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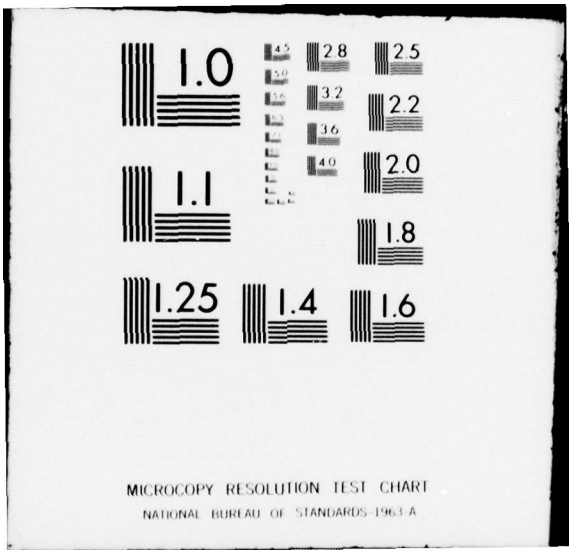
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HABITAT DEVELOPMENT FIELD INVESTIGATIONS WINDMILL POINT MARSH DEVELOPMENT SITE JAMES RIVER, VIRGINIA.

APPENDIX E: ENVIRONMENTAL IMPACTS OF MARSH DEVELOPMENT WITH DREDGED MATERIAL: METALS AND CHLORINATED HYDROCARBON COMPOUNDS IN MARSH SOILS AND VASCULAR PLANT TISSUES.

by

(10) John D. Lunz

Environmental Laboratory

U. S. Army Engineer Waterways Experiment Station

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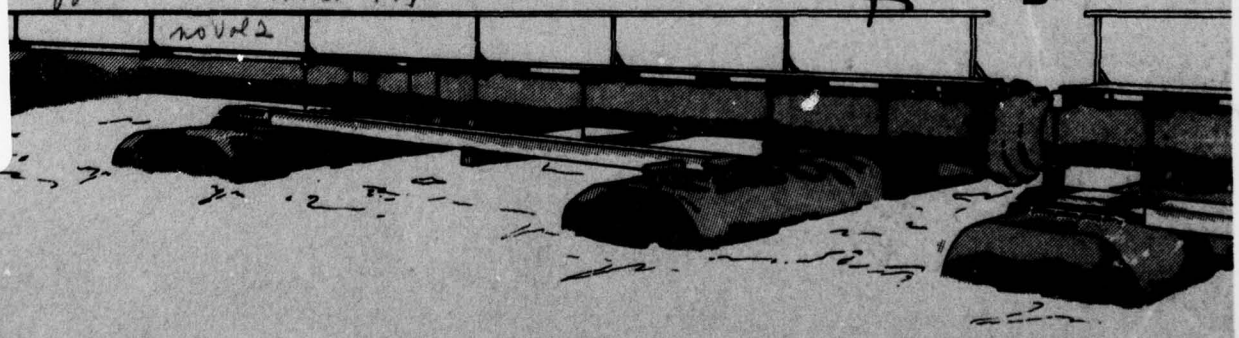

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HABITAT DEVELOPMENT FIELD INVESTIGATIONS, WINDMILL POINT MARSH DEVELOPMENT SITE, JAMES RIVER, VIRGINIA

Appendix A: Assessment of Vegetation on Existing Dredged Material Island

Appendix B: *Propagation of Vascular Plants*

Appendix C: Environmental Impacts of Marsh Development with Dredged Material: Acute Impacts on the Macrobenthic Community

Appendix D: Environmental Impacts of Marsh Development with Dredged Material: Botany, Soils, Aquatic Biology, and Wildlife

Appendix E: Environmental Impacts of Marsh Development with Dredged Material: Metals and *Chlorinated Hydrocarbon Compounds in Marsh Soils and Vascular Plant Tissues*

Appendix F: Environmental Impacts of Marsh Development with Dredged Material: Sediment and Water Quality

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SUBJECT: Transmittal of Technical Report D-77-23, Appendix E

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1. The technical report transmitted herewith represents the results of one of a series of research efforts (work units) undertaken as part of Task 4A (Marsh Development) of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 4A was part of the Habitat Development Project (HDP) and had as its objective the development and testing of the environmental, economic, and engineering feasibility of using dredged material as a substrate for marsh development.

2. Marsh development using dredged material was investigated by the HDP under both laboratory and field conditions. The study reported herein (Work Unit 4A11L) was an integral part of a series of research efforts jointly developed to achieve Task 4A objectives at the Windmill Point Marsh Development Site, James River, Virginia, one of six marsh establishment sites located in several geographic regions of the United States. Interpretation of this report's findings and recommendations is best made in context with the other reports in the Windmill Point site series (4A11A-M).

3. This report, "Appendix E: Environmental Impacts of Marsh Development with Dredged Material: Metals and Chlorinated Hydrocarbon Compounds in Marsh Soils and Vascular Plant Tissues," is one of six appendices relative to the Waterways Experiment Station's Technical Report D-77-23, entitled "Habitat Development Field Investigations, Windmill Point Marsh Development Site, James River, Virginia; Summary Report" (4A11M). The appendices to the Summary Report are studies that provide technical background and supporting data and may or may not represent discrete research products. Appendices that are largely data tabulations or that clearly have only site-specific relevance were published as microfiche; those with more general application were published as printed reports.

4. Research described in this document deals with the comparison of heavy metals and chlorinated hydrocarbons in marsh soils and marsh plant tissues in three freshwater marshes in the James River, Virginia. Two of these marshes were natural; the third was developed on dredged material. Evaluations of chemical transfer routes and comparisons between sites are presented and discussed.

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5. Data from this report are included in the Windmill Point Summary Report (4A11M) and synthesized in the Technical Reports entitled "Upland and Wetland Habitat Development with Dredged Material: Ecological Considerations" (2A08), and "Wetland Habitat Development with Dredged Material: Engineering and Plant Propagation" (4A22).

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Soil and vascular plant tissue samples were collected in October 1976 from three freshwater marshes located on the James River in Virginia. One marsh known as the Windmill Point marsh development site had been constructed using dredged material during the 1974-75 maintenance dredging of the James River navigation channel. The two other marshes were natural marshes. The marshes studied were similar in their substrate characteristics. All were fine-textured silt and clay with volatile solids values between 10 and 20 percent, and

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contained about 50 percent water. Elevation and plant community characteristics were similar. Soil samples were collected from the same three elevation zones in each marsh. Arrow arum (*Peltandra virginica*) seeds, barnyard grass (*Echinochloa sp.*) seeds, stems and leaves, and roots, and cattail (*Typha sp.*) stems and leaves and tubers were also collected from each marsh. Soil and plant tissue samples were analyzed for the metals nickel, zinc, chromium, lead, and cadmium and the chlorinated hydrocarbon compounds DDT, DDD, DDE, lindane, heptachlor, heptachlor epoxide, chlordane, endrine, dieldrin, Kelthane, Kepone, PCBs, and toxaphene. Plant stem and leaf tissue samples were treated before analysis to remove sorbed metal and chlorinated hydrocarbon materials. Marsh soil concentrations of chromium, cadmium, and lead were higher in the dredged material marsh; nickel and zinc concentrations were higher in the natural marsh. Low detectable levels of DDD, chlordane isomers, and Arochlor 1260 (PCB) occurred most frequently in dredged material marsh soils. Nickel was the only metal studied which could be identified in an experimental marsh plant tissue at higher levels than existed in a similar plant tissue from a natural marsh. DDE and Kelthane were detected most frequently in plant samples collected from the experimental marsh. Kepone was detected in all marsh soils studied. Concentrations were highest (about 500 ppb, dry weight) at the experimental marsh. However, there were no differences in plant tissue Kepone concentrations between the experimental and natural marshes. There was no apparent relationship between total sediment chemical composition and plant available metal and chlorinated hydrocarbon compounds. Soil characteristics occurrent in marshes, including near neutral pH, high organic content, and reduced oxidation reduction conditions, appeared to restrict chemical mobility and bioavailability and favored chlorinated hydrocarbon degradation. Potential soil chemical to plant transfer routes including surface sorption and adsorption and translocation were evidenced and discussed.

PREFACE

This report presents the results of an investigation of metals and chlorinated hydrocarbon compounds in soils and vascular plant tissues collected from a dredged material marsh and natural marshes. The study was one of several conducted at the Windmill Point marsh development site, James River, Va. The research was sponsored by the Office, Chief of Engineers (DAEN-CWO-M), under the Civil Works Dredged Material Research Program (DMRP), which was planned and implemented by the Environmental Laboratory (EL), U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The study was undertaken as part of Task 4A, Marsh Development, of the DMRP Habitat Development Project (HDP).

The report was written by John D. Lunz, Natural Resources Development Branch, EL, under the supervision of Dr. Hanley K. Smith, Manager, HDP, Dr. C. J. Kirby, Chief, Environmental Resources Division, EL, and Dr. John Harrison, Chief, EL.

The following persons are acknowledged for their cooperation during the study: Mr. David Harrison, owner of the Windmill Point experimental marsh; Ms. Bruce Crane Fischer, owner of the Ducking Stool Point natural marsh; the U. S. Fish and Wildlife Service; and Mr. Harold Olson, Refuge Manager of the Presquile National Wildlife Refuge in which the Turkey Island natural marsh was located.

The U. S. Army Engineer District, Norfolk, provided contracting support for metals analysis by the Virginia Institute of Marine Science (VIMS), Gloucester Point, Va. (Contract No. DACW 39-76-C-0040), and for chlorinated hydrocarbon analysis by Analytical Biochemistry Laboratories, Inc., Columbia, Mo. (Contract No. DACW 65-77-C-0052).

VIMS provided field logistical support during sample collection. The assistance of Mr. Damon Doumlele and Mr. Arthur Harris in collecting plant tissues and of Dr. Richard Wetzel, who directed collecting of soil samples, is particularly acknowledged.

EL personnel also benefitted the study. Dr. Robert Terry Huffman and Ms. L. Jean Hunt participated in collecting plant tissues,

Dr. Robert J. Diaz assisted in statistical analysis and data presentation, and Ms. Mary K. Vincent provided editorial review and technical writing support.

The Director of WES during the study was COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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HABITAT DEVELOPMENT FIELD INVESTIGATIONS, WINDMILL POINT MARSH DEVELOPMENT SITE, JAMES RIVER, VIRGINIA

APPENDIX E: ENVIRONMENTAL IMPACTS OF MARSH DEVELOPMENT WITH DREDGED MATERIAL: METALS AND CHLORINATED HYDROCARBON COMPOUNDS IN MARSH SOILS AND VASCULAR PLANT TISSUES

PART I: INTRODUCTION

1. In 1973, the Dredged Material Research Program (DMRP) was undertaken by the U. S. Army Engineer Waterways Experiment Station (WES) to investigate a wide variety of problems concerning environmental aspects of dredged material disposal operations. The Habitat Development Project (HDP) of the DMRP had, as one of its tasks, to evaluate, as an alternative to disposal, the possibility of developing marsh habitat on dredged material substrate. A major part of the research involved a field program with study sites located in a variety of coastal environments. One of the sites was located near Windmill Point on the James River, Va. (Figure 1).

Setting

2. The Windmill Point marsh development site is a 9.3-ha dredged material island in the James River, 0.4 km west of Windmill Point, Prince George County, Va. The site was constructed during the 1974 to 1975 maintenance dredging of the Windmill Point and Jordan Point navigation channels. Approximately 61,000 m^3 of sand were used for dike construction and about 167,000 m^3 of fine-textured channel sediments were disposed within the 152- by 396-m confinement. For more detailed site description and site construction information the reader is referred to the main text of the summary report on the site (Lunz et al. 1978).

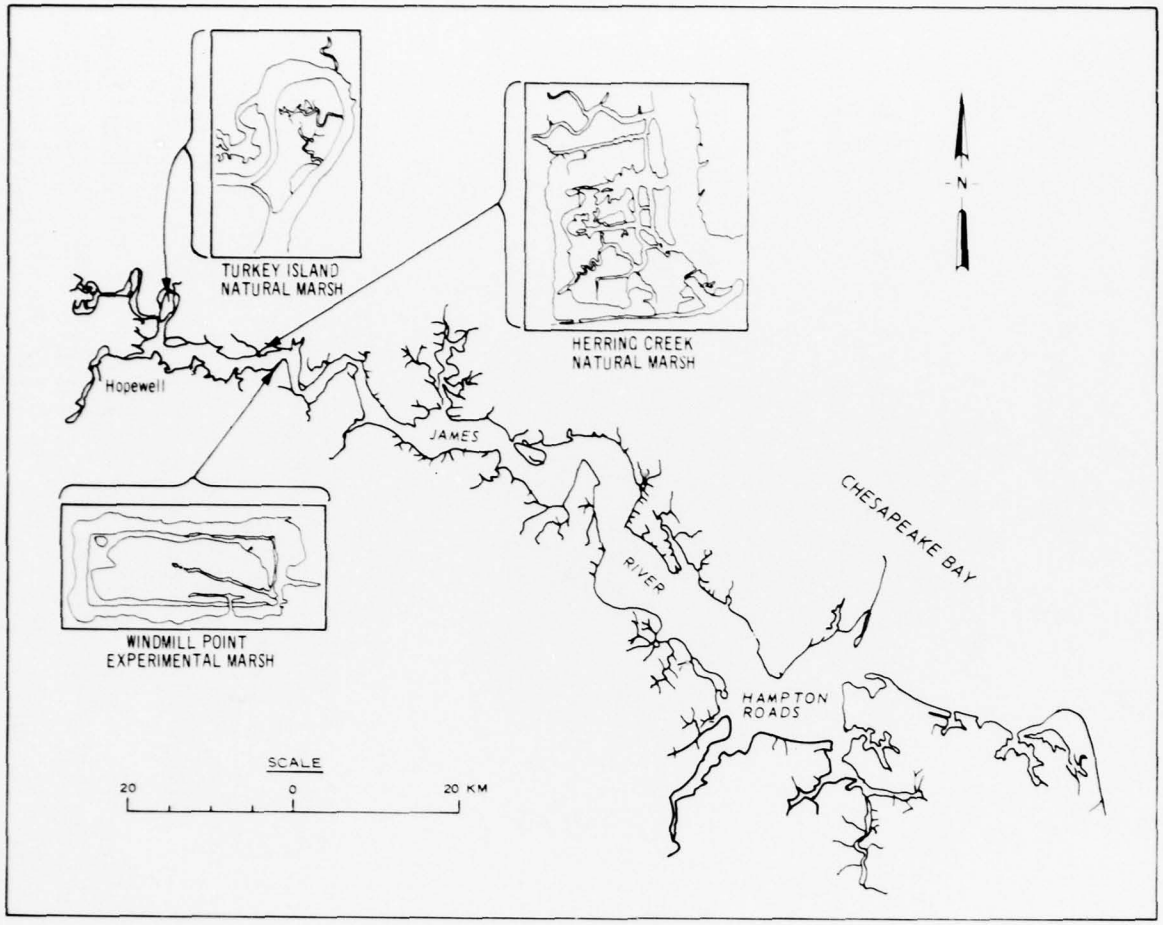

Figure 1. Location of the Windmill Point experimental march (dredged material island) and the natural marshes at Ducking Steel Point and Turkey Island

Background to Problem

3. Freshwater marsh vascular plants are important primary producers of organic material that provide nutrition directly to grazing plant eating animals (herbivores) including various ducks and geese and mammals that inhabit marsh areas. Additionally, these plants provide an indirect source of nutrition to a diversity of smaller aquatic animals including worms, insects, and shellfish that live on top of or in the marsh, river, or lake sediments and that feed on decomposing plant fragments (detritus) or the abundant microscopic life (bacteria, fungi, diatoms etc.) associated with detrital particles.

4. The HDP was concerned with the potential transfer of metals and chlorinated hydrocarbon compounds from a dredged material substrate to the freshwater vascular plants growing on that substrate as a consequence of marsh development.

5. Plant uptake of soil applied metals and chlorinated hydrocarbons are well documented in the scientific literature. The majority of these studies deal with the uptake of sewage sludge incorporated metals or metallic radionuclides or common pesticidal and herbicidal compounds by important agricultural crops such as corn, soybeans, cotton, alfalfa, etc. Where appropriate these studies have been cited in the results and discussion portions of this report.

6. In contrast to studies of crop plants, prior to the DMRP, very little information existed that might be applied to assessing the potential for either metals or chlorinated hydrocarbon uptake by marsh vegetation. Gambrell et al. (1977) reviewed information relevant to metals in marsh vascular plants and presented the results of laboratory studies examining the influence of salinity, pH, and oxidation-reduction potential on metals transfer to marsh plant tissues. Lee et al. (1978) examined a variety of both freshwater and saltwater marsh plant species in a laboratory hydroponic study and demonstrated the potential for metals transfer to some of these tissues. Walsh

and Hollister* studied the uptake of Tordon 101 (an organic compound composed of the herbicide 2,4-D mixed with Picolinic acid), the polychlorinated biphenyl (PCB) Arochlor 1254 and Mirex by turtle grass (*Thallassia testudinum*). The 2,4-D component of Tordon 101 was concentrated by the chromes of turtle grass by a factor of 0.05 to 0.12 after 10-days exposure to 1 and 5 ppm, respectively. Arochlor 1254 was not concentrated by turtle grass even after exposure for 10 days to concentrations as high as 5.8 ppm. Mirex was concentrated by a factor of 0.36 after a 10-day exposure to only 0.1 ppb. A study by Walsh et al.** of red mangrove's (*Rhizophora mangle*) ability to concentrate Tordon 101 documented concentration factors from 0.064 to 9.0 in all the plant's tissued after 20-days exposure to 14.4 ppb.

7. In 1974, before the commencement of channel dredging and dredged material disposal and construction of the marsh Windmill Point development site, the fine-textured sediments of the Jordan Point navigation channel were collected and analyzed to describe their metals composition (Lunz et al. 1978). Table 1 summarizes the results of these analyses. Channel sediments collected before dredging were further screened for organic contaminants that would be associated with the proposed marsh substrate.*** The organic characterization suggested the possible presence of the following compounds: aldrin, dieldrin, endrin, chlordane, heptachlor, heptachlor epoxide, p,p' DDT, p,p' DDD,

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* Unpublished data. Prepared by G. E. Walsh and T. A. Hollister, 1971. Environmental Protection Agency, Gulf Breeze Research Laboratory, Gulf Breeze, Fla.

** Unpublished data. Prepared by G. E. Walsh, R. Barrett, and G. H. Cook, 1972. Environmental Protection Agency, Gulf Breeze Research Laboratory, Gulf Breeze, Fla.

*** "The alteration of fine-grained channel sediments and interstitial water during and after pipeline dredging and deposition within a sand-diked island near Windmill Point, James River, Virginia," by D. O. Adams, D. A. Darby, and A. J. Diefenderfer (unpublished). Prepared in 1976 under contract to the U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

Table 1

Interstitial Water and Total Sediment Concentrations of Nickel, Zinc, Cadmium and Lead in Samples Collected from the James River Navigation Channel near Windmill Point*

(Concentrations are in parts per million; sediment concentrations are based on dry weight)

Metal	Sample Type	Mean	Standard Deviation	No. of Samples
Nickel	Total sediment	31.6	7.1	15
	Interstitial water	0.051	0.019	21
Zinc	Total sediment	230.0	51.9	15
	Interstitial water	0.183	0.304	17
Cadmium	Total sediment	1.26	0.55	15
	Interstitial water	0.009	0.004	23
Lead	Total sediment	60.9	11.38	15
	Interstitial water	0.078	0.021	21

* Adapted from Adams et al. (1978) from concentrations in the upper (0 to 43 cm) core sections collected from the James River Navigation Channel near Windmill Point.

p,p' DDE, Kelthane, lindane, methoxychlor, Kepone, polychlorinated biphenyls (PCBs) and tetrachlorethylene (doubtful).

Approach and Objective

8. The approach to the investigation was based on the following tenents:

a. The known occurrence of metal contaminated sediments in the navigation channel to be dredged for habitat development and the probable occurrence of a variety of chlorinated hydrocarbon compounds in these sediments;

b. The release of Kepone into the James River during the period preceeding marsh site construction (unknown at the time of habitat development site planning and construction) and the potential bioaccumulative and toxic nature of the coumpound (U. S. Army Engineer District, Norfolk 1976, Hansen et al. 1976); and

c. The well-documented transfer of metals and chlorinated hydrocarbons from soils to upland plants and the limited evidence of these chemical transfers through marsh and aquatic vegetation systems.

9. The objective of this study was to collect and analyze soils and plant tissues in order to document the concentration of various metals and chlorinated hydrocarbon compounds in tissues of selected freshwater vascular plants collected from a dredged material marsh and natural reference marshes.

PART II: METHODS AND MATERIALS

Experimental Design

10. Vascular plant and soil/sediment samples were collected from three marshes. Three zones or strata were sampled in each marsh and samples were collected from each zone according to a stratified random sampling design. The stratified random sampling scheme was selected to reduce some of the chemical variability expected as a function of elevation and based on the relationship between elevation, vegetation zonation, tidal inundation, and sedimentation. Random sampling within each strata was selected in preference to systematic sampling so that information resulting from the analysis of collected samples could be used to describe each zone as a collective unit.

Marsh sites

11. The locations of the three marshes are identified in Figure 1. They are:

a. The experimental marsh development site at Windmill Point, which served as the dredged material treatment;

b. A natural reference marsh at Ducking Stool Point, near Herring Creek, approximately 3.2 km upriver from Windmill Point; and

c. A natural reference marsh located on Turkey Island, Presquile National Wildlife Refuge, approximately 22.5-km upriver from Windmill Point and approximately 8-km upriver from Hopewell, Va., the source of Kepone input to the James River.

Sampling strata

12. Soils and/or plant samples were collected from three intertidal strata. There were:

a. The mud flat zone, the lowest of the three zones sampled, and characterized by having no vegetation;

b. The pickerel weed - arrow arum zone, defining the lowest vegetated zone of the marshes and consisting of pickerel weed (*Pontederia cordata*) and/or arrow arum (*Peltandra virginica*) and/or arrowhead (*Sagittaria latifolia*);

c. The cattail - beggar tick zone, the middle and upper marsh zones inundated less frequently than either the mudflat or pickerel weed - arrow arum zones and comprised

of plant species including cattails (*Typha spp.*), beggar ticks (*Bidens spp.*) and barnyard grass (*Echinochloa spp.*).

Sampling locations

13. Five sampling locations in each strata were chosen based on the random occurrence of selected plant species identified below. One sample was defined as the amount of a specific tissue type estimated as necessary for chemical analysis. Thus each of the five replicate samples per strata were pooled samples.

Plant Species

14. Plant species were chosen considering their direct value as food items for local wildlife species. Additionally, only portions (tissues) of the plant actually eaten or preferred by wildlife were collected. Collections consisted of arrow arum seeds, cattail stems and leaves, cattail tubers, barnyard grass seeds, barnyard grass stems and leaves, and barnyard grass roots.

Tissue Treatments

15. The collected stems and leaves of both cattail and barnyard grass from each location were divided into two portions. One portion was treated by wiping with methyl alcohol, dilute hydrochloric acid and distilled water to remove most of the chemical contaminants on the surface of these materials (Elias and Patterson 1975, Lee et al. 1978); the other portion was left untreated.

Collection Methodology

16. Plant and soils samples were collected from all sites during October 1976. Plant tissues were collected by hand, separated into tissue components in the field, and placed into precleaned (dilute hydrochloric acid, distilled water, and acetone) 1-litre glass jars. Soil samples were collected by hand push coring using pre-

cleaned 5-cm ID by 50-cm long acrylic core liner tubes. All samples were transported to the laboratory on the day of collection where they underwent immediate processing or were refrigerated at $4^{o}C$ for processing as soon as practical.

Sample Processing

17. Sample processing consisted of (a) dividing samples for a scheme of metals and chlorinated hydrocarbon analyses, (b) cleaning the stems and leaves of certain of the cattail and barnyard grass subsamples as described in the above tissue treatments section, (c) recording sample weights, and (d) transferring the samples to individual precleaned (acid, distilled water, and acetone) mason jars for storage preceding their analytical processing. All samples were stored at $4^{o}C$. Caps of jars containing samples identified for metals analyses were lined with Parafilm; jars with samples for chlorinated hydrocarbon analysis had aluminum foil lined caps to prevent contamination by the rubber seal or regular cap liner material.

Parameters

18. Soil and plant tissue samples from the three marsh sites were analyzed for chlorinated hydrocarbons. Samples from two sites were analyzed for metals. The natural marsh located on Turkey Island, upstream from Windmill Point and Hopewell, Va., was selected as an upstream control for Kepone studies. Information presented by Gregory (1976) suggested that Kepone was concentrated at the mouth of and downstream from Bailey's Creek on the James River at Hopewell, Va. In the interest of economy, the Turkey Island marsh samples were not analyzed for metals.

19. For metals, samples were analyzed to document concentrations of nickel, zinc, cadmium, chromium, and lead. For chlorinated hydrocarbons, samples were analyzed to document concentrations of aldrin, dieldrin, DDT, DDE, DDD, α and γ chlordane, heptachlor, heptachlor epoxide,

endrin, lindane, Kelthane, Kepone, polychlorinated biphenyls (PCBs), and toxaphene.

Analytical Methodology

20. Metals analyses were conducted by the Virginia Institute of Marine Science (VIMS), Gloucester Point, Va., by agreement with WES and the U. S. Army Engineer District, Norfolk, under Contract No. DACW 39-76-C-0040. Analytical Biochemistry Laboratories, Inc., Columbia, Mo., conducted chlorinated hydrocarbon analyses under Contract No. DACW 65-77-C-0052.

Metals in soil and plant tissues

21. Soil and plant tissue samples were analyzed for metals using atomic absorption spectrophotometry following a nitric acid digestion designed to estimate the total metals levels. All glassware used for metals analysis was washed with concentrated nitric acid and rinsed with deionized water.

22. A soil or plant tissue sample (approximately 1 g) of known weight and moisture content was added to a flask with 10 ml concentrated nitric acid, heated to just boiling and removed from the heat. A second 10 ml of concentrated nitric acid was added and again the sample was heated to just boiling. The sample was removed from the heat, allowed to cool and centrifuged for 5 min at 8000 rpm. The supernatant was decanted, measured and stored until analysis. Minimum levels of detection using these procedures are presented in Table 2.

Chlorinated hydrocarbons in soils and plant tissues

23. The following methodology information was provided by Analytical Biochemistry Laboratories, Inc., as procedures used for the development of chlorinated hydrocarbon data presented in this report.

a. Analysis of soil for Kepone: A 25.0-g subsample was weighed into a stainless steel cup. To this sample, 25 g of hexane-extracted sand (Mallinkrodt washed and ignited) was added. After the sample and sand were mixed, the sample composites were transferred to extraction thimbles. The stainless steel cups were then rinsed with methanol/benzene (50/50) to remove any sample remaining in them. The methanol/benzene rinse was

Table 2

Minimum Levels of Detection for Nickel, Zinc, Cadmium, Chromium and Lead in Soil and Plant Samples

Metal	Sample Type	Concentration ppm, Dry Weight
Nickel	Soil	0.13
	Plant tissue	1.0
Zinc	Soil	0.03
	Plant tissue	2.5
Cadmium	Soil	0.03
	Plant tissue	0.4
Chromium	Soil	0.1
	Plant tissue	0.9
Lead	Soil	0.3
	Plant tissue	2.5

poured through the extraction thimbles set in the soxhlet extractors. The remainder of the 300 ml of methanol/benzene was then poured into the extractor. The apparatus was connected to a reflux condenser and heating mantel and allowed to extract for 12 hr. After the extraction period, the samples were allowed to cool. The soxhlet was then rinsed with an additional 100 ml of methanol/benzene mixture. The sample extract was then evaporated on a rotary evaporator until only water remained. To this aqueous layer, 25 ml of acetone was added. The combined layers were then passed through a sodium sulfate funnel to remove the water. The sample flask was rinsed with two additional 25 ml portions of acetone. After the sample extracts had been passed through the sodium sulfate funnel, it was rinsed with 3-m to 10-ml portions of acetone. The combined acetone rinses were then evaporated to dryness using a rotary evaporator. The sample residue was then transferred to a marked culture tube with ethyl acetate and evaporated under an air stream to 5 ml. A 0.5-ml aliquot of this extract was then submitted to further cleanup on a mini florisil column.

The florisil column was prepared by dry-packing 1.75 g of florisil into a 4-mm ID by 140-mm long column. The column was then topped with 10 mm of anhydrous sodium sulfate and prewet with 20 ml of hexane. A 0.5-ml aliquot of the extract was then added to the column and eluted with 2.5 ml of eluant B (50 percent methylene chloride/0.35 percent acetonitrile/49.65 percent hexane), which was discarded. The Kepone was then eluted with 15 ml of ethyl acetate. The ethyl acetate fraction was then evaporated to dryness. Any sample residue was transferred to a marked culture tube with ethyl acetate and then analyzed by gas liquid chromatography (G.L.C.). Operating parameters were as follows:

1.5 percent OV-17 on GCQ 100/120 mesh

2.0 percent OV-210

Column Temperature: 205°C

Inlet Temperature: 225°C

Detector ^{63}Ni Temperature: 300°C

Column used: 1.8-m coiled and 1.8-m "U" column

N_2 flow: 100 mℓ/min

b. Analysis of soil for remaining compounds: Soil samples were thawed and mixed thoroughly. Twenty-five-g subsamples were weighed into 33- by 94-mm cellulose extraction thimbles. Twenty-five g of ignited and washed sand was mixed into the subsample and the thimble placed

in the soxhlet extraction assembly. Approximately 300 ml of acetone/petroleum ether (1+1) was poured through the extraction tube. The condensers were fitted to the soxhlet extractor and the solvent heated to a gentle boil. After at least 12 hr the heaters were turned off and allowed to cool. The extracts were concentrated to just dryness by rotary evaporator. Residues were transferred to a 2.5- by 100-cm florisil column. PCBs, toxaphene, lindane, aldrin, chlordanes, heptachlor, DDT and metabolites, mirex, and some Kelthane were eluted with 100 ml of eluent A (20 percent dichloromethane in petroleum ether). Separation of PCBs from chlordane and DDTs was accomplished with woelm silica gel mini columns. "A" eluents from florisil were concentrated to 2 ml and a 1-ml aliquot was placed on the column. PCBs, mirex, and some DDE were eluted with 16 ml of eluent 1(0.5 percent benzene in petroleum ether). The eluate was concentrated to 10 ml for G.L.C. analysis. Lindane, aldrin, heptachlor, chlordanes and DDTs were eluted with 15 ml eluent 2 (4 percent ethyl acetate in benzene). Heptachlor epoxide, dieldrin, endrin, and methoxychlor were eluted from florisil with 180 ml of eluent B (50 percent methylene chloride/49.65 percent petroleum ether/0.35 percent acetonitrile). The eluate was concentrated to 10 ml for G.L.C. analysis. Microlitre aliquots were injected into G.L.C.'s equipped with a ^{63}Ni electron capture detector. Operating parameters were as follows:

Column: 1.5 percent OV-17, 2.0 percent OV-120 on G.C.G. 100/120 mesh

Column Temperature: 200°C

Inlet Temperature: 225°C

Detector Temperature: 300°C

N_2 flow: 100 mℓ/min

c. Analysis of plant tissue for Kepone: The samples were macerated with a 3.8-litre Waring blender. A 25-g subsample was weighed into a cellulose extraction thimble, loaded into a soxhlet extraction tube, and the extraction tube fitted with a 500-ml boiling flask. Three hundred ml of methanol/benzene (1+1) was poured into the extractor. The extractor was fitted with a reflux condenser and heating mantle and allowed to extract for 12 hr at a rate of approximately 4 times per hour. After the extraction period, the samples were allowed to cool. The soxhlet was then rinsed with an additional 100 ml of methanol/benzene mixture. The sample extract was then evaporated on a rotary evaporator until only water remained. To this aqueous layer, 25 ml of acetone was added. The combined layers were then

passed through a sodium sulfate funnel to remove the water. The sample flask was rinsed with two additional 25-ml portions of acetone. After the sample extracts had been passed through the sodium sulfate funnel, it was rinsed with three 10-ml portions of acetone. The combined acetone rinses were then evaporated to dryness using a rotary evaporator. The sample residue was then transferred to a marked culture tube with ethyl acetate and evaporated under an airstream to 5 ml. A 0.5-ml aliquot of this abstract was then submitted to further cleanup on a mini-florisil column.

The florisil column was prepared by dry-packing 1.75 g of florisil into a 4-mm ID by 140-mm long column. The column was then topped with 10 mm of anhydrous sodium sulfate and prewet with 20 ml of hexane. A 0.5-ml aliquot of the extract was then added to the column and eluted with 2.5 ml of eluant B (50 percent methylene chloride/49.65 percent hexane/0.35 percent acetonitrile), which was discarded. The Kepone was then eluted with 15 ml of ethyl acetate. The ethyl acetate fraction was then evaporated to dryness. Any sample residue was transferred to a marked culture tube with ethyl acetate and then analyzed by G.L.C. Operating parameters were as follows:

1.5 percent OV-17 on GCQ 100/120 mesh

2.0 percent OV-210

Column Temperature: 205°C

Inlet Temperature: 225°C

Detector ^{63}Ni Temperature: 300°C

Column used: 1.8-m coiled and 1.8-m "U" column

N_2 flow rate: 100 mℓ/min

d. Analysis of plant tissue for remaining coumpounds: Twenty-five g of the macerated sample were weighed into a 600-ml Sorval blender cup and blended with approximately 100 ml of acetone/petroleum ether (1+1) for 5 min. The sample was filtered through glass fiber filter paper with vacuum. The filtrate was set aside while the filter cake and glass fiber paper were placed into an extraction thimble. Approximately 300 ml of acetone/petroleum ether (1+1) was poured through the extraction tube. The condensers were fitted to the soxhlet extractor and the solvent heated to a gentle boil. After at least 12 hr the heaters were turned off and allowed to cool. The extracts were concentrated to just dryness by rotory evaporator. Residues were transferred to a 2.5- × 100-cm florisil column. PCBs,

toxaphene, lindane, aldrin, chlordanes, heptachlor, DDT and metabolites, mirex, and some Kelthane were eluted with 100 ml of eluent A (20 percent dichloromethane in petroleum ether). Separation of PCBs from chlordane and DDTs was accomplished with Woelm silica gel mini columns. "A" eluents from florisil were concentrated to 2 ml and a 1 ml aliquot was placed on the column. PCBs, mirex, and some DDE were eluted with 16 ml of eluent 1 (0.5 percent benzene in petroleum ether). The eluate was concentrated to 10 ml for G.L.C. analysis. Lindane, aldrin, heptachlor, chlordanes, and DDTs were eluted with 15 ml eluent 2 (4 percent ethylacetate in benzene). Heptachlor epoxide, dieldrin, endrin, and methoxychlor were eluted from florisil with 180 ml eluent B (50 percent methylene chloride/49.65 percent petroleum ether/0.35 percent acetonitrile). The eluate was concentrated to 10 ml for G.L.C. analysis. Microlitre aliquots were injected into G.L.C.'s equipped with a ^{63}Ni electron capture detector. Operating parameters were as follows

Column: 1.5 percent OV-17, 2.0 percent OV-210 on GCQ 100/120 mesh

Column Temperature: 200°C

Inlet Temperature: 225°C

Detector Temperature: 300°C

N_2 flow: 100 mℓ/min

24. Minimum levels of detection are presented in Table 3. Samples containing detectable Kepone concentrations were confirmed by G.L.C. analysis using a 1.8 m x 4 mm I.D. coiled column using 5.0 percent SE-30 on GCQ 100/120 mesh.

Column Temperature: 200°C

Inlet Temperature: 225°C

^{63}Ni Detector Temperature: 300°C

Confirmation analyses substantiated the presence of Kepone in all samples tested. Confirmed Kepone values in all soil samples were within 16 percent. Percent recovery values for chlorinated hydrocarbon

Table 3

Minimum Levels of Detection for Chlorinated Hydrocarbon Compounds in Soil and Plant Samples

Compound	Concentration ppb, Wet Weight
Aldrin	10
Dieldrin	10
DDT	10
DDT	10
DDE	10
DDE	10
DDD	10
α chlordane	10
γ chlordane	10
Heptachlor	10
Methoxychlor	25
Heptachlor epoxide	10
Endrin	10
Lindane	10
Kelthane	50
Kepone	10
Polychlorinated biphenyls	30
Toxaphene	200

compounds from spiked soil and plant tissue samples are presented in Table 4.

Data Analysis

25. Metals concentrations for both soils and plant tissues were subjected to analysis of variance (ANOVA) and Duncan's Multiple Range Comparison using the Statistical Analysis System (Barr et al. 1976). To achieve a balanced design, a concentration value equal to 0.5 the minimum detection limit for the particular metal (Table 3) was substituted for concentrations below detection. When dealing with the chlorinated hydrocarbon data, the number of missing valued associated with less than detectable concentrations contra-indicated the use of ANOVA and so a two-tailed t-test or a completely subjective data analysis was employed. Exceptions to this are noted in the appropriate portions of the results and discussion sections.

Table 4

Percent Recovery Values for Chlorinated Hydrocarbon Compounds from Spiked Soil and Plant Tissue Samples

Compound	Concentration Spike ppb, Wet Weight	No.	Mean Percent Recovery
Arochlor 1254 (PCB)	158.0	5	82
Lindane	4.1	1	68
	41.0	9	75
Heptachlor	3.6	1	97
	40.0	9	61
Aldrin	4.0	1	80
	38.0	9	79
Heptachlor epoxide	8.4	1	93
	53.0	9	63
γ chlordane	8.1	1	94
	42.0	9	78
α chlordane	7.8	1	108
	45.0	8	76
DDE	11.8	1	73
	42.0	9	79
Dieldrin	11.4	1	108
	39.0	9	83
Endrin	20.4	1	88
	36.0	9	73
DDT	19.6	1	71
	42.0	10	73
DDT	19.8	1	95
	95.0	10	82
DDD	19.8	1	96
	39.0	10	78
Mirex	24.0	1	36
	42.0	5	37
Methoxychlor	36.8	1	48
	42.0	10	76
Kepone	40.0	22	93
Toxaphene	262.0	1	67
	330.0	1	56
Kelthane	248.0	1	79
	26.0	1	77

PART III: RESULTS

Metals

26. Interacting physical conditions and chemical and biological characteristics influence metal concentrations in plant tissues. Some of the major factors are sediment particle size, soil dryness or wetness, concentrations of organic and inorganic substances, and plant tissue structure as it affects the potential routes of metals transfer. The single greatest problem affecting defendable conclusions about the uptake or chemical substances by vascular plant materials is probably the high variability of the data caused by these complex interactions. Marshes are, by definition, transitional areas between terrestrial and aquatic habitats. The transitional character of marsh environments adds to high natural variability in soil conditions believed to be important in effecting metals transfer to plant tissues.

27. Given the above, the reader is forewarned that the presentation of results in this report has been tempered by considering the highly variable data (Table 5). Eyeball estimates of trends in mean metals concentrations among areas, soil zones, and plant tissues often suggest differences that may be only natural variability. Unless otherwise qualified, statements about metals concentrations indicating that areas, soils, or plant tissue samples are different from each other are made at $\alpha = 0.05$ or less.

Zinc in plant tissues

28. Zinc concentrations among various plant tissues at the experimental and natural marsh were different but there were no differences between comparable plant tissues at the two marshes. Figure 2 presents mean zinc concentrations in plant samples. There was no consistent trend in plant zinc concentrations between the two marshes. The highest mean zinc concentration values were associated with barnyard grass roots from the reference marsh. When compared with other plant tissues there were no real differences between barnyard grass root zinc concentrations at the reference marsh and con-

Table 5

Concentrations of Metals in Marsh Plant Tissues Collected from the Windmill Point Experimental Marsh and a Natural Marsh

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight: Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
a. Windmill Point Experimental Marsh						
Peltandra, seeds	1	<0.5	30.0	<0.2	2.0	<1.3
	2	7.0	31.0	<0.2	<0.5	<1.3
	3	1.0	24.0	0.6	<0.5	<1.3
	4	<0.5	51.0	<0.2	<0.5	<1.3
	5	2.0	43.0	<0.2	<0.5	<1.3
	Total	11.0	179.0	1.4	4.0	6.5
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	2.2	35.8	0.28	0.80	1.3
Echinochloa, seeds	1	2.0	139.0	<0.2	3.0	3.0
	2	5.0	68.0	0.5	4.0	<1.3
	3	1.0	49.0	<0.2	2.0	<1.3
	4	3.0	76.0	0.3	4.0	<1.3
	5	<0.5	54.0	0.8	3.0	<1.3
	Total	11.5	386.0	2.0	16.0	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	2.3	77.2	0.4	3.2	1.64
Echinochloa, roots	1	5.0	40.0	<0.2	2.0	3.0
	2	7.0	70.0	0.9	8.0	13.0
	3	8.0	63.0	0.6	6.0	6.0
	4	6.0	63.0	1.1	4.0	5.0
	5	7.0	46.0	0.8	4.0	5.0
	Total	33.0	282.0	3.6	24.0	32.0
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	6.6	56.4	0.72	4.8	6.4

(Continued)

Table 5 (Continued)

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight: Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
a. Windmill Point Experimental Marsh (Continued)						
Echinochloa, stems/ leaves unwashed	1	5.0	16.0	<0.2	4.0	<1.3
	2	1.0	54.0	0.3	<0.5	3.0
	3	3.0	39.0	<0.2	2.0	<1.3
	4	2.0	66.0	<0.2	2.0	<1.3
	5	<0.5	49.0	<0.2	3.0	<1.3
	Total	11.5	224.0	1.1	11.5	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	2.3	44.8	0.22	2.3	1.64
Echinochloa, stems/ leaves washed	1	4.0	36.0	<0.2	2.0	<1.3
	2	2.0	127.0	0.4	<0.5	<1.3
	3	6.0	56.0	<0.2	2.0	<1.3
	4	1.0	66.0	<0.2	2.0	<1.3
	5	2.0	55.0	<0.2	3.0	<1.3
	Total	15.0	340.0	1.2	9.5	6.5
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	3.0	68.0	0.24	1.9	1.3
Typha, tubers	1	2.0	14.0	<0.2	2.0	<1.3
	2	4.0	144.0	<0.2	3.0	<1.3
	3	1.0	37.0	0.3	2.0	3.0
	4	6.0	61.0	<0.2	4.0	<1.3
	5	3.0	32.0	0.4	<0.5	<1.3
	Total	16.0	288.0	1.3	11.5	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	3.2	57.6	0.26	2.3	1.64

(Continued)

Table 5 (Continued)

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight: Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
a. Windmill Point Experimental Marsh (Concluded)						
Typha, stems/leaves unwashed	1	3.0	16.0	0.3	<0.5	<1.3
	2	8.0	18.0	0.3	<0.5	3.0
	3	4.0	45.0	0.7	2.0	5.0
	4	5.0	20.0	<0.2	2.0	3.0
	5	5.0	29.0	<0.2	3.0	<1.3
	Total	25.0	128.0	1.7	8.0	13.6
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	5.0	25.6	0.34	1.6	2.7
Typha, stems/leaves washed	1	4.0	12.0	<0.2	2.0	<1.3
	2	7.0	16.0	0.3	<0.5	<1.3
	3	5.0	15.0	<0.2	3.0	3.0
	4	4.0	22.0	<0.2	<0.5	<1.3
	5	3.0	76.0	0.4	<0.5	<1.3
	Total	23.0	141.0	1.3	6.5	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	4.6	28.2	0.26	1.3	1.64
b. Ducking Stool Point						
Peltandra, seeds	1	<0.5	39.0	<0.2	<0.5	<1.3
	2	1.0	32.0	1.6	2.0	15.0
	3	1.0	52.0	<0.2	2.8	<1.3
	4	<0.5	46.0	<0.2	2.0	<1.3
	5	<0.5	40.0	0.3	<0.5	<1.3
	Total	3.5	209.0	2.5	7.8	20.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	0.7	41.8	0.5	1.56	4.04

(Continued)

Table 5 (Continued)

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight				
		Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
b. Ducking Stool Point (Continued)						
Echinochloa, seeds	1	<0.5	44.0	<0.2	4.0	<1.3
	2	<0.5	68.0	<0.2	<0.5	<1.3
	3	1.0	45.0	<0.2	2.0	<1.3
	4	<0.5	75.0	<0.2	2.0	<1.3
	5	3.5	88.0	0.3	7.0	9.0
	Total	6.0	320.0	1.1	15.5	14.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	1.2	64.0	0.22	3.10	2.84
Echinochloa, roots	1	9.0	92.0	1.6	2.0	15.0
	2	5.0	275.0	0.8	5.0	9.0
	3	2.0	38.0	<0.2	2.3	<1.3
	4	1.0	30.0	<0.2	<0.5	<1.3
	5	15.0	95.0	0.8	10.0	20.0
	Total	32.0	530.0	3.6	19.8	46.6
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	6.4	106.0	0.72	3.96	9.3
Echinochloa, stems/ leaves unwashed	1	3.0	46.0	<0.2	5.0	<1.3
	2	2.0	84.0	<0.2	<0.5	<1.3
	3	1.0	44.0	0.3	<0.5	<1.3
	4	1.0	41.0	<0.2	3.0	<1.3
	5	<0.5	32.0	0.3	<0.5	<1.3
	Total	7.5	247.0	1.2	9.5	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	1.50	49.4	0.24	1.90	1.31

(Continued)

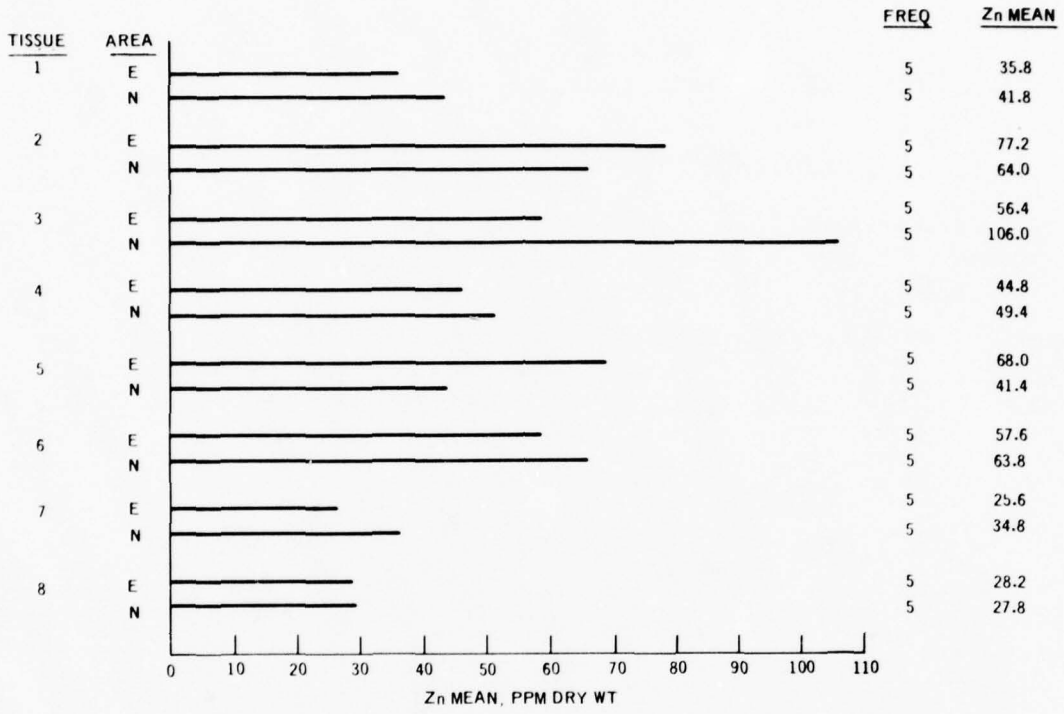
Table 5 (Continued)

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
b. Ducking Stool Point (Continued)						
Echinochloa, stems/ leaves washed	1	3.0	45.0	0.7	<0.5	<1.3
	2	1.0	30.0	<0.2	0.2	<1.3
	3	1.0	41.0	<0.2	<0.5	<1.3
	4	<0.5	33.0	<0.2	4.0	<1.3
	5	1.0	58.0	<0.2	3.0	3.0
	Total	6.5	207.0	1.5	8.2	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	1.3	41.4	0.3	1.64	1.64
Typha, tubers	1	4.0	63.0	<0.2	3.0	<1.3
	2	4.0	71.0	0.4	3.0	4.0
	3	3.0	38.0	<0.2	2.0	<1.3
	4	4.0	73.0	<0.2	3.0	6.0
	5	3.0	74.0	0.4	4.0	7.0
	Total	18.0	319.0	1.4	15.0	19.6
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	3.6	63.8	0.28	3.0	3.92
Typha, stems/leaves unwashed	1	1.0	14.0	<0.2	2.0	<1.3
	2	1.0	15.0	0.3	3.0	4.0
	3	1.0	14.0	<0.2	2.0	<1.3
	4	2.0	106.0	0.4	<0.5	<1.3
	5	2.0	25.0	<0.2	2.0	<1.3
	Total	7.0	275.0	1.3	9.5	9.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	1.4	34.8	0.26	1.90	1.84

(Continued)

Table 5 (Concluded)

Marsh Plant Tissue	Sample No.	Metal and Minimum Level of Detection ppm, Dry Weight: Nickel 1.0	Zinc 2.5	Cadmium 0.4	Chromium 0.9	Lead 2.5
b. Ducking Stool Point (Concluded)						
Typha, stems/leaves washed	1	3.0	45.0	0.7	<0.5	<1.3
	2	<0.5	17.0	<0.2	3.2	3.0
	3	3.0	16.0	<0.2	3.0	<1.3
	4	3.0	37.0	0.4	<0.5	<1.3
	5	3.0	24.0	<0.2	2.0	<1.3
	Total	12.5	139.0	1.7	9.2	8.2
	N	5.0	5.0	5.0	5.0	5.0
	$\bar{X}$	2.5	27.8	0.34	1.84	1.64



LEGEND

TISSUE

1– ARROW ARUM SEEDS
2– BARNYARD GRASS SEEDS
3– BARNYARD GRASS ROOTS
4– BARNYARD GRASS STEMS/LEAVES, UNWASHED
5– BARNYARD GRASS STEMS/LEAVES, WASHED
6– CATTAIL TUBERS
7– CATTAIL STEMS/LEAVES, UNWASHED
8– CATTAIL STEMS/LEAVES, WASHED

AREA

E – WINDMILL PT. EXPERIMENTAL MARSH
N– DUCKING STOOL PT. NATURAL MARSH

Figure 2. Mean zinc concentrations in plant tissues collected from the Windmill Point experimental marsh and a natural marsh at Ducking Stool Point

centrations in barnyard grass roots at the experimental marsh or cattail tubers at either marsh. Barnyard grass seed zinc concentrations also existed within the wide range of zinc values associated with the barnyard grass roots from the natural marsh.

29. Zinc concentrations in barnyard grass roots from the natural marsh were higher than concentrations in other plant tissues from both marshes. These included the barnyard grass stems and leaves, cattail stems and leaves, and the arrow arum seeds.

30. There were concentration trends within plant species. These trends were not consistent between sites and none were significant when subjected to the routine parametric statistics used in this study. By applying Duncan's Multiple Range Comparison, plant tissues are divided into two groups based upon their zinc concentrations (Figure 3).

Zinc concentration, soil and plant relationships

31. Estimates of total zinc soil concentrations were highest in the pickerel weed - arrow arum soil zone of the natural marsh, followed by the cattail - beggar tick zone of the natural marsh and the cattail - beggar tick and pickerel weed - arrow arum zones of the experimental marsh, respectively (Table 6). Estimates of total soils zinc did not correlate with plant tissue zinc concentrations (Figure 2).

Nickel in plant tissues

32. Nickel was the only metal studied with concentration differences between the same type of plant tissue from both marshes. Nickel concentrations in plant tissues from the experimental marsh were generally higher than concentrations in natural marsh plant tissues (Figure 4). Comparisons between nickel concentrations in unwashed cattail stems and leaves indicate that concentrations at the experimental marsh were higher. These differences did not persist after the stem and leaf surfaces were cleaned, indicating the possibility of surface contamination that was removed by the washing procedure. As was the case with zinc, barnyard grass roots contained

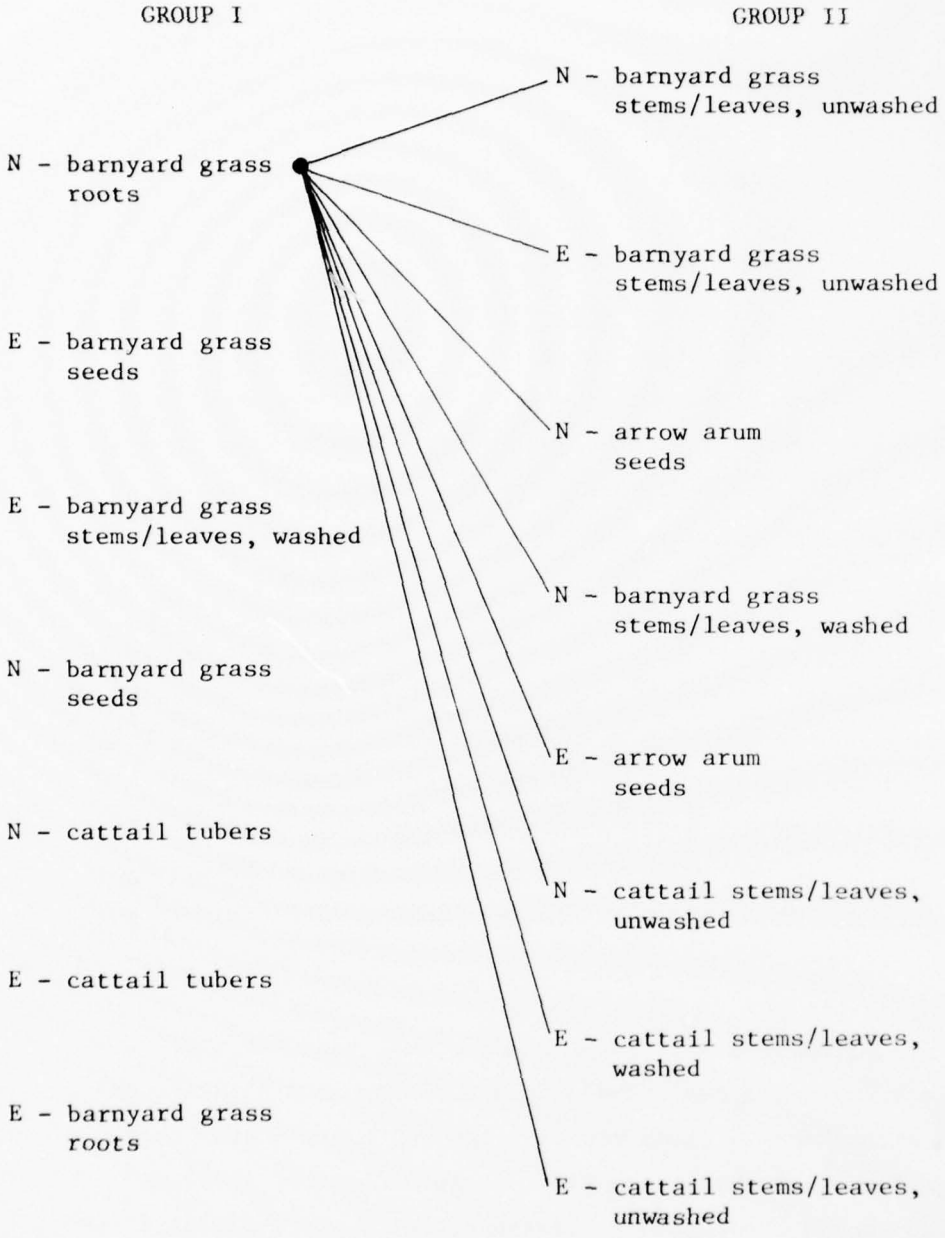


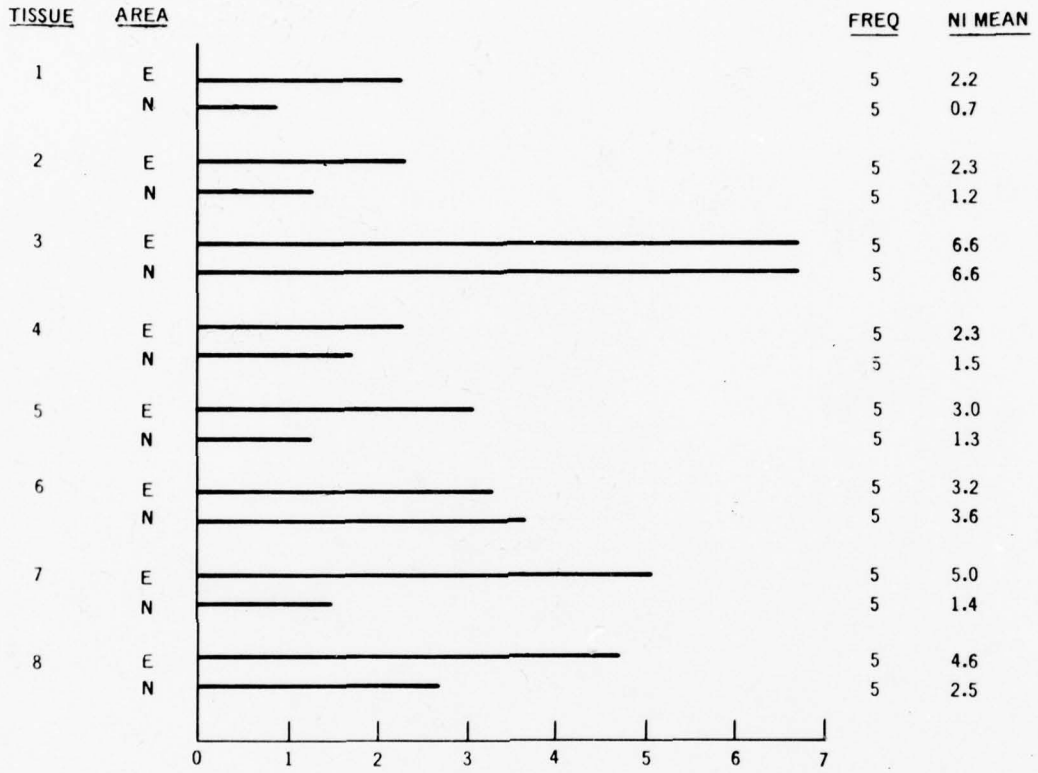
Figure 3. Differences in zinc concentrations between marsh plant tissues. The prefixes N and E are used to identify the samples as natural or experimental marsh tissues, respectively. Tissues are listed from top to bottom, left to right in order of decreasing mean zinc concentration. Connecting lines identify significant concentration differences. Tissues in the same group did not contain different zinc concentrations.

Table 6

Mean Soil Concentrations of Metals in the Pickerel Weed-Arrow Arum and Cattail-Beggartick Soil Zones of the Windmill Point Experimental Marsh and Ducking Stool Point Natural Marsh

Soil Zone	Metal Concentration*									
	Nickel		Zinc		Chromium		Cadmium		Lead	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
a. Windmill Point Experimental Marsh										
Pickerel weed-arrow arum zone	15.2	2.4	73.0	20.5	131.0	26.0	10.9	1.7	61.4	8.4
Cattail-beggartick zone	17.0	1.5	82.3	5.2	206.5	123.6	14.5	3.2	65.5	7.6
b. Ducking Stool Point Natural Marsh										
Pickerel weed-arrow arum zone	26.8	14.1	173.9	50.8	100.3	35.0	10.8	4.0	43.7	15.0
Cattail-beggartick zone	24.0	6.1	125.1	59.4	60.6	22.1	6.4	1.4	30.8	7.1

* Concentrations are in parts per million, dry weight, and represent the mean of five values.



LEGEND

TISSUE

1 ARROW ARUM SEEDS
2 BARNYARD GRASS SEEDS
3 - BARNYARD GRASS ROOTS
4 - BARNYARD GRASS STEMS/LEAVES, UNWASHED
5 - BARNYARD GRASS STEMS/LEAVES, WASHED
6 - CATTAIL TUBERS
7 - CATTAIL STEMS/LEAVES, UNWASHED
8 - CATTAIL STEMS/LEAVES, WASHED

AREA

E - WINDMILL PT. EXPERIMENTAL MARSH
N - DUCKING STOOL PT. NATURAL MARSH

Figure 4. Mean nickel concentrations in plant tissues collected from the Windmill Point experimental marsh and a natural marsh

the highest concentration of nickel among the plant tissues of both marshes, higher than in all tissues except for the unwashed and washed cattail stems and leaves collected from the experimental marsh. A different pattern of nickel uptake is suggested by comparisons between barnyard grass tissues and cattail tissues collected from the experimental marsh: barnyard grass tissues followed a concentration pattern of roots > leaves; cattail tissues followed a pattern of leaves > roots. Plant tissues were grouped by their mean nickel concentration in Figure 5, which was developed from application of Duncan's Multiple Range Comparison technique.

Nickel concentration, soil and plant relationships

33. The patterns of the estimated total nickel concentrations in the natural and experimental marshes are similar to that for zinc (Table 6). Estimated total nickel concentrations were highest in the pickerel weed - arrow arum zone of the natural marsh followed by the cattail - beggar tick zone of the natural marsh and the cattail - beggar tick and pickerel weed - arrow arum zones of the experimental marsh, respectively. The lack of a positive correlation between estimated total nickel soil concentrations and plant uptake is especially evident when the nickel-soil-plant tissue relationship is examined. The general pattern of experimental marsh-plant tissue nickel concentrations is not supported by any suggestion that the greater the soil nickel, the greater the plant tissue concentration. The highest mean nickel value occurred in a soil's zone supporting arrow arum, whose seeds contained the smallest nickel concentration observed in a plant tissue during this study (Figure 4).

Cadmium in plant tissues

34. Cadmium concentrations among various plant tissues at the experimental and reference marsh were different but there were no differences observed between the same plant tissues at the two marshes. Consistent with zinc and nickel concentration observations, the highest cadmium concentrations were observed in barnyard grass roots. Experimental and natural marsh mean cadmium concentrations in barnyard grass

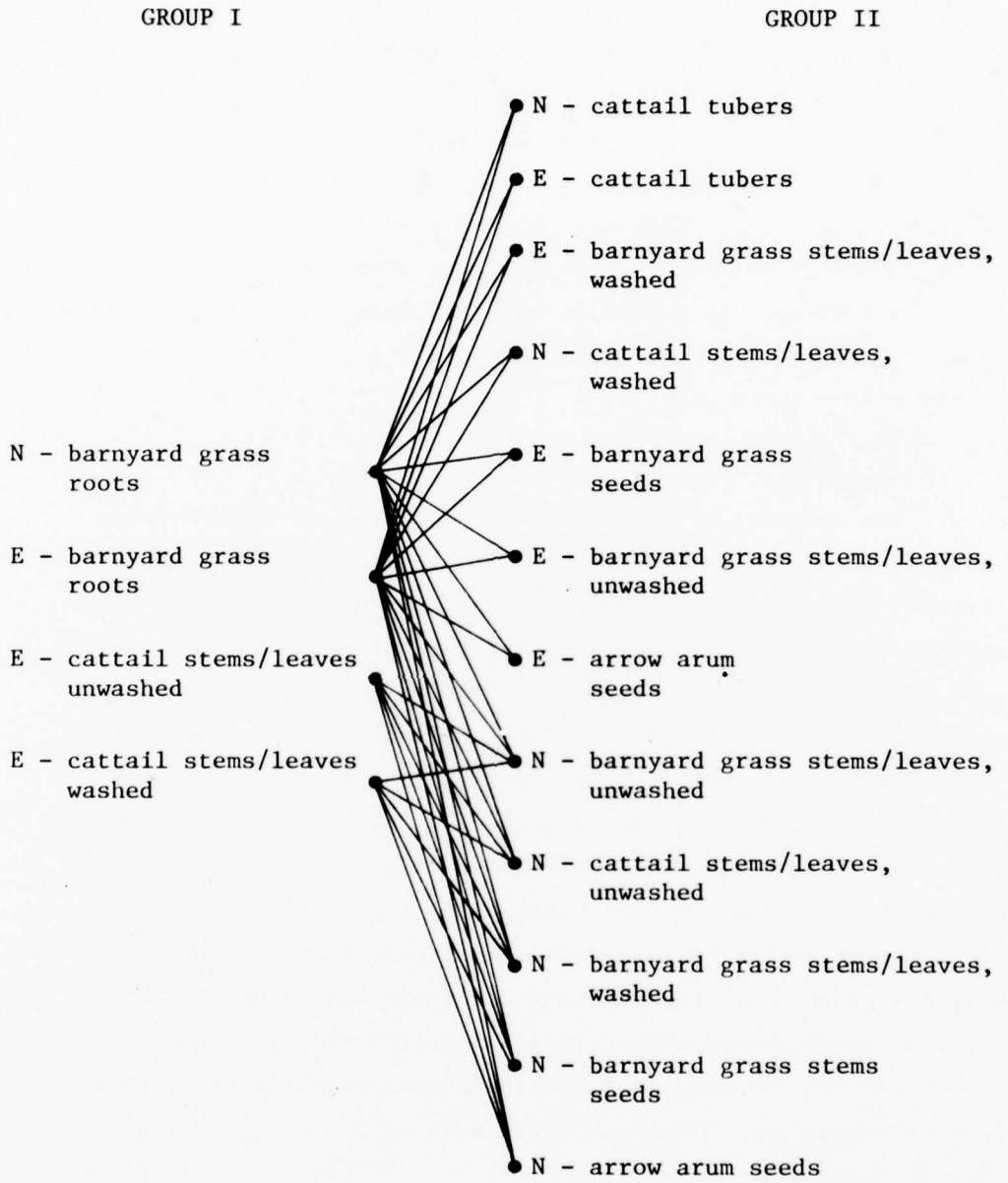


Figure 5. Differences in nickel concentrations between marsh plant tissues. The prefixes N and E are used to identify the samples as natural or experimental marsh tissues, respectively. Tissues are listed from top to bottom, left to right in order of decreasing mean nickel concentration. Connecting lines identify significant concentration differences. Tissues in the same group did not contain different nickel concentrations.

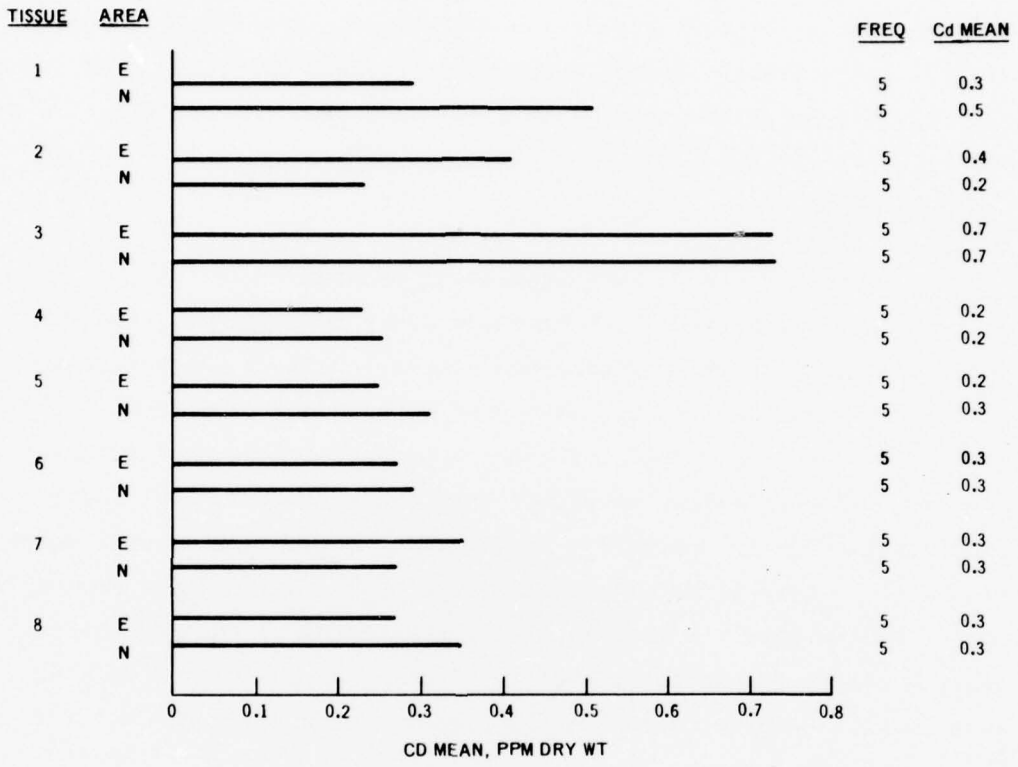
root tissues were higher than concentrations in all other plant tissues with two exceptions. Arrow arum seeds from the natural marsh and barnyard grass seeds from the experimental marsh were not different from the barnyard grass root tissue concentrations. There were no consistent concentration trends among plant tissues at either site (Figure 6). Plant tissues are grouped by their mean cadmium concentration in Figure 7.

Cadmium concentration, soil and plant relationships

35. The pattern of estimated total cadmium concentrations in the soil of the natural and experimental marshes is different from the concentration patterns for zinc and nickel. Cadmium concentrations in the pickerel weed - arrow arum zone of both the experimental and natural marshes and in the cattail - beggar tick zone of the experimental marsh are similar or higher than the estimated total cadmium concentration in the cattail - beggar tick zone of the natural marsh (Table 6). There is no clear pattern of plant-soil cadmium concentration relationships. A correlation is frustrated by the greater concentrations in the soils of the experimental marsh and the lack of any dominant cadmium concentration trends in the plant tissues from the experimental marsh.

Chromium in plant tissue

36. Chromium concentrations among various plant tissues at the experimental and reference marsh were different but there were no differences between the same plant tissues collected from the two marshes. There was no general marsh related trend in chromium concentrations among plant tissues (Figure 8). Consistent differences with barnyard grass roots containing higher concentrations of chromium than barnyard grass stems and leaves occurred in samples from both sites. Barnyard grass roots from both the experimental and natural marshes contained the highest chromium concentrations observed during the study. Barnyard grass samples from the experimental marsh were higher in their chromium concentrations than all other tissues studied. Plant tissues were divided into two groups based on cadmium concentrations (Figure 9).



LEGEND

TISSUE

1–ARROW ARUM SEEDS
2–BARNYARD GRASS SEEDS
3–BARNYARD GRASS ROOTS
4–BARNYARD GRASS STEMS/LEAVES, UNWASHED
5–BARNYARD GRASS STEMS/LEAVES WASHED
6–CATTAIL TUBERS
7–CATTAIL STEMS/LEAVES, UNWASHED
8–CATTAIL STEMS/LEAVES, WASHED

AREA

E–WINDMILL PT. EXPERIMENTAL MARSH
N–DUCKING STOOL PT. NATURAL MARSH

Figure 6. Mean cadmium concentrations in plant tissues collected from the Windmill Point experimental marsh and a natural marsh

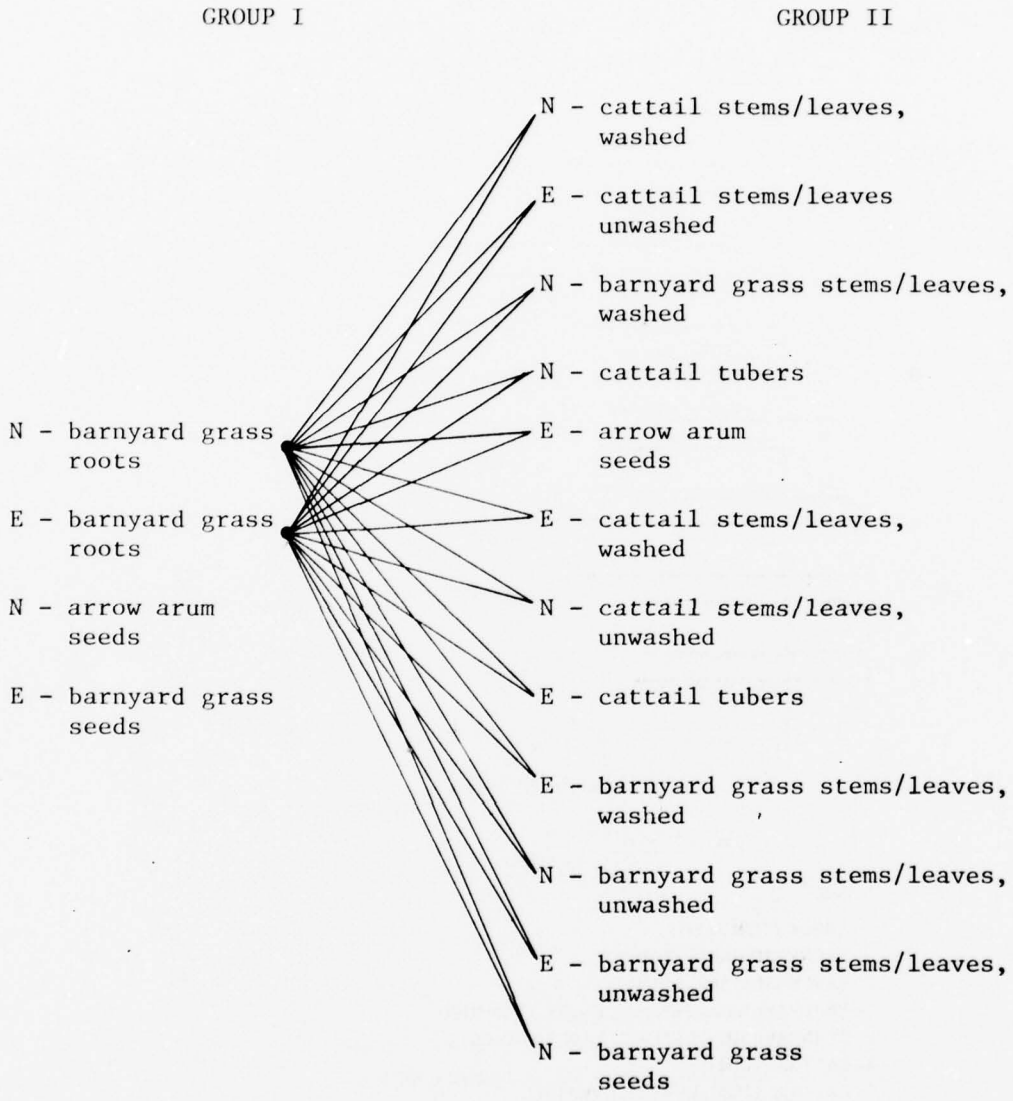
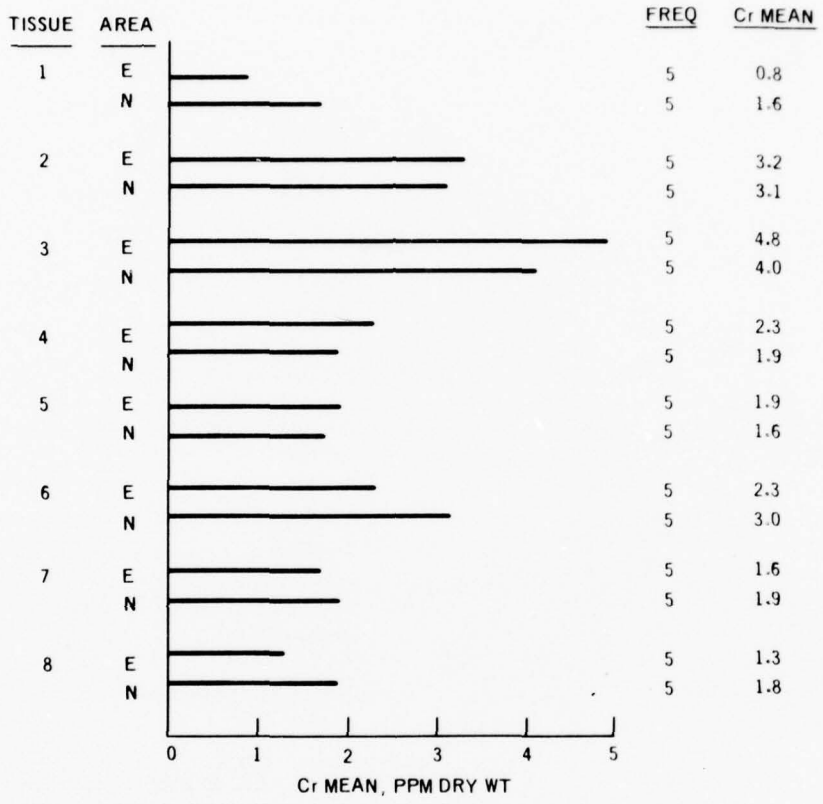


Figure 7. Differences in cadmium concentrations between marsh plant tissues. The prefixes N and E are used to identify the samples as natural or experimental marsh tissues, respectively. Tissues are listed from top to bottom, left to right, in order of decreasing mean cadmium concentration. Connecting lines identify significant concentration differences. Tissues in the same group did not contain different cadmium concentrations.



LEGEND

TISSUE

1–ARROW ARUM SEEDS
2–BARNYARD GRASS SEEDS
3–BARNYARD GRASS ROOTS
4–BARNYARD GRASS STEMS/LEAVES, UNWASHED
5–BARNYARD GRASS STEMS/LEAVES, WASHED
6–CATTAIL TUBERS
7–CATTAIL STEMS/LEAVES, UNWASHED
8–CATTAIL STEMS/LEAVES, WASHED

AREA

E–WINDMILL PT. EXPERIMENTAL MARSH
N–DUCKING STOOL PT. NATURAL MARSH

Figure 8. Mean chromium concentrations in plant tissues collected from the Windmill Point experimental marsh and a natural marsh

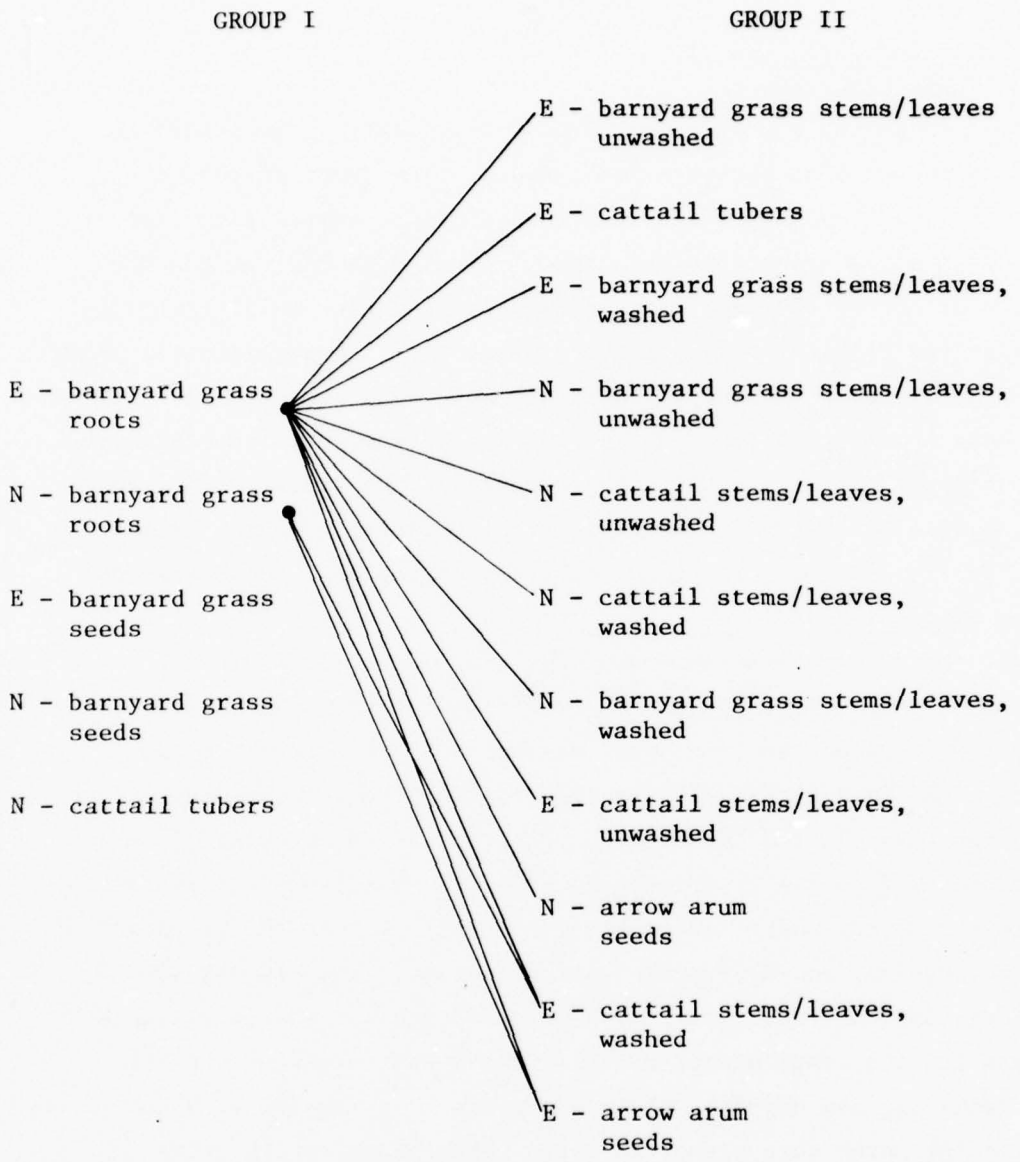


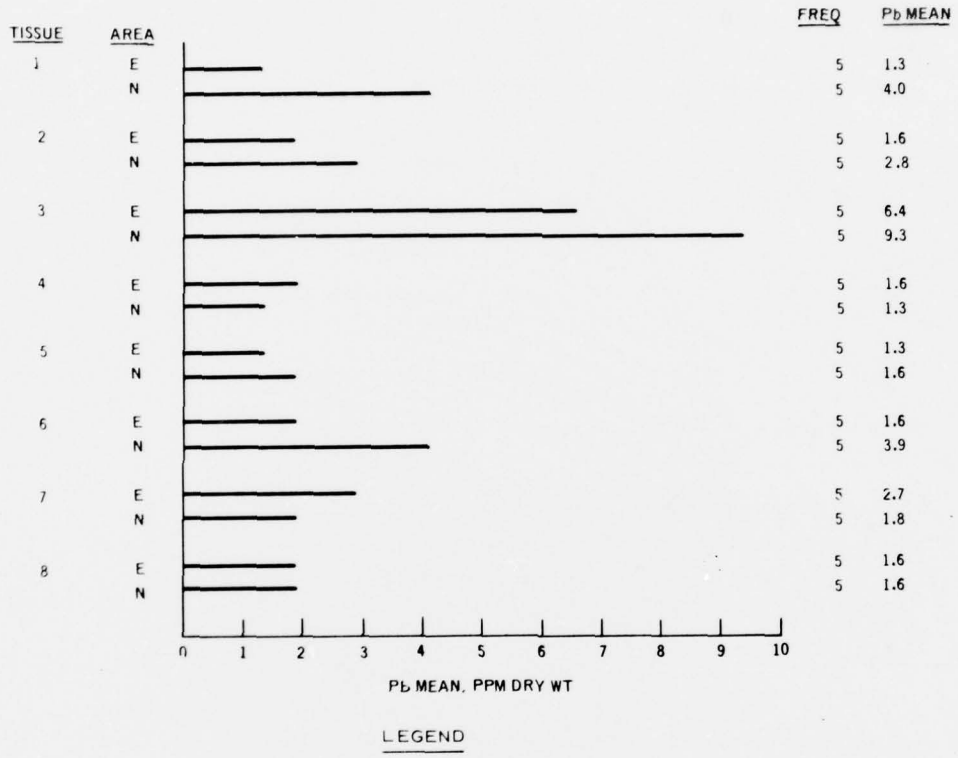
Figure 9. Differences in chromium concentrations between marsh plant tissues. The prefixes N and E are used to identify the samples as natural or experimental marsh tissues, respectively. Tissues are listed from top to bottom, left to right, in order of decreasing mean chromium concentration. Connecting lines identify significant concentration differences. Tissues in the same group did not contain different chromium concentrations.

Chromium concentration, soil and plant relationships

37. Estimates of total chromium soil concentrations suggest a trend similar to that observed for cadmium. The trend in mean values (Table 6) indicates that soils from the cattail - beggar tick zone of the experimental marsh contained higher chromium concentrations than exist in either of the natural marsh soil zones. The soil chromium values in the pickerel weed - arrow arum zone of the experimental marsh suggest no distinct concentration differences when compared with other soil zones of either marsh. Except for the occurrence of the highest chromium level in the plant tissue (barnyard grass roots) collected from the soil zone with the highest chromium level, no correlations between soil and plant tissue chromium concentrations are suggested.

Lead in plant tissue

38. Lead concentrations among various plant tissues in the experimental and reference marshes were different but there were no differences between the same plant tissues collected from the two marshes. The lead in plants data (Figure 10) suggests the possibility that plant tissues from the natural marsh contained more lead than plant tissues from the experimental marsh. This difference exists at an α level = 0.13, which for consistency with the rest of this study's reported results, would be called not different. The highest lead concentrations were associated with barnyard grass roots, but as was the case for all other metals studied, there was no difference for this tissue between marshes. Barnyard grass root samples from the experimental marsh were higher in their lead concentrations than washed cattail stems and leaves from the experimental marsh suggesting a reduction in cattail stem and leaf lead effected by the tissue washing procedure. A common tissue type-plant species concentration trend existed at both marshes where barnyard grass root lead concentration trend existed at both marshes where barnyard grass root lead concentrations were higher than concentrations in the stems and leaves and seeds. Plant tissues were divided into the two groups based on lead concentrations (Figure 11).



LEGEND

TISSUE

1 - ARROW ARUM SEEDS
2 - BARNYARD GRASS SEEDS
3 - BARNYARD GRASS ROOTS
4 - BARNYARD GRASS STEMS/LEAVES, UNWASHED
5 - BARNYARD GRASS STEMS/LEAVES, WASHED
6 - CATTAIL TUBERS
7 - CATTAIL STEMS/LEAVES, UNWASHED
8 - CATTAIL STEMS/LEAVES, WASHED

AREA

E - WINDMILL PT. EXPERIMENTAL MARSH
N - DUCKING STOOL PT. NATURAL MARSH

Figure 10. Mean lead concentrations in plant tissues collected from the Windmill Point experimental marsh and a natural marsh

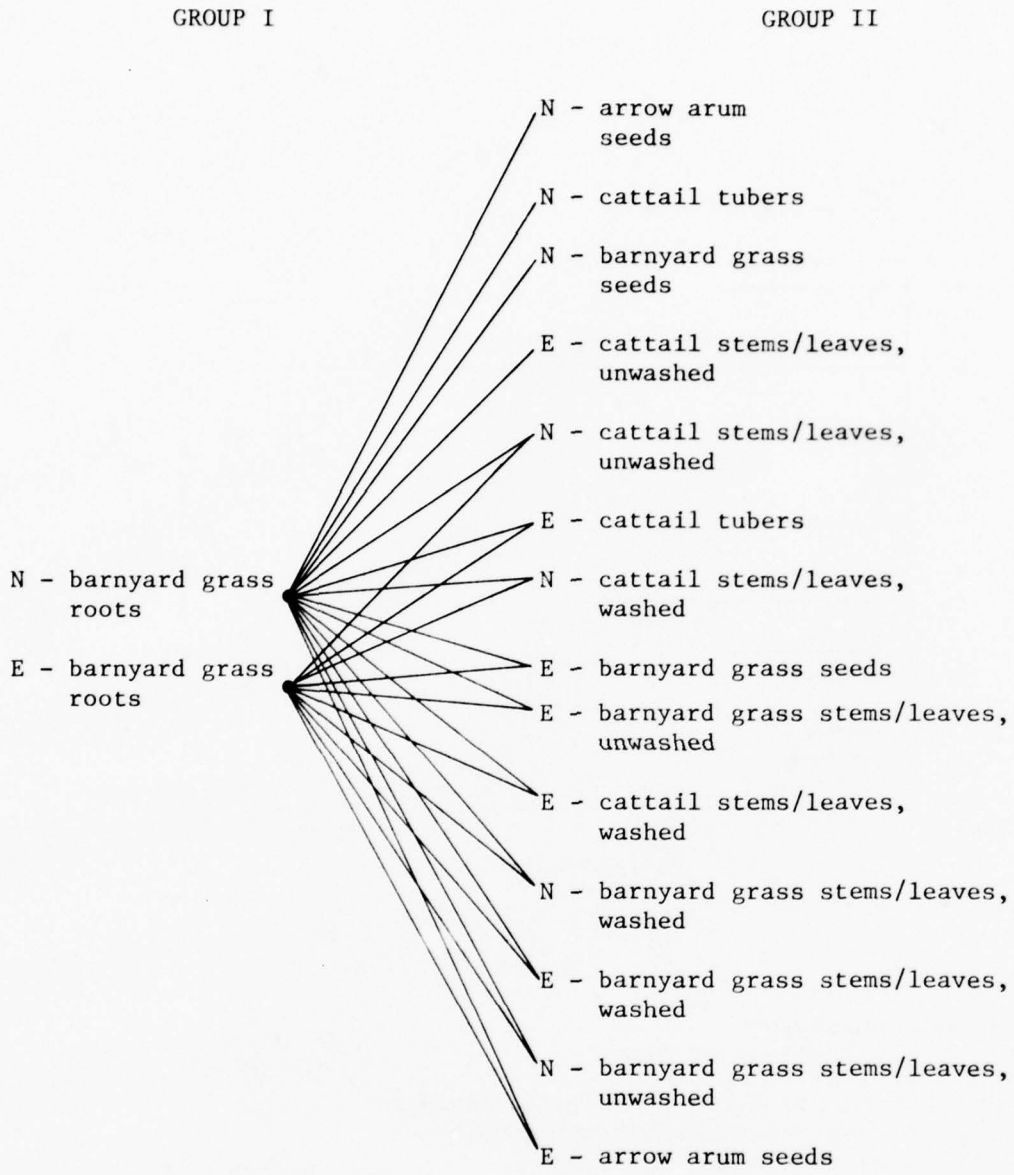


Figure 11. Differences in lead concentrations between marsh plant tissues. The prefixes N and E are used to identify the samples as natural or experimental marsh tissues, respectively. Tissues are listed from top to bottom, left to right, in order of decreasing mean lead concentration. Connecting lines identify significant concentration differences. Tissues in the same group did not contain different lead concentrations.

Lead concentration, soil and plant relationships

39. Estimates of total lead soil concentrations suggest that experimental marsh soil lead concentrations were higher than natural marsh soil lead concentrations (Table 6). Lead concentrations in soils did not correlate with lead concentrations in plant tissues. Mean plant tissue lead concentrations ranged from 1.3 to 9.32 ppm (Figure 10). At the experimental marsh, barnyard grass roots contained 6.4 and arrow arum seeds contained 1.3 ppm lead. Soil lead concentrations within the zones supporting these tissues had mean values equal to 65.48 and 61.40 ppm, respectively (Table 6).

Chlorinated Hydrocarbons

40. Studies of the behavior of chlorinated hydrocarbon compounds in natural systems are hampered by the variable and poorly understood concentration distributions of these compounds. The low frequency occurrence of detectable concentrations of most of the chlorinated hydrocarbon compounds in samples of marsh soils and vascular plant tissues collected during this study precluded the use of a rigorous statistical data analysis. With notable exceptions, the results of this portion of the study are presented descriptively and do not pretend any probability significance.

Chlorinated hydrocarbon compounds in marsh soils

41. Of the 15 chlorinated hydrocarbon compounds investigated by this study (aldrin, dieldrin, endrin, chlordane (both α and γ isomers), heptachlor, heptachlor epoxide, DDT, DDD, DDE, Kelthane, lindane, methoxychlor, Kepone, and Arochlor 1260 (PCB)), 7 were present in soils samples collected from any one of the three study marshes with a frequency of occurrence great enough to allow some estimate of variation. An estimate of variation was based on the occurrence of detectable concentrations of a compound in at least two of the five

soil samples collected from any soil zone of any study marsh. Mention is afforded those compounds that did not satisfy the frequency occurrence criteria. DDT and heptachlor each occurred in one soil sample collected during this study. DDT was collected in one sample from the Windmill Point experimental marsh; heptachlor was collected in one sample from the natural marsh located on Turkey Island. Table 7 identified the soils concentrations of singularly occurring compounds.

42. Of the 15 compounds studied, 7 were present in at least two out of five soil samples collected from a soil zone of at least one study marsh. These are identified in Table 8 with information on their location and frequency of detection.

Chlorinated hydrocarbon compounds in marsh plant tissues

43. The same frequency occurrence criteria applied to soils was applied to plant tissues to identify the variability of detectable chlorinated hydrocarbon concentrations (Table 9). Mention is afforded those compounds that were detected in only one of five plant tissues or tissue treatment samples collected from any marsh zone. DDD, heptachlor, and lindane occurred in single plant tissues from the Windmill Point experimental marsh; heptachlor and heptachlor epoxide occurred in single plant tissue samples from the natural marsh at Ducking Stool Point; DDD and dieldrin occurred in single plant tissue samples collected from the natural marsh located on Turkey Island. Table 10 identifies the plant tissue concentrations of singularly occurring compounds.

44. A comparison of the chlorinated hydrocarbon compounds detected in soils and plant tissue samples from either the singular occurrence or multiple occurrence categories identified three compounds detected in a plant tissue sample that were not detected in any soil samples. These were lindane and heptachlor at the Windmill Point experimental marsh, heptachlor and heptachlor epoxide at the natural Ducking Stool Point natural marsh, and dieldrin and heptachlor at the natural marsh on Turkey Island. Figures 12 through 16 present chlorinated hydrocarbon concentration distributions and variations in plant tissues by

Table 7

Chlorinated Hydrocarbon Concentrations in Soil Collected from the Windmill Point Experimental Marsh and Two Natural Marshes

(Concentrations are in parts per billion dry weight)

Soil Zone	DDT	DDD	DDE	α Chlordane	γ Chlordane	Heptachlor	Kelthane	Kepone	Arochlor 1260
a. Windmill Point Experimental Marsh									
Cattail-beggartick zone	b.d.*	13	26	5.0	4.2	b.d.	71	108	73
	b.d.	22	28	4.6	3.8	b.d.	70	220	56
	b.d.	7	28	3.9	3.3	b.d.	b.d.	300	92
	b.d.	18	35	3.9	3.7	b.d.	b.d.	260	91
	b.d.	7.6	29	b.d.	b.d.	b.d.	b.d.	312	94
Pickerel weed-arrow arum zone	6.5	42	14	7.2	5.6	b.d.	65	260	70
	b.d.	23	47	6.2	5.1	b.d.	b.d.	230	74
	b.d.	19	43	5.9	5.2	b.d.	b.d.	280	61
	b.d.	17	27	5.2	42	b.d.	b.d.	200	73
	b.d.	10	27	b.d.	b.d.	b.d.	b.d.	210	b.d.
Mudflat zone	b.d.	20	22	5.1	4.7	b.d.	23	450	94
	b.d.	16	27	3.8	3.5	b.d.	5.9	420	79
	b.d.	16	29	3.3	2.9	b.d.	82	510	61
	b.d.	14	15	4.1	3.5	b.d.	b.d.	240	75
	b.d.	14	35	b.d.	b.d.	b.d.	b.d.	820	71
b. Ducking Stool Point Natural Marsh									
Cattail-beggartick zone	b.d.	9.6	48	5.6	4.8	b.d.	35	60	b.d.
	b.d.	27	55	b.d.	b.d.	b.d.	b.d.	100	b.d.
	b.d.	14	24	b.d.	b.d.	b.d.	b.d.	148	b.d.
	b.d.	18	61	b.d.	b.d.	b.d.	b.d.	350	b.d.
	b.d.	b.d.	37	b.d.	b.d.	b.d.	b.d.	160	b.d.
Pickerel weed-arrow arum zone	b.d.	16	16	4.2	2.7	b.d.	61	24	50
	b.d.	11	11	b.d.	b.d.	b.d.	b.d.	37	b.d.
	b.d.	20	20	b.d.	b.d.	b.d.	b.d.	100	b.d.
	b.d.	26	26	b.d.	b.d.	b.d.	b.d.	15	b.d.
	b.d.	29	29	b.d.	b.d.	b.d.	b.d.	84	b.d.
Mudflat	b.d.	35	35	4.2	3.6	b.d.	86	130	61
	b.d.	32	32	b.d.	b.d.	b.d.	b.d.	59	47
	b.d.	22	22	b.d.	b.d.	b.d.	b.d.	170	75
	b.d.	36	36	b.d.	b.d.	b.d.	b.d.	120	b.d.
	b.d.	23	23	b.d.	b.d.	b.d.	b.d.	55	b.d.
c. Turkey Island Natural Marsh									
Cattail-beggartick zone	b.d.	28	28	b.d.	b.d.	4.2	82	38	b.d.
	b.d.	5.5	9	b.d.	b.d.	b.d.	86	15	b.d.
	b.d.	10	34	b.d.	b.d.	b.d.	b.d.	37	b.d.
	b.d.	9.4	33	b.d.	b.d.	b.d.	b.d.	61	b.d.
	b.d.	b.d.	31	b.d.	b.d.	b.d.	b.d.	31	b.d.
Pickerel weed-arrow arum zone	b.d.	6.8	8.7	b.d.	b.d.	b.d.	28	15	b.d.
	b.d.	b.d.	16	b.d.	b.d.	b.d.	41	10	b.d.
	b.d.	b.d.	13	b.d.	b.d.	b.d.	b.d.	39	b.d.
	b.d.	b.d.	16	b.d.	b.d.	b.d.	b.d.	14	b.d.
	b.d.	b.d.	26	b.d.	b.d.	b.d.	b.d.	13	b.d.
Mudflat zone	b.d.	15	25	2.5	3.7	b.d.	58	55	35
	b.d.	5.9	27	5.2	b.d.	b.d.	94	18	29
	b.d.	32	34	b.d.	b.d.	b.d.	110	70	110
	b.d.	b.d.	17	b.d.	b.d.	b.d.	81	46	b.d.
	b.d.	b.d.	64	b.d.	b.d.	b.d.	b.d.	88	b.d.

* b.d.-below detectable concentration for that particular compound.

Table 8

Frequency of Detectable Concentrations of Chlorinated Hydrocarbon Compounds of Soil Samples Collected from the Windmill Point Experimental Marsh and Two Natural Marshes

Area	Soil Code*	DDD	DDE	α Chlordane	γ Chlordane	Kelthane	Kepone	Arochlor 1260
Windmill Point	1	5	5	4	4	2	5	5
experimental	2	5	5	4	4	1	5	4
marsh	3	5	5	4	5	3	5	5
Ducking Stool	1	4	5	1	1	1	5	0
Point natural	2	1	5	1	1	1	5	1
marsh	3	3	5	1	1	1	5	3
Turkey Island	1	4	5	0	0	2	5	0
natural marsh	2	1	5	0	0	2	5	0
	3	3	5	2	1	4	5	3

* Numbers refer to soil study zones. Zones 1, 2, and 3 are the cattail-beggartick, pickerel weed-arrow arum, and mudflat zones, respectively.

Table 9

Frequency of Detectable Concentrations of Chlorinated Hydrocarbon Compounds in Plant Tissues Collected from the Windmill Point Experimental Marsh and Two Natural Marshes

Area	Plant Tissue Code*	DDE	Chlordane	Kelthane	Kepone	Arochlor 1260
Windmill Point	E - 1**	9	0	3	4	0
experimental	T - 1†	3	0	2	4	0
marsh	P - 2††	2	0	1	0	0
Ducking Stool	E - 1**	6	1	0	6	3
Point nat-	T - 1†	2	0	0	4	2
ural marsh	P - 2††	1	0	0	0	0
Turkey Island	E - 1**	2	2	0	2	0
natural	T - 1†	1	0	0	1	0
marsh	P - 2††	0	0	0	0	0

* Plant tissue codes refer to plant species (letter) and marsh soil zone (number). E - Echinochloa spp (barnyard grass), T - Typha spp (cattail), P - Peltandra virginica (arrow arum). For information on particular plant tissue concentrations, see Table 10.

** Out of a possible 20 samples: considering barnyard grass, roots, seeds, unwashed and washed stem/leaf tissues.

† Out of a possible 15 samples: considering tubers, washed and unwashed stem/leaf tissues.

†† Out of a possible 5 samples: considering seed tissue only.

Table 10

Chlorinated Hydrocarbon Concentrations in Plant Tissue Collected from the Windmill Point Experimental Marsh and Two Natural Marshes

(Concentrations are in parts per billion, wet weight)

Plant Tissue or Tissue Treatment	DDD	DDE	α Chlordane	γ Chlordane	Dieldrin	Heptachlor	Heptachlor-epoxide	Kelthane	Lindane	Kepone	Arochlor 1260
a. Windmill Point Experimental Marsh											
Arrow arum seeds	b.d.	3.3	b.d.	b.d.	b.d.	3.8	b.d.	23.0	b.d.	b.d.	b.d.
	b.d.	3.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass seeds	b.d.	9.7	b.d.	b.d.	b.d.	7.0	b.d.	13.0	b.d.	b.d.	b.d.
	b.d.	7.3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	9.5	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass roots	b.d.	6.5	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	26.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	39.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	56.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	83.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass stems and leaves, unwashed	b.d.	18.0	b.d.	b.d.	b.d.	7.4	b.d.	16.0	5.5	b.d.	b.d.
	b.d.	3.3	b.d	b.d.	b.d.	b.d.	b.d.	14.0	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass stems and leaves, washed	b.d.	9.5	b.d.	b.d.	b.d.	4.5	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	4.6	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	3.6	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail tubers	9.3	12.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	12.0	b.d.
	b.d.	3.9	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	23.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	20.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	28.7	b.d.
Cattail stems and leaves, unwashed	b.d.	3.0	b.d.	b.d.	b.d.	b.d.	b.d.	14.0	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail stems and leaves, washed	b.d.	b.d.	b.d.	2.5	b.d.	b.d.	b.d.	27.0	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.

(Continued)

Note: b.d. indicates below detectable concentration for the particular compound.

Table 10 (Continued)

Plant Tissue or Tissue Treatment	DDD	DDE	α Chlordane	γ Chlordane	Dieldrin	Heptachlor	Heptachlor-epoxide	Kelthane	Lindane	Kepone	Arochlor 1260
b. Ducking Stool Point Natural Marsh											
Arrow arum seeds	b.d.	7.4	b.d.	5.4	b.d.	8.0	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass seeds	b.d.	6.2	2.4	b.d.	b.d.	2.6	2.7	b.d.	b.d.	b.d.	b.d.
	b.d.	5.3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass roots	b.d.	5.1	b.d.	b.d.	b.d.	3.2	b.d.	b.d.	b.d.	25.0	27.0
	b.d.	9.6	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	14.0	31.0
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	48.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	42.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	40.0	b.d.
Barnyard grass stems and leaves, unwashed	b.d.	2.9	b.d.	b.d.	b.d.	2.5	3.2	b.d.	b.d.	b.d.	16.0
	b.d.	3.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass stems and leaves, washed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	10.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail tubers	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	18.0	16.0
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	38.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	29.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	45.0	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail stems and leaves, unwashed	b.d.	5.2	b.d.	b.d.	b.d.	3.7	b.d.	b.d.	b.d.	b.d.	35.0
	b.d.	5.2	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail stems and leaves, washed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.

(Continued)

Table 10 (Concluded)

Plant Tissue or Tissue Treatment	DDD	DDE	a Chlordane	γ Chlordane	Dieldrin	Heptachlor	Heptachlor-epoxide	Kelthane	Lindane	Kepone	Arochlor 1260
					c. Turkey Island Natural Marsh						
Arrow arum seeds	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	o.d.	b.d.	b.d.	b.d.
Barnyard grass seeds	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	43	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass roots	4.7	1.9	1.6	b.d.	5.5	b.d.	b.d.	b.d.	b.d.	11	b.d.
	b.d.	3.9	7.4	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass stems and leaves, unwashed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Barnyard grass stems and leaves, washed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail tubers	5.5	2.4	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	11	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail stems and leaves, unwashed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b .d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cattail stems and leaves, washed	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.

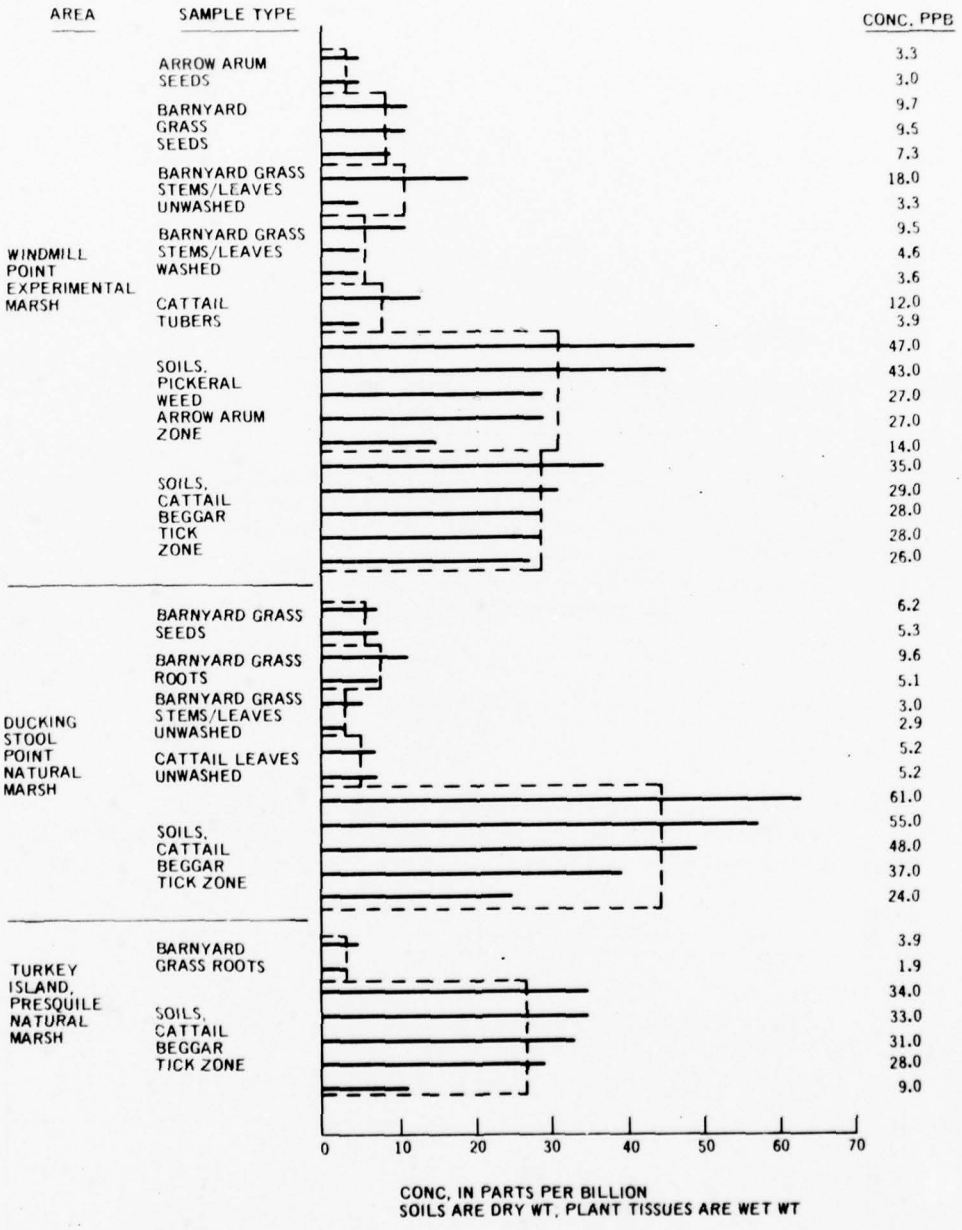


Figure 12. DDE concentrations in marsh soils and plant tissues collected from the Windmill Point experimental marsh and two natural marshes

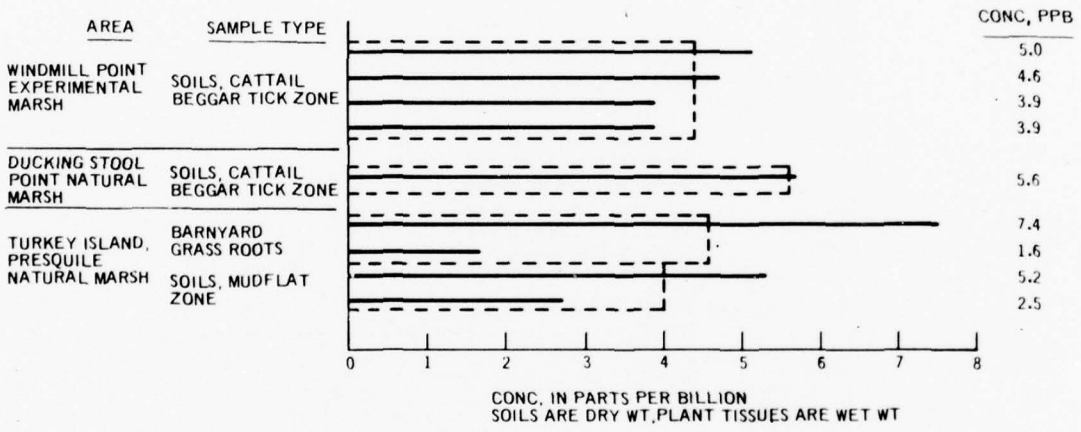


Figure 13. α chlordane concentrations in marsh soils and plant tissues collected from the Windmill Point experimental marsh and the two reference marshes

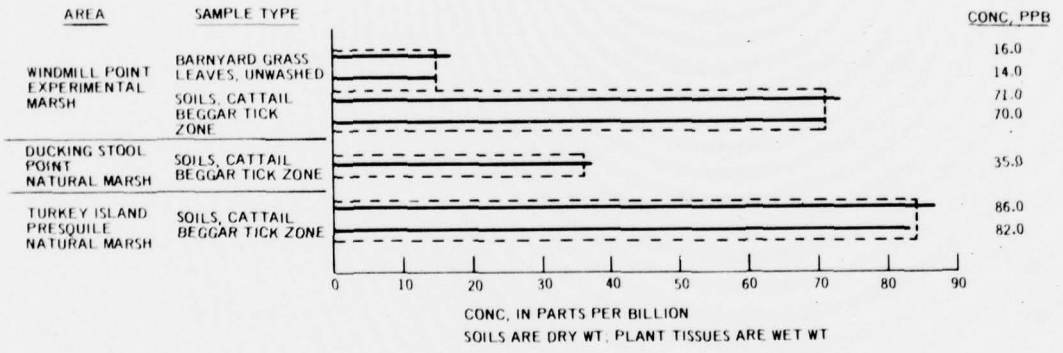


Figure 14. Kelthane concentrations in marsh soils and plant tissues collected from the Windmill Point experimental marsh and the two reference marshes

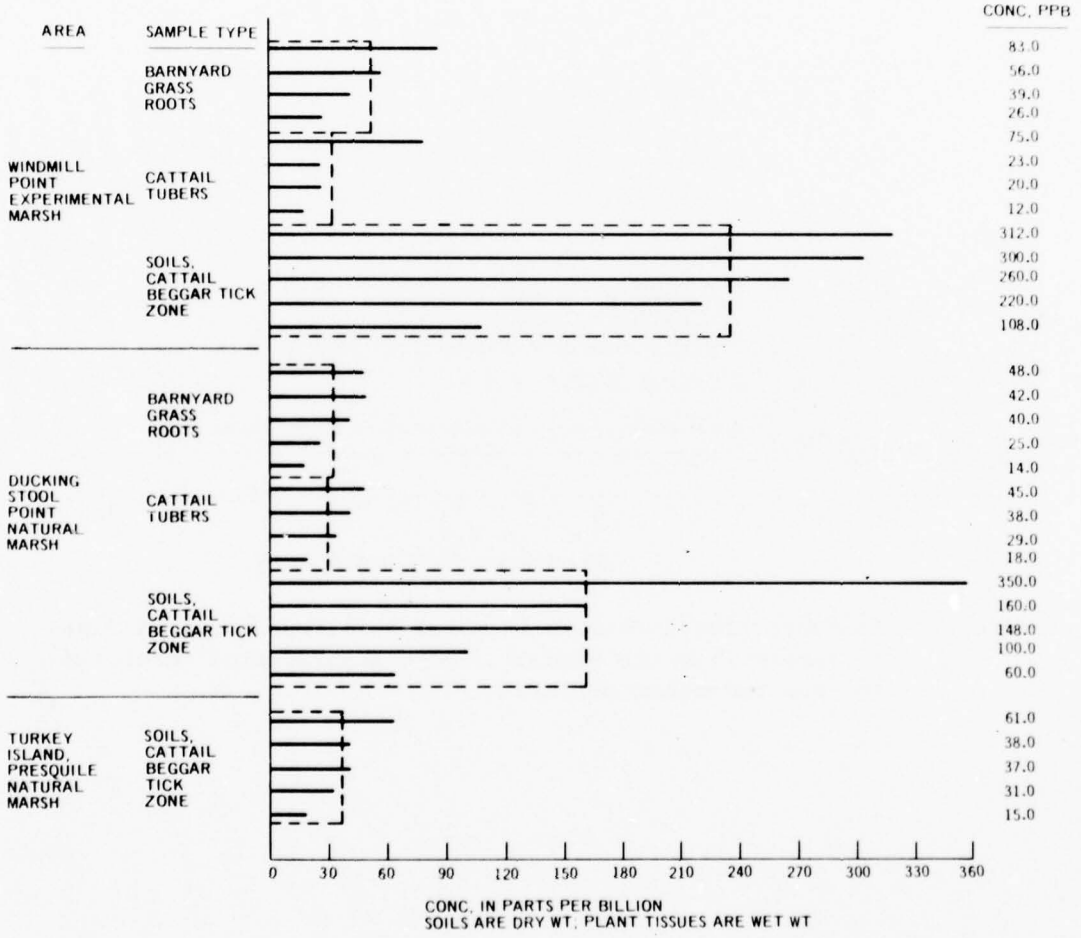


Figure 15. Kepone concentrations in marsh soils and plant tissues collected from the Windmill Point experimental marsh and the two reference marshes

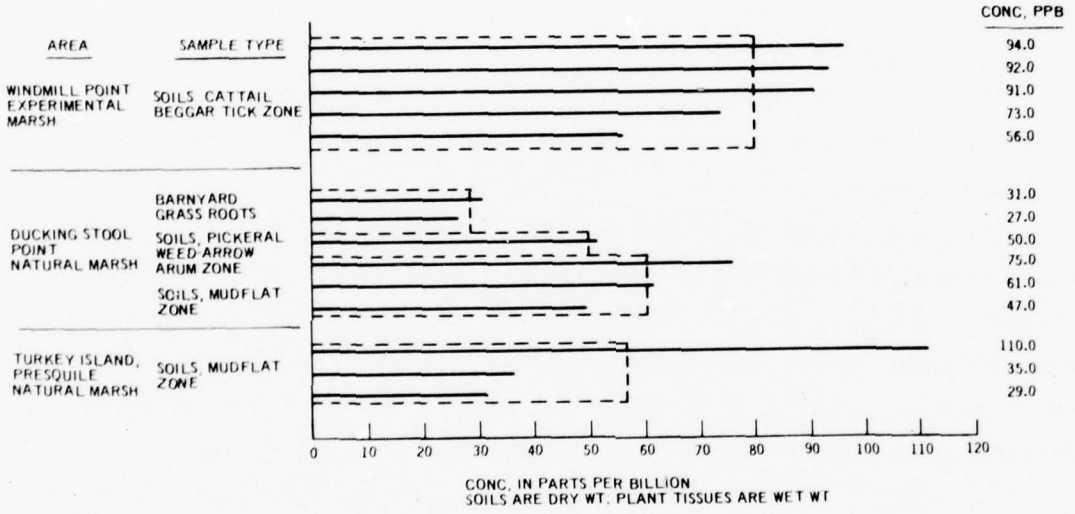


Figure 16. Arochlor 1260 (PCB) concentrations in marsh soils and plant tissues collected from the Windmill Point experimental marsh and the two reference marshes

compound and area. Soil zone concentrations are presented for the soil zone in which the plant tissue demonstrating detectable uptake occurred. If a plant species contained a compound not detected in its own soil zone, but in another soil zone of the same marsh, data for the other soil zone is presented in the figures. For example, α chlordane exhibited a significant frequency occurrence in barnyard grass roots collected from the Turkey Island natural marsh; the only Turkey Island soil zone containing α chlordane was the mudflat zone. The α chlordane concentration of soil samples from other mudflat zones is therefore presented in Figure 13.

Summary of results by compound

45. DDT. DDT was detected in only one soils sample collected from the Windmill Point experimental marsh. DDT was not detected in any plant tissue.

46. DDD. More soils samples collected from the Windmill Point experimental marsh contained detectable DDD concentrations than from either of the two natural marshes. Soil concentrations of DDD were not different between the three marshes. DDD occurred in one cattail tuber tissue sample from the Windmill Point experimental marsh and one cattail tuber tissue sample from the natural marsh at Turkey Island.

47. DDE. All soils samples from all marshes contained detectable DDE concentrations. The amount of data on DDE concentrations permitted a statistical analysis that suggested there were no DDE concentration differences between the three marshes. There were differences between soil zones but zone concentration trends were not consistent between marshes. Soil zone concentration trends are given in the following:

a. Windmill Point experimental marsh:

   low marsh = high marsh = mudflat

b. Ducking Stool Point natural marsh:

   high marsh > low marsh = mudflat

c. Turkey Island natural marsh:

   mudflat > high marsh = low marsh

48. DDE concentrations in soils and plant tissues at the three marshes are given in Figure 12. At the Windmill Point experimental marsh, DDE was present in seeds from both marsh zones, and in washed, unwashed stem and leaf tissues and root tissues from the high marsh zone. At the Ducking Stool Point marsh, DDE was detected in seeds, unwashed stem and leaf root tissue from the high marsh zone. Only barnyard grass roots from the high marsh on Turkey Island contained detectable DDE concentrations. The tissue washing procedure removed DDE from stem and leaf tissues from both the Windmill Point experimental marsh and the Ducking Stool Point natural marsh.

49. α chlordane. α chlordane was detected most frequently in soils from the Windmill Point experimental marsh, the frequency of occurrence in soils from the three marshes being: Windmill Point > Ducking Stool Point = Turkey Island. Soil α chlordane concentration differences between marshes could not be reliably compared because of the low number of detectable concentrations at both natural marshes. There were soil zone concentration differences at Windmill Point experimental marsh with the low marsh-pickerel weed - arrow arum soil zone containing higher α chlordane concentrations than either the high marsh or mudflat soil zones. α chlordane was not detected in any plant tissue samples collected at the Windmill Point experimental marsh, but did occur in one barnyard grass seed sample from the Ducking Stool Point marsh and in two barnyard grass root tissue samples from the Turkey Island marsh (Figure 13).

50. γ chlordane. γ chlordane exhibited a trend in soils very much like α chlordane. Based on the frequency of detectable γ chlordane concentrations, the soils of the Windmill Point experimental marsh contained more of this compound than either of the natural marshes. No statement could be made about soil γ chlordane concentration differences between the three marshes because the relative differences in concentration information prevented a fair comparison. An analysis of variance of the soil γ chlordane concentration data from the Windmill Point experimental marsh suggested there were no soil zone differences (this contrasts with the α chlordane results).

γ chlordane was detected in only one plant tissue sample, arrow arum seeds from the Ducking Stool Point marsh.

51. Dieldrin. Dieldrin was not detected in any marsh soils but was found in one barnyard grass root tissue sample from the Turkey Island natural marsh.

52. Heptachlor. Heptachlor was detected in one soils sample collected from the high marsh, cattail - beggar tick zone on Turkey Island. The frequency occurrence of detectable plant tissue heptachlor concentrations was very low at both the Windmill Point experimental marsh and the Ducking Stool Point natural marsh. Heptachlor occurred in single samples of four and five plant tissue or plant tissue treatments at the Windmill Point and Ducking Stool Point marshes, respectively. No plant tissues collected from the Turkey Island marsh contained any detectable heptachlor concentrations.

53. Heptachlor epoxide. Heptachlor epoxide was not detected in any marsh soils. One barnyard grass seed tissue sample and one unwashed stem and leaf tissue sample collected from the Ducking Stool Point natural marsh contained detectable heptachlor epoxide.

54. Kelthane. Soil Kelthane concentrations were most often detected in samples collected from the Turkey Island natural and Windmill Point experimental marshes. Kelthane was least often detected in Ducking Stool Point marsh soils. Based on sparse soil concentration data, it appeared that Kelthane concentrations in the high marsh soils of Turkey Island could be higher than those from the Windmill Point experimental marsh. Kelthane was detected only in plant tissues from the Windmill Point marsh, in most cases in a single tissue sample. The exception was its occurrence in two unwashed barnyard grass stem and leaf samples (Figure 14). No Kelthane concentration trends among the Windmill Point plants were observed.

55. Kepone. Kepone was detected in all soil samples from the three marshes. A statistical analysis of the soils Kepone concentration data indicated that, in general, the Windmill Point experimental marsh soils contained higher Kepone concentrations than the soils from the Ducking Stool Point natural marsh. Ducking Stool Point

marsh soils contained higher Kepone concentrations than soils collected from the natural marsh at Turkey Island. There were differences in concentrations between soil zones but there was no uniform trend among the marshes. Soil zone concentration trends are given in the following:

a. Windmill Point experimental marsh:

mudflat > low marsh = high marsh

b. Ducking Stool Point natural marsh:

high marsh = mudflat > low marsh

c. Turkey Island natural marsh:

mudflat = high marsh > low marsh

What this study defines as significant numbers of plant tissue samples containing Kepone were collected only from the Windmill Point experimental marsh and Ducking Stool Point natural marsh. At both marshes, Kepone was detected in barnyard grass roots and cattail tubers (Figure 15). There were adequate numbers of samples of both tissue types from both marshes to allow a two-tailed t-test of the concentration data which showed that there was no difference among the tissues at either marsh or between the tissue from the two marshes.

56. Arochlor 1260. More Windmill Point experimental marsh soil samples contained detectable Arochlor 1260 (PCB) than soil samples from the two natural marshes. Statistical analysis of the Windmill Point soils data suggested no concentration differences among the Windmill Point soil zones. A comparison between the mudflat PCB concentration data from the three sites showed no differences within this zone between the three marshes. Only plant tissues from the Ducking Stool Point marsh contained detectable PCB concentrations. The small number of these samples permit questionable inter-tissue comparisons. Arochlor 1260 was detected in the root and unwashed stem and leaf tissues from the Ducking Stool Point marsh (Figure 16).

PART IV: DISCUSSION

Metals

57. A decade of agricultural research has been concerned with the uptake of metals and their effects on the growth and reproduction of crop plants. More recently, since 1973 there have been many studies concerned with the effects of land application of municipal wastes, primarily sewage sludges. These studies have emphasized the effects of land waste-application on plant growth and reproduction and on the potential veterinary and public health hazards of metals accumulation in edible plant tissues.

58. Because marsh vascular plants are not considered agricultural crops and because marshes have not been candidates for sewage sludge disposal, studies have in most all cases not included them. But there are soil-plant-metal specific relationships that have emerged from these studies that are applicable to assessing the transfer of metals from marsh soils to marsh plants.

Bioavailability

59. The chemical state of a metal is crucial if it is to be incorporated by one organism and passed to another in a food web. The solubility and reactivity of trace metal complexes, whether they are around a plant root or in a food residue of an animal's digestive tract, are among the fundamental determinants of the distribution and fate of trace metal ions in plants and animals (Tiffin 1977). The bioavailability of a metal is related to its potential for solubility in a soil-water system coupled with characteristics of plant species exposed to the soluble metal forms. Jenne and Luoma (1976) suggested that the biological importance of solid forms of trace elements may be principally due to their regulation of equilibrium solute concentrations in the associated waters via sorption, desorption, and dissolution-precipitation reactions. These authors also stated that organic complexation of trace elements may enhance their availability to biota. Increased trace element uptake through complexation may

result from: (a) a decrease in the rate and extent of trace element sorption by sediments, (b) solubilization of solid forms of trace elements in soil and sediments, (c) a valence reduction or stabilization of the reduced valence state or vise versa, and (d) formation of physiologically active complexes.

Bioavailability of metals from sediment-water systems

60. The lack of correlation between the estimated total metals concentrations in the soils and marsh vascular plant tissues from the Windmill Point experimental marsh and the natural marsh is consistent with the experience of agricultural scientists and those few who have attempted to predict metal concentrations in marsh vascular plants based on total metals concentrations. Chemical extractants have been used to estimate the availability of trace elements to agricultural crops (Jenne and Luoma 1977) and marsh vascular plants (Lee et al. 1978) by removing a labile fraction of the element from the soil. The procedure is based on the natural partitioning of metals among various fractions of a soil-water solution and the fact that certain of these fractions represent reservoirs of metals more or less capable of being solubilized and thereby made available for plant uptake. Metals in solution within the soil/sediment interstitial water and exchangeable metal category are examples of readily available materials. Metals bound within the crystalline lattice of primary minerals are essentially unavailable. Between these two extremes, there may be quantities of metals associated in the fractions capable of releasing metals into solution as a result of chemical transformation in the sediment water system (Gambrell et al. 1977). A discussion of the plant-metals examined in this study and of the marsh soil-water conditions, in light of what is known about the bioavailability of these metals, follows.

Nickel

61. Nickel is the outstanding exception in this study as the only metal associated with the Windmill Point experimental marsh in higher concentrations than existed in the natural marsh. Nickel is

found in all soils, plants, and waters. The total nickel content in soils is commonly in the range of 10 to 100 ppm (Council for Agricultural Science and Technology 1976). The soil nickel concentrations at the experimental and natural marshes were about 16 and 25 ppm, respectively (Table 6). Extractable (labile) nickel seemed to be governed by the surfaces of iron and manganese hydroxides and oxides that act as a "sink" for nickel as well as by organic chelates, which complex weakly with nickel (Council for Agricultural Science and Technology 1976). Based on a study by Nivens (1978) as cited by Adams et al. (1978), who characterized metals in sediment samples collected from the experimental and natural marshes according to their various chemical fractions, the experimental marsh sediments contained more nickel in the easily reducible phase than the natural marsh sediments. The concentrations of nickel in the easily reducible phase (hydrous manganese hydroxides and oxides) in the sediments from the experimental and reference marshes were 4.22 and 1.07 ppm, respectively. Sediments in the reference marsh were generally less oxidized than sediments in the experimental marsh. The redox potential of the high marsh surface sediments at the experimental and natural marshes were measured at +274 mV and +192 mV, respectively. Toxicity of nickel to plants has been observed only on acid soils (Council for Agricultural Science and Technology 1976). Soil treatments such as liming reduce the solubility of nickel and its toxicity. Conditions of pH at the experimental site are not believed responsible for the observed nickel concentrations in plant tissue differences. Experimental marsh soil pH values were higher than pH values in the marshes at the natural marsh. Experimental marsh pH values averaged 6.41 ± .47 with values usually around 0.5 units higher than natural marsh sediments (Adams et al. 1978). Nickel has no known essential function in plants. It is toxic to plants in concentrations above 50 ppm in plant tissues (Council for Agricultural Science and Technology 1976). Mean concentrations ranged from 0.7 to 6.6 ppm in the various plant tissues analyzed during this study.

62. The occurrence of higher nickel concentrations in unwashed cattail stems and leaves from the experimental marsh, compared with

the reference marsh, and the reduction in those differences after washing the stems and leaves suggests the possibility of nickel transfer to these tissues from the water. There is no way to positively verify this possibility from this study's observations, but the importance of considering both water and sediments as sources of metals to plants is discussed by Mayes et al. (1977), who experimentally manipulated a rooted aquatic vascular plant (*Elodea canadensis*) among different substrate and water lead and cadmium concentration combinations and demonstrated the importance of both uptake routes.

Zinc

63. Zinc occurred in soils from the experimental and natural marshes in total mean concentrations from about 80 to 150 ppm, respectively. This compares with a total mean zinc concentration of 49 ppm in sediments collected from 25 marshes along the South Atlantic coast of the United States (Windom 1976). Windom described this mean South Atlantic concentration as representative of what metals levels in unpolluted sediments in the coastal littoral salt marsh environment should be. Zinc is an essential component of enzyme systems of both plants and animals. The most important mechanisms for zinc retention in soils are clay and hydrous iron oxide surfaces and chelation by organic matter. Zinc is taken up by plants as Zn^{+2}, which occurs in solutions under acid conditions. In excessive quantities it can be toxic to plants. When zinc toxicity does occur, tissues of most crops studied contain zinc at concentrations of several hundred ppm (Council for Agricultural Science and Technology 1976). Mean zinc concentrations in plant tissues analyzed during this study ranged from 25 ppm for cattail stems and leaves at the experimental marsh to 106 ppm in barnyard grass roots at the natural marsh.

64. Studies by Gambrell et al. (1977) with sediments containing zinc concentrations from 100 to 200 ppm indicated that pH and Eh strongly influence the soluble and exchangeable zinc fractions. Exchangeable zinc concentrations generally exceed soluble concentrations were .060 and 7.56 ppm. Soluble and exchangeable zinc fractions at the natural marsh were 0.067 and 8.56 ppm (Adams et al. 1978). The

same study indicates that zinc concentrations in the easily reducible fraction consisting of manganese oxides and hydroxides were 25.1 and 19.6 ppm, and organic fraction zinc concentrations were 12.0 and 14.1 ppm in the experimental and reference marshes. Concentrations of organic material were higher in the reference marsh (about 18 percent) than the experimental marsh (about 10 percent) and pH values were lower (by about 0.5 units) in the reference marsh. The characterization of the soil conditions at the two marshes together with the plant tissue zinc concentration results combines to produce a complex set of potential interactions effecting zinc solubility and availability for plant uptake. It is suggested that the higher concentrations of total zinc and lower pH values of soils at the natural marsh, which together might enhance potential for zinc soil to plant transfer, were mitigated by the higher concentration of organic material binding zinc to a solid, less available phase. The apparently high zinc concentrations in the roots of barnyard grass relative to concentrations in the other plant tissues is suggested to be at least in part surface contamination by adherent soil particles. The fine roots of barnyard grass made them more difficult to clean than the coarser form of cattail tubers. There is less of a suggestion of zinc transfer to plant tissues from water than occurred with nickel. There was no apparent effect from washing. The zinc tissue concentrations suggest more of an internal uptake or substrate transfer mode based on relative tissue concentration trends of relatively high values for all barnyard grass roots and cattail tuber tissues, barnyard grass and arrow arum seeds and lower values in cattail stems and leaves (Figure 2). These suggested uptake modes are speculative on the part of the author, based upon tissue zinc concentrations that were not different from each other at $\alpha = 0.05$.

Zinc toxicity by ingestion

65. A wide margin of safety exists between normal dietary intakes of zinc and the higher intake that may produce toxicity in birds and mammals (Council for Agricultural Science and Technology 1976). Pigs showed no ill effect when they received zinc sulfate and zinc carbonate in quantities to supply zinc concentrations of 1000 ppm in their diet.

Chromium

66. Unlike nickel and zinc, which are ubiquitous in plants, water, and soils, chromium is not readily available to plants from soils. Chromium in soils is not readily extracted by ionic exchange leaching solutions or chelating agents, but is extracted by strong acids indicating its association with less bioavailable soils fractions. Information in the literature presenting concern with chromium toxicity refers to the haxavalent chromium form, which is soluble and toxic to plants but which is reduced to the less soluble trivalent form under the reduced soil conditions characteristic of marshes. Chromium is unessential to plant growth and reports of its requirement by humans or animals are contradictory. McKee and Wolf (1971) state that there is no evidence that chromium salts are essential or beneficial to human nutrition. The Council for Agricultural Science and Technology (1976) states that chromium is required in the diets of animals and humans.

67. There were no clear patterns in chromium distribution among plant tissues examined in this study. Concentrations in plant tissues collected from both the experimental and reference marshes were similar (Figure 8) even though chromium concentrations in the experimental marsh soils were higher than natural marsh soil chromium levels (Table 6). Actual concentrations in plant tissues were consistent with values reported for upland experimental crops.

68. Clapp et al.* reported 4 ppm in corn stem/leaf tissues. Chromium is not generally considered an essential plant element, though the Council for Agricultural Science and Technology (1976) cites the existence of reports of slight plant yield increases with chromium additions. A question may be raised about the effects of chromium uptake on marsh plant growth and development because of information from literature citations of upland experiments. Schueneman (1974) observed field beans with 30 ppm chromium grown on soil containing 200 ppm and reported a yield reduction of 25 percent. Yield reductions

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* Unpublished data prepared by C. E. Clapp, R. H. Dowdy, and E. Larson, 1976. Agricultural Research Service, U. S. Department of Agriculture, St. Paul, Minn.

in tomato plants, which achieved chromium concentrations as high as 35 ppm, were observed at tissue concentrations as low as 5 ppm.

69. Chromium concentrations presented by this study were highest in the root tissues of barnyard grass and the seeds of barnyard grass at both the experimental and the natural sites. The tissue washing procedure effected a reduction in the concentration of chromium in cattail stems and leaves suggested the possibility of transfer by surface contamination. The naked seeds of barnyard grass could have been exposed to the same contamination as the cattail leaves. As was the case for zinc, the relatively high root tissue concentrations are believed, in part at least, to be caused by chromium contamination for adherent soil particles.

Cadmium

70. Like chromium, cadmium concentrations in plant tissues analyzed by this study were no different between the experimental and reference marshes. Soil concentrations of about 12 and 3 ppm at the experimental and natural marshes were higher than the soil values from 0.01 to 7.0 ppm reported by Allaway (1968) for upland areas and the mean concentration of 1.4 ppm reported by Windom (1976) for 25 South Atlantic unpolluted coastal salt marshes. Cadmium concentrations in marsh plant tissues including the barnyard grass roots that contained the highest concentrations of 0.72 ppm were within or below the range of concentrations for untreated (control) experimental crops grown on fine-textured upland soils by Giordano and Mays (1977).

71. Cadmium is probably the source of more plant uptake concern than any other metal studied because of its linkage to certain human and veterinary health problems and the cumulative characteristics of cadmium in humans and animals from low level exposure.

72. The concentration and speciation of cadmium in soil and water systems appears to be influenced by organic and water contents, clay content and type, the presence of iron and manganese oxides and hydroxides, inorganic salts like carbonates, sulfides and chlorides, and soil pH and redox potential (Gambrell et al. 1977, Council for Agricultural Science and Technology 1976). More than

the other metals studied, cadmium mobilization to available forms is controlled by soil pH and redox conditions potentially modified by dredged material disposal options. Conditions effecting an increase in soil oxidation and a reduction in soil pH increase soluble cadmium concentrations and plant uptake. In reduced sediment conditions at pH 5.0 to 6.6, cadmium is not solubilized even with increasing concentrations (Gambrell et al. 1977). Under the soil conditions of reduced to slightly oxidized Eh values and soil pH values between 5 and 6.6 of the experimental and natural marsh substrates (Adams et al. 1978) cadmium uptake by plants was the same and suggested as unproductive of any potential health hazard.

73. Tissue cadmium concentration trends, based on a subjective evaluation of mean tissue cadmium concentrations, suggest possible internal translocations of cadmium through the plant species studied. This is based on the cadmium concentrations in the roots and seeds of plants from both types of marshes relative to stem and leaf tissue concentrations and the absence of any apparent reduction in cadmium concentrations after the tissue washing procedure. Based on the studies of cadmium uptake by the rooted freshwater marsh plant *Elodea canadensis* (Mayes et al. 1977) the sources of cadmium to the plants studied could have been either the marsh soils or the waters flooding the marshes.

Lead

74. Mean total concentrations of lead in the soils of the experimental and natural marshes were about 63 to 37 ppm. Soils from unpolluted coastal salt marshes of the South Atlantic coastal United States (Windom 1976) contained a mean lead concentration of 17 ppm. Despite the higher soil lead values at the Windmill Point experimental marsh relative to the natural marsh, lead concentrations in plant tissues of the experimental marsh were not elevated. The possibility that lead was more concentrated in the natural marsh plant tissues was mentioned in the results section. As with all other metals studied during this project, concentrations of lead were highest in the roots of barnyard grass. This was evident at both marshes and is attributed

primarily to contamination of the root tissue by adherent soils particles. A reduction in the lead concentration of cattail stem/leaf tissues from the experimental site suggests a site specific importance of plant tissues surface contamination from either air or water sources.

75. Lead is a non-essential element with low toxicity to plants and high potential animal toxicity. Plants take up lead in the ionic form from soils. Soluble lead added to soils reacts with clays, labile phosphates and organic material all of which effect a reduction in lead solubility. The Council for Agricultural Science and Technology (1976) cites Cox and Rains (1972), who observed a reduction in lead uptake by 5 plant species from lead contaminated soils after liming, and Hassett (1974), who related the lead sorption capacity of Illinois soils to cation exchange capacity, pH, and extractable phosphorous content.

76. Studies by Gambrell et al. (1977) indicate that lead availability is most influenced by pH, the availability increasing with lower pH. This same study identified the association of lead with hydrous oxides and found that much of the potentially available lead was associated with large molecular weight humic acids.

77. Data from Adams et al. (1978) identify a number of soil conditions relevant to considerations of the lead availability in soils at the Windmill Point area natural marshes.

78. Lead concentrations associated with the various soluble, exchangeable, reducible, organic, and residual soil fractions were not different. The pH of the soils from the natural marsh were lower by an average of about 0.5 pH units while cation exchange values at the natural marsh were approximately twice the values at the experimental marsh (60 vs 30 meq/100 g NaEc). Statements of cause and effect between soil lead species concentrations and plant tissue concentrations would be purely speculative given the data available from this study. As with zince, the solubility of lead is the net result of a number of interrelated physical and chemical conditions. Naturally reduced aquatic or marsh substrate conditions appear to limit the availability and potential toxicity of lead.

Chlorinated Hydrocarbons

79. Chlorinated hydrocarbon concentration data from marsh soils and plant tissues was reviewed considering: (a) available information documenting the uptake of chlorinated hydrocarbon compounds by plants, (b) the mechanisms of transfer to plant tissues, and (c) soil conditions affecting plant chlorinated hydrocarbon uptake.

Relationships among the chlorinated hydrocarbon compounds detailed in this study

80. For purposes of streamlining the discussion, compounds are grouped according to known chemical similarities or relationships that can be useful in understanding reasons for some of the observed concentration trends.

81. DDT, DDD, DDE, and Kelthane. DDD and DDE are both degradation products of the insecticide DDT. Dicofol, known by the commercial name Kelthane, is a DDT-like compound without insecticidal properties and is classified as an acaricide for use in the control of mites on a wide range of crops. DDT can be converted to dicofol by insects (Brooks 1974) and dicofol was converted to DDE by rats (Menzie 1978). The interrelationship between these compounds therefore is established by their identification as common breakdown products of different chlorinated hydrocarbon compounds or their existence as parent compounds of the same degradation products.

82. α-chlordane, γ-chlordane, heptachlor and heptachlor epoxide. Technical chlordane is contaminated by technical heptachlor and vise versa. Technical chlordane is a misture of chemically similar chlordane isomers including α, β, and γ chlordanes present in ratios that vary between production batches. Heptachlor degrades to heptachlor epoxide in plants and animals and heptachlor epoxide was detected in plant tissues following chlordane applications (Nash 1974, Menzie 1978). Like DDT and its related compounds this group of chlorinated hydrocarbons is interrelated by common degradation products.

83. Dieldrin. Dieldrin is the degradation product of aldrin.

Aldrin conversion to dieldrin by a variety of plants has been demonstrated (Nash 1974, Menzie 1978).

84. Kepone. Kepone is the trademark for the chlorinated hydrocarbon compound chlordecone and is unrelated to any other compound studied by this project.

84. Arochlor 1260. Arochlor 1260 is the trademark for a specific form of polychlorinated biphenyl (PCB) and is unrelated to any other compound studied by this project.

Bioavailability of chlorinated hydrocarbon compounds

85. The concept of bioavailability presented in the discussion about metals is also relevant to chlorinated hydrocarbon compounds. Nash (1974), in a review of the literature on plant uptake of insecticides and other organic compounds, suggests that there are two mechanisms effecting plant uptake. Plants may take up chlorinated hydrocarbons by adsorption with translocation to aerial plant parts or by sorption by root crops or aerial tissues. The potential for either uptake mode depends on an array of conditions including the characteristics of the compound, its concentration in the environment, and the plant species and soil characteristics. As with metals, uptake appears to be enhanced by solubility in the soil reservoir and reduced by conditions that tend to bind the chlorinated hydrocarbons to solid soil particles.

Marsh plant-soil relationships and chlorinated hydrocarbons

86. There was no consistent correlation considering either the frequency occurrence or the concentration data between marsh soils and marsh plant tissues even though there were differences in soils chlorinated hydrocarbon concentrations between the Windmill Point experimental marsh and the two natural marshes. This observation suggests the existence of conditions that limited the transfer of chlorinated hydrocarbon compounds from marsh soils to marsh vascular vegetation.

87. DDT, DDD, DDE, and Kelthane. DDT and its degradation products (excepting Kelthane) have been studied more than any other chlorinated

hydrocarbon insecticide. The persistance of DDT is apparently decreased by the conversion of DDT to DDD and DDE under conditions characteristic of marsh environments. DDT conversion to DDD occurs rapidly under reduced conditions where its degradation is catalyzed by reduced iron porphyrins. DDT conversion to DDE occurs slowly in soil but rapidly in animal tissues (Zoro et al. 1974). Concentrations of DDT in plants range from 7.5 ppm in root crops to 0 to 10 ppm in field crops with values at the high end of the range associated with suspected plant tissue soil contamination (Nash 1974). Plant tissues are readily contaminated by foliar sorption of volatilized DDT, DDE, or DDD, which seems to be a more important mechanism for soil to plant transfer than root adsorption (Nash and Woolson 1967). Volatilization is a mechanism of loss from soils (Farmer and Letey 1974). Volatilization is enhanced by physical disturbance and microtillage by bioturbation (either plant or animal), a type of physical distrubance (Nash and Woolson 1967). Conditions that enhance volatilization such as temperature gradients, air flow, etc., i.e., conditions that effect the vapor pressure of volatile compounds at a soil-air or soil-water interface, are favored by marsh conditions. Reduced soils and periodic inundation and exposure of marsh soils compared with a constantly inundated aquatic environment favor volatilization.

88. The occurrence of DDT in the experimental marsh recently constructed with navigation channel sediments, although detected in only one sample, could be explained in this fashion. The foliar sorption via volatilization of DDE transfer to plant tissues collected from both the Windmill Point experimental and Ducking Stool Point natural marshes is supported by the reduction in DDE concentrations by washing stem and leaf tissues collected from both sites. Organic material in soils effected a decrease in DDT uptake in soybeans and cotton (Nash et al. 1970); uptake of DDT by wheat was decreased in soils with near neutral pH, higher CEC and higher organic matter.

89. Windmill Point experimental marsh and Ducking Stool Point natural marsh soils data was reported by Adams et al. (1978). It can be assumed that soil conditions at the Turkey Island marsh were

similar to the Ducking Stool Point marsh than at the experimental marsh, these soil conditions help explain the frequency occurrence of DDE in plant tissue between sites. DDE occurred more often and in a greater variety of plant tissues from the Windmill Point marsh. The soil conditions at the Windmill Point marsh were less acid (avg pH = 6.4) than the natural marsh soils, and had a lower organic content (10 vs 18 percent) and cation exchange capacity (30 vs 60 meq/100 g). The Kelthane data are mysterious and no information was available in the author's literature to assist its interpretation. Based on its chemical structure it would be expected to be more hydrophilic and less lipophilic than DDT suggesting a greater bioavailability and lower bioaccumulation potential. Its detection in small numbers (5 of 40) of a large variety of plant tissue or tissue treatment samples (5 of 8) from the Windmill Point experimental marsh compared with the lack of detectable Kelthane concentrations in any tissues from the Turkey Island natural marsh under similar soil concentrations and frequency detection conditions remains unexplained.

90. α-chlordane, γ-chlordane, heptachlor, and heptachlor epoxide. Chlordane isomers and heptachlor have been studied during experiments with root crops because of their tendency for root sorption. Residues were found mostly in the root peel or surface with very little in the plant (Beall and Nash 1971, Nash 1974). As with DDT, organic matter effected a decrease in heptachlor uptake by soybeans and cotton (Nash et al. 1970). Heptachlor applied to soils (which occurs with either technical heptachlor application or technical chlordane application) was recovered in plant tissues as heptachlor epoxide (Nash 1974). No chlordane isomers were detected in the plant tissue samples collected from the Windmill Point experimental marsh, and except for the occurrence of γ chlordane in two barnyard grass root tissue samples collected from the Turkey Island marsh, there was no mentionable chlordane transfer to marsh plants. The reasons for the observed data cannot be explained. Heptachlor and heptachlor epoxide concentrations were detected only in single tissues or tissue treatments of plants collected from the Windmill Point and Ducking Stool Point marshes. Based on

the sparse data (Table 10) no defendable interpretation could be presented.

91. Dieldrin. The lack of detectable concentrations in any of the marsh soil samples and its detectable presence in only one plant tissue sample collected from the Turkey Island natural marsh excludes it from further discussion.

92. Kepone. The discharge of Kepone from the Life Science Products Company in Hopewell, Va., to the sewage treatment plant, followed by the closure of Life Science Products Company on 23 July 1975, led to the HDP awareness of the contamination of the James River sediments with Kepone. Subsequent studies reported by Hansen et al. (1976), U. S. Army Engineer District, Norfolk (1976) and Gregory (1976)* identified Kepone as a highly toxic and bioaccumulative chlorinated hydrocarbon compound. The concentration distribution of Kepone in the James River sediments was reported by Gregory (1976) as 10,000 ppb in Bailey's Creek sediments at the mouth of the Hopewell sewage treatment plant (Figure 17) and 20 to 90 ppm at Windmill Point (Figure 18). If it is assumed that a simple relationship exists between the water solubility of Kepone and its availability to plant tissues, then Kepone uptake might be expected by the plant tissues studied. According to Brooks (1974), Kepone is stable, dissolves in strong aqueous alkaline solutions, and readily forms hydrates. Brooks states that water solubility is low, as usual (for chlorinated hydrocarbon insecticides**). Saleh et al. (1978) reported that only lindane (which is 2,000 times more water soluble than DDT according to Nash (1974)), Kepone, and total PCBs were present in measurable concentrations in centrifuged supernatent elutriate from Bailey Creek sediments. These authors suggested that Kepone and PCBs exhibited a behavior different from other chlorinated hydrocarbons under investigation.

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* "Kepone levels in sediments and water in the Chesapeake Bay System," by R. Gregory. Paper presented at the Kepone Workshop at Virginia Institute of Marine Science, Gloucester Point, Va.

** Author's statement of clarification.

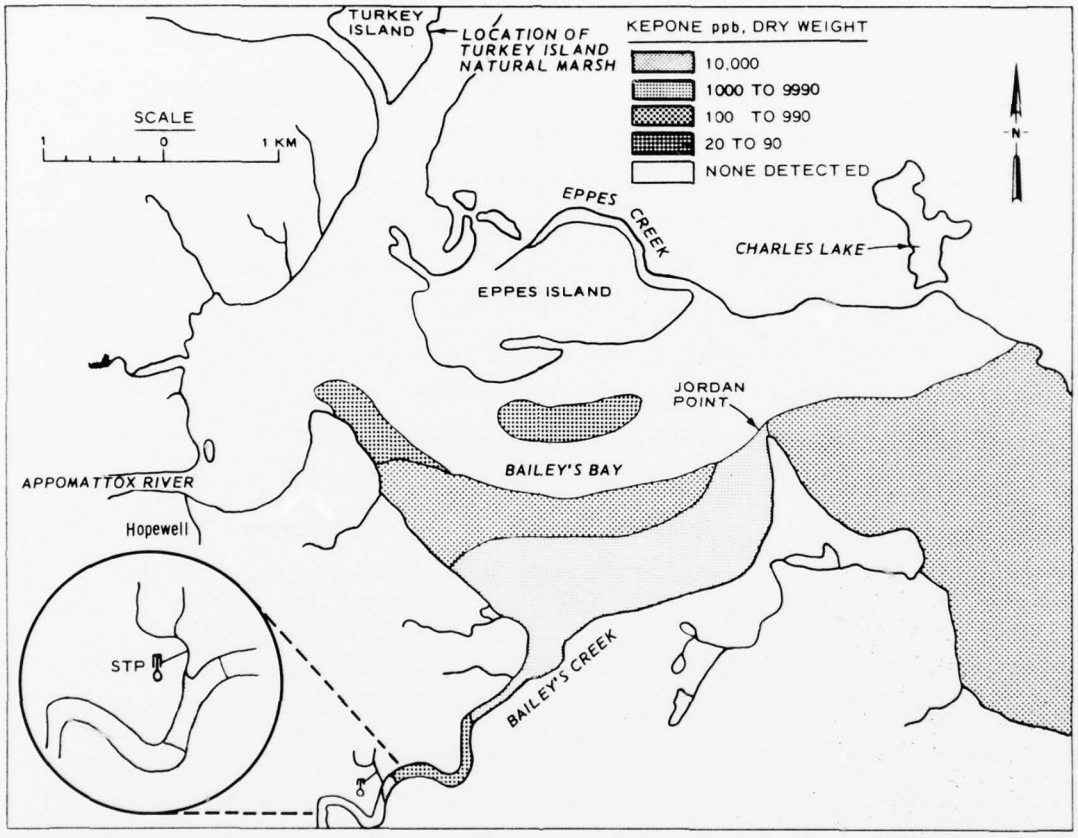

Figure 17. Sediment Kepone concentrations in the top four centimetres, Bailey's Bay area

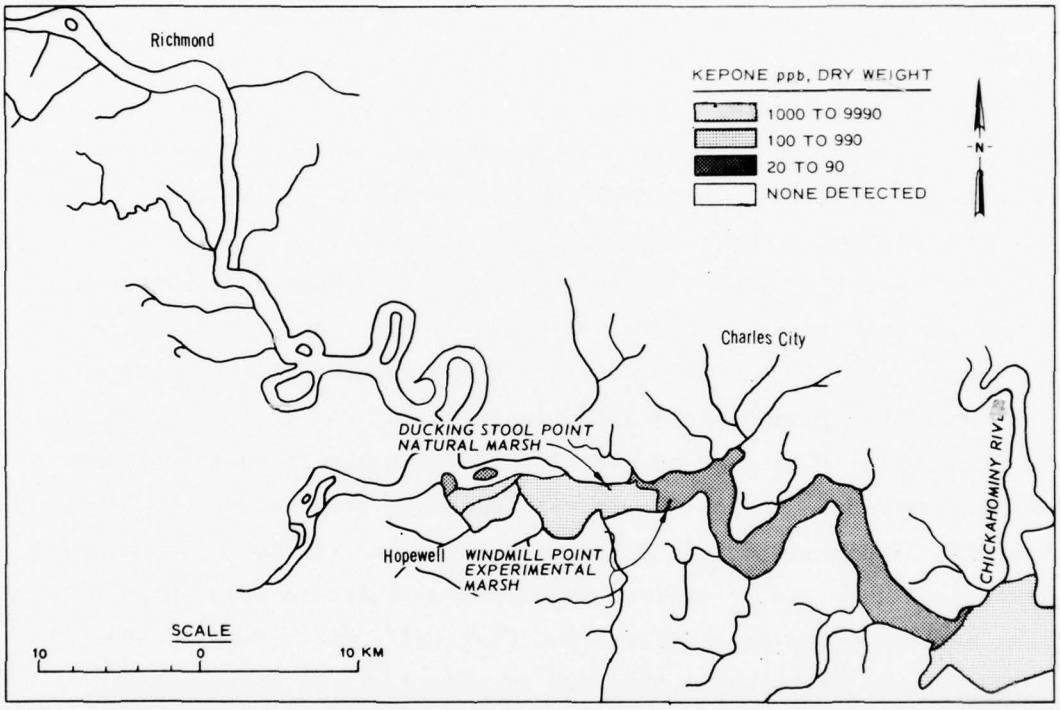

Figure 18. Sediment Kepone concentrations in the top four centimetres, Richmond to Chickahominy River

93. The large differences in the soil concentration of Kepone collected from the Windmill Point experimental and the two natural marshes do not correlate with plant tissue concentration relationships. Despite the large differences between soil sample concentrations from the Windmill Point experimental marsh and the Ducking Stool Point natural marsh, plant tissues containing detectable Kepone were not different in their concentrations. The lack of detectable Kepone in any aerial plant tissues suggests that there was no absorption and translocation to aerial tissues. The concentrations in the root tissues of barnyard grass and cattail at both downstream marshes identifies conditions that could be the result of either root surface sorption or adherent soils contamination.

94. Arochlor 1260. Unlike the other chlorinated hydrocarbon compounds studied during this project, Arochlor 1260 is not an insecticide. It has not been studied by the agricultural community concerned with plant uptake effecting reduced crop yield. Arochlor 1260 and other PCBs such as Arochlor 1254 are structurally related to DDT-like compounds and subject to the same properties of resistance to rapid degradation, relatively low water solubility, and high fat solubility. As a result they have been characterized as persistent and bioaccumulative (Zitko and Choi 1971, Risebrough and de Lappe 1972). Based on numerous observed incidents of PCB accumulation in filter-finding and suspension-feeding shellfish like oysters and mussels (Lincer et al. 1976), PCB concentrations have been related to particulate organic material. Information about factors affecting the solubility of PCBs are useful for interpreting plant uptake data. Pavlou et al. (1978) reported that PCBs are distributed by equilibrium partitioning between the water, sediments and suspended material (living or dead) and indicates that a reequilibration may occur when PCB contaminated sediments are moved to a less contaminated environment. Saleh et al (1978) state that PCBs behave differently than a variety of other chlorinated hydrocarbons including DDT, DDD, DDE, dieldrin, endrin, heptachlor, etc. These authors suggest that PCBs are either more soluble or more assoicated with colloidal particles

than most other chlorinated hydrocarbon compounds.

95. The high frequency of occurrence of detectable PCB concentrations in the Windmill Point experimental marsh soils and the apparently higher concentrations of Arochlor 1260 in the soils of the experimental marsh (if soil zones are pooled) than occurred in either of the natural marshes was not reflected in plant tissue samples. Neither Windmill Point nor Turkey Island marsh plant tissue samples contained detectable PCB residues. At the Ducking Stool Point natural marsh, detectable Arochlor 1260 in root tissues of cattail and barnyard grass and unwashed stem and leaf tissues of barnyard grass and cattail suggests that root sorption and foliar contamination might have been the plant uptake routes.

PART V: CONCLUSIONS

Metals

96. Estimated total soil metals concentrations resulting from a wet ashing (nitric acid) extraction procedure cannot be used to evaluate the potential transfer of nickel, zinc, chromium, cadmium, or lead from dredged material to marsh plant tissues under conditions of freshwater marsh habitat development.

97. Total concentrations of chromium, cadmium, and lead in the soil of a dredged material marsh did not effect an increase in those metals in marsh plants growing in those soils, as indicated by comparison with marsh plant metal uptake from natural marsh soils containing lower concentrations.

98. Nickel was the only metal studied that could be identified in an experimental (dredged material) marsh plant tissue at higher levels than existed in a similar plant tissue from a natural marsh.

99. Metal concentrations within the same plant tissue types and among different plant tissue types generally exceeded metal concentration differences between samples collected from a dredged material and natural marsh.

100. Gross plant tissue morphology, related to a potential for metals contamination by adherent soil particles, is probably a primary determinant of tissue metal concentrations. Plant tissue washing procedures designed to remove metal contaminants from plant leaf and stem surfaces are valuable in assisting the interpretation of metals uptake data.

101. Natural, physical, and chemical processes dominating marsh soil-water systems seemed to effectively immobilize nickel, zinc, cadmium, chromium, and lead to insoluble soil fractions, thereby reducing the transfer of these metals from the freshwater marsh substrate to marsh vascular vegetation.

Chlorinated Hydrocarbons

102. Chlorinated hydrocarbon compound levels in marsh soils, based on frequency occurrence of detectable concentrations or actual concentration values, were not correlated with the frequency occurrence of detectable concentrations or actual concentration values in marsh vascular plant tissues.

103. A higher frequency of detectable concentrations of DDD, α and γ chlordane, and Arochlor 1260, observed in soil samples collected from the Windmill Point experimental marsh as compared with observations in two natural marshes, was not related to the frequency of detection of these compounds in plant tissues. DDE and Kelthane were detected most frequently in plant samples collected from the Windmill Point experimental marsh.

104. Kepone was detected in all marsh soils studied. Soil Kepone concentrations were higher at the Windmill Point experimental marsh, compared with the natural marsh at Ducking Stool Point, and Ducking Stool Point marsh soil concentrations were higher than concentrations in the soils collected from the Turkey Island marsh located upstream from Hopewell, Va. Kepone was detected with the same frequency in the same plant tissues of both the Windmill Point and Ducking Stool Point marshes, and there were no differences in relative plant tissue Kepone concentrations between these marshes. A few of the same kinds of plant tissue samples collected from the Turkey Island natural marsh contained apparently lower Kepone concentrations, but significance of the data was not testable because of the low number of detectable concentrations.

105. DDE and Kepone were detected more often in marsh soils and plant tissue samples than any other compound studied.

106. Heptachlor epoxide and dieldrin were detected in marsh plant tissues but not in marsh soils.

107. Soil conditions affecting the association of chlorinated hydrocarbon compounds with particulate soil phases, thereby decreasing solubility or volatilization, reduce the transfer of these compounds

from marsh soils to marsh vegetation. Important conditions appear to be soil organic content, cation exchange capacity and pH.

108. Chlorinated hydrocarbon compounds may be transferred from marsh soils to marsh vegetation by either root absorption and tissue translocation or by sorption to root or aerial plant tissues.

109. Plant tissue washing procedures designed to remove chlorinated hydrocarbon contaminants from stem and leaf surfaces are valuable in assisting the interpretation of chlorinated hydrocarbon uptake data.

109. Chlorinated hydrocarbon concentration levels detected in marsh soils and marsh plant tissues during this study were generally lower than values reported in upland soils and crop plants by the scientific literature.

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