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M.S. degree in Entomology

Major professor

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PESTICIDE RESIDUE SURVEY
ON THE RED CEDAR RIVER, SOUTHCENTRAL MICHIGAN

by
Kouame Adou

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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ABSTRACT

PESTICIDE RESIDUE SURVEY ON THE RED CEDAR RIVER, SOUTHCENTRAL MICHIGAN

by

Kouame Adou

Pesticide use has in part resulted in the contamination of most environments. In Michigan, the Red Cedar River has been described as contaminated by DDT and DDT analogues, with the level of pollutants increasing in a downstream direction (Zabik et al., 1971).

To check the Red Cedar River for pesticide contamination, seven sampling stations were set out on it. Duplicate water and sediment samples were then collected monthly from each station, from May 1992 to October 1992.

Analysis of the collected samples by Gas Chromatography showed residues of DDT, DDD, DDE, atrazine, alachlor, 2,4-D, and dicamba in the river. The level of DDT and its metabolites was approximately 1,000 times less than in 1971 and was related to the samples organic matter content. Atrazine and dicamba showed a relationship with their major period of application, while the concentration of alachlor was rather related to the volume of surface run-off.

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I- INTRODUCTION

The use of pesticides has undoubtedly led to many positive results, enhancing the capability of man to combat various threats to public health and increase the productivity in agriculture. Yet, once applied, these chemicals may undergo several processes resulting in the contamination of the environment and groundwater as well as our drinking water and food. In particular, pesticides may be carried by surface water in a dissolved or bound state to oceans, lakes streams, rivers, and ponds.

The widespread use of pesticides, along with the potential for runoff of these compounds, has resulted in the pollution of most of our aquatic environments (Bedford et al., 1968). For example, the Red Cedar River (Michigan, Ingham County) has been described as contaminated by pesticides. In research to check whether the freshwater mussel could be used as a good monitor of pesticide

concentrations in surface waters, Bedford et al. (1968) found residues of methoxychlor, aldrin, and DDT and its metabolites (DDE and DDD) in the Red Cedar River.

They also found that the content of DDT and its metabolites increased in a downstream direction. In 1971, Zabik et al. not only confirmed the presence of DDT and its metabolites in the river, but also observed the downstream pollution pattern indicated by Bedford et al.. Moreover, they reported the waste water treatment plants on the study section as the major source of pollution. Beside these studies, other research projects have been undertaken to evaluate the water quality of the river with respect to varied pollutants and factors. Investigating the river water with regard to the urbanization of the river watershed, Jensen (1966) observed that the water quality decreased in a downstream direction and pointed out the drain effluents as the primary source of contamination. Similar results were obtained by Talsma in 1972.

Overall, these past works have described the Red Cedar River as a contaminated river, with the amount of pollutants coming principally from drain effluents and increasing in a downstream direction. As a follow-up on the research done by Zabik et al. (1971), this study was designed to check for the presence of pesticide residues in the Red Cedar River. However, in addition to the chlorinated hydrocarbons studied in their work, this research was also concerned with other

groups of pesticides. Organophosphate insecticides, chlorinated herbicides, and triazine herbicides were also part of our compounds of interest because some of them have been listed among the most commonly used pesticides in Michigan. For the same reason, alachlor was also included in this study.

Chlorinated hydrocarbon and organophosphate compounds were analyzed through water and sediment samples; the remaining groups through water samples only. Certainly, analysis of more types of sample including biological samples could give a better picture of the river's pesticide contamination. Unfortunately, the shortness of the time allocated to this research did not allow us to do so. Nevertheless, the collected samples were representative of the study area and provide a useful indicator of changes of water quality in the study section since the 1971 study.

II- LITERATURE REVIEW

A- Pesticide residues in the environment

Earlier we alluded to the environmental effects of pesticides, discussing the particular case of the Red Cedar River. Based on the literature, this section is designed to give a general idea of pesticide residues in the environment.

