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Pesticide Residue in Barrier Island Salt Marshes Along the Indian River Lagoon

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This project was to document the occurrence and mobility of chlorinated pesticides in the St. Lucie County Mosquito Control salt marsh impoundments. A total of 128 sediment samples were collected and analyzed. The results show that ten sediment samples from eight impoundments were found to contain p,p'-DDE. The concentration ranged between 1.87 ng/g and 31.2 ng/g. Six sediment samples from three impoundments contained dieldrin ranging between 2.54 ng/g to 43.2 ng/g. Lindane (y-BHC) was found in most of the impoundments. A total of 33 sediment samples from 11 impoundments were found to contain lindane and the concentration ranged between 0.85 ng/g to 34.4 ng/g. Core water samples from each impoundment, surface water samples, discharging water from both impoundments 1 and 2, and water samples from the Indian River Lagoon were also collected in order to examine the potential for water-borne exchange of pesticides between the estuary and the impoundments. A total of 146 water samples were analyzed and found to have non-detectable concentrations ($\leq$0.01 ug/l). The study concludes that either lindane, dieldrine, or p,p'-DDE were found in most of the impoundments. They were largely concentrated in the surficial layer of sediment, which had proportionately higher levels of organic muck. Pesticide levels in the impoundment waters and adjacent watersof the Indian River Lagoon were non-detectable, thus restoration of marsh flushing appears to play no role in pesticide mobility within the scope of this study.

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EXECUTIVE SUMMARY
CM - 260
Pesticide Residue in Barrier Island Salt Marshes Along the Indian River Lagoon
Saint Lucie County, Florida

The purpose of the project was to determine the occurrence, flux and distribution of chlorinated pesticides in the Mosquito Control impoundments of Saint Lucie County and the possible role of marsh restoration in their existence and mobility. A total of 18 impoundments located on the barrier islands between the Indian River Lagoon and the Atlantic Ocean (on east coast of Florida) were screened by analyzing cores of sediment, groundwater and the above ground water-column for pesticides. The presence or absence of pesticides in the marsh substrate was established from the core samples. Water samples were obtained from each core and from perimeter culvert sites and from adjacent marsh and river areas, in order to document the presence or absence and mobility of the pesticides in the water column under contrasting management techniques. Two sediment core samples and two core hole water samples were collected from each impoundment. Each core sample was approximately six feet in length and was subdivided into two or three segments for analysis based upon major lithologic units. Each sediment core was subjected to grain-size analysis, compositional analysis and/or faunal analysis. Sediment composition was determined by the Loss on Ignition technique. The results of the pesticide survey indicated that 10 sediment samples from eight impoundments were found to contain p,p′-DDE (a degradation compound of DDT). The detected concentration ranged from 1.87 ng/g at impoundment 10A (site 2, top layer) to 31.2 ng/g at impoundment 23 (site 1, top layer). Impoundments 1, 2, 5, 10A, 16A, 18, 19B and 23 were detected to contain p,p′-DDE in at least one core sample. These impoundments are located on the central and north sections of the study area. Six sediment samples from three impoundments contained dieldrin, ranging from 2.54 ng/g at impoundment 3 (site 1, middle layer) to 43.2 ng/g at impoundment 3 (site 1, top layer). Lindane (-BHC) was found in most of the impoundments located on both north and south ends of the study area. Impoundments 5, 7, 8, 9, 10A, 12, 16A, 17A, 18, 19B, 23, and 24 were found to have lindane contamination. The detected concentration ranged from 0.85 ng/g at impoundment 24 (site 1, top layer) to 34.4 ng/g at impoundment 12 (site 2, top layer). The lindane concentration was higher in the surficial layer and lower in the deeper portions of the sediment samples. The core water samples, the marsh surface water samples, the culvert discharge water samples and the Indian river water samples did not contain detectable levels of pesticide (0.01 g/l). Impoundment 1 (unmanaged impoundment) and Impoundment 2 (managed impoundment) were selected for detailed water and sediment analysis to determine the extent of pesticide contamination. Both, core water and sediment cores of the surficial layer of the substrate were collected from 10 and 11 sites in each impoundment, respectively. Three sampling sites [I1/T4 (D), I1/T7 (G), and I1/S1] in impoundment 1 contained p,p'-DDE. The concentration ranged between 2.41 ng/g at I1/T4 to 7.54 ng/g at I1/T7. Results show that most of p,p'-DDE contamination for the two impoundments (1 and 2) occurred in the north section of impoundment 1. Lindane was found in four sites in impoundment 2, with the concentration ranging from 2.80 ng/g at T3/S3 (I) to 5.92 ng/g at T1/S2 (B). Dieldrin concentrations of 15.6 ng/g and 26.9 ng/g were also detected in the impoundment 2 sites (at T2/S2 (E) and T3/S3 (I), respectively). Only one site in impoundment 2 contained p,p'-DDE concentration (2.29 ng/g at T1/S3 (C)). Pesticide residues were non-detectable (0.01 g/l) in all of water samples collected in all of the cores in impoundments 1 and 2 during the intensive screening process. The potential for water-borne exchange between the above impoundments and the estuary was also examined in this study, by collecting water samples from impoundments 1 and 2; (1) at the end of the open session, (2) during mid-closure period, and (3) at the end of the closure period. Samples were taken from; (a) the marsh surface 50 feet from culvert in the interior of the impoundments, (b) at culvert on the riverside during low tide (while the impoundment was discharging), and (c) 100 feet into the river. A total of 88 exchanging-water samples were analyzed. The pesticide residues in all of the water samples were non-detectable even though large amounts of organic material were constantly being exported during the closure period through the bottomwater release devices, as well as through the open culverts in the restored areas (restoration of flushing) of the impoundments. The study concludes that residues of either lindane, dieldrin or p,p'-DDE, which were applied in the 1940's and 1950's, were found in most of the impoundments, but not at all stations. Higher concentrations were found in the surface layer portion of the marsh substrate sampled. Organic muck, which is concentrated in the suface layer of the sediments, has a strong tendency to adsorb these pesticide compounds. The more organic matter in soil, the longer the pesticides are theorized to persist in it. Microbial degradation of these pesticides (DDE, dieldrin, and lindane) in the soil play an important role to breakdown these compounds, however, in this case there was no strong evidence that the bacteria could completely break the pesticides down due to their prolonged persistance. Enhancement of microbial activity in the impoundment could possibly stimulate and increase the degradation rates of these contaminants in the impoundment. In addition, the examination of the effect of the restoration of marsh flushing by the Mosquito Control District, within the scope of this study, indicated that restoration did not appear to play a role in pesticide mobility or pesticide transport from the impoundments to the Indian River Lagoon.

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INTRODUCTION

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INTRODUCTION

The advent of DDT as a contact insecticide in the early 1940's marked the beginning of the era of synthetic organic pesticides. A large family of organochlorine pesticides emerged and were widely used. These pesticides included DDT, BHC, lindane, heptachlor, heptachlor epoxide, dieldrin and aldrin. The migration of these pesticides into various compartments of the environment has generated considerable public apprehension concerning their fate and effects. Certain pesticides applied to crops and soil for pest and mosquito control do not remain on site, but are transported in runoff and on eroded soil particles into receiving waters (1-8) where they may be absorbed directly by living organisms (9-13) that are subsequently consumed by larger organisms. In this manner, organochlorine pesticides may be passed on to secondary consumers and up through the food chain. Several instances of poisoning have been reported as a final step in the biological magnification process (14-17).

Due to the persistent and long residual effectiveness of the pesticides, quantities of DDT, BHC, dieldrin, and chlordane mixed with fuel oil were applied from both ground and air by the St. Lucie County Mosquito Control District in the late 1940's and early 1950's (c.f., Annual Reports of the St. Lucie County Mosquito Control District, 1947 through 1955). Unknown quantities were also applied to the marshes by the military during World War II. Of concern in this study are the concentrations of these pesticides which may still remain within the marsh substrate.

How do mosquito control techniques which disturb the marsh sediment (e.g., rotary ditching) or modify the exchange of estuarine waters (e.g., RIM) influence the concentration or mobility of any remaining organochlorine pesticides? As a first approximation, both mosquito control techniques described above could increase the flux of these compounds (if present) into the Indian River Lagoon (IRL).

Project Goal

The goal of this project is to (1) document the presence or absence of chlorinated pesticides within the marsh substrate of 18 St. Lucie County mosquito control impoundments along the IRL (Figure 1), and (2) document the mobility of these pesticides into the IRL under contrasting marsh management techniques (well-flushed vs. poorly flushed).

This project makes two important contributions in the area of mosquito control and coastal zone management: (1) immediately improving the decision making capabilities of the St. Lucie County Mosquito Control District by providing additional baseline data, and (2) documenting the effect of standard impoundment management techniques on Indian River water quality.

Project Description

The project consists of two components: (1) screening of all impoundments for the presence of pesticides and (2) detailed analysis of pesticide distribution and mobility associated with 2 impoundments managed under contrasting hydrodynamic conditions (e.g., well-flushed vs. poorly-flushed).

Eighteen impoundments are located within the St. Lucie County Mosquito Control District (Figure 1). All 18 were screened for the presence of pesticides using 2 randomly selected sediment cores. In addition, 2 water samples were collected from the base of each core hole.

Two impoundments were selected for detailed study. One impoundment (#1) covers 639 acres and is connected to the IRL by 5 culverts (Figure 1 and 2). It is considered to be a poorly-flushed impoundment (acreage:culvert = 128) as the impounded water levels oscillate only a few centimeters over the tidal cycle (range ~1.3 ft). In contrast Impoundment #2 covers 188 acres and is connected to the IRL by 7 culverts (Figure 1 and 3). It is considered to be a well-flushed impoundment (acreage:culvert = 27) with little tidal dampening (<10%) or time lag observed.

In addition to the detailed sampling of the marsh substrate, 3 field sessions focused on the characteristics of the waters exchanging between the 2 impoundments selected for detailed study and the estuary. Water samples were collected (1) at the end of the open season, when the marsh exchanges freely with the estuary, (2) at the end of the closed season, when the marsh is isolated from the estuary, and (3) at drawdown, when the impoundments are completely drained during the mid-closure period (Impoundment 2 only).

The following three sections describe (1) geotechnical methods and results, (2) chemical methods and results, and (3) data synthesis and discussion.

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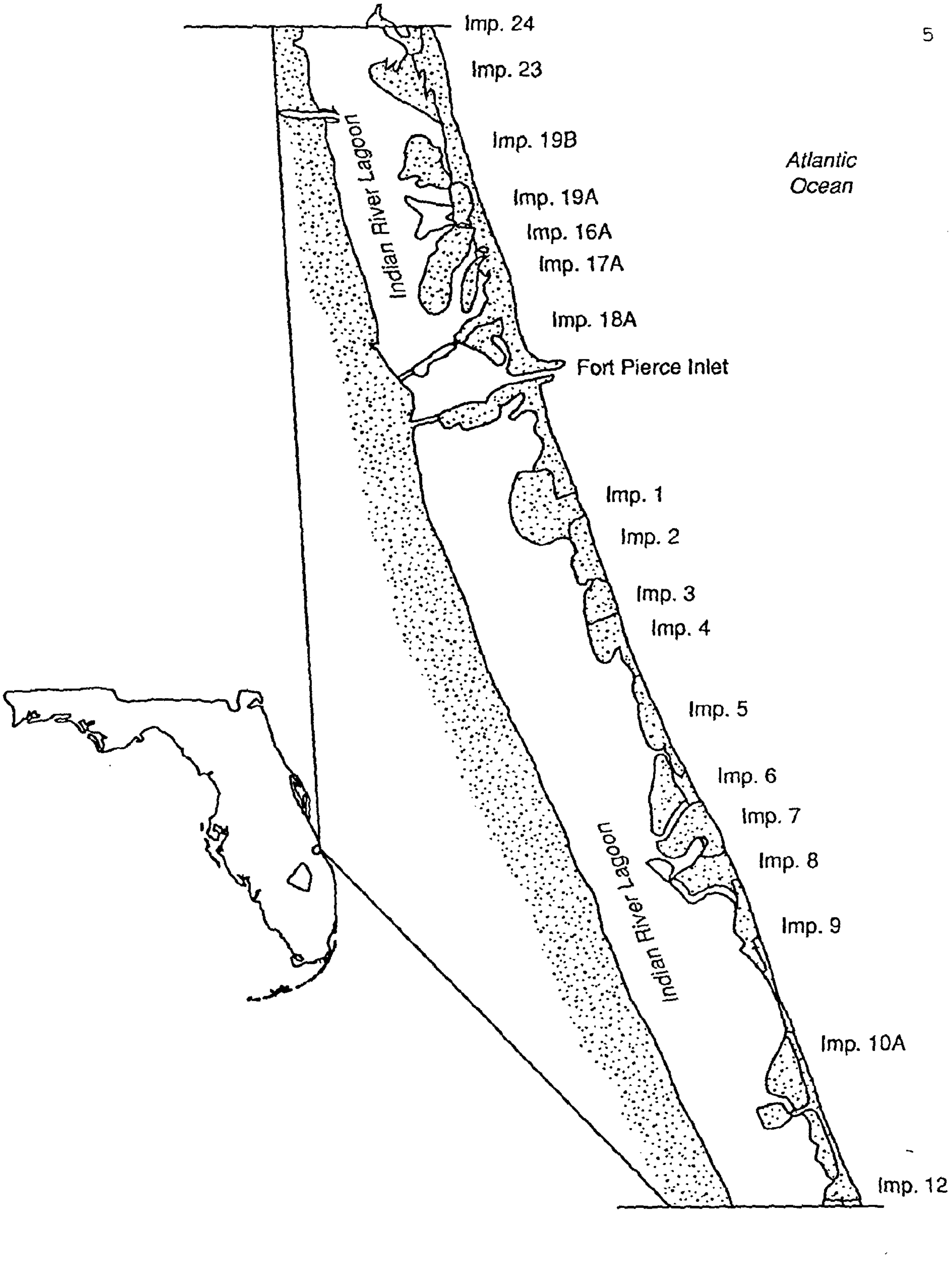

Figure 1 - Regional Location Map of Study Area

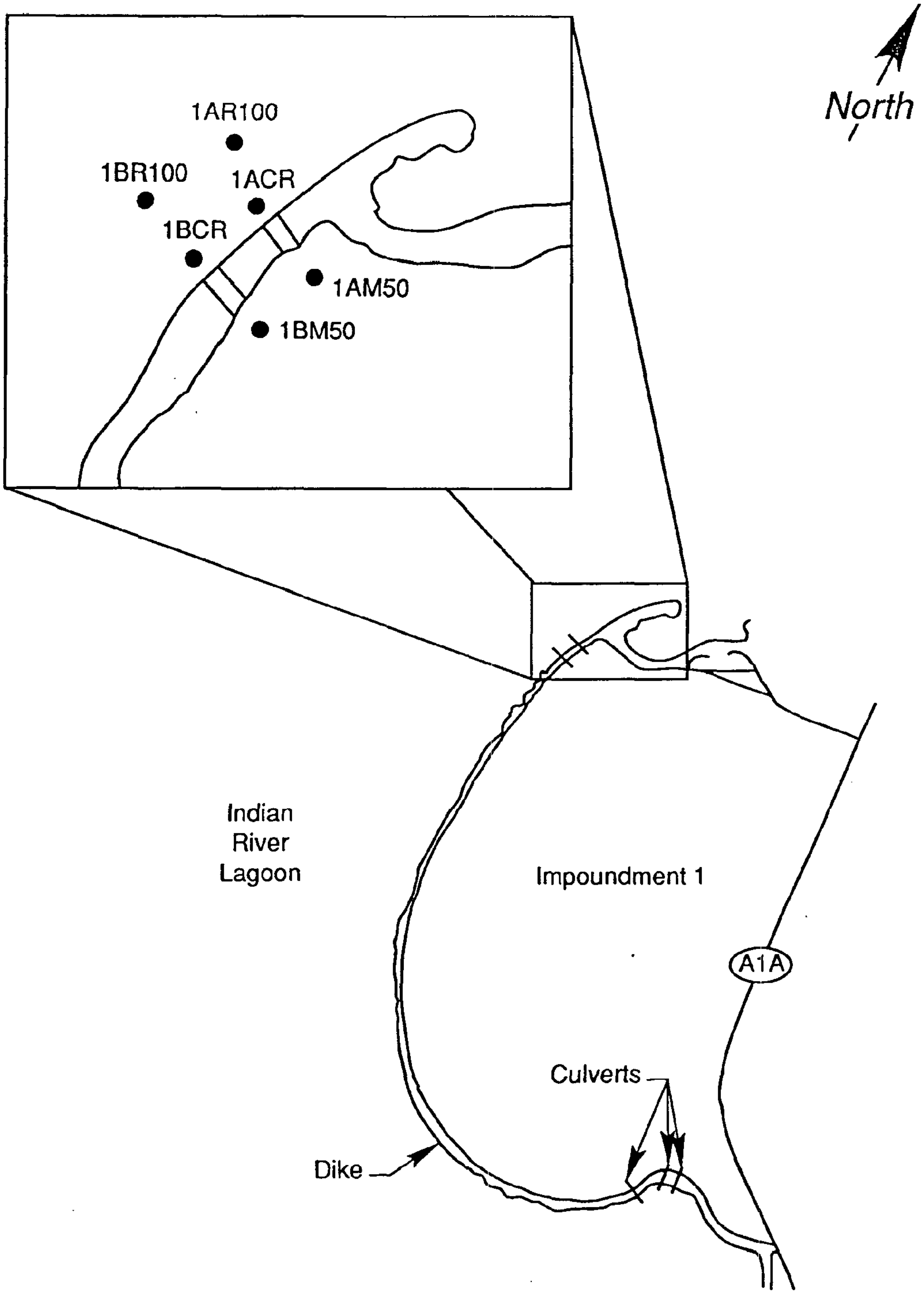

Figure 2 - Location of Culvert Water Sampling Stations: Impoundment 1

SECTION 2

GEOTECHNICAL ANALYSIS

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GEOTECHNICAL METHODS

Selection of Field Stations

Impoundment Survey

The initial phase of field work consisted of the collection of two sediment cores from all 18 mosquito control impoundments on the St. Lucie County barrier island (Figure 1). These were collected from sites determined in a random or haphazard fashion. If an impoundment was dissected by the coastal highway (A1A), one site was established on each side of the highway. The point of entry into the impoundment was selected by Mr. James David (St. Lucie County Mosquito Control). Site selection was based upon: (1) accessibility, (2) proximity to probable historical application sites, (3) the degree to which marsh sediments had been disturbed by post application activity, and (4) degree of flushing by mosquito control water management programs. Entry points were either located along the coastal highway or the dike which separates each impoundment from the Indian River Lagoon. The distance traveled into the impoundment was determined using a random number generator and ranged from between 0 and 100 feet. If the point of entry was from the highway, an additional 100 feet was added to the random number to avoid sampling an area of the impoundment that may have been altered by road construction. Location of all cores obtained during random screening of 18 impoundments are shown in Appendix A1.

Detailed Impoundment Sampling

Impoundments 1 and 2 (Figure 1) were initially proposed to be the sites of a detailed geotechnical and chemical survey. This selection was based upon the fact that these two impoundments were located immediately adjacent to the city of Ft. Pierce and therefore they were most likely to have been treated in an effort to reduce the urban mosquito and sandfly problem. The results of the random pesticide survey confirmed this speculation as three of the four random cores collected from Impoundments 1 and 2 contained pesticides. These two impoudments were also selected for study because one (#1) is considered poorly flushed (acreage:culvert = 128) and the other (#2) well flushed (acreage:culvert = 27). Hence the influence of water management on pesticide distribution and mobility could also be addressed in this study.

Detailed coring transects were established for each impoundment (Figure 2 and 3). The transects were initially laid out in a grid like fashion to maximize coverage of the impoundment.

Impoundment 2 was small enough that the planned coring program was accomplished and a total of 11 cores were collected (including the two randomly selected cores). The center of Impoundment 1 proved to be inaccessible. A total of 10 cores (including the two randomly selected cores) were collected although none were taken from the center of the impoundment.

Water Sampling Stations

Pore water samples were taken at each core site. These were taken from waters that entered the void created by removal of the sediment core. In addition, a water sampling program was established in the viscinity of Impoundment 1 and 2, adjacent to culverts which pass through the dike and connect the impoundment perimeter ditch to the Indian River Lagoon. The culverts to be monitored were selected by Mr. James David (St. Lucie County Mosquito Control District). Selection was limited to sites of continuous bottom water release. Figure 4 and 5 illustrate the location of sampling stations.

Sample Collection

General Procedures

All sampling containers used in this study were composed of either glass or metal. No plastic material was allowed to come into contact with the samples. All glass containers used for storage of water samples were cleaned using the laboratory techniques of Dr. Tsen Wang. Any object that was to be reused in a field sampling procedure was cleansed using distilled water and subjected to a final rinse of acetone. If a sample was not subjected to immediate analysis after returning from the field, it was temporarily stored in a refrigerated room.

Core Collection

At each core site a 3" diameter aluminum pipe was forced into the soil using brute force and pounding weight. The initial meter or so of penetration was typically quick and easy, reflecting the constitution of the marshy substrate. Penetration eventually stopped at a depth of between 1 and 2 meters. At that time the core was driven still further into the soil using a pounding weight. This ensured that the core sample completely penetrated through the marsh sediments and into premarsh sediments. After removing each core, the base was inspected to ensure that it had penetrated completely through the marsh sediment sequence. If the initial attempt was unsuccessful, another core was taken. The core was then sealed and returned to the laboratory refrigeration unit where it was stored in an upright position.

Water Sample Collection

Water samples collected from the core holes were recovered using a 100 ml glass dipper. The dipper was inserted towards the base of the hole and upon filling, was transferred into a four liter glass jar. Water sampling was repeated until the four liter jar was full. During the screening of the 18 impoundments, water levels were low and most of the water sampled from the core holes was collected at the base as it began to fill the void space. Two core sites (Impoundment 23, site 2 and Impoundment 18, site 1) yielded no water.

Impoundments 1 and 2 were partially submerged at the time the detailed sampling program was initiated. Therefore, core holes immediately filled upon removal of the core tubing. Water samples were collected by submerging a "corked" dipper about 25 cm into the hole and was then uncorked to collect the water sample. The core was withdrawn as slowly as possible in an attempt to maximize the volume of pore water to enter the void and minimize the volume of surface water collected.

All core hole water samples were transferred to the HBOI refrigeration unit within 4 hrs.

Culvert water sampling was conducted on three separate occasions during the project: (1) at the end of the open period, when estuarine water circulated freely through the culverts during the tidal cycle, (2) after opening the culverts at the end of the closed period, when the impounded marsh surface was kept submerged by mechanical pumping and closure of culverts, and (3) during mid-closure drawdown, when impounded water was released to draw down the water levels (Impoundment 2 only). During each sampling event, water was collected at three stations (Figure 4 and 5) once a day over a five day period. The samples were always taken while water was draining the impoundment.

Water samples were collected at the three culvert stations by submerging a one liter glass jar about 25 cm below the water surface. Two samples were collected at each station. One was delivered to HBOI within 3 hrs and subjected to chemical analysis at a later date. The other sample was stored at FIT in a refrigeration unit until it was subjected to further geotechnical analysis (described below).

Geotechnical Analysis

Sediment Cores

Sediment cores were split longitudinally, photographed, and measured. A core log was generated by visually describing the sediment according to its texture and composition.

Based upon visual inspection, each core was subdivided into major lithologic units. For detailed geotechnical analysis, 5 cm thick sediment samples were collected at 30 cm intervals or at the contact between two major lithologic units. Utilizing the other half of the core, a continuous sediment sample was taken from within each major lithologic unit. This typically generated three pesticide samples which were transferred to HBOI. Chemical analysis of the survey cores indicated that if pesticides were present at a core site they were present at the surface. Therefore, during the detailed survey of pesticide distribution in Impoundments 1 and 2 only surface samples were analysized for pesticides.

Each sediment subsample was subjected to one or more of the following laboratory procedures: (1) grain size analysis, (2) compositional analysis, and (3) faunal analysis. Standard sieve analysis was used during this project to determine weight percent gravel (>2mm), sand (<2mm but >62 um), and mud (<62um).

Sediment composition was determined using the Loss on Ignition (LOI) technique described by Dean (1974). This procedure distinguished between total organic matter (TOM), carbonate, and noncombustibles (primarily clastic sediment).

Faunal elements were identified using Abbott (1974).

Water Samples

Water samples collect during the three sampling intervals were filtered through preweighed 0.45 um opening paper. Total particulate organic matter (POM) was then determined by LOI following the techniques of Dean (1974). A number of blanks were also run to determine the accuracy of this technique.

GEOTECHNICAL RESULTS

Appendix A2 contains all of the geotechnical data including sediment description, composition, geotechnical sample location, grain size, and fauna. In addition chemical sample intervals and concentrations are also shown. The results of the geotechical analysis are decribed below.

Cores

General Observations

In general, the sediment cores collected during this study consisted of an upper, organic rich mud or muddy peat underlain by a skeletal sand. The presence of large amounts of organic material within the upper portion of most cores made standard grain size analysis inappropriate. The organic material binds the sediment to generate an apparent grain size distribution that does not reflect the true sediment size, but instead, the size distribution of bound sediment clumps and detritus. Therefore, trends in grain size were not determined independently, but inferred from the visual core descriptions.

Compositional trends were effectively determined using the LOI technique.

In only 5% of the samples were faunal elements identifiable. All other samples were barren or contained skeletal material that was chemically or physically degraded to such an extent that recognition was not possible.

In general, the thickness of the sediment sequence recovered by coring was less than the actual depth to which the core penetrated the marsh. This is commonly referred to as compaction. For example, assume a core penetrated 1 m of marsh but upon opening the core only 0.5 m of sediment was present. The sediment is assumed to have compacted 50%. This is common in water laden, organic rich marsh soils. No attempt was made to "decompact" the cores because different sediment types have different compactibility. All sediment depths discussed in this report were measured directly for the compacted core.

Specific Observations

Four major sediment types were recognized in the impoundment cores. They are as follows:

(1) Mangrove peat and detritus: A brownish, spongy sediment consisting of between 30 and 80 wt% organic material. The organic material consisted of fibrous rootlets, roots, and leaf material. Mud content varied inversely with organic content. The sediment averaged about 0.5 m in thickness.

(2) Muddy quartz sand: A tan or light brown, muddy, fine to medium grained quartz sand. Visible rooting and rootlets were recognizible. Organic content varied between 5 and 20 wt%. Mud content averaged about 10%. The sediment appeared mottled; a consequence of the irregular distribution of mud. Typical thicknesses were about 0.4 m.

(3) Skeletal quartz sand: A light gray, clean, medium grained skeletal quartz sand. Skeletal content ranged from between 5 and 35 wt%. Shells were very poorly preserved, except within discrete shell layers or towards the base of the sequence. Organic contents were typically <5%. Sediment thickness could not be determined because the cores never penetrated completely through this sediment type.

(4) Mud: Typically blue-gray, although white and medium gray examples were also encountered. Organic contents averaged between 10 and 20 wt%. Rarely contained any material >62um. Some mangrove roots were identified. Thickness averaged <0.4m.

The sediments described above typically were found to occur in a repeatable sequence consisting of (in descending order): (1) mangrove peat or mud, (2) muddy quartz sand, and (3) skeletal quartz sand. Only Impoundments 23 and 24 did not yield this sequence. In these impoundments the muddy quartz sand was exposed at the surface and underlain by skeletal quartz sand. Both of these areas are at high marsh elevations and lack red mangrove vegatation.

The compositional trend generated by this sediment sequence was one of decreasing organic content and increasing clastic content with depth (Figure 6 and 7). Calcium carbonate values were low and did not vary as a function of depth (Figure 8).

Culvert Water Samples

Average POM data for the culvert transects is shown in Figures 9 and 10. Each data point represents the mean value of five samples collected over a five day interval. Raw data is included in Appendix A3. Impoundment 1 water samples were collected at the end of the open period and end of the closed period. Except for the marsh stations sampled at the end of the closed period, there is no significant difference between the samples as a function of culvert location, station location, or sample period. The marsh stations yielded statistically higher POM at the end of the closed period.

Impoundment 2 water samples were collected at the end of the open period, end of the close period and during mid-closure drawdown. There is no significant difference between the samples as a function of culvert location, station location or sample period.

DISCUSSION OF GEOTECHNICAL RESULTS

Significance of Sediment Types

Sediment types 1 and 4, which were always found at the top of cores, are clearly a product of sedimentation processes currently active in the impoundments. Sediment type 1 is a mangrove associated deposit. The origin of sediment type 4 remains enigmatic. It always lies above sediment type 2 and at the same stratigraphic position as sediment type 1. Therefore it is interpreted to have been deposited within a marsh environment.

Sediment type 2, the muddy quartz sand, consistently occurred beneath sediment type 1 or 4 and above sediment type 3. This sequence is interpreted to have been deposited prior to marsh formation, perhaps as a barrier island overwash fan or inlet related backbarrier deposit. Shell, when present, consisted of trace (<5%) amounts of unrecognizable skeletal fragments that were usually abrained and etched.

The rooting within sediment type 2 is interpreted to have developed as coastal vegetation associated with sediment type 1 colonized the surface of this sedimentary deposit.

Sediment type 3, a clean, skeletal quartz sand, is distinguished from sediment type 2 by the abundance of skeletal material and paucity of rooting, although the contact between sediment type 2 and 3 is often gradational. These distinctions suggest that sediment types 2 and 3 are genetically related. In all likelihood they were probably deposited within the same depositional environment as a single unit. Post depositional modification by rooting, slowly transformed the upper layers of a clean, skeletal sand (sediment type 3) into a muddy quartz sand (sediment type 2). The absence of significant quantities of skeletal material within sediment type 2 can be attributed to the slightly acidic groundwater conditions that are often associated with organic rich marsh sediments. Skeletal material within sediment type 3 was difficult to identify but appeared to consist primarily of a restricted marine fauna (e.g., Anomolacardia sp., Cerithium sp.)

Anticipated Pesticide Sediment Intervals

Based upon the sedimentological evidence provided above, it is most probable that Sediment Types 1 and 4 were present at the land-air interface at the time the impoundments were treated with organoclorine pesticides. Sediment types 2 and 3 were not exposed to direct treatment and could only have acquired pesticides through vertical and lateral migration away from the contaminated surface layer.

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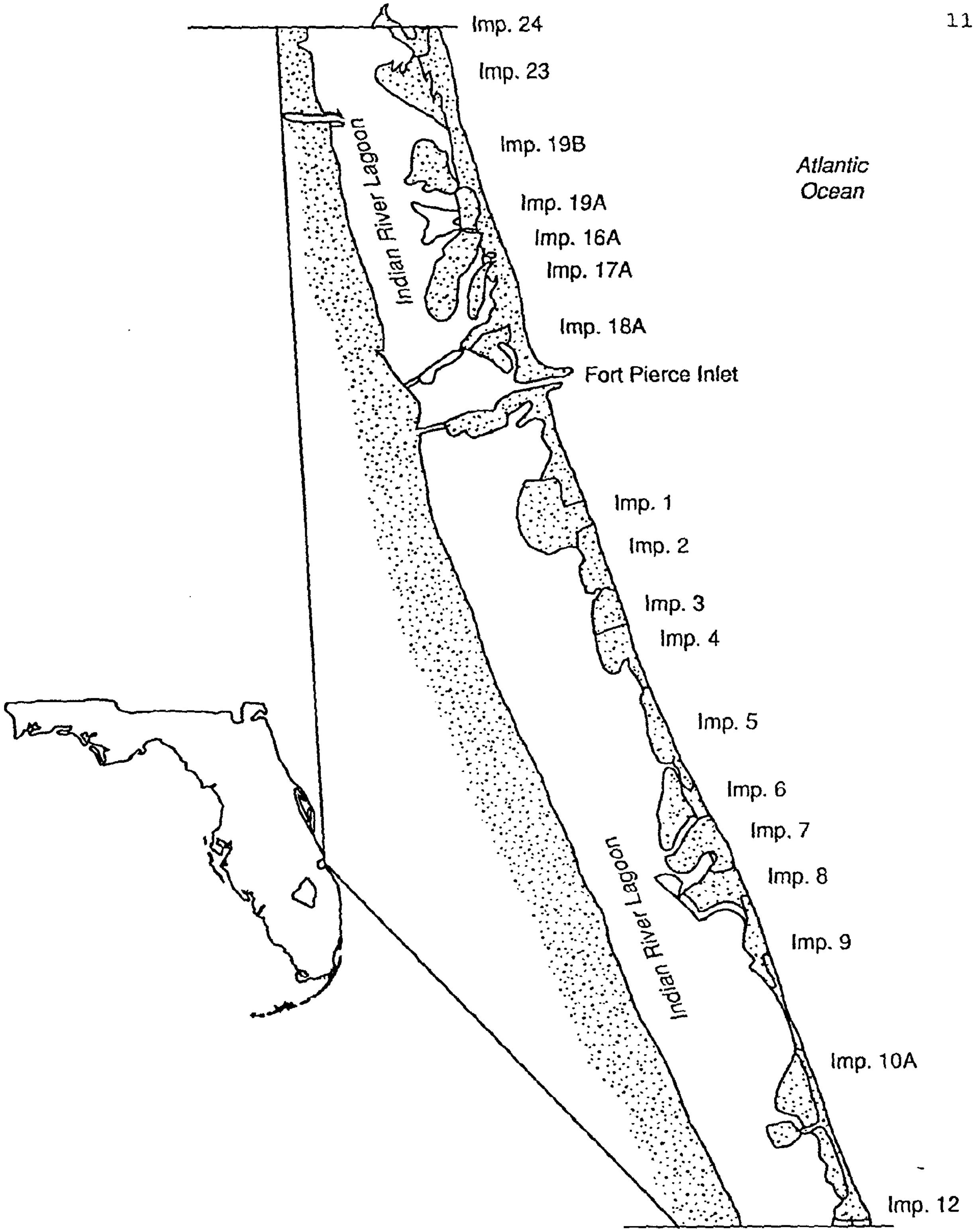

Figure 1 - Regional location map of study area

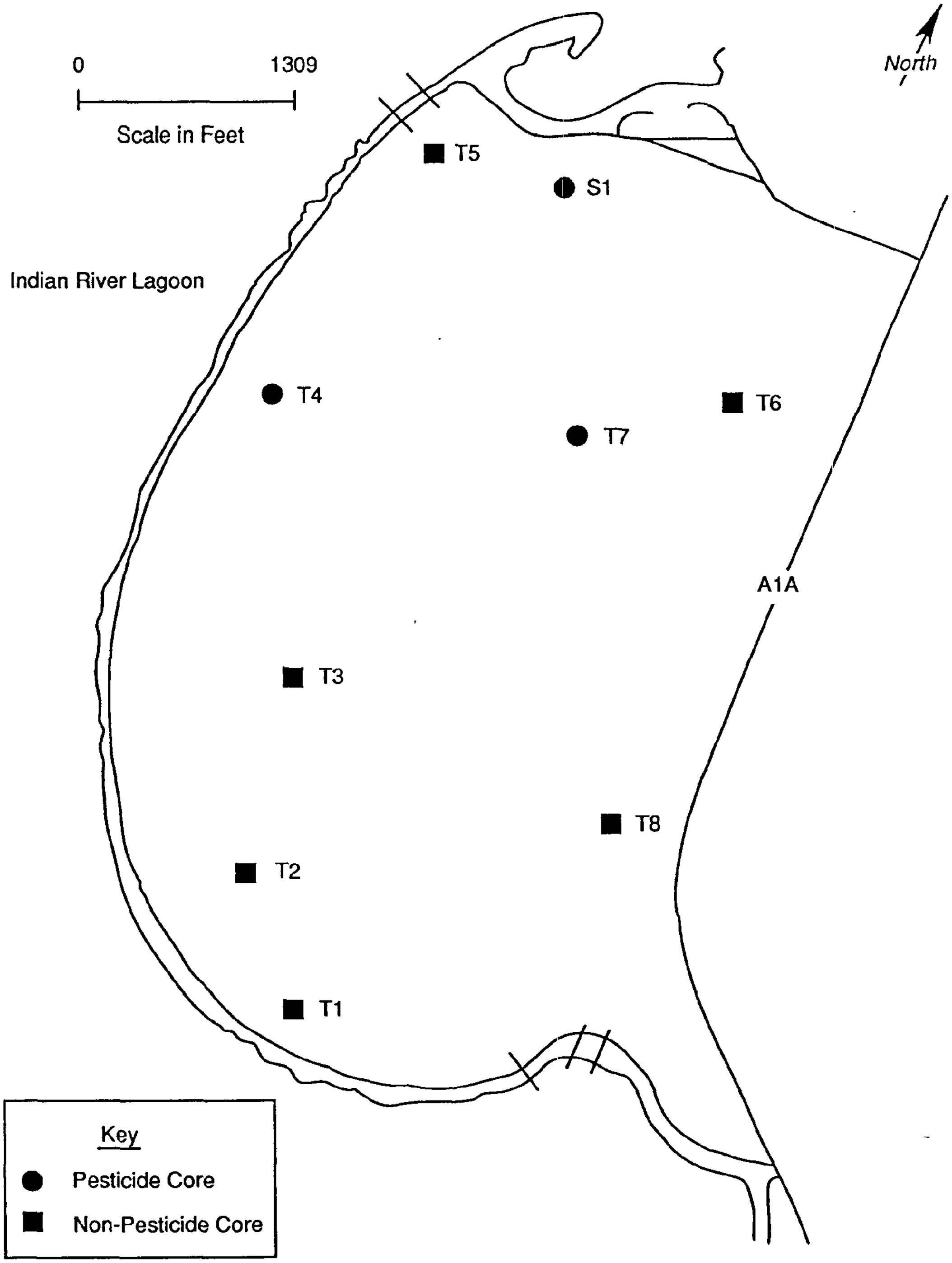

Figure 2 - Core locations: Impoundment 1

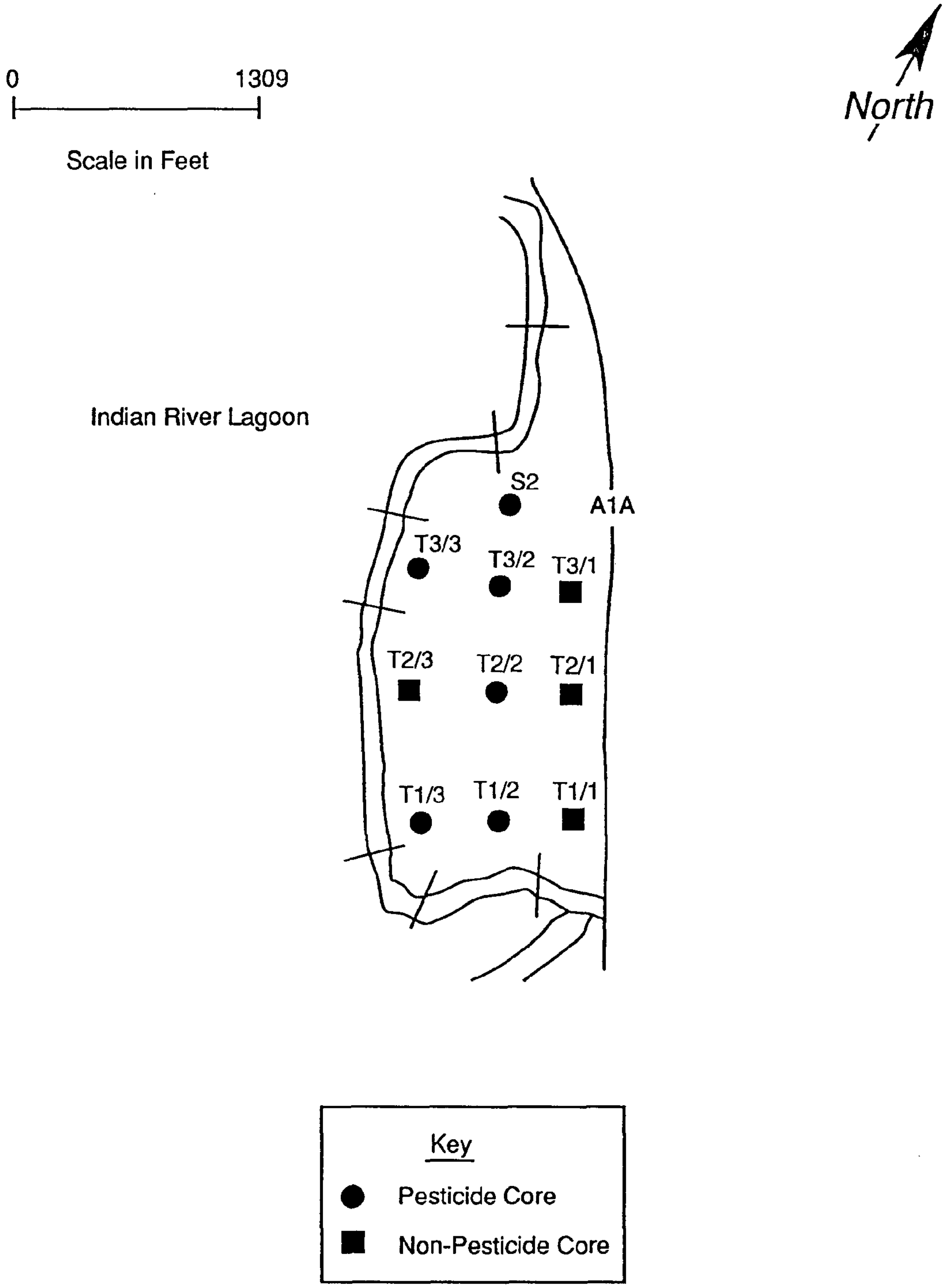

Figure 3 - Core locations: Impoundment 2

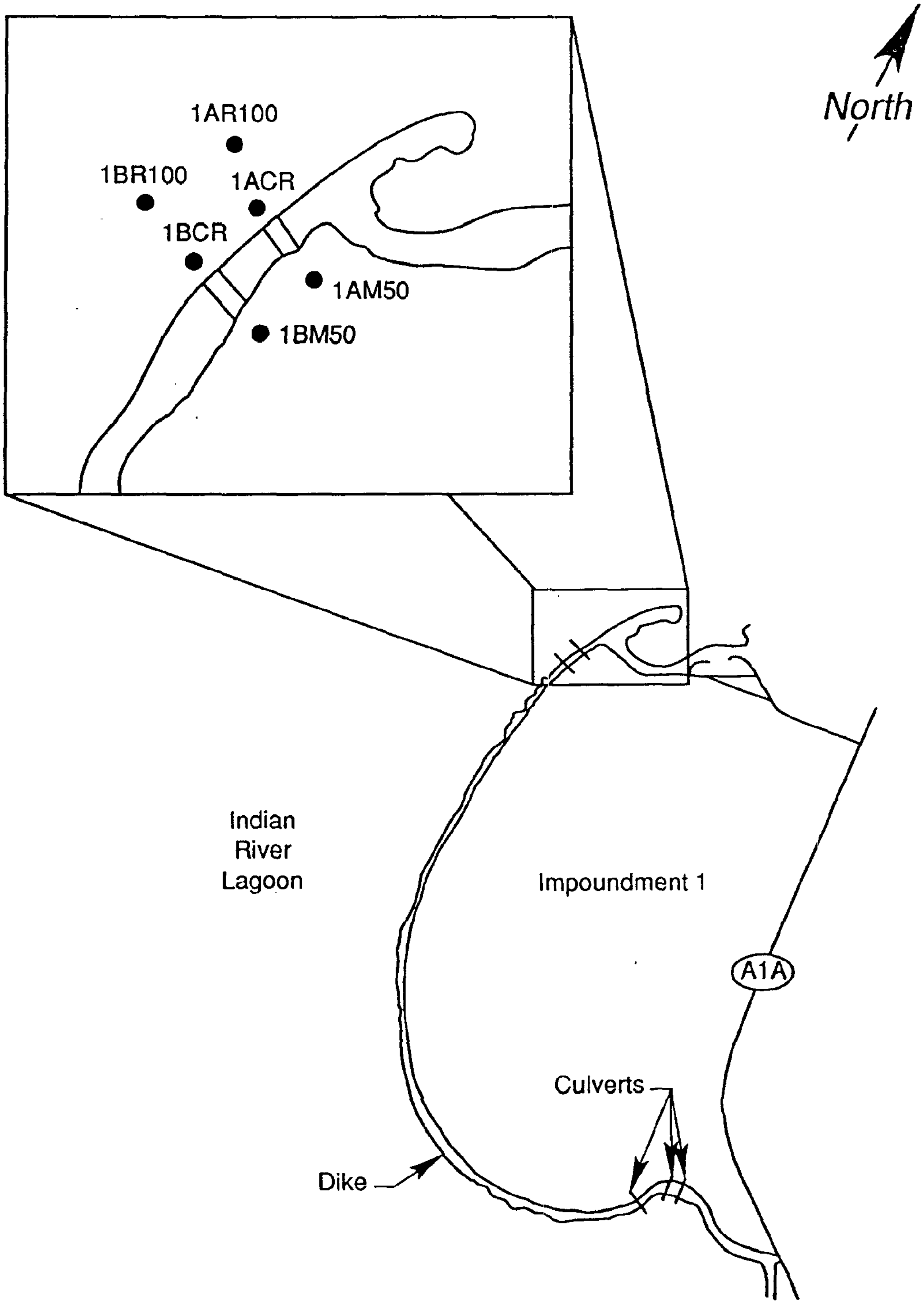

Figure 4 - Location of culvert water samples: Impoundment 1

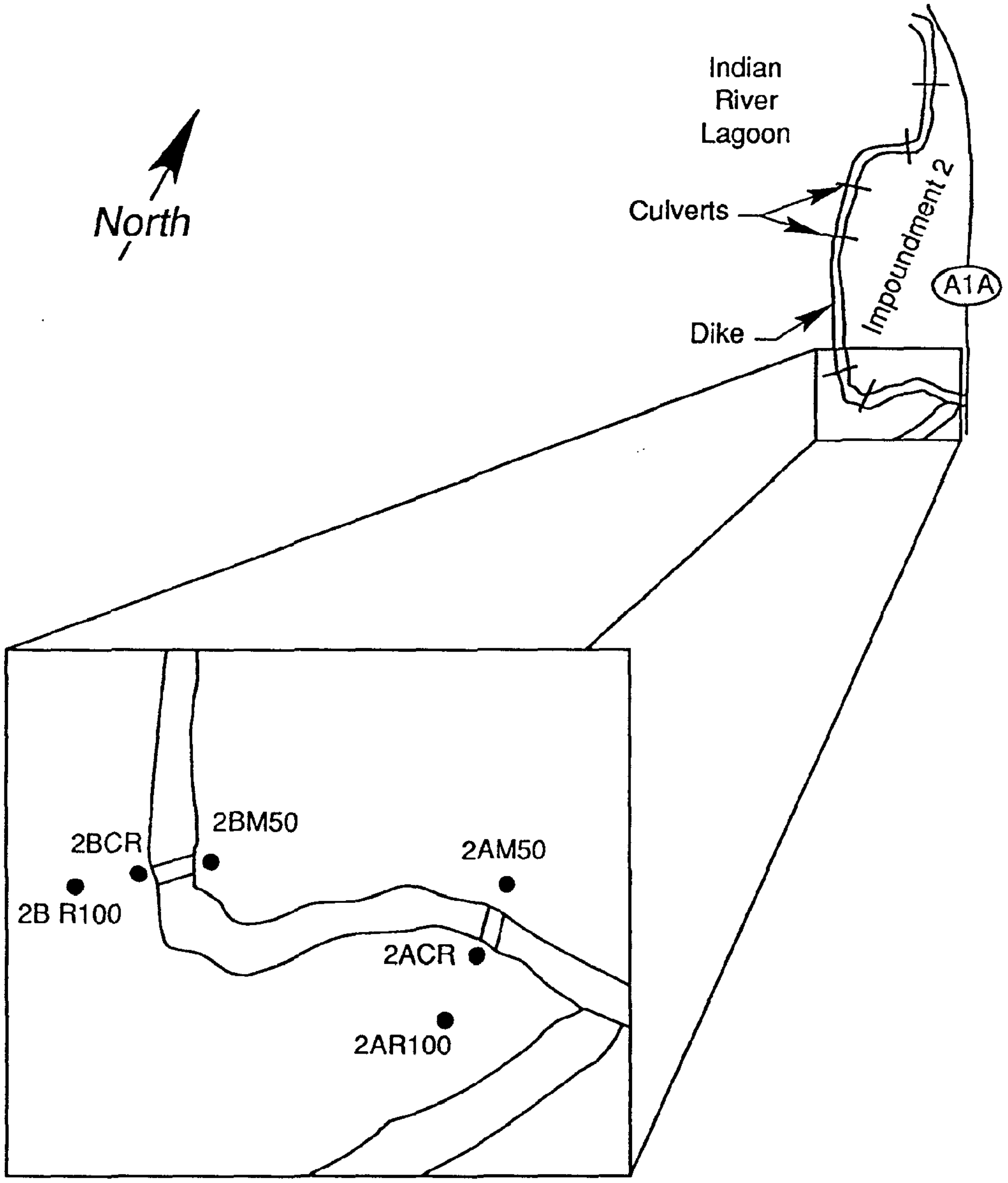

Figure 5 - Location of culver water samples: Impoundment 2

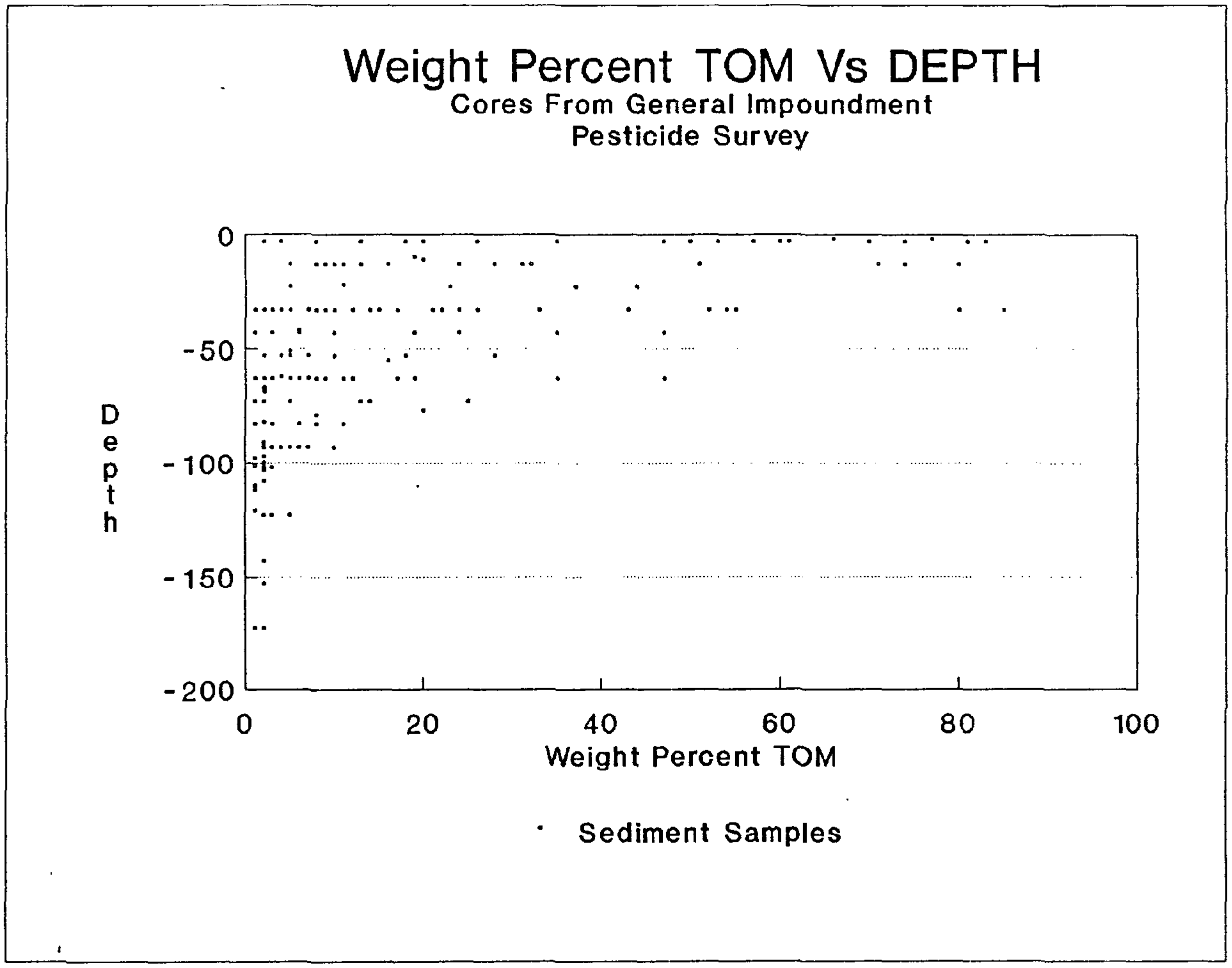

Figure 6 - Weight percent TOM vs depth: 18 general survey cores

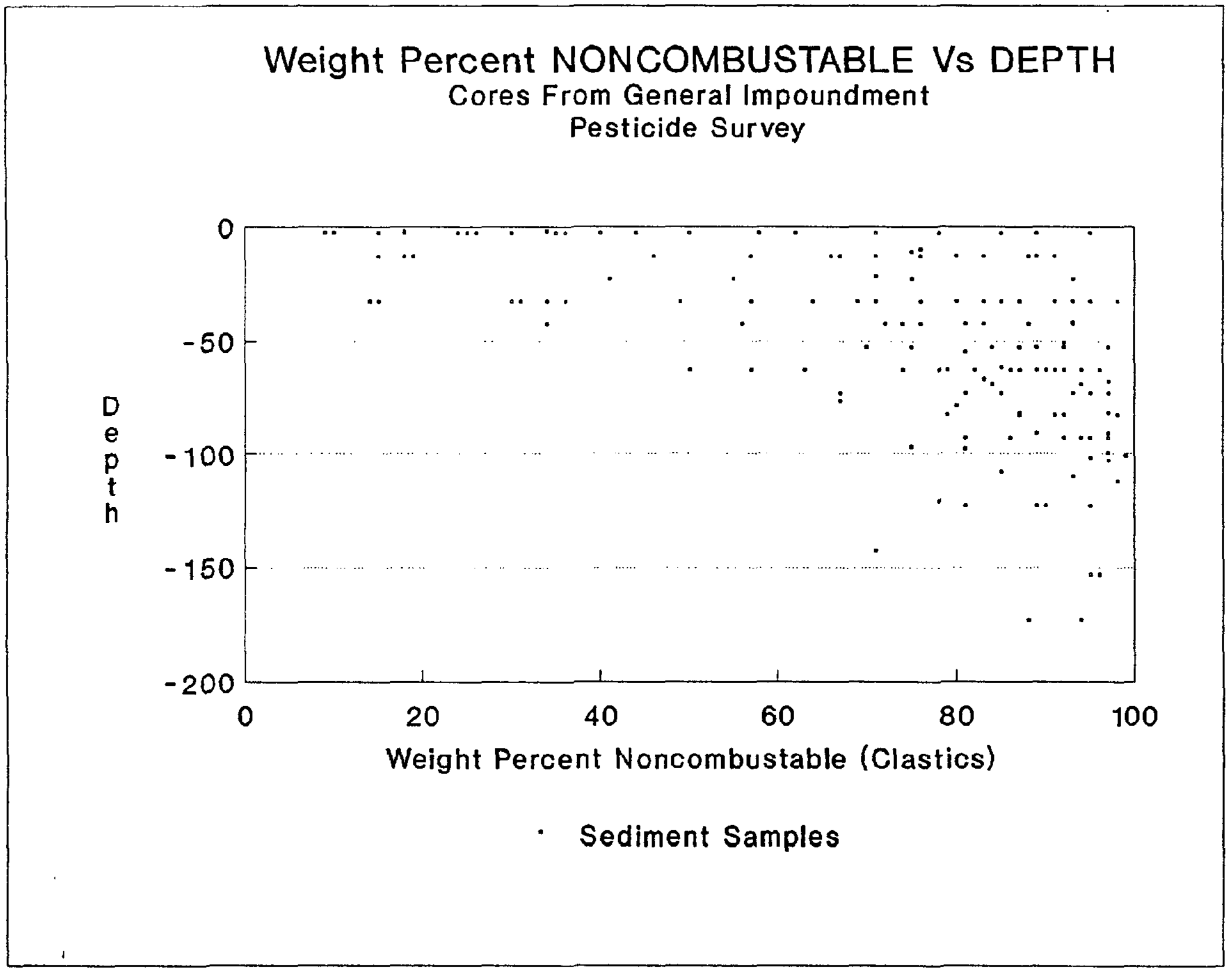

Figure 7 - Weight percent clastics vs depth:
cores 18 general survey

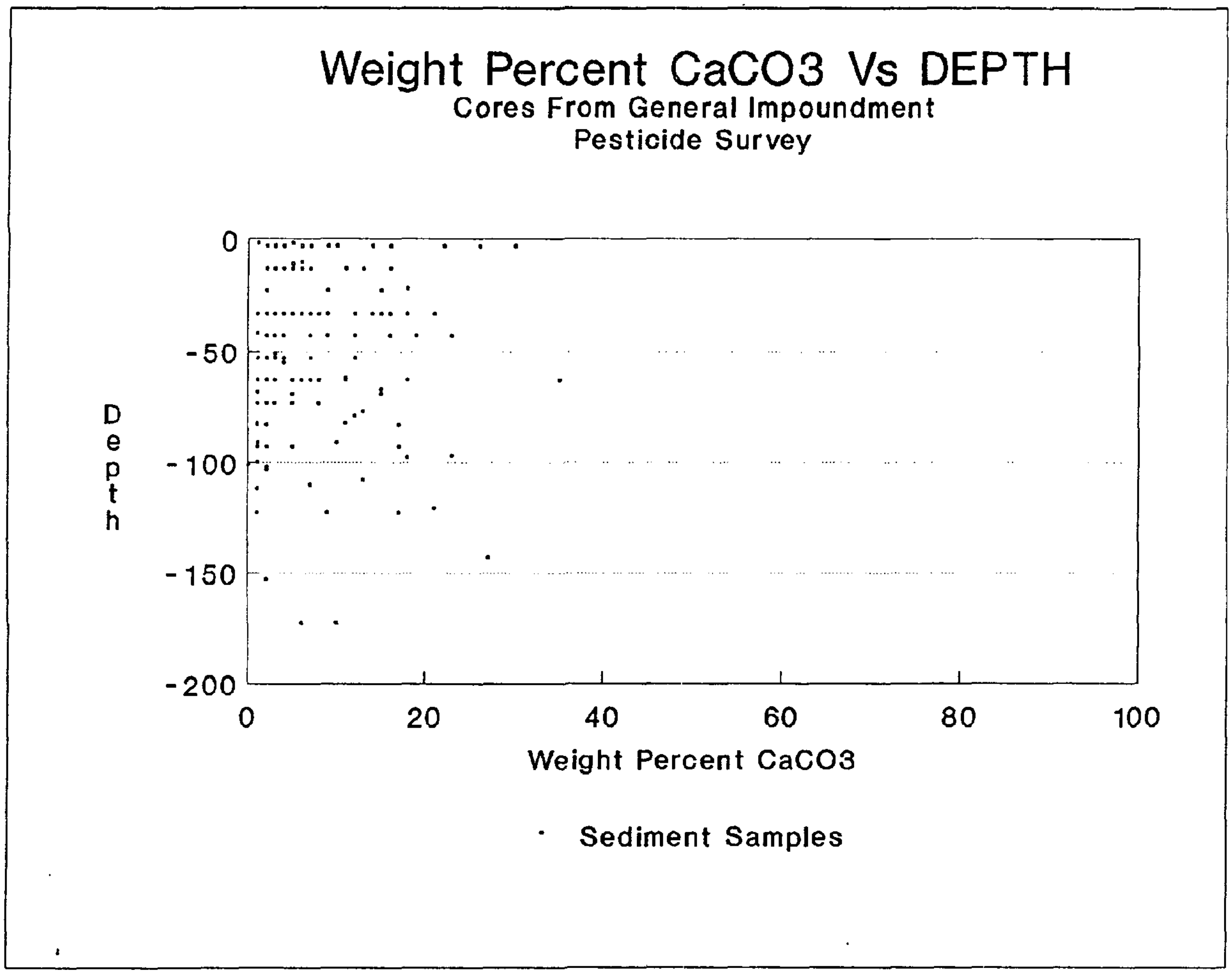

Figure 8 - Weight percent CaCO3 vs depth:
18 general survey cores

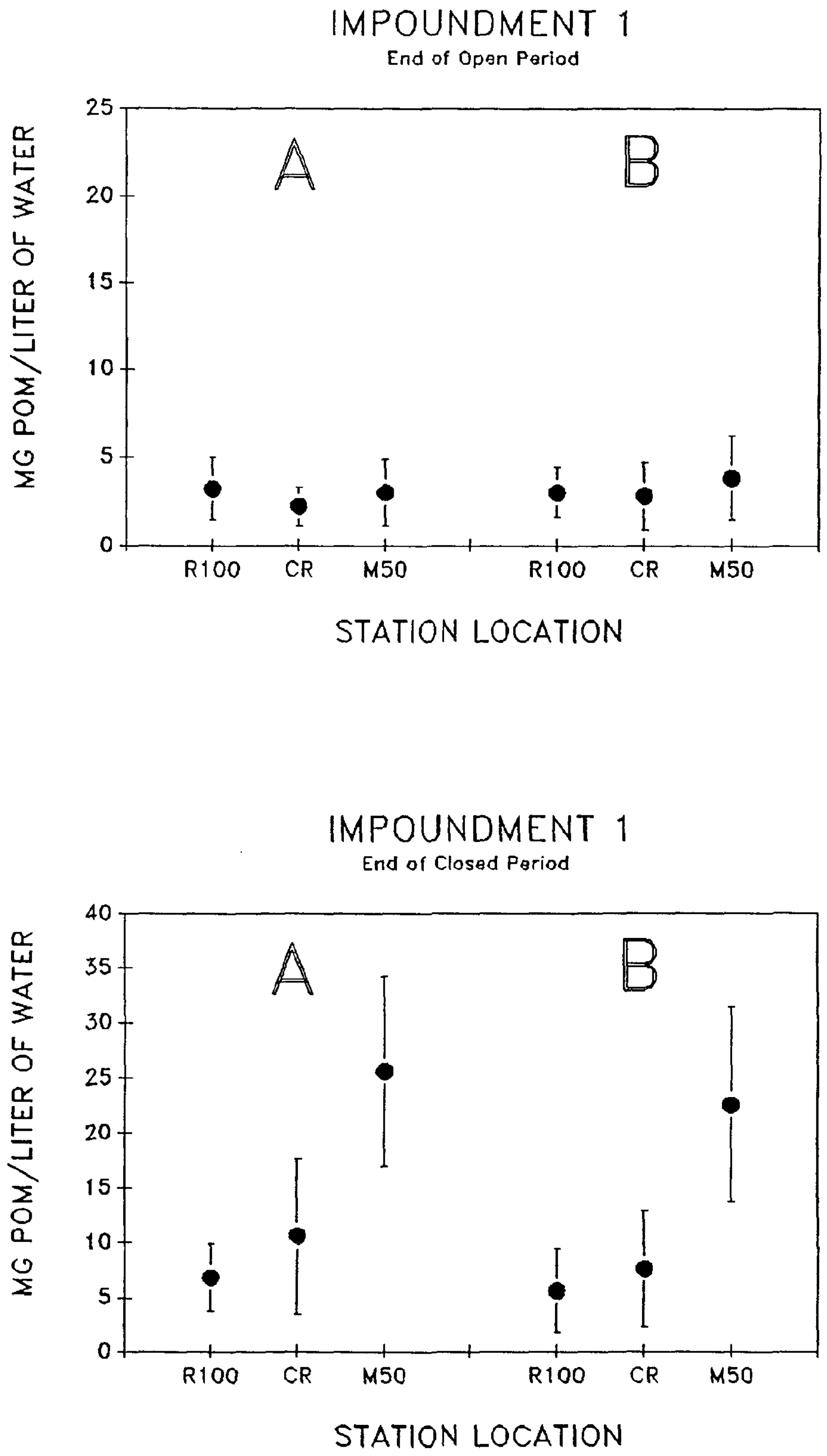

Figure 9 - Culvert water sample data: Impoundment 1 POM

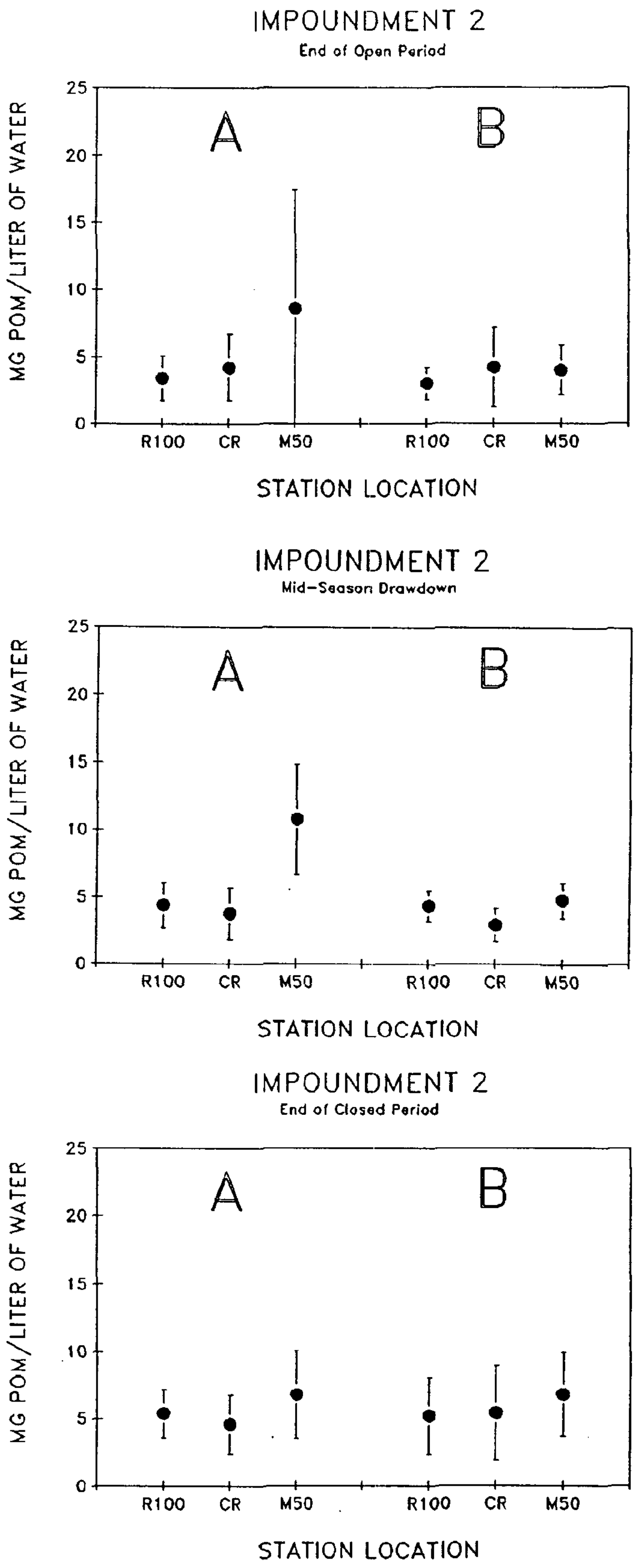

Figure 10 - Culvert water sample data: Impoundment 2 POM

SECTION 3

CHEMICAL ANALYSIS

Pesticide Residue Occurrence and Distribution in the St. Lucie County Mosquito Control Impoundments, Florida

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Summary - Pesticide Residue Occurrence and Distribution in the Mosquito Control Impoundments

This project was to determine the occurrence and distribution of chlorinated pesticides in the St. Lucie County mosquito control impoundments. A total of 18 impoundments located on the barrier islands between the Indian River lagoon and Atlantic Ocean on east coast of Florida were screened to determine the presence or absence of pesticides. Two random core sediment samples and two core hole water samples from each impoundment were collected. Each core sample was approximately six feet in depth and was subdivided into three sections (top, middle, and bottom layer) for analysis. The results show that 10 sediment samples from eight impoundments were found to contain p,p'-DDE (a degradation compound of DDT). The detected concentration ranged from 1.87 ng/g at impoundment 10A (site 2, top layer) to 31.2 ng/g at impoundment 23 (site 1, top layer). Impoundments 1, 2, 5, 10A, 16A, 18, 19B and 23 were detected at least once with p,p'-DDE. These impoundments are located on the central and north sections of the study area.

Six sediment samples from three impoundments contained dieldrin ranging from 2.54 ng/g at impoundment 3 (site 1, middle layer) to 43.2 ng/g at impoundment 3 (site 1, top layer). Dieldrin was mostly found in impoundments 2, 3, and 17A, which are located on the central section of the study area. Lindane (γ-BHC) was found in most of the impoundments located on both north and south ends of the study area. Impoundments 5, 7, 8, 9, 10A, 12, 16A, 17A, 18, 19B, 23, and 24 were found to have lindane contamination. The detected concentration ranged from 0.85 ng/g at impoundment 24 (site 1, top layer) to 34.4 ng/g at impoundment 12 (site 2, top layer). The lindane concentration was generally higher at the top layer and then gradually reduced to bottom samples. The core water samples collected from each impoundment were also analyzed. The results show that pesticide residues were non-detectable ($\lesssim$ 0.01 µg/l) in all of the water analyzed.

Impoundment 1 (unmanaged impoundment) and Impoundment 2 (managed impoundment) were selected for detail water and sediment analysis to determine the extent of pesticide contamination. Both water and top layer of sediment samples were collected from 10 to 11 sites in both impoundments, respectively. Three sampling sites [I1/T4 (D), I1/T7 (G), and I1/S1] in impoundment 1 contained p,p'-DDE. The concentration ranged between 7.54 ng/g at I1/T7 to 2.41 ng/g at I1/T4. Results show that most of p,p'-DDE contamination occurred at the north section of impoundment 1. Lindane was found in four sites from impoundment 2 [I2/T1/S2 (B), I2/T1/S3 (C), I2/T2/S2 (E), I2/T3/S3 (I)]. The concentration ranged from 2.80 ng/g at T3/S3 (I) to 5.92 ng/g at T1/S2 (B). Dieldrin concentration of 15.6 ng/g and 26.9 ng/g were also detected in the impoundment 2 site T2/S2 (E) and T3/S3 (I), respectively. Only one site at T1/S3 (C) in impoundment 2 contained 2.29 ng/g p,p'-DDE concentration. A total of 22 water and sediment samples from both impoundments were analyzed. Pesticide residues were non-detectable ($\lesssim$ 0.01 µg/l) in all of water samples collected.

Water exchange between impoundments and the estuary was examined in this study. Water samples from impoundments 1 and 2 were collected (1) at the end of the open session, (2) during mid-closure period, and (3) at the end of the closure period. Samples taken from (a) 50 feet from culvert into the impoundments, (b) at culvert on the riverside, and (c) 100 feet into the river, were analyzed. A total of 88 water samples were analyzed. The pesticide residues in all of the water samples were non-detectable.

The study concludes that lindane, dieldrin and p,p'-DDE were found in most of the impoundments. They were mostly concentrated on the top layer of sediment. Pesticide compounds have a low solubility in water and once released to the aqueous environment, have a tendency to be adsorbed by particulate matter. This particulate matter gradually sinks to the bottom. Pesticides normally do not remain long in the water. The soil or mud bottom acts as a sink source for pesticides. Organic muck concentrated mostly on the top layer of sediments have a strong tendency to adsorb these pesticide compounds. The more organic matter in soil, the longer the pesticides can persist in it. Microbial degradation of these pesticides (DDE, dieldrin, and lindane) in the soil play an important role to breakdown these compounds. However, there was no strong evidence that they could completely break them down. Enhancement of microbial activity in the impoundment could possibly stimulate and increase the degradation rates of these contaminants in the impoundment.

Chlorinated Pesticide Residue Analysis

Water samples were centrifuged at 8000 G for 25 min at 10 °C to separate suspended solids from the water. A 900 ml water sample was extracted with 60 ml of methylene chloride three times. The extract was then passed through a Na_2SO_4 and florisil column for clean-up procedures. Activated copper was added to remove sulfur compounds prior to gas chromatographic analysis. The analytical procedure is presented in Table 1.

EPA method 3540 (18) was used to extract sediment samples for chlorinated pesticide analysis. A dried sediment sample (100 g) was soxhlet extracted with 300 ml hexane/acetone (1:1) mixture for 24 hours. The extract was then passed through Na_2SO_4 and florisil columns. Copper was also added to remove sulfur. The analytical procedure for sediment samples is presented in Table 2.

A 30 m X 0.25 mm DB-5 fused silica column equipped with an electron capture detector in a Perkin Elmer Sigma 3B gas chromatograph was used to analyze water samples. Argon/methane (6 ml/min) was used as carrier gas. The temperature program was set at 180 °C for 6 min. to 280 °C at a rate of 3 °C/min. The gas chromatograph operating conditions and calibrations curves for each chlorinated compound are included in Table 3. The minimum detectable concentration for each compound is 0.01 µg/l. The mean recovery (84% to 99%) and relative deviation (7% to 16%) for water samples for each compound are shown in Table 4. A gas chromatograph/mass spectrometer (A DB-5 capillary column equipped with Varian GC 3400 and Finnigan ITDS 806A) was used to analyze sediment samples. The GC/MS was also used to confirm water sample analysis. The operating conditions and retention times for each compound are present in Table 5. The minimum detectable concentration for sediment samples ranged between 0.17 ng/g for α-BHC to 0.49 ng/g for endrin. Twelve chlorinated pesticides were analyzed for both water and sediment samples. The accuracy and precision of sediment analysis for chlorinated pesticides shown in Table 6 ranged between 77% to 98% and 6% to 13%, respectively. The analytical standard for each compound was obtained from Supelco, Inc. For each set of samples, a method blank, a spiked sample and the unknown samples were performed. Prior to each unknown sample analysis, dibutyl chlorendate was spiked as a surrogate standard to monitor sample extraction efficiency.

Results and Discussion

Two random sampling sites for each impoundment were selected for sampling both core sediment and core water samples. Each core sample was approximately 6 ft in depth and was subdivided into three sections (top, middle, and bottom) for analysis. During the screening phase, a total of 34 water samples and 92 sediment samples were analyzed to screen for the presence and distribution of pesticides in 18 impoundments. Pesticide residues were non-detectable ($\leq$ 0.01 µg/g) in all the 34 water samples analyzed. The analytical results of each water sample analysis are included in addendum Table 1. Dieldrin, p,p'-DDE, and lindane were detected in some of the sediment samples collected. A summary of the detected compounds in the sediment samples at each impoundment are shown in Table 7. Figure 1 shows the location and distribution of pesticide occurrence in the 18 impoundments. The exact sampling site for each impoundment and concentration of detected compounds in each layer of sediment samples are presented in Figure 2A to 2L.

A total of ten sediment samples from eight impoundments were found to contain p,p'-DDE. The concentration ranged between 31.2 ng/g at impoundment 23 (site 1, top layer) to 1.87 ng/g at impoundment 10A (site 2, top layer). Figure 1 shows that the p,p'-DDE occurred mostly in the top soil of the north part of the mosquito impoundments. Impoundments 1, 2, 5, 10A, 16A, 18, 19B, and 23 were detected with DDE at least once during the study period. A total of six sediment samples from three impoundments (2, 3, 17) contained dieldrin. Top layer sediment samples of both impoundments 2 and 3 had a dieldrin concentration of 34.0 and 43.2 ng/g, respectively. Figure 1 shows dieldrin contamination mostly occurred in the middle section of the study area (i.e. Impoundment 2, 3, and 17 were detected once with dieldrin). Lindane (γ-BHC) was another pesticide detected in the sediment. A total of 33 sediment samples from 11 impoundments were found to contain lindane. The compound was distributed mostly at the south and north end of the study area (impoundments 7 to 12 and 16A to 24) as shown in Figure 1 and Figure 2. Lindane was detected in the top and middle or bottom core samples at impoundment 8, 12, 17A, 19A, 19B, and 24. The concentration of each sampling site is shown in Figure 2. The concentration was generally higher at the top layer and then gradually reduced to bottom samples. The highest concentration detected was 34.4 ng/g lindane at impoundment 12 (site 2, top layer) and reduced to 9.4 ng/g at the bottom layer in the same site. The analytical results of each sediment sample analysis are shown in Appendix B Tables 2-19.

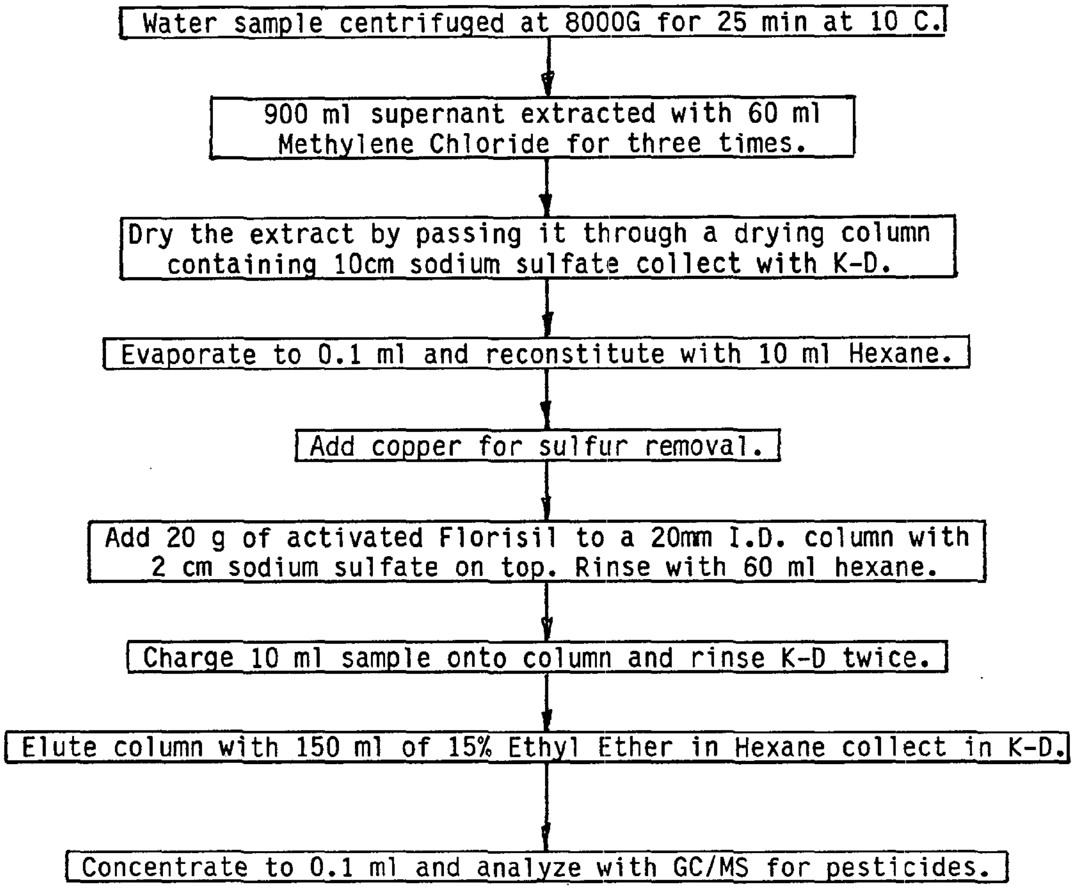
Impoundments 1 and 2 were selected for detail analysis to determine the extent and distribution of pesticide contamination. Transect sampling for both water and sediment in both impoundments was performed. Ten and eleven sampling sites approximately 1500' and 600' apart in both impoundments 1 and 2 were chosen as shown in Figures 3A and 3B. Only top layer sediment and core hole water samples from each site were collected. A total of 22 water and sediments samples each were analyzed. The analytical results of each water and sediment analysis were included in Appendix B Tables 20 - 23. The detected pesticides in the transect sediment samples are summarized in Table 8 and Figures 3A and 3B. Only p,p'-DDE was detected in the two sites from impoundment 1. The concentration was 2.41 and 7.54 ng/g at transect site D and G, respectively. Both samples plus the sample from the random sampling site (I1/S1) indicate that DDE contamination mostly occurred at the north section of impoundment 1 (Figure 3A). Lindane was found in 4 samples (B, C, E, and I) collected at impoundment 2. The concentration ranged from 2.80 ng/g at transect 3 (site I) to 5.92 ng/g at transect 1 (site B). Dieldrin was found in two samples from impoundment 2. A concentration of 15.6 ng/g and 26.9 ng/g was detected at transect 2 (site E) and transect 3 (site I), respectively.

Water exchanging between impoundments and the estuary was also studied. Water samples in impoundments 1 and 2 were collected (1) at the end of the open session (March 8, 1990 for impoundment 1 and April 17, 1990 for impoundment 2), (2) Mid-closure period - impoundment 2 only on July 12, 1990, and (3) the end of the closure period on October 8, 1990. Samples were taken from (1) 50 ft from culvert into the marsh, (2) at culvert on the river side, and (3) 100 ft into the river. Two culverts were selected for each impoundment in this study. The sampling sites for both impoundments 1 and 2 are shown in Figure 4A and 4B. A total of 88 water samples were analyzed to study the water quality between the impoundments and the estuary. The pesticide concentration in all of 88 water samples analyzed was non-detectable. The analytical results of each water analysis run are shown in Appendix B Tables 24 - 29.

The study concludes that lindane, dieldrin, and p,p'-DDE were concentrated on the top layer of the core sample. Analysis of impoundment water and core hole water did not detect any chlorinated pesticides. Pesticide compounds once released to the aqueous environment, have a tendency to be adsorbed by particulate matter and gradually sink to the bottom. Pesticides normally do not remain long in the water and the soil or mud bottom act as a sink source for pesticides. There are many factors that could determine the persistence and degradation of pesticides on the soil or sediment environment. Pesticides can be adsorbed by soil constituents, leached by impoundments or rain water, taken up by plants or animals, broken down by microbial activities, photooxidized by natural sunlight. The soil type greatly influences the adsorption of insecticides. Normally, pesticides are largely adsorbed in organic muck and followed by clay loam, sandy loam, silty clay, coarse silt, light sandy clay loam, and silty clay loam (19). The ways in which soil structure affects the persistence of pesticides is closely linked with organic matter, clay content, and hydrogen ion concentration. It seems that the more organic matter in a soil, the longer an insecticide persists in it.

The soil type influences not only the persistence and activity of insecticide in soil, but also the rate at which they are converted or degraded into other compounds. Micro-organisms in different types of soil could play an important role in breaking down the pesticides. However, several studies have shown little evidence that they can completely break them down. The major microbial metabolic steps are reductive dechlorination, dehydrochlorination and the oxidative systems. DDT and lindane can be dehydrochlorinated via microbial breakdown to DDE and pentachlorocyclohexene (PCCH). Dieldrin undergoes microbial reaction or other biological oxidation to form photodieldrin. The complete degradation pathways for each compound are attached in Figures 5 to 7 for DDT, dieldin, and lindane, respectively. The intermediate degradation compounds and the persistence or disappearance rate can be varied with different types of environmental conditions. The persistence and degradation rates of insecticides in the St. Lucie County mosquito impoundments has not been studied. This project only focuses on the occurrence and distribution of chlorinated pesticides in the impoundments.

Table 1. ANALYTICAL PROCEDURES FOR WATER SAMPLES



Water sample centrifuged at 8000G for 25 min at 10 C.

900 ml supernant extracted with 60 ml Methylene Chloride for three times.

Dry the extract by passing it through a drying column containing 10cm sodium sulfate collect with K-D.

Evaporate to 0.1 ml and reconstitute with 10 ml Hexane.

Add copper for sulfur removal.

Add 20 g of activated Florisil to a 20mm I.D. column with 2 cm sodium sulfate on top. Rinse with 60 ml hexane.

Charge 10 ml sample onto column and rinse K-D twice.

Elute column with 150 ml of 15% Ethyl Ether in Hexane collect in K-D.

Concentrate to 0.1 ml and analyze with GC/MS for pesticides.

Table 2. ANALYTICAL PROCEDURES FOR SEDIMENT SAMPLES

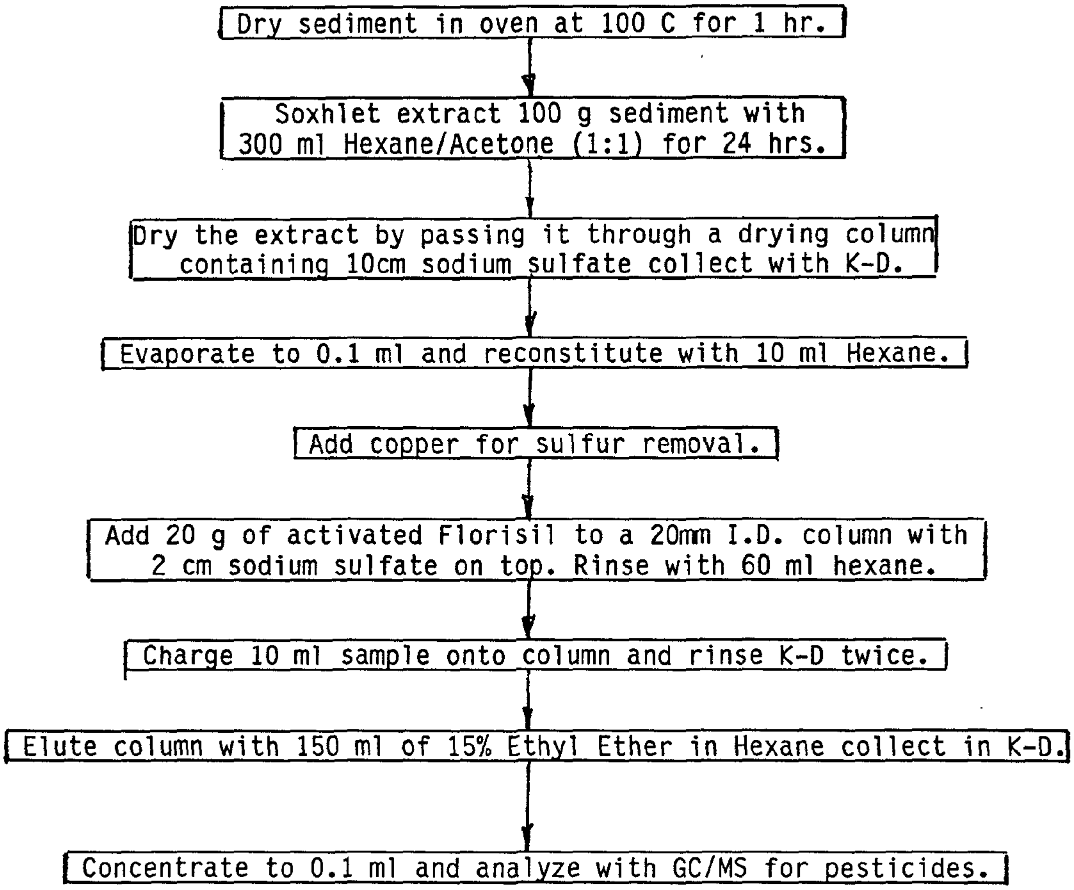


Table 3. GAS CHROMATOGRAPH OPERATING CONDITIONS AND CALIBRATION CURVES

G.C. Model: Perkins Elmer Sigma 3B
Column: 30m x 0.53 mm Id. J&W DB-5 P/N 125-5032
Carrier: $Ar\text{-}CH_4$ 6 mℓ/min.
Oven: 180°C for 6 min. to 280°C at rate of 3°C/min.
Detector: Electron capture at 330°C
Make-up gas 30 mℓ/min.

COMPOUNDS	CALIBRATION RANGE (ng)	CALIBRATION CURVES (5 pt.) Y=area X= amt.(ng)	CORRELATION COEFFICIENT
α-BHC	0.25-2.5	Y=1.471X+0.0466	0.998
β-BHC	0.25-2.5	Y=0.514X+0.00388	0.999
γ-BHC	0.25-2.5	Y=1.310X+0.00981	0.999
δ-BHC	0.25-2.5	Y=1.308X+0.0463	0.999
Heptachlor	0.25-2.5	Y=1.1155X-0.0324	0.999
Aldrin	0.25-2.5	Y=1.316X-0.0438	0.999
Heptachlor Epoxide	0.25-2.5	Y=1.178X+0.209	0.999
p.p'-DDE	0.5-5.0	Y=0.877X+0.208	0.999
Dieldrin	0.5-5.0	Y=1.1280X-0.0333	0.999
Endrin	0.5-5.0	Y=0.741X-0.0150	0.998
p.p'-DDD	1.5-9.0	Y=0779X+0.205	0.999
p.p'-DDT	1.5-9.0	Y=1.344X-0.164	0.999
SURROGATE STANDARD			
Dibutyl Chlorendate	(5.40)	Y=0.480X+1.359	0.994

Table 4. Quality Control for Water Sample Analysis

COMPOUNDS	MEAN RECOVERY % X ± S.D	RELATIVE DEVIATION (%)	MINIMUM DETECTABLE (ng/g)
α-BHC	92.8 ± 12.5	13.5	0.01
β-BHC	89.1 ± 13.8	15.5	0.02
γ-BHC	97.4 ± 13.7	14.1	0.01
δ-BHC	83.9 ± 13.3	15.9	0.01
Heptachlor	95.3 ± 11.5	12.1	0.01
Aldrin	98.9 ± 13.1	13.2	0.01
Heptachlor Epoxide	95.5 ± 12.4	13.0	0.01
p.p'-DDE	96.5 ± 11.7	12.1	0.01
Dieldrin	94.8 ± 11.6	12.2	0.01
Endrin	85.2 ± 11.5	13.5	0.01
p.p'-DDD	89.9 ± 6.08	6.76	0.01
p.p'-DDT	94.1 ± 8.95	9.51	0.01
Surrogate Standard			
Dibutyl Chlorendate	97.6 ± 9.44	9.67	0.05

*Minimum detectable concentration (μg/ℓ) basis on 900 ml water sample.

$$= \frac{(5 \text{ X G.C. noise})}{\text{std.inj. pk area}} \times \underline{(\text{inj.amt.})} \times \frac{(\text{final ext.})}{(\text{inj. vol.})} \times \frac{1}{(\text{sample size})} \times \frac{1}{(\text{recovery})}$$

Table 5. GAS CHROMATOGRAPH/MASS SPECTROMETER (ION TRAP DETECTOR) OPERATING CONDITIONS

Model:	Varian GC 3400 & Finnigan ITD 800
Column:	DB-5, 30m x 0.25mm ID
Carrier:	Helium (25 cm/sec) Head pressure = 11 psi
Oven:	80°C for 1 min to 225°C at 8°C/min and to 280°C at 3°C/min
Detector:	Ion trap with open split interface

COMPOUNDS	RETENTION TIME (MIN.)	BASE PEAK	SCAN NO.	SENSITIVITY (ng)
α-BHC	20.00	181	1218	0.5
β-BHC	20.50	181	1269	0.5
γ-BHC	21.04	181	1282	0.5
δ-BHC	21.49	181	1329	0.5
Heptachlor	23.33	272	1412	0.5
Aldrin	24.51	263	1419	0.5
Heptachlor Epoxide	26.24	355	1583	0.5
p.p'-DDE	28.47	246	1727	1.00
Dieldrin	29.06	263	1745	1.00
Endrin	30.08	263	1807	1.00
p.p'-DDD	30.48	235	1846	1.00
p.p'-DDT	32.42	235	1953	3.00
Surrogate Standard				
Dibutyl Chlorendate	36.22	388	2181	0.50

Table 6. QUALITY CONTROL FOR SEDIMENT SAMPLE ANALYSIS

COMPOUNDS	MEAN RECOVERY % X ± S.D	RELATIVE DEVIATION (%)	MINIMUM DETECTABLE (ng/g)
α-BHC	84.3 ± 11.1	13.2	0.17
β-BHC	98.3 ± 6.35	6.46	0.19
γ-BHC	85.1 ± 5.69	6.69	0.18
δ-BHC	89.3 ± 2.45	2.74	0.21
Heptachlor	85.8 ± 8.88	10.3	0.46
Aldrin	86.3 ± 10.0	11.6	0.18
Heptachlor Epoxide	80.2 ± 6.56	8.18	0.24
p,p'-DDE	96.8 ± 9.63	9.95	0.24
Dieldrin	76.5 ± 5.48	7.16	0.32
Endrin	81.1 ± 5.71	7.04	0.49
p,p'-DDD	93.2 ± 5.61	6.02	0.29
p,p'-DDT	88.8 ± 9.35	10.5	0.40

Note:

1. $\bar{X}$: Mean value of a set of n = 5 samples.
2. S.D.: Standard deviation.
3. Minimum Detectable: Corrected with recovery efficiency for each compound, basis on 100g sample size.

Table 7. SUMMARY OF DETECTED COMPOUNDS IN THE SEDIMENT SAMPLES AT EACH IMPOUNDMENT (ng/g)

Sampling Location	p,p'-DDE (ng/g)	Dieldrin (ng/g)	Lindane (γ-BHC) (ng/g)
I1/S1/01	2.65	N.D.	N.D.
I1/S1/02	3.05	N.D.	N.D.
I2/S1/01	N.D.	34.0±2.36	N.D.
I2/S2/01	17.0	N.D.	N.D.
I3/S1/01	N.D.	43.2±2.11	N.D.
I3/S1/02	N.D.	2.54	N.D.
I3/S2/01	N.D.	6.31	N.D.
I3/S2/02	N.D.	5.52	N.D.
I5/S1/01	N.D.	N.D.	2.28
I5/S1/02	N.D.	N.D.	2.83
I5/S2/01	14.8	N.D.	N.D.
I7/S1/01	N.D.	N.D.	4.45
I7/S2/01	N.D.	N.D.	4.84
I7/S2/02	N.D.	N.D.	4.06
I8B+C/S2/01	N.D.	N.D.	3.55±1.31
I8B+C/S2/02	N.D.	N.D.	2.30
I9/S1/01	N.D.	N.D.	2.99±0.13
I9/S2/01	N.D.	N.D.	3.87
I10A/S1/01	N.D.	N.D.	1.58
I10A/S2/01	1.87	N.D.	4.94
I12/S1/01	N.D.	N.D.	8.95±0.29
I12/S1/02	N.D.	N.D.	1.66

Table 7. cont.

Sampling Location*	p,p'-DDE (ng/g)	Dieldrin (ng/g)	Lindane (γ-BHC) (ng/g)
I12/S1/03	N.D.	N.D.	6.03
I12/S2/01	N.D.	N.D.	34.4
I12/S2/02	N.D.	N.D.	4.46
I12/S2/03	N.D.	N.D.	9.40
I16A/S1/01	0.39	N.D.	5.14
I16A/S2/01	N.D.	N.D.	5.37
I17A/S1/01	N.D.	28.1	8.50
I17A/S1/02	N.D.	N.D.	3.42
I17A/S2/01	N.D.	N.D.	7.84
I17A/S2/02	N.D.	N.D.	6.79
I17A/S2/03	N.D.	N.D.	5.26
I18/S2/01	3.83	N.D.	8.08
I19A/S1/01	N.D.	N.D.	3.69
I19A/S1/02	N.D.	N.D.	3.07
I19A/S2/01	1.97	N.D.	12.9
I19B/S1/01	3.55±0.87	N.D.	13.7±1.30
I19B/S1/02	N.D.	N.D.	3.51
I23/S1/01	31.2	N.D.	3.35
I24/S1/01	N.D.	N.D.	0.85
I24/S2/01	N.D.	N.D.	8.53±0.70
I24/S2/02	N.D.	N.D.	5.93
I24/S2/03	N.D.	N.D.	2.62

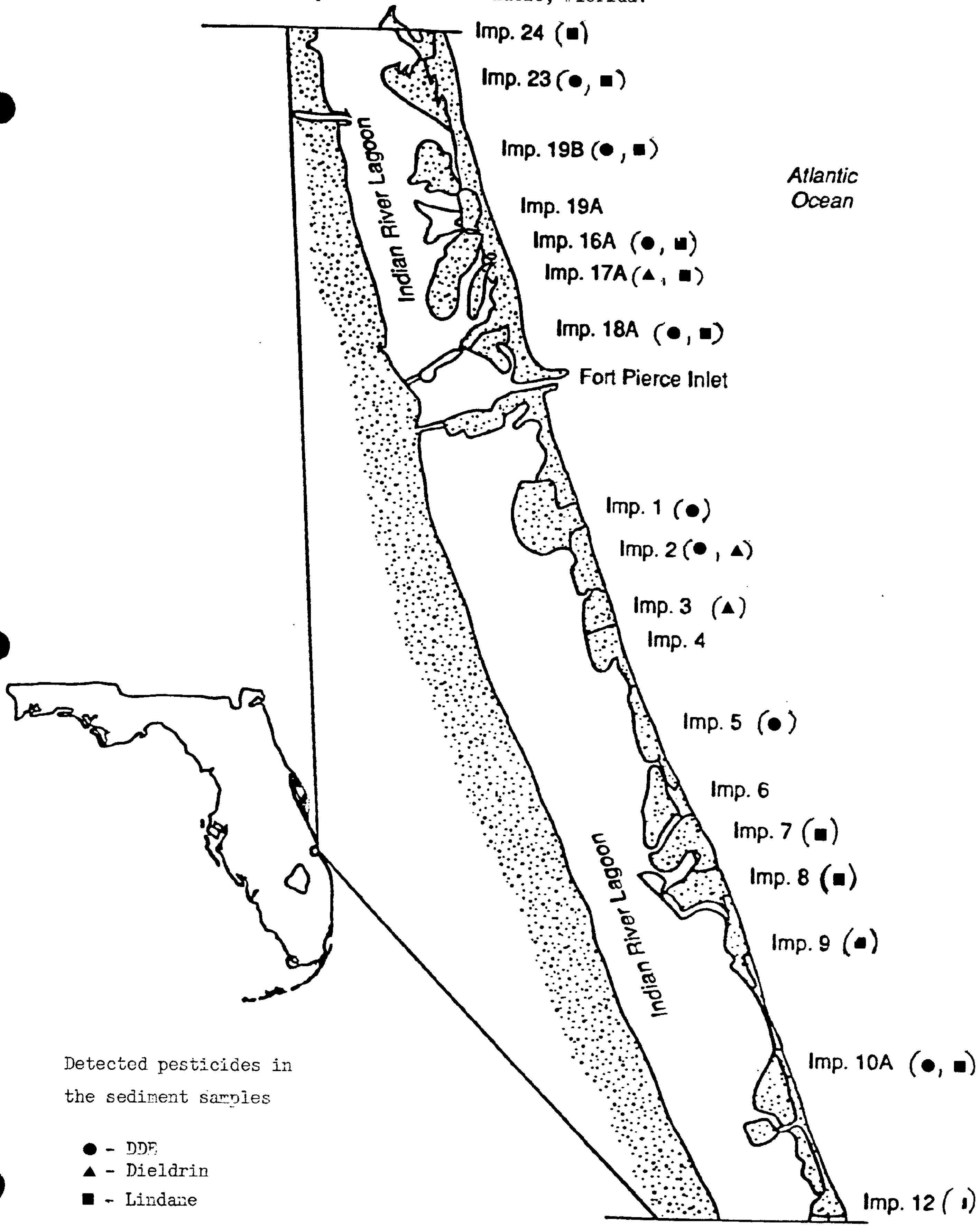
* Impoundment no./ site no./ layer no.

Table 8. SUMMARY TRANSECT SEDIMENT SAMPLING FOR IMPOUNDMENTS 1 AND 2

Sampling Location*	p,p'-DDE (ng/g)	Dieldrin (ng/g)	Lindane (γ-BHC) (ng/g)
I1/T4 (D)	2.41	N.D.	N.D.
I1/T7 (G)	7.54	N.D.	N.D.
I2/T1/S2 (B)	N.D.	N.D.	5.92
I2/T1/S3 (C)	2.29	N.D.	3.52
I2/T2/S2 (E)	N.D.	15.6	4.02
I2/T3/S3 (I)	N.D.	26.9	2.80

* Impoundment No./ site No./ layer No. (Sample identification No.)

in each Impoundment at St. Lucie, Florida.

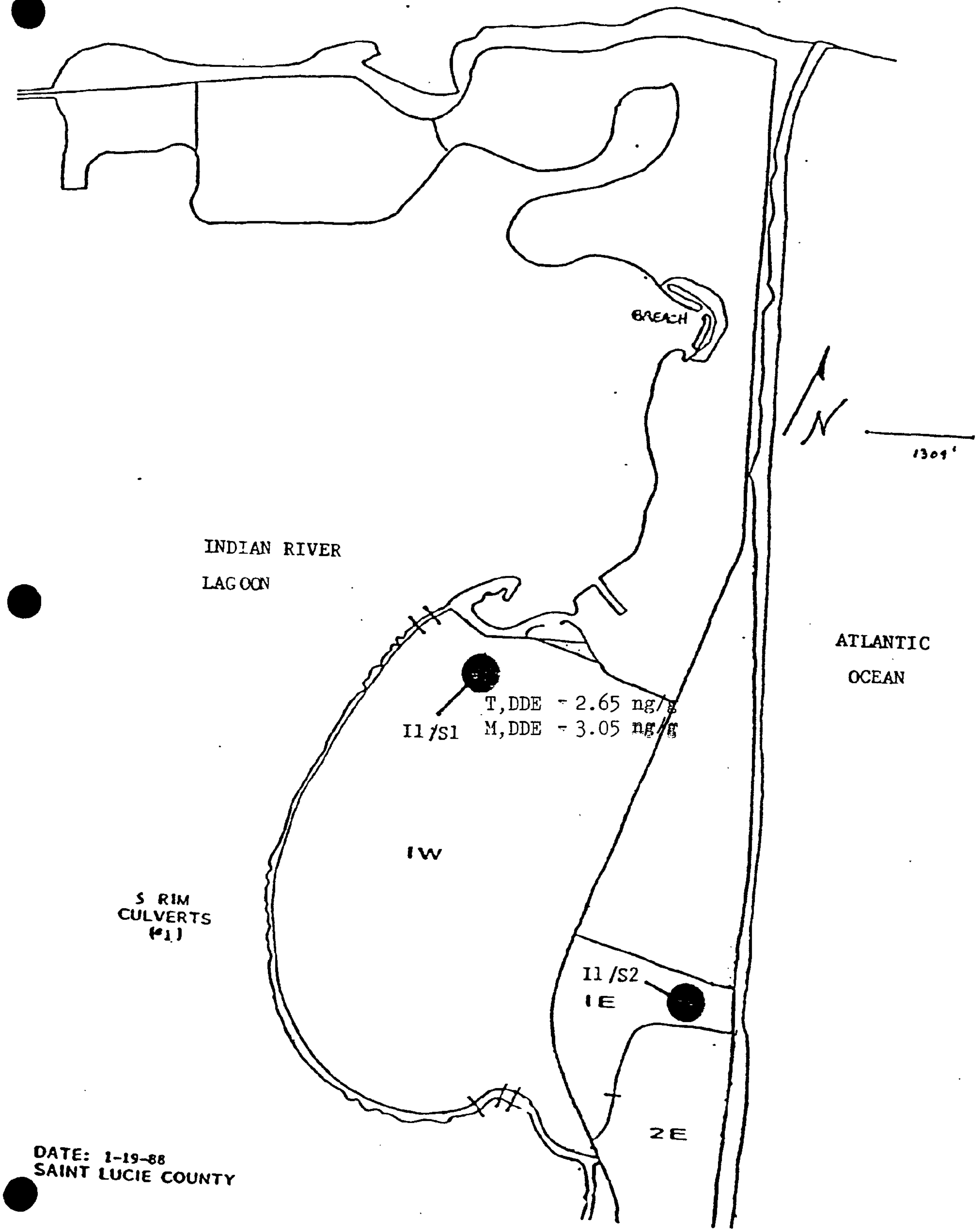


Detected pesticides in the sediment samples

● - DDE
▲ - Dieldrin
■ - Lindane

Figure 2A. Pesticide Distribution in the sediment at each Impoundment

(T-Top Layer, M-Middle Layer, B-Bottom Layer)



T,DDE - 2.65 ng/g
M,DDE - 3.05 ng/g

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Figure 2B. Pesticide Distribution in the Sediment at each Impoundment
(Top-Top Layer, M-Middle Layer, B-Bottom Layer)

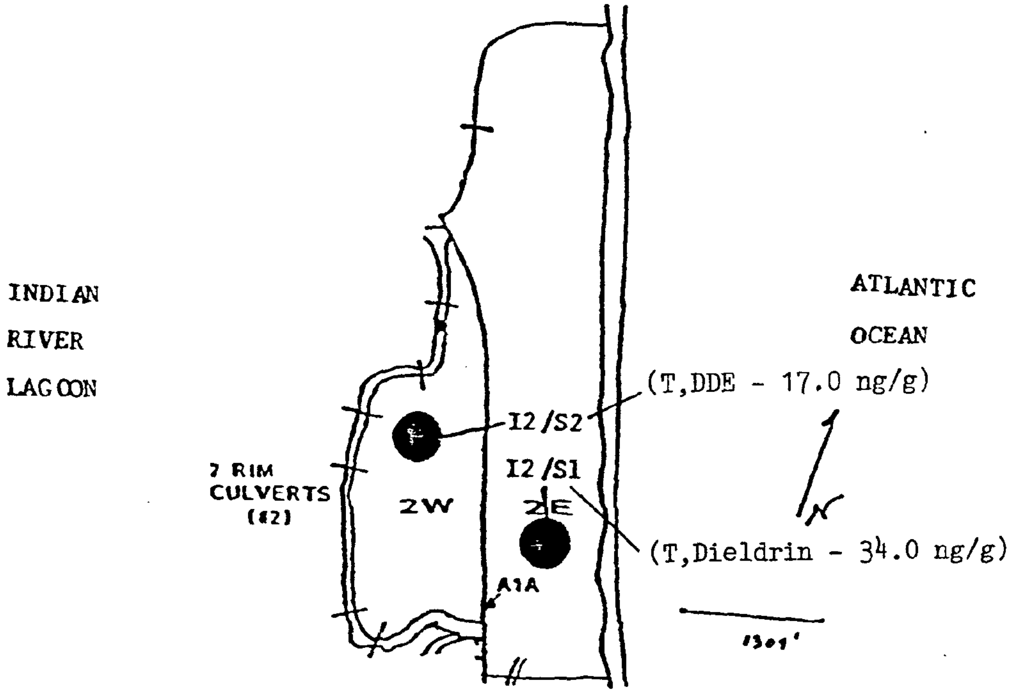


Figure 2C. Pesticide Distribution in the Sediment at each Impoundment
(T-Top Layer, M- Middle Layer, B- Bottom Layer)

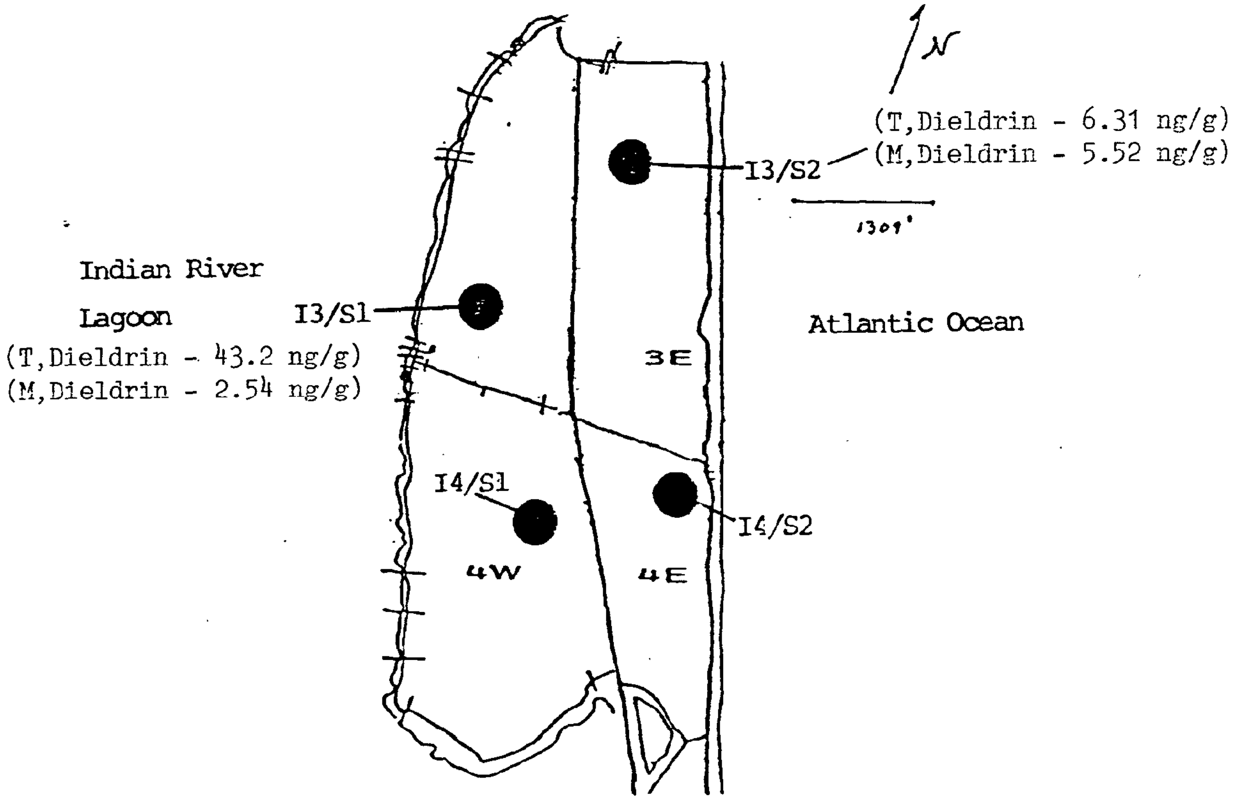


Figure 2D. Pesticide Distribution in the Sediment at each Impoundment
(T-Top Layer, M-Middle Layer, B-Bottom Layer)

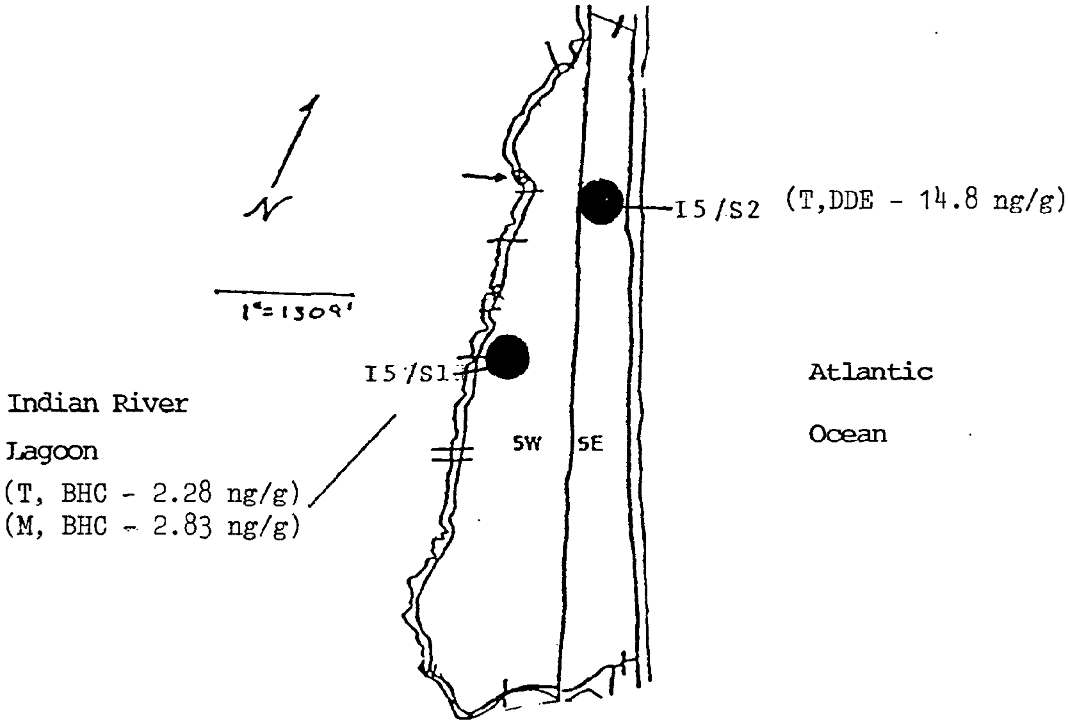


Figure 2E. Pesticide Distribution in the Sediment at each Impoundment (T-Top Layer, M-Middle Layer, B-Bottom Layer)

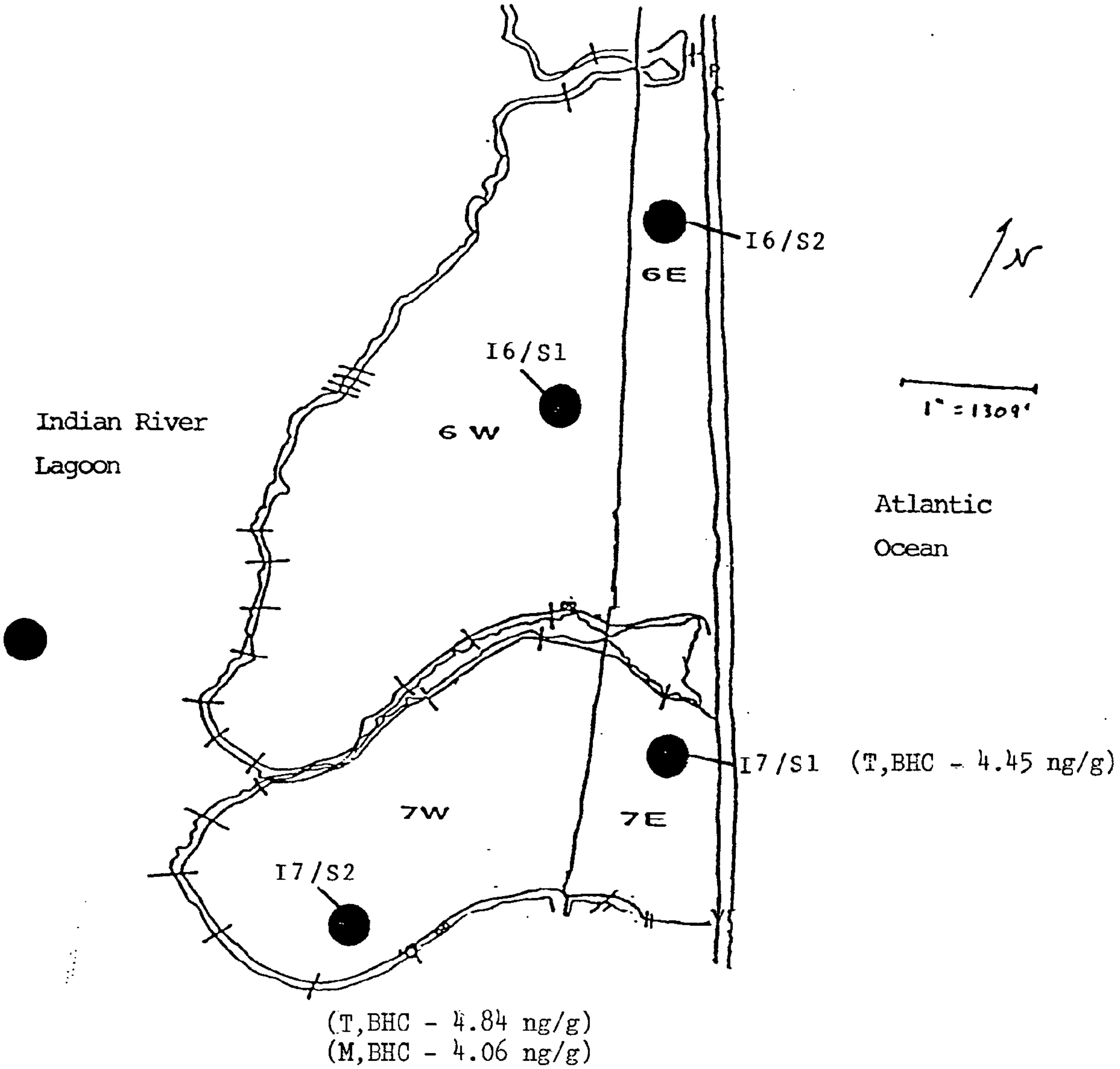
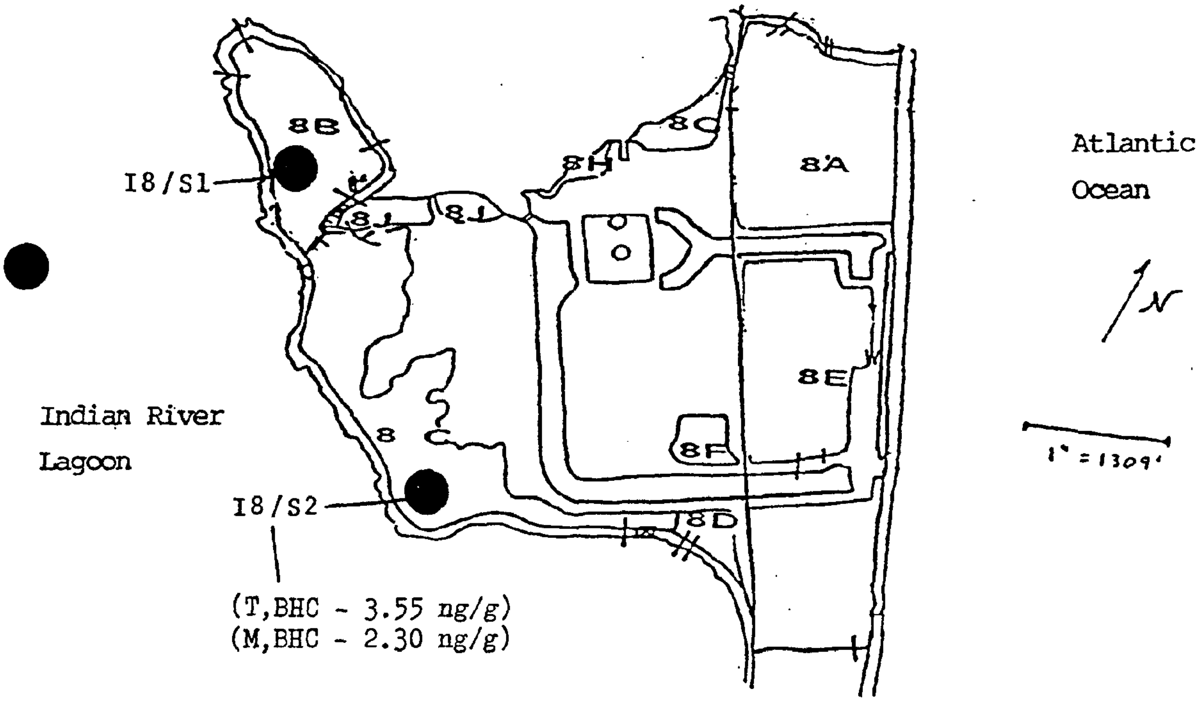


Figure 2F. Pesticide Distribution in the Sediment at each Impoundment
(T-Top Layer, M-Middle Layer, B- Bottom Layer)



(T,BHC - 3.55 ng/g)
(M,BHC - 2.30 ng/g)

Figure 2G. Pesticide Distribution in the Sediment at each Impoundment
(T-Top Layer, M-Middle Layer, B-Bottom Layer)

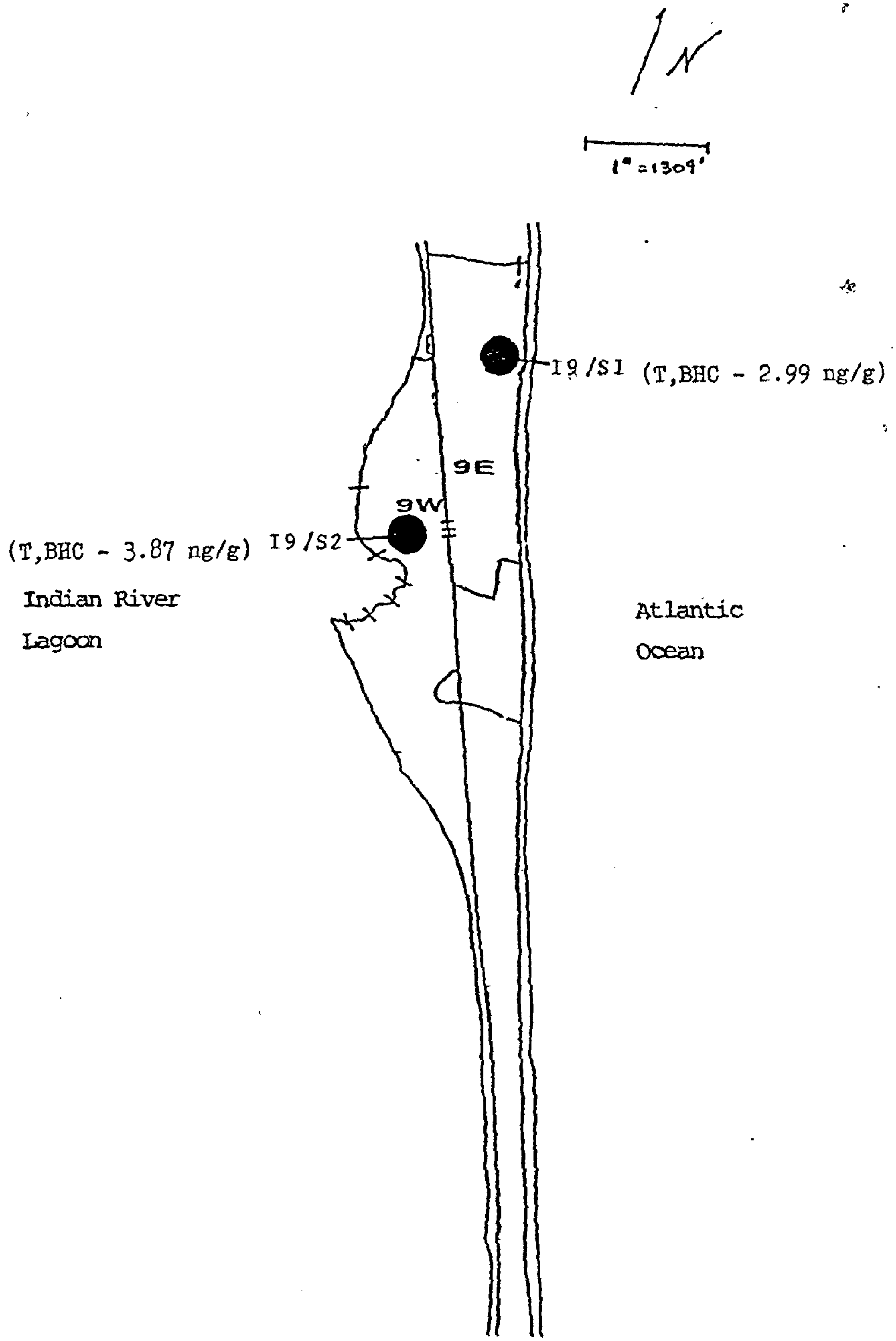


Figure 2H. Pesticide Distribution in the Sediment at each Impoundment (T-Top Layer, M-Middle Layer, B-Bottom Layer)

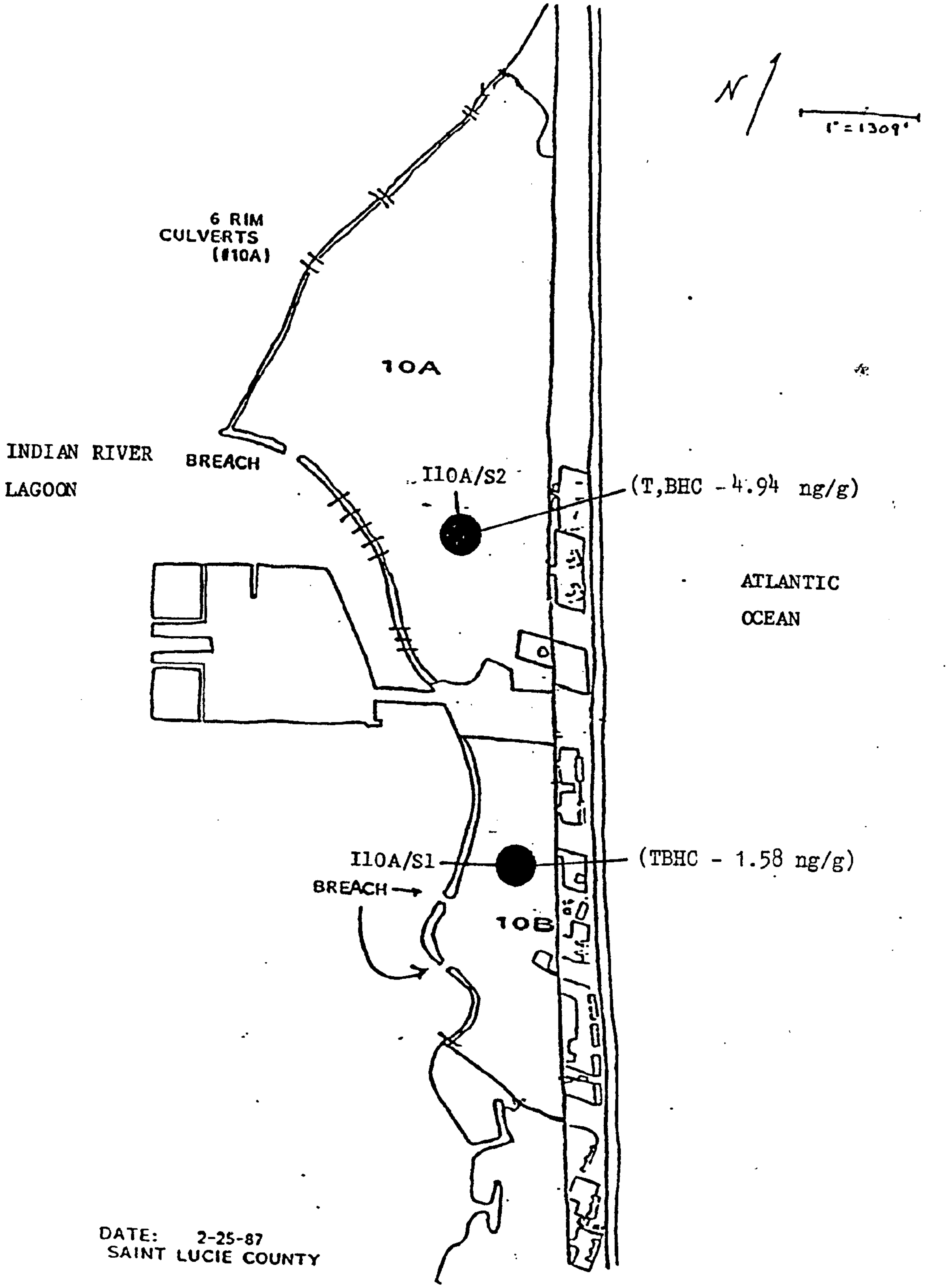


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Figure 21. Pesticide Distribution in the Sediment at each Impoundment
(T-Top Layer, M-Middle Layer, B-Bottom)

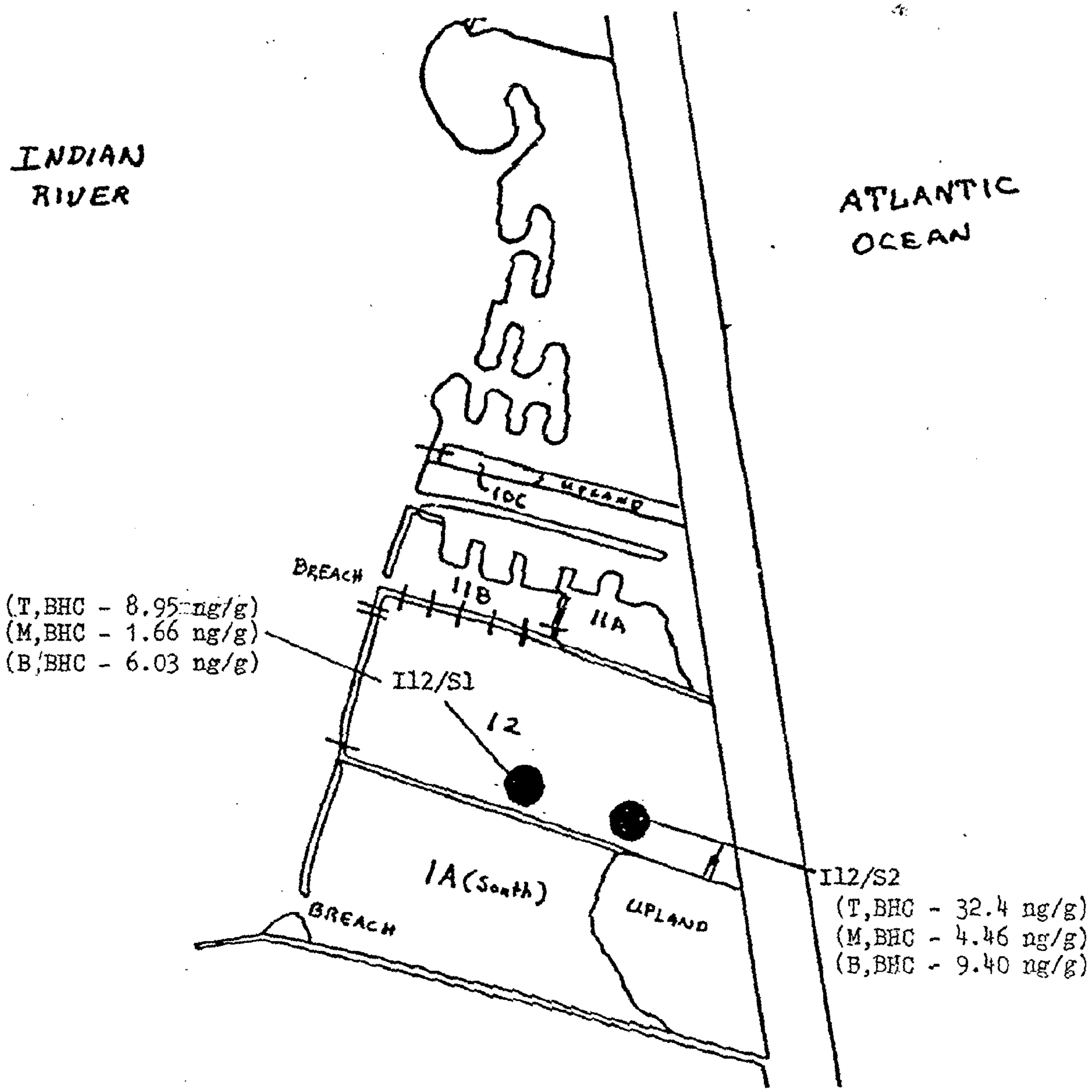


Figure 2J. Pesticide Distribution in the Sediment at each Impoundment (T-Top Layer, M-Middle Layer, B-Bottom Layer)

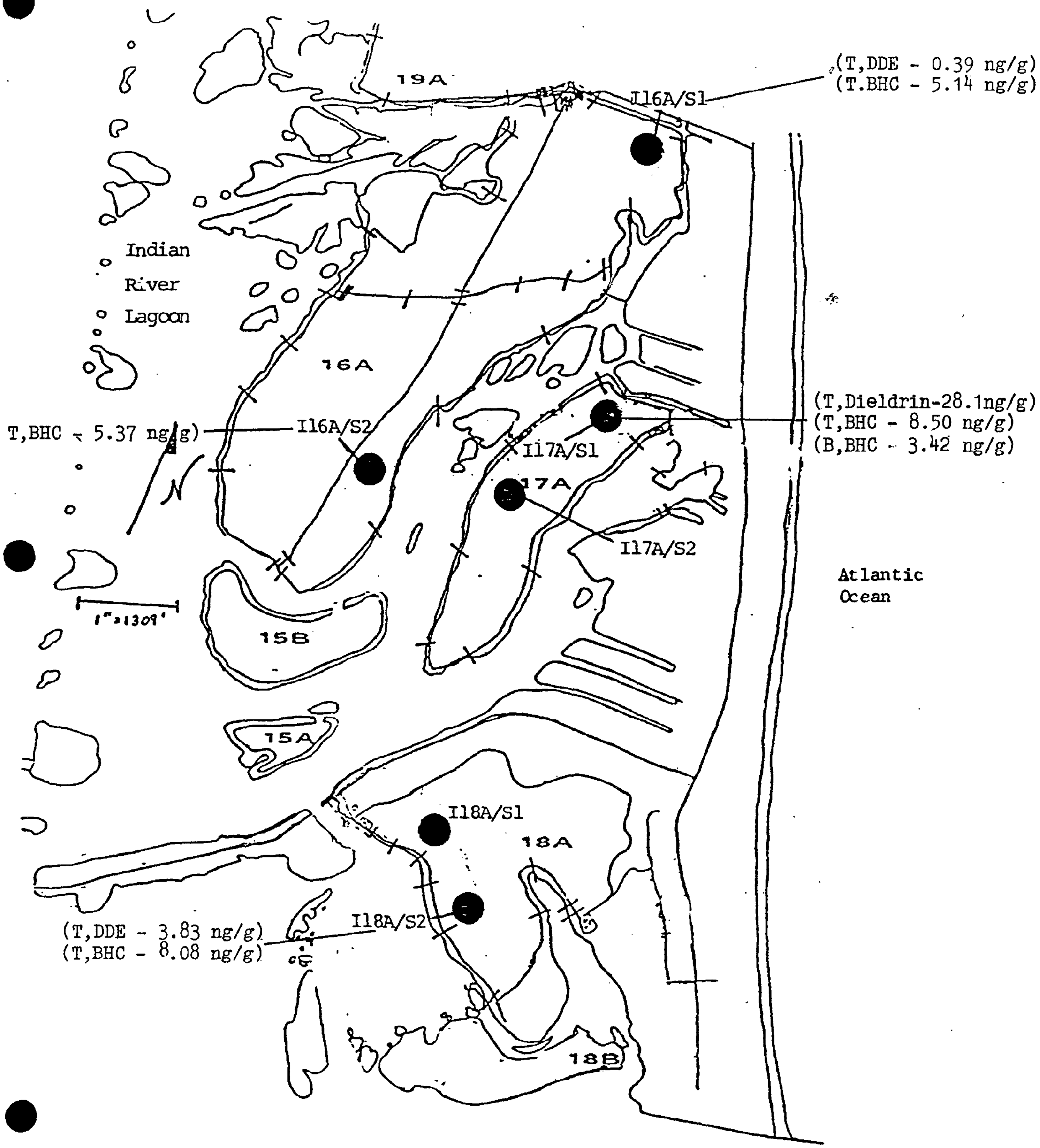


Figure 2K. Pesticide Distribution in the Sediment at each Impoundment (T-Top Layer, M-Middle Layer, B-Bottom Layer)

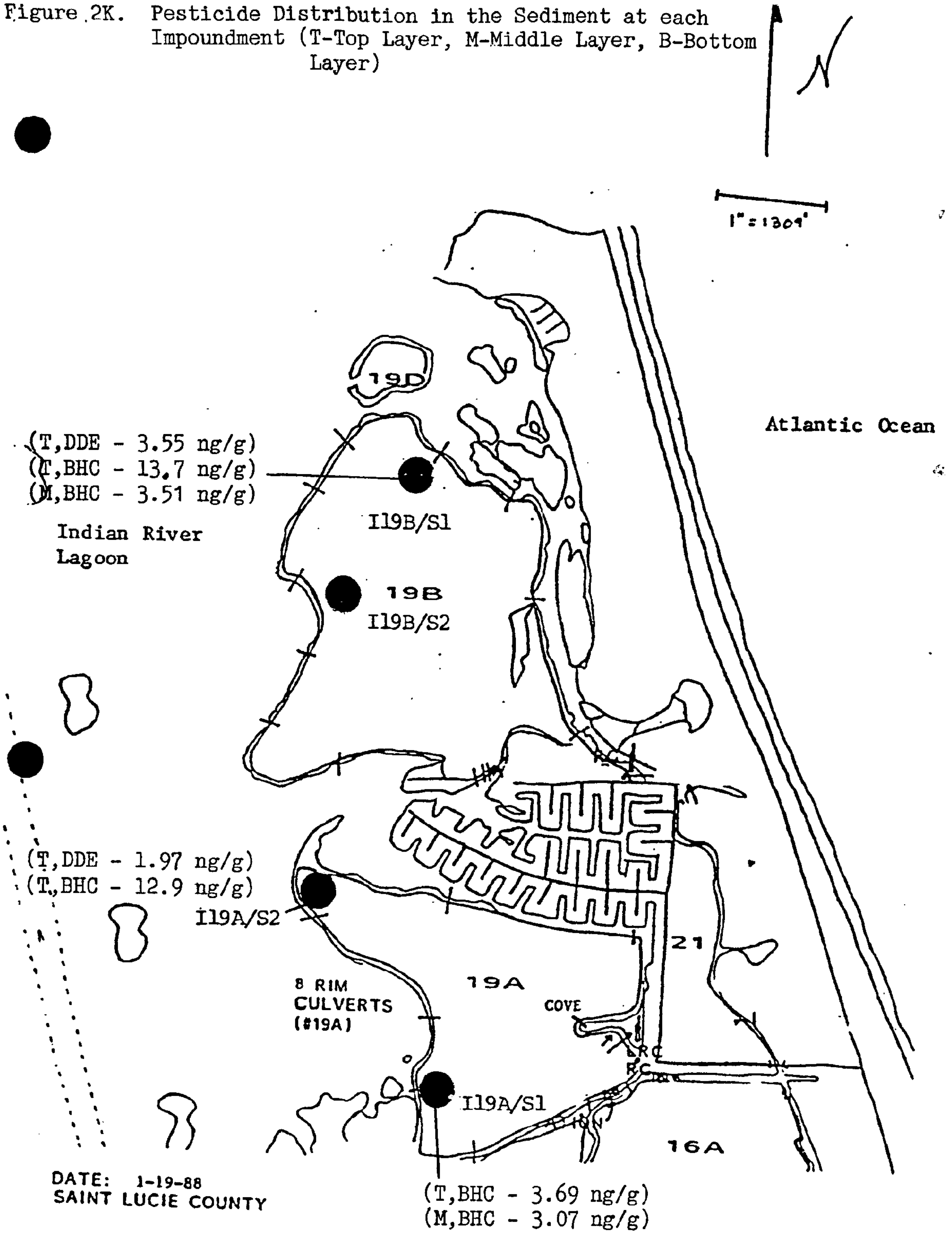


Figure 2L. Pesticide Distribution in the Sediment at each Impoundment (T-Top Layer, M-Middle Layer, B-Bottom Layer)

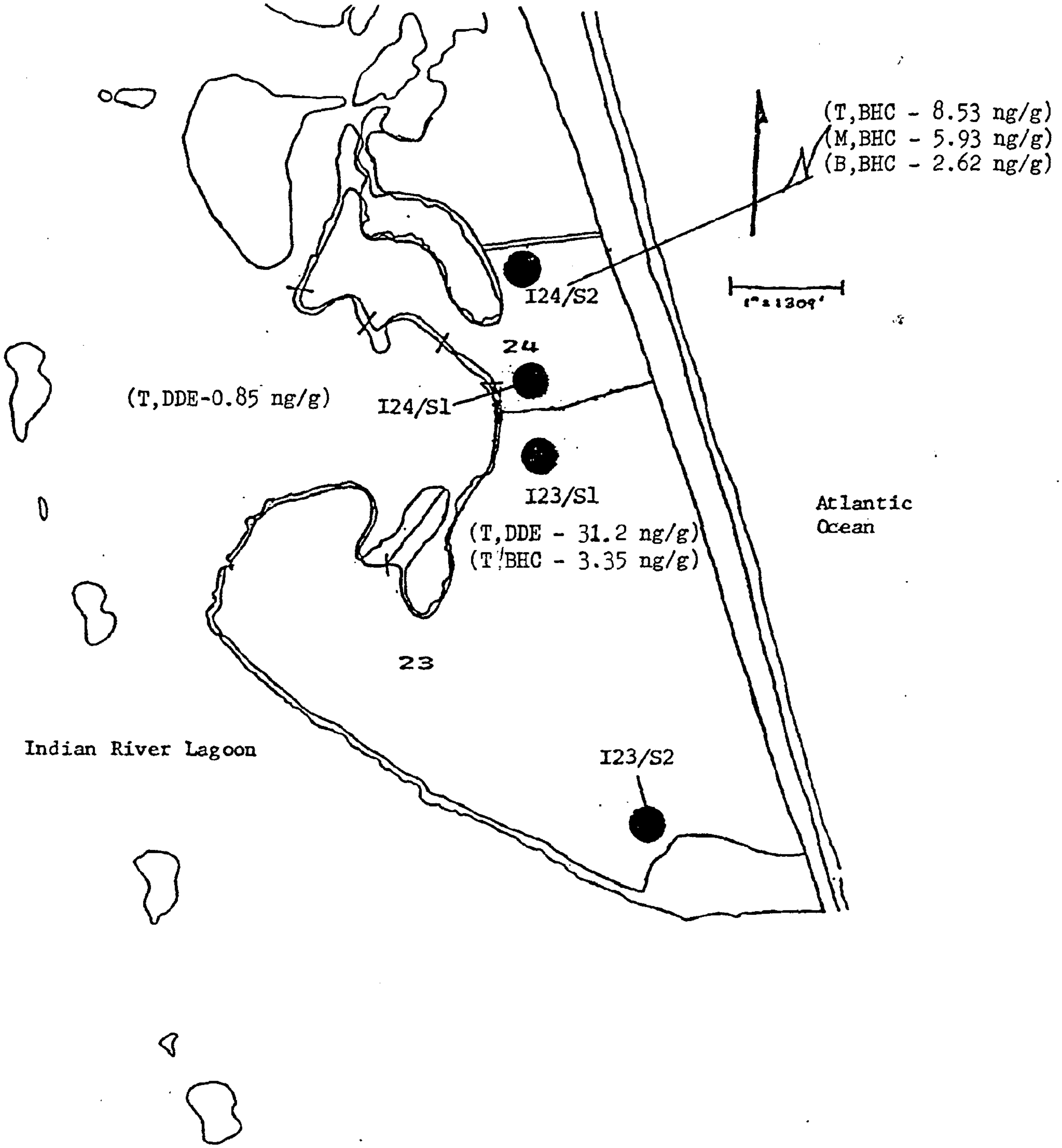


Figure 3A. Transect Sediment Sampling at Impoundment 1

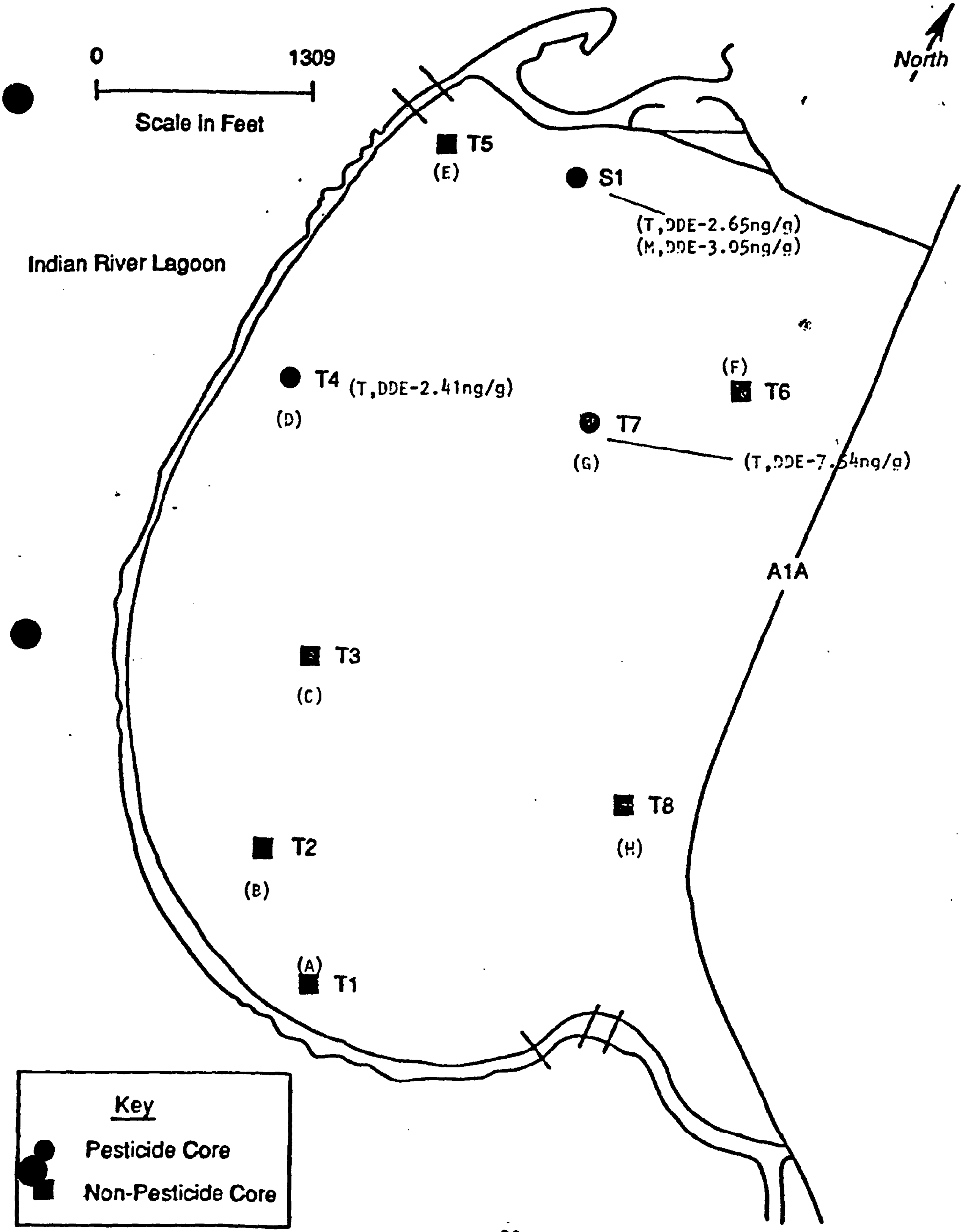
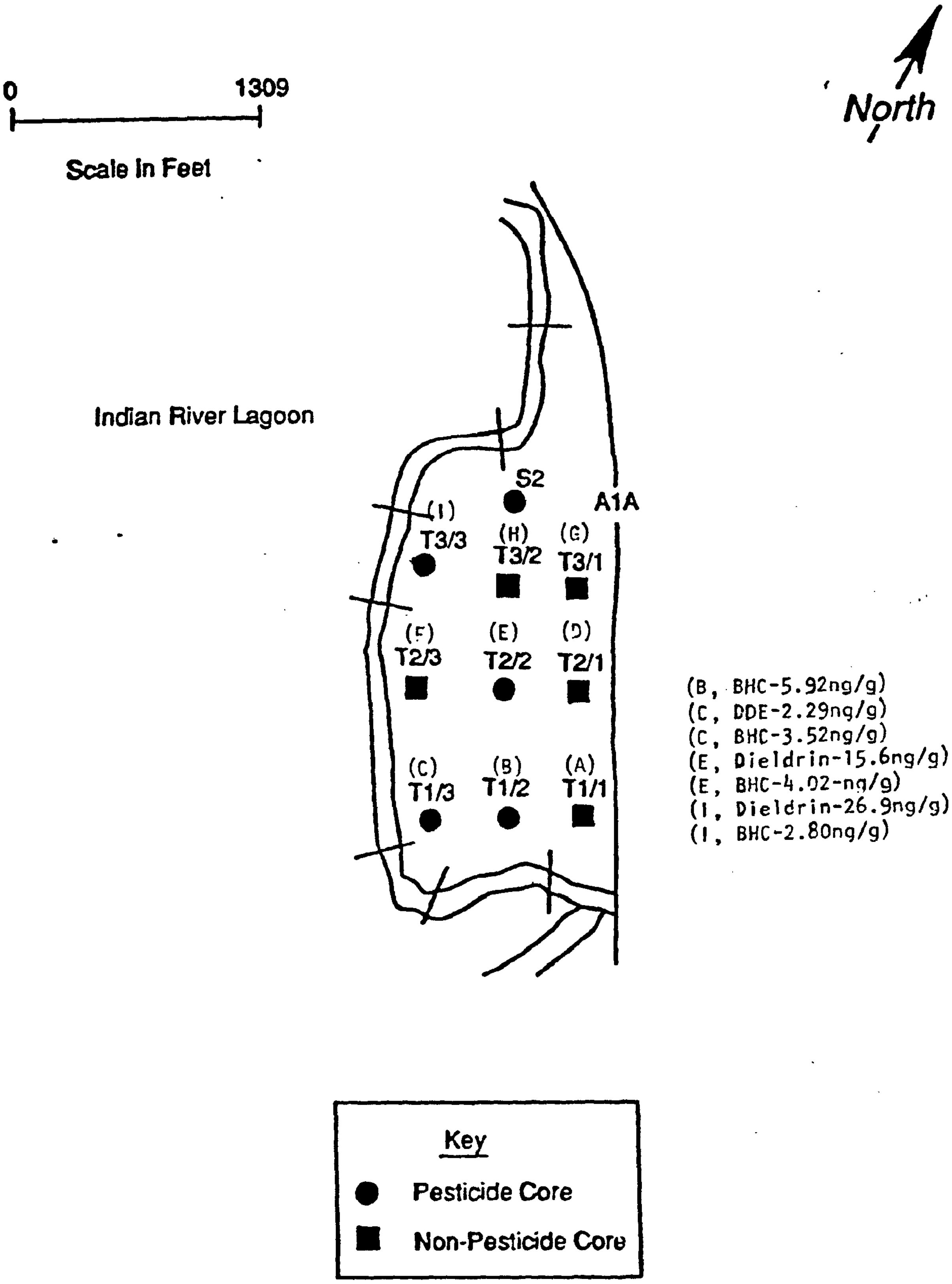


Figure 3B. Transect Sediment Sampling at Impoundment 2



(B, BHC-5.92ng/g)
(C, DDE-2.29ng/g)
(C, BHC-3.52ng/g)
(E, Dieldrin-15.6ng/g)
(E, BHC-4.02-ng/g)
(I, Dieldrin-26.9ng/g)
(I, BHC-2.80ng/g)

Figure 4A. Impoundment 1 Water Flushing Sampling

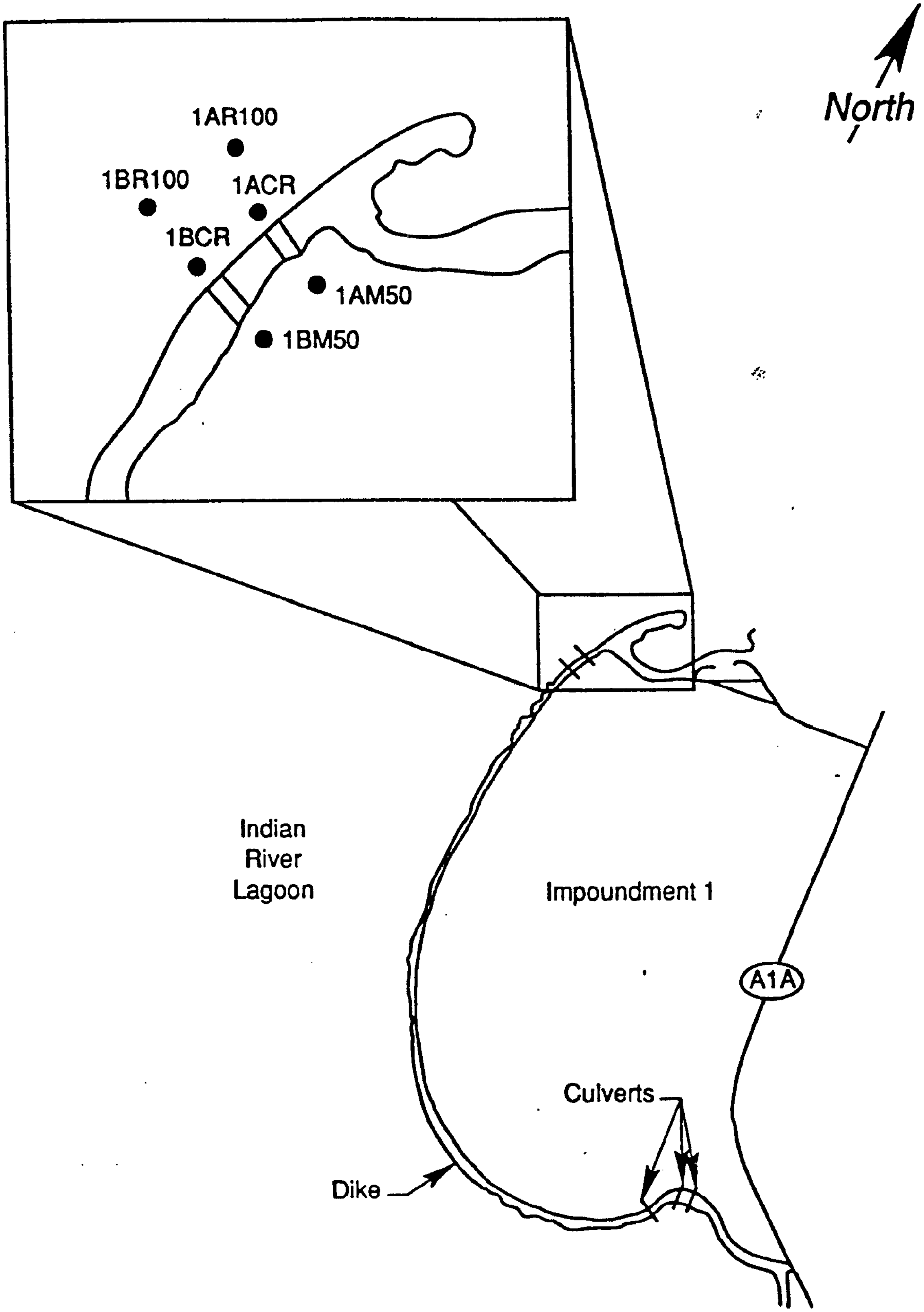
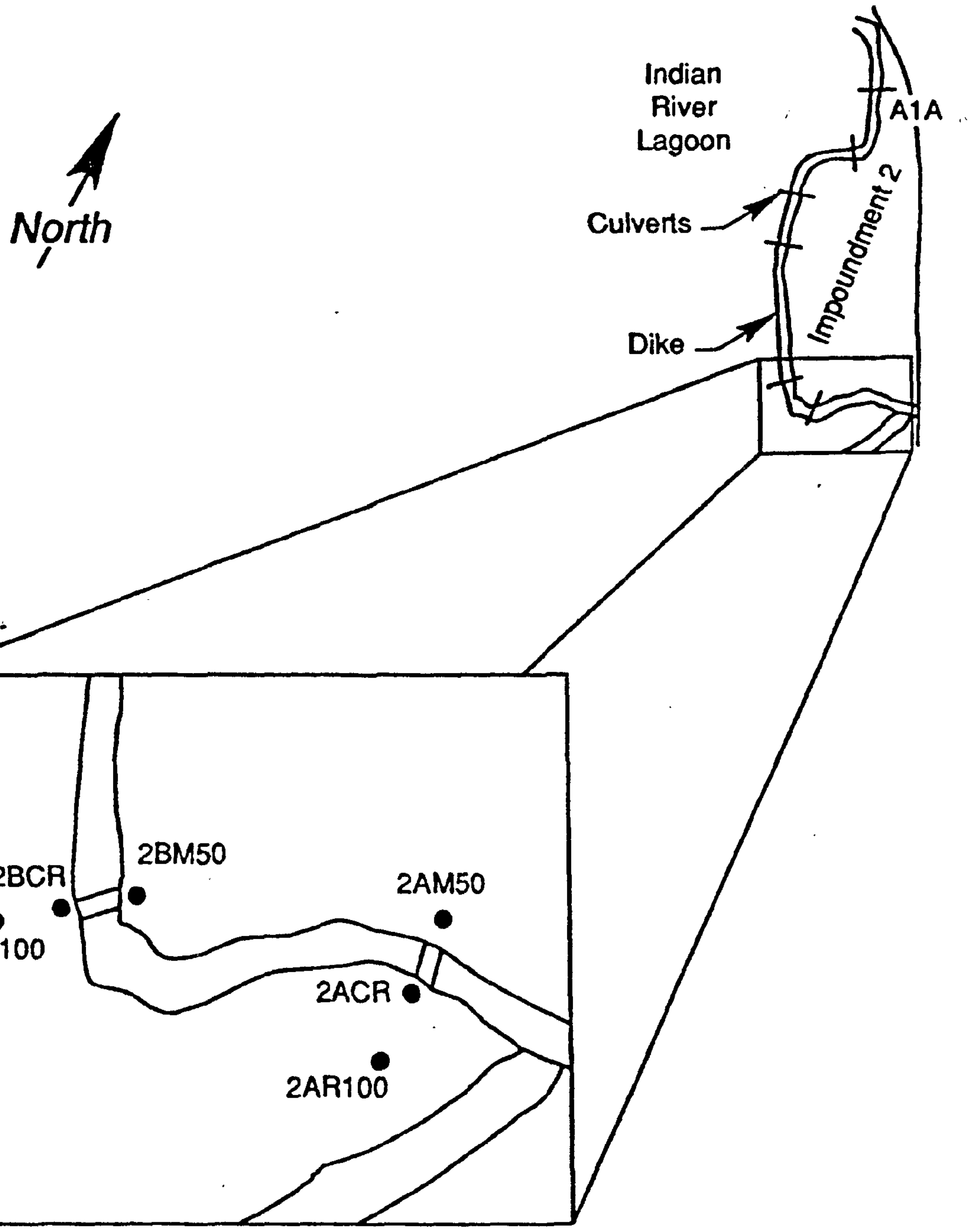


Figure 4B. Impoundment 2 Water Flushing Sampling



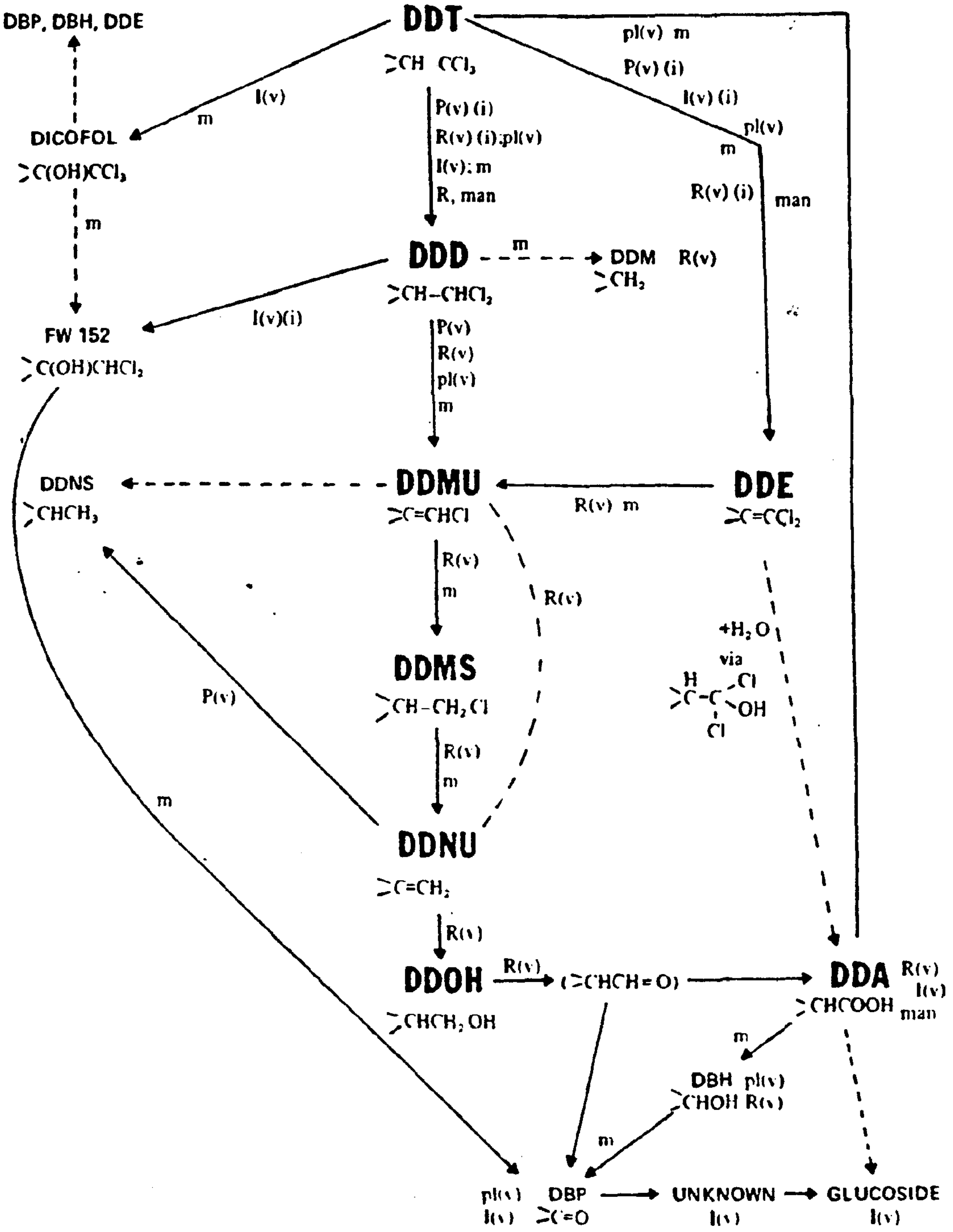


FIGURE 5. Pathways and products of DDT metabolism in some living organisms. I = insects; m = microorganisms; P = pigeon; pl = plants; R = rat; i = in vitro; v = in vivo (20)

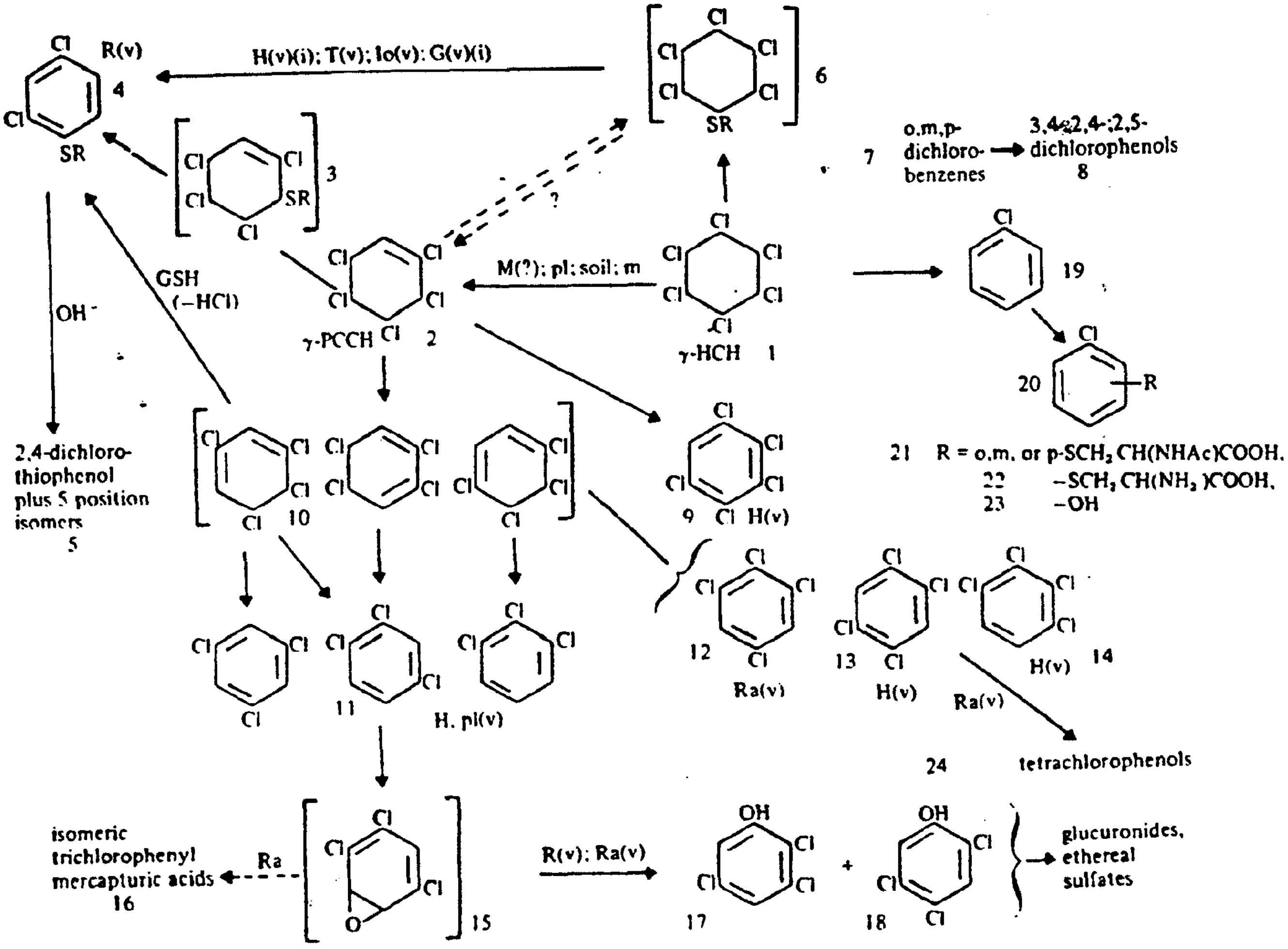


FIGURE 6. Pathways (some speculative) of metabolism of lindane and related compounds. G = grass grub; H = housefly; lo = locust; M = mammal; m = microorganisms; pl = plants; Ra = rabbit; R = rat; T = cattle tick; i = in vitro; v = in vivo; in structure 4, -SR = glutathione for H, T, lo and G; mercapturic acid for the rat. (20)

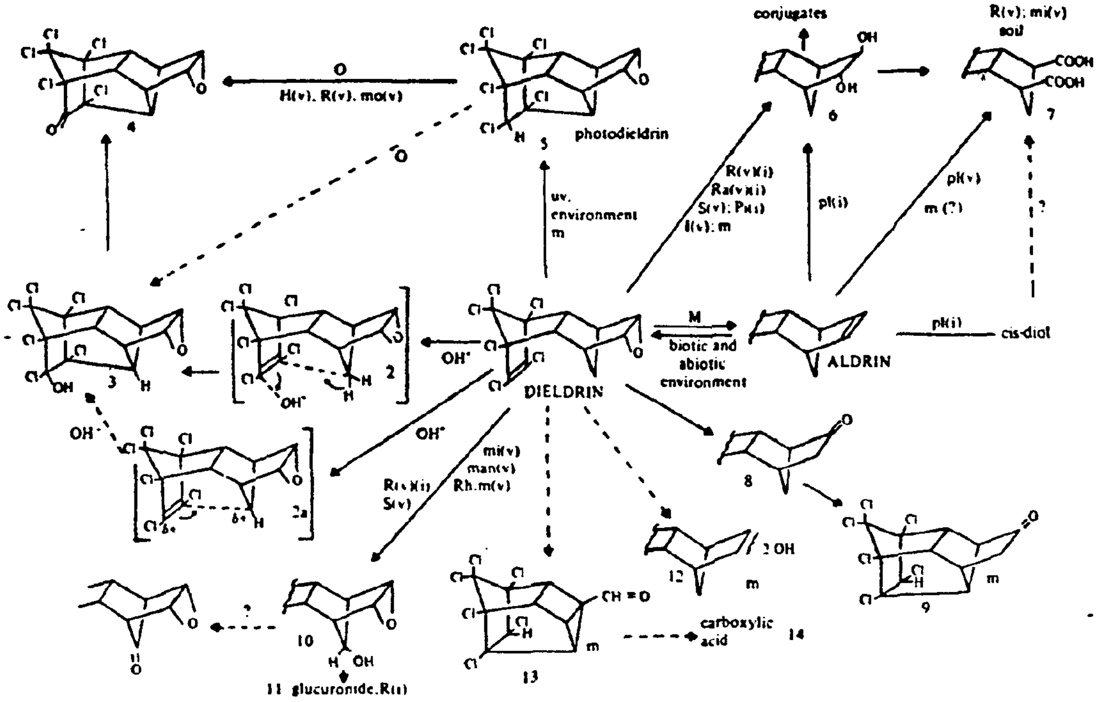


FIGURE 7. Metabolic conversions of aldrin, dieldrin and photodieldrin. H = housefly; I = other insects; m = microorganisms; mi = mice; mo = mosquito; Pi = pig; pl = plants; R = rat; Ra = rabbit; Rh.m = Rhesus monkey; S = sheep; i = in vitro; v = in vivo. (20)

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SECTION 4

CONTROLS ON PESTICIDE DISTRIBUTION AND MOBILITY

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Tsen Wang
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James David
St. Lucie County Mosquito Control

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Sediments

Pesticide Distribution Trends

Chemical analysis of 53 sediment cores taken in 18 St. Lucie County mosquito control impoundments suggests organochlorine pesticide distribution is widespread. 89% of the impoundments contained pesticides. However, this distribution is very patchy. Detailed analysis of Impoundments 1 and 2 suggest the distribution of pesticide residue within <u>each</u> impoundment is also patchy. 33% of the cores in Impoundment 1 contained pesticide residue and 60% in Impoundment 2. In several cases these cores were <150m apart.

Geographically, gamma BHC (a residual of BHC mixed compounds applied in the mid to late 1950's) appears to be concentrated in northern and southern areas, while dieldrin (a residual of sandfly control experiments conducted in the mid 1950's) is more prevalent in the central areas.

In most cases the concentration of organochlorine compounds, if present, decreases with depth (Appendix A2). Pesticides were only found in subsurface samples if the overlying surface sample contained pesticides.

Controls on Pesticide Distribution

The patchy distribution of organochlorine compounds within salt marsh sediments of St. Lucie County mosquito control impoundments can be attributed to a number of processes including: (1) application, (2) post treatment breakdown by microbial or microbial-related activity, (3) sunlight, and (4) migration.

County records are not sufficiently detailed to determine the degree to which pesticide application techniques have influenced the distribution patterns identified during this study. Post-treatment breakdown by microbial activity and sunlight are widely recognized as processes which alter the distribution of pesticides in marsh substrates. However, this study was not designed to investigate post treatment breakdown reaction pathways and therefore the degree to which pesticide distribution is controlled by these processes remains unevaluated at present.

The third factor which can influence the distribution of pesticides in St. Lucie County mosquito control impoundments is migration. All or some of the pesticide residue can potentially migrate from a contaminated layer into what were originally pristine sediments. This migration can occur in both the vertical and horizontal direction. Vertical migration is detectable by identifying the contact between sediments that were deposited prior to pesticide treatment and those sediments which were at the marsh surface when pesticides were being applied. In the case of St. Lucie County impoundments, the contact lies between sediment type 2 (premarsh) and either sediment type 1 or 4 (marsh). If sediment type 2 contains pesticides, migration has occurred. Lateral migration is a more difficult to recognize. It may have occurred if pretreatment sediments (e.g., sediment type 2 or 3) contain pesticides but the overlying sediment type 1 or 4 is barren of residue. In this case, pesticides may have migrated laterally from an adjacent subterranean contaminated zone. On the other hand, it could be argued that this contamination profile is the result of complete removal of pesticides from the overlying sediment through either breakdown or migration processes.

In 13 (36%) of 36 cores, pesticides were detected in the premarsh sediments. In all of these cases, the overlying marsh sediment sequence was also contaminated. Pesticides were never detected in premarsh sediments if the overlying marsh sediment was not contaminated. Hence, although vertical migration of pesticides has occurred in St. Lucie County mosquito control impoundments, mean migration distances are difficult to quantify because the pesticide samples were taken over the entire length of the sediment type. In addition, there is no evidence of lateral migration.

It was initially hypothesized that organic rich sediments would preferentially adsorb pesticide residue and hence a direct correlation between TOM and pesticide concentration was thought to be obtainable. However, the results of this study did not support this hypothesis (Figure 1 and 2). There were a number of instances in which pesticides were detected in surface sediments with low or no organic content. The apparent correlation between TOM and pesticides may be coincidental since Marsh sediments are typically organic rich. Hence most of the marsh surface exposed to pesticide was organic rich at the time of treatment. Subsequent to treatment, the pesticide may have either remained in place, or migrated downward and into the premarsh, organic poor, sediments (Figure 2). This migration produced a pesticide concentration profile that decreased with depth, as did the organic content of the host sediment.

This project was also designed to determine whether the water management by the Mosquito Control District had any effect on pesticide mobility. Of particular concern was whether a well flushed marsh facilitated pesticide migration and the flux of pesticides into the Indian River Lagoon. It was initially hypothesized that a well-flushed impoundment would promote migration and hence pesticide levels might be lower in a well flushed-marsh in comparison to a poorly-flushed marsh. This relationship was not apparent. Impoundment 1 was selected for detailed study as a poorly-flushed site. Impoundment 2 was selected to represent a well-flushed site. Thirty three percent of the cores in Impoundment 1 contained pesticides. Sixty percent of the cores in Impoundment 2 contained pesticides. This provides supporting evidence that water management for mosquito control does not influence pesticide mobility. Water quality data, described below, supports this assessment.

Water

Pesticide Distribution Trends

Water samples were taken from each of the 36 core holes (pore water) and in four transects proximal to Impoundment 1 and 2 paired bottom water release culverts (which continuously release bottom water throughout the closed season). A total of 51 pore water and 170 culvert samples were collected and analyzed for TOM and pesticide content. None of the water samples contained detectible levels of pesticides.

Controls on Pesticide Distribution

Initially it was hypothesized that pesticides entering the Indian River Lagoon would be associated with impoundment water high in POM because of the binding capacity of the organic material. Water samples were collected at the end of the open and closed period and at mid-closure drawdown to determine (1) what effect water management has on POM exchanging with the estuary, (2) whether pesticides are associated with this water, and (3) whether or not water management was enhancing the flux of pesticides into the Indian River Lagoon. The results of this study indicate that the water management practices of St. Lucie County mosquito control have no detectable effect on the concentration of pesticides entering the Indian River Lagoon.

CONCLUDING REMARKS

(1) Pesticides were detected within the sediments of St. Lucie County mosquito control impoundments.

(2) Pesticides have migrated from the treated sediments downward into sediment layers that were not contaminated during the original application of pesticides.

(3) There is no obvious graphical relationship between the presence or absence of pesticides and sediment TOM.

(4) Pore waters collected from the sediment core holes did not contain pesticides even if the sediment yielded positive results.

(5) Water management of the impoundments does not appear to have any effect of pesticide mobility through the sediments.

(6) Estuarine water circulating through the impoundments never contained detectible levels of pesticide.

(7) The significance of pesticide levels detected during this study is unknown and beyond this study's scope of work. Additional studies will be required to determine the effect of pesticide residue on biological systems in this area.

ADDITIONAL STUDIES

(1) Examine pesticide levels in adjacent estuarine areas.

(2) Examine biological uptake of pesticides by the organisms that inhabit the impoundments.

(3) Examine the impact of increased microbial activity resulting from management practices on pesticide degradation.

(4) Examine the applicability and practicality of mechanical or bio-remediation for the impoundment sediments.

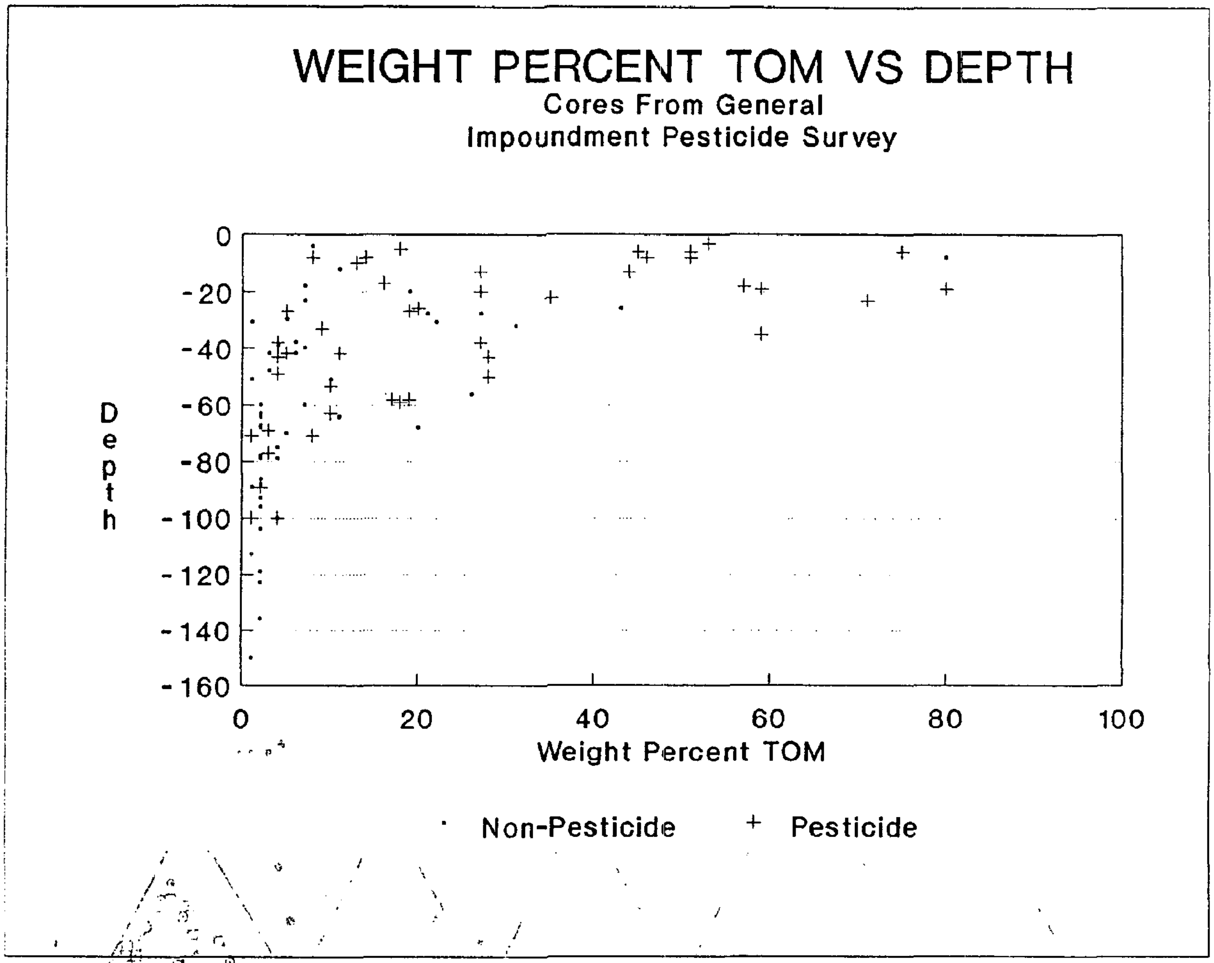

Figure 1.- Pesticide presence as a function of weight percent TOM and depth. Samples plotted are from the 18 general survey cores.

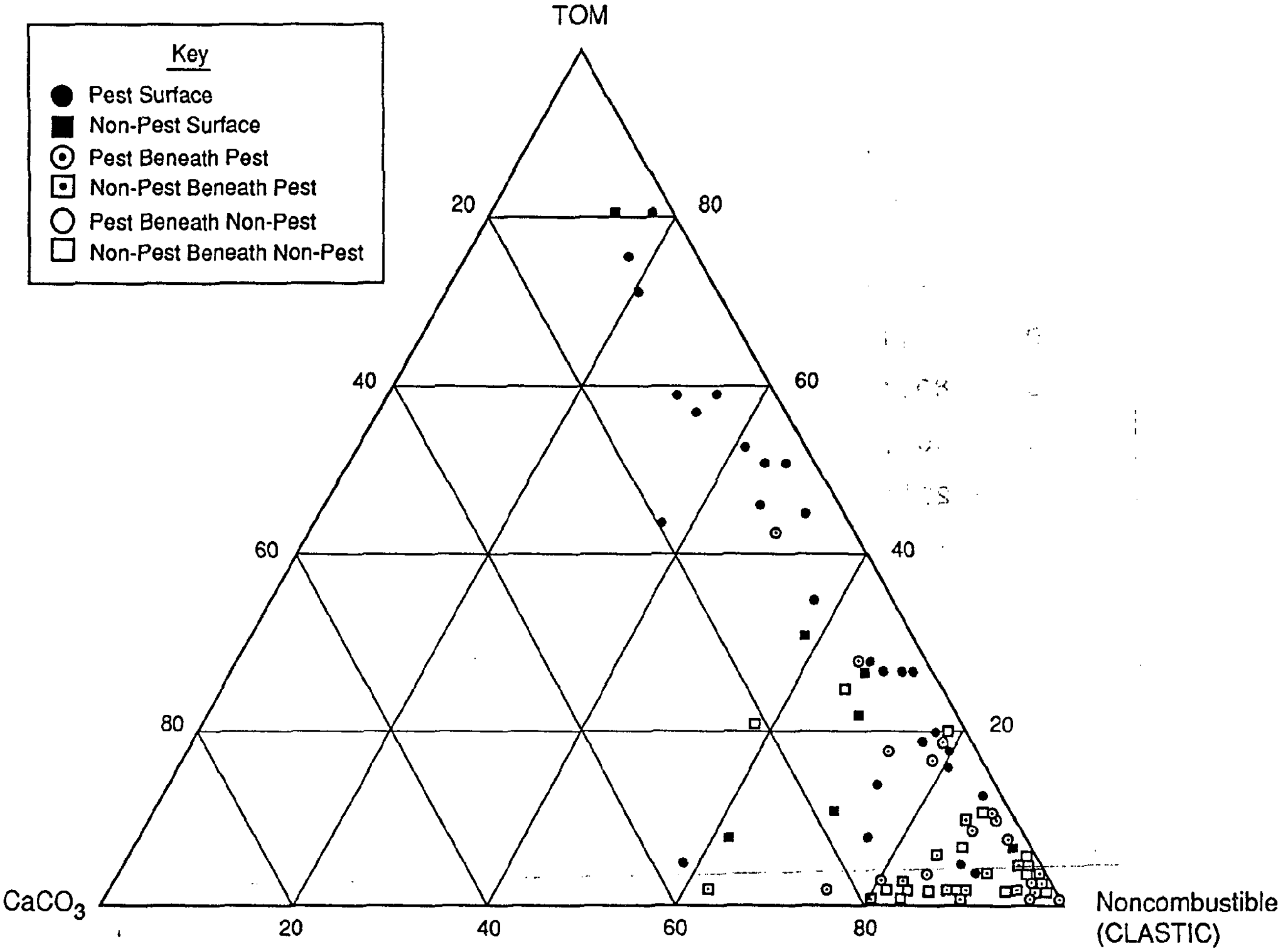

Figure 2 - Ternary diagram illustrating relationship between sediment composition, depth, and pesticide content

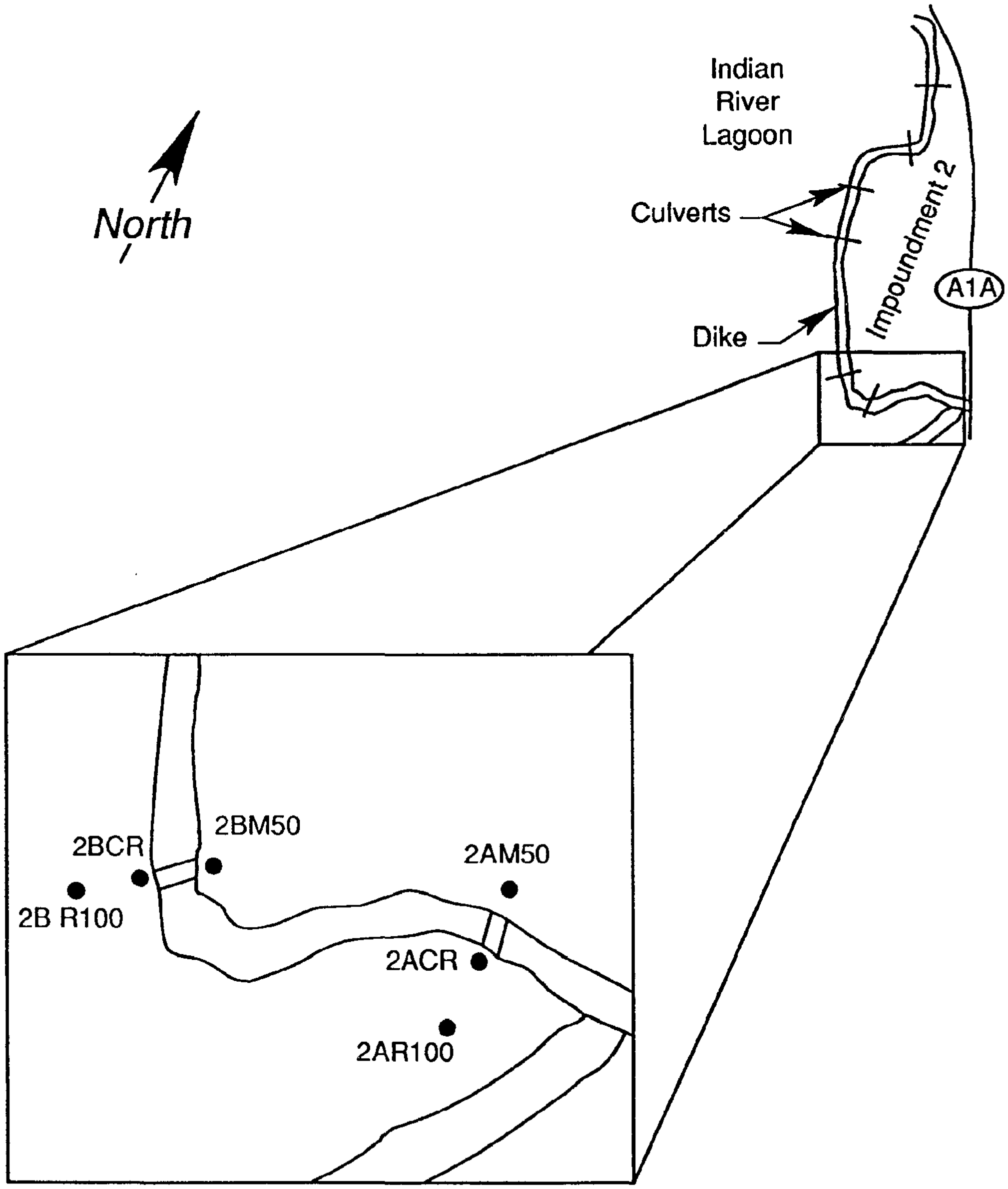

Figure 3 - Location Map of Culvert Water Sampling Stations: Impoundment 2