminating the Club. Existing federal programs, unfortunately, are directed toward reclaiming wetlands that have been destroyed by farming, not those like the Club's marshes that have been maintained in their original position in the landscape. A program to sell development rights for $1,000 an acre is a pittance when waterfront lots sell for $50,000 to $100,000 per acre.

The partial exception is wetland banking. While this does not apply to the two marshes, totaling about 1200 acres, where the Club is diverting farm runoff, it is currently reclaiming a portion that has been inundated by Muddy Creek Bay for the past 60 years. Originally this area of 250 acres, where Muddy Creek flows into Sandusky Bay, was a low lying area known as the Horseshoe Island marsh. The first protective measures are evident on an 1894 map, where rock revetments were placed by hand at the most erodible points. In 1937 the Club built dikes, but the dike was eroded and permanently breached by increased Lake Erie water levels in 1957. As the water level continued to increase, the once lush wetland was relegated to near sterile open lake conditions. The fertile organic soils were scoured away, leaving bare clay and silt on the bottom.

In 1997 the Club began to reclaim the Horseshoe Island Marsh. This required permission of the Corps of Engineers, which could only grant it on the condition that in past years the Club had maintained this marsh with a dike. Once this was proven with historical records, the Club began to dredge and build a dike around the area at a cost of $450,000. It received partial funding under the North American Waterfowl Management Plan, administered by the US Fish and Wildlife Service. Two years later, the work was complete and the water pumped out. Native plants are now recolonizing the area. The wealth of the Shooting Club made possible this costly recreating of an historic wetland. Very few other property owners could afford such a project. Because this is restoration, it may qualify for banking under the federal government program.

New technology may help by reducing the amount of fertilizer spread on fields. At present farmers tend to buy and use too much because it is easier than measuring and calculating amounts scientifically. Now mechanized testing kits can evaluate the fertility of the soil in various parts of a field and synchronous global positioning satellites can automatically distribute the optimal amount in each place. Fertilizer, after all, is expensive, and using less will improve profits. On the other hand, encouraging farmers to use low till cultivation methods instead of plowing up the entire field reduces erosion, a major source of water pollution, but at the same time requires more herbicides to compensate for the lack of plowing.

Planning for land management may be an alternative. The Gottgens, Spongberg and Muller studies, along with others, clearly point to the benefits of wetlands for abating pollution. This would suggest encouraging hunting clubs by zoning and reduced property taxes. Flood control is an additional benefit for society. While the national and state governments may not be willing to spend money up front on purchasing wetlands, they may be willing to zone coastal areas and to reduce taxes. A related method is to require real estate developers to maintain or even restore wetlands as a condition of receiving permission to build resorts and condominiums along the Great Lakes and oceans.

5. Summary

- Soils in the watersheds had low to very low permeabilities and were dominated by the very poorly-drained Toledo Silty Clay. Land-use practices in the watersheds of either marsh changed little since 1950; however, both watersheds were marked by decrease area dedicated to orchards and a concurrent increase in residential and road area. Comparing land-use between the two watersheds showed that a higher percentage of the West Marsh was used for row crops and that the North Marsh contained substantial forested marsh and old-field areas that may have functioned as a filter for farm runoff.

- We generated eight reliable core chronologies (four from each marsh) using ^{210}Pb, ^{137}Cs analyses. The use of *Ambrosia* pollen as an ancillary age-marker provided only slight support for separating pre-European agricultural deposits from more recent sediments. This was likely due to abundant *Ambrosia* in this wet-prairie region even before European agricultural development .

- TP and BAP accumulation during the last 10 years in the North Marsh more than tripled compared with the accumulation rates during 1920-1977 interval. These increases were less in the West Marsh. Only the increase in TP accumulation in the North Marsh was statistically significant. Additionally, the North Marsh ratios of TP to TC and TP to TN accumulation were higher since 1988, whereas these ratios remained fairly constant in West Marsh sediments since 1920. However, overall accumulation rates for sediment, TC, TN, TP and OM were higher in the West Marsh relative to North Marsh since 1920.

- The ratio of TC to TN accumulation rates remained fairly constant in both marshes since 1920. The correlations between the accumulation rates of these two elements were highly significant for both marshes over all time periods. The absence of a sedimentary signal of increased trapping of these elements in the North Marsh may be because both elements had a significant atmospheric sink in addition to sediment storage.

- North Marsh sediments accumulated TP at a greater rate than Al, Fe, and Mn since 1988. This trend was not evident in the West Marsh. Therefore, it appeared that the increased retention of TP in the North Marsh since 1988 was not caused by increased Al, Fe, or Mn. This implied that the increased retention of TP accumulation was not limited by the availability of these metals.

- North Marsh sediments were composed of approximately 80% silt and clay until the mid-1960s when a dramatic increase in sand-sized proportion began. This increase may be associated with a period of high water in Lake Erie since the early 1970s. Conversely, low proportions of sand-sized clasts coincided with periods of low water levels. West Marsh sediments were composed of approximately 60% clay and silt since 1920. Contrary to expectations, core sections with the highest TP accumulation rates also had the lowest percent clay.

- The pesticide data from Winous Point showed variations of aldrin, endrin, HCHs, and DDT with depth that can be attributed to agricultural use. High concentrations of HCHs and endrin in West Marsh sediments since mid-1960's point to a possible airborne source. The ratio of metabolite to parent molecule did not appear to change with sediment age. Also, there appeared to be a delay between pesticide application and deposition in the marshes.

- Several national government programs can be tapped to support nonpoint source pollution mitigation by means of wetlands. These programs include grants under Section 319 of the Clean Water Act, various U.S Department of Agriculture programs (such as the wetland reserve and buffer strip initiatives), Department of Interior grants to states to purchase wetlands for restoration, and others.

6. Recommendations

- In the absence of decades of data, sedimentary records can be used to evaluate long-term biological and chemical dynamics in wetlands. These records integrate short-term variations and provide information on historic deposition rates and recent trends. Our study is the first of its kind for Lake Erie marshes since no long-term record (i.e., decades) of the capacity of these marshes to accumulate nutrients, pesticides, and suspended matter exists. We recommend that additional studies of this nature be undertaken in conjunction with real-time studies, to determine the long-term utility of these marshes to reduce nonpoint-source pollution.

- The use of the *Ambrosia* horizon as an independent age marker in sediment cores from the coastal areas of northwestern Ohio is of limited value because this region lacked contiguous forest even prior to the period of agricultural development.

- The continued ability of the North Marsh to sequester TP and BAP from nonpoint-source agricultural runoff suggests that these marshes can play an important role in removing excess P over the long term. These marshes may also remove C and N from runoff. TC and TN, however, did not appear to have been sequestered in the sediments but may have been lost to the atmosphere via biological and chemical pathways. Our results suggest that, over the long term, southwestern Lake Erie wetlands may play an important role in mitigating the effects of nonpoint-source agricultural runoff on downstream systems. In the case of Winous Point, the use of these marshes to trap P from runoff, does not seem to impact the use of these marshes by waterfowl and wildlife.

- The use of a relational database for this project enhanced our ability to manage the data and allowed us to track progress and maintain a verifiable and unique data set. The database and programs developed for this project should form the basis for all data collected at this site.

- Our research focused on quantifying net accumulation in the sediment and did not address comprehensive nutrient budgets. Long-term, real-time research on nutrient and contaminant budgets in Laurentian marshes, linking sedimentary signals to a record of concentrations of target analytes in inflows and outflows, is needed.

- Linking our database to a GIS would allow analysis of the spatial distribution of target analyte accumulation in the sediments. Such a system should include variables that impact this accumulation, such as distance to inflow and outflow, water depth, sediment composition, as well as type and quantity of aquatic macrophytes. This information would optimize the management of marshes for use as filtering systems.

- At the present time pesticides that have been banned appear to still be entering the marsh. Therefore, continued monitoring for these compounds is recommended.

- A number of national government programs can be utilized to promote the reduction of nonpoint source pollution using wetlands. The total amount of available funds, however, is not large relative to the extent of the problem. Linking nonpoint-source pollution control to agricultural programs, waterfowl management, and wetland banking may increase the opportunities.

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8. Appendices

8.1. Lake Erie Environmental Database (LEED)

BORINGS

Table BORINGS contains field data for sampling locations. Total records for this project: 20

NAME	NULL?	TYPE
PROJECT_NAME		VARCHAR2(30)
CORE_ID		VARCHAR2(30)
LATITUDE		VARCHAR2(20)
LONGITUDE		VARCHAR2(20)
EASTING		VARCHAR2(20)
NORTHING		VARCHAR2(20)
TOTAL_DEPTH		NUMBER
TD_UNITS		VARCHAR2(20)
SAMPLERS		VARCHAR2(30)
BORING_DATE		DATE
TIME		VARCHAR2(20)
COMMENTS		VARCHAR2(100)
FLAG		VARCHAR2(30)
CHRON_STATUS		VARCHAR2(3)

LAB_SAMPLES

Table LAB_SAMPLES contains data on subsamples taken from cores or other field samples. Total records for this project: 577.

NAME	NULL?	TYPE
CORE_ID		VARCHAR2(30)
PROJECT_ID		VARCHAR2(30)
SAMPLE_ID		VARCHAR2(30)
SAMPLE_DATE		DATE
M_COLOR		VARCHAR2(30)
TOP_DEPTH		NUMBER
BOTTOM_DEPTH		NUMBER
DEPTH_UNITS		VARCHAR2(30)
DESCRIPTION		VARCHAR2(100)
COMMENTS		VARCHAR2(255)
TYPE		VARCHAR2(15)

LAB_RESULTS

Table LAB_RESULTS contains data on analyses performed on subsamples taken from cores or other field samples. Total records for this project: 19,668.

NAME	NULL?	TYPE
PROJECT_NAME		VARCHAR2(30)
CORE_ID		VARCHAR2(30)
LATITUDE		VARCHAR2(20)
LONGITUDE		VARCHAR2(20)
EASTING		VARCHAR2(20)
NORTHING		VARCHAR2(20)
TOTAL_DEPTH		NUMBER
TD_UNITS		VARCHAR2(20)
SAMPLERS		VARCHAR2(30)
BORING_DATE		DATE
TIME		VARCHAR2(20)
COMMENTS		VARCHAR2(100)
FLAG		VARCHAR2(30)
CHRON_STATUS		VARCHAR2(3)

8.2. Publications and Presentations Resulting from this Work

Davis, D.H., 1999, "The frustrations of an environmental good citizen", PA Times 22:10:3-5.

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Gottgens, J.F., B.E. Muller, and A.L. Spongberg, 1999, "Longterm nonpoint pollution abatement by a Lake Erie marsh and its implication for wetland restoration policies", Annual Ohio Lake Erie Conference, Huron, Ohio.(invited).

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