Pesticides have been intensively used throughout the world to control a variety of pests. In the United States for example, the amount of formulated pesticides applied per year is roughly estimated at 2.6 billion pounds (Mott and Snyder, 1987). Yet the properties of these chemicals give them the potential to contaminate all component parts of our environment(agricultural soils, atmosphere, ground water, surface waters, living organisms, foods) in small amounts. Adsorption to soil particles, volatization, photodegradation, microbial degradation, chemical degradation, plant uptake, crop removal, surface runoff, and leaching are the possible fates of a pesticide in the environment (Renner and Kells, 1992).

The presence of pesticide residues in cropland soils primarily results from the process of adsorption which is the adhesion of the chemical molecules to the surface of

soil colloids. The binding of a given compound to soil particles is a function of a variety of factors including the chemical properties of the compound itself.

Organochlorine pesticides such as DDT, chlordane, and lindane may be held by the soil particles for years due to their low water solubility, hydrophobicity, and resistance to chemical and microbial degradation. In research to investigate the persistence of DDT, dieldrin, and lindane in the soil over a long period, Martijn et al.(1993) reported that residues of these compounds were still present in soil 21 years after application. Use of DDT, as well as other organochlorine insecticides (lindane, dieldrin, aldrin, heptachlor, aldrin,...) has been restricted in most countries because of their great persistence in the environment and detrimental effects on living organisms. In the United States, their use was cancelled in 1972 by the United States Environmental Protection Agency (Mott and Snyder, 1987). Despite this cancellation, the soil environment is still contaminated by pesticides. Hitch and Day (1992) indicated that high amounts of DDT and its metabolites were found in some western USA soils in 1980. In 1992, they also found that some Texas agricultural soils still had residues of these compounds, with the level of DDT being even higher than of DDE. Although they have been classified as the most persistent in the environment, organochlorine compounds are not the only chemicals which

leave residues in soils. Soil pesticide contamination involves other groups of compounds as well. A recent study by Jabbar et al. (1993) revealed the presence of monocrotophos, dimethoate, profenofos, cyhalothrin, fenvalerate, and cypermethrin in some Pakistan agricultural soils.

Pesticides may also be present in the atmosphere through the process of volatilization. Gaseous chemicals can move along with air current in the atmosphere, process known as vapor drift (Renner and Kells, 1992). Transport by air currents, either in a gaseous form or in a dust-particle-adsorbed form, has been described as the major path of DDT redistribution in the world (Woodwell et al. in Filonow, 1974). Pesticides having a high vapor pressure may be redistributed through the same process.

Another environmental component contaminated by pesticides is groundwater. The major process involved in groundwater contamination is leaching or movement of the compound through the soil pores as influenced by water flow. Like adsorption and volatilization, leaching is a function of several factors including the pesticide itself. Highly water soluble compounds are more likely to leach and reach groundwater. Several studies have reported examples of groundwater to be contaminated by pesticides. In Pakistan, Jabbar et al. (1993) studied the possible contamination of cropland soils and shallow groundwater in the Punjab as

related to pesticide use in the area. They detected residues of monocrotofos, cyhalothrin, and endrin in the shallow groundwater of the studied area. The residue level ranged from traces to 0.2 ppm for cyhalothrin, 0.1 to 0.2 ppb for endrin, and 40 to 60 ppb for monocrotofos. A similar study was undertaken by Bushway et al. (1992) to evaluate the water quality of some wells in Central Maine with respect to the use of alachlor, atrazine, and carbofuran in the area. Of the 58 samples analyzed, 18 were atrazine positive, with 2 samples having a residue level greater than the 3.0 ppb MCLG (Maximum Contaminant Level Goal); 19 samples contained alachlor above the zero ppb MCLG whereas carbofuran was only present in 4 samples. Contamination of groundwater by pesticides is then a reality. Effective ways to prevent this situation are needed as groundwater is still a major source of drinking water in the world. In the United States, 95 percent of the rural population and 50 percent of the whole population rely on groundwater as source of drinking water; yet a 1987 EPA report indicated that residues of more than 20 pesticides have been found in at least 24 states groundwater (Mott and Snyder, 1987).

Like groundwater, surface waters have also been victim of pesticide contamination. A study conducted by Mugachia et al. (1992) in Kenya revealed the presence of organochlorine pesticides in the Athi River, Kenya. Of the analyzed fish, 73 percent of the samples contained residues

of the following compounds: p,p'-DDE, p,p'-DDT, p,p'-DDD, o,p'-DDT, o,p'-DDD, HCH, and heptachlor. Similar cases of surface water pollution have also occurred elsewhere in the world. For example, from March 1988 to April 1989, Fingler et al. (1992) performed a residue survey on the Kupa River, in Croatia. They found the river water to be polluted by a variety of compounds including organochlorine pesticides such as hexachlorobenzene and DDT and its metabolites. In 1983, the East Central Michigan Planning and Development Region (ECMPDR) reported the Pine River, East Central Michigan, to be contaminated by high levels of DDT. In the United States, several currently used pesticides have also been detected in surface waters. In the Midwest U.S., the herbicide alachlor has been detected not only in groundwater, but also in surface waters (Mott and Snyder, 1987). In the Ohio area, Baker (1987) undertook a study of surface water contamination on the Lake Erie Basin, in relation with land use activities. Along with other findings, he reported that many pesticides are transported to river waters during runoff events following their application. Giving a particular attention to atrazine, alachlor, metolachlor, and cyanazine in the Honey Creek Watershed at Melmore, in the northwestern Ohio, he observed that these four herbicides had similar Spring runoff patterns and were primarily carried to the watershed between May and July. Like in the previously named areas of the

world , surface waters in Canada are also victim of pesticide contamination. From 1971 to 1985, Canadian governmental agencies evaluated the river quality of some Ontario, Canada rural ponds with regard to pesticide use in the corresponding areas. The results of this study indicated that 12 ponds were polluted by the insecticides carbofuran, chlorpyrifos, diazinon, DDT, endosulfan, parathion; 5 ponds with the fungicide PCP, and 122 ponds with the herbicides alachlor, 2,4-D, cyanazine, dicamba, simazine, diquat, glyphosate, and atrazine (Frank et al., 1990). The same research observed atrazine as the most frequently detected herbicide, which is in support of the U.S EPA new rules to modify the atrazine label with regard to surface water contamination. Indeed, in order to reduce the potential of atrazine for surface water contamination, the EPA has recently required the use of lower rates and the establishment of buffer zones between application areas and surrounding surface waters (Kells et al., 1993).

Hence, pesticides are everywhere; on the ground, in the air surrounding us, in drinking water, groundwater, streams, lakes, ditches, rivers, oceans,.... As a result, all living organisms including man are exposed to them on a regular basis. Effective ways to monitor these chemicals are strongly needed.

B-Most commonly used pesticides in Michigan

As pesticide regulations change, pesticide use change. As a result, a given agricultural chemical described as most frequently used in a given area over a given period of time may be subject to changes in terms of use. Adapted from various sources, the following tables show the most frequently used pesticides in Michigan over the past three years.

Table 1: Most commonly used Pesticides on Field Crops in Michigan, 1992

	total applied (1,000 lbs) 1/	leaching potential 2/	run-off potential 2/	water solubility (ppm at 20-27°C) 3/
	corn			
	potatoes			
herbicides				
atrazine	2,504	high	medium	33
metolachlor	1,775	medium	medium	530
alachlor	1,481	medium	medium	242
cyazafos	970	high	medium	*
dicamba	138	high	low	4,500
2,4-D	75	low	medium	600
linuron	11	medium	medium	81,000
metribuzin	5	high	medium	1,200
chlorpyrifos	401	low	high	*
terbufos	127	low	medium	*
phosmet	37	*	*	*
methyl parathion	26	low	medium	*
endosulfan	20	*	*	*
fungicides				
malic hydrazide	31	*	*	*

1/: source: NASS and ASB, 1992a. Agricultural Chemical Usage 1992 Field Crops Summary. USDA, Washington, D.C.
 note: NASS = National Agricultural Statistics Service
 ASB = Agricultural Statistics Board

2/: source: Renner, A. R., L.G. Olsen and J.N. Lendle. 1991. Managing Pesticides
 On Corn to Avoid Contaminating Water. Extension Bulletin, Michigan State University,
 E. Lansing, Michigan.

3/: Farm Chemicals Handbook. 1990. Meister, Willoughton, Ohio.

* : not provided by the indicated source

Table 2: Most commonly used Pesticides on Vegetables in Michigan, 1992

		total applied (1,000 Lbs)
herbicides	metolachlor	35.2
	pendimethalin	24.4
	EPTC	24.1
	simazine	23.8
	atrazine	15.5
insecticides	carbaryl	51
	disulfoton	16.1
	carbofuran	13.6
	chlorpyrifos	12.7
fungicides	chlorothalonil	153.5
	mancozeb	39.3
adapted from: NASS and ASB. 1992b. Agricultural Chemical Usage		
Vegetables 1992 Summary. USDA, Washington, D.C..		

Table 3: Most commonly used Pesticides on Fruits in Michigan, 1991

		total applied (1,000 Lbs)
herbicides	simazine	20.5
	glyphosate	11.4
	paraquat	10.8
	diuron	10.3
	2,4-D	5.5
insecticides	petroleum distillate	1,409.70
	azinphosmethyl	147.8
	phosmet	131.5
	chlorpyrifos	91.1
	propargite	62.4
fungicides	captan	1,003.20
	sulfur	639.2
adapted from: NASS and ASB. 1991. Agricultural Chemical Usage 1991 Fruits and Nuts Summary. USDA, Washing. D.C..		

III- DESCRIPTION OF STUDY AREA

Previous studies have described the Red Cedar River as a warm-water stream located in southcentral Michigan, originating from Cedar Lake (Livingston County, Michigan), and flowing through Livingston and Ingham counties before joining the Grand River in Lansing, Michigan (Talsma, 1972; Zabik et al., 1971). Small grain agriculture and pasturage are the main activities upstream whereas the downstream region is characterized by an extensive agricultural development, urbanization, and industrialization (Zabik et al., 1971). The current usage of the river water is restricted to agricultural irrigation, recreational purposes, and treated water disposal.

For the purpose of this study, seven permanent sampling stations were set out in the vicinity of East Lansing, from just above the M-52 bridge to below the East Lansing Wastewater Treatment Plant (Fig. 1). Station 1 is located just above the M-52 bridge. The bottom material primarily consists of sand. The river water is relatively clean and agriculture is the major activity above this station (Zabik et al., 1971). Station 2 is located approximately 4 Km downstream from station 1, at the Williamston wastewater treatment outlet. The river bottom comprises sand and stones in the middle, detritus and silt

on the sides. Station 3 lies approximately 8 Km downstream station 2, at the M-43 bridge. The bottom at this station consists of small stones mixed with sand. This area has also been described as agricultural.

Station 4 is situated just below the Okemos bridge, about 15 Km downstream from station 3. The river bed is primarily comprised by sand covered by approximately one inch of silt. The surrounding area is mainly residential. Station 5 lies above the Hagadorn bridge, about 1 Km from station 4. The bottom material is made up of sand covered by beds of sludge, decaying leaves, and silt. Station 6 is located on the Michigan State University campus, approximately 500 m downstream from station 5. Here, the riverbed consists of large stones and coarse gravel in the middle, silt and detritus along the edges. Station 7 is situated below the East Lansing Wastewater Treatment Plant, about 2 Km from station 6. The bottom is covered with 2 to 3 inches of sludge beds, silt, and detritus.

Station 4, 5, 6, and 7 are located in highly residential areas. Consequently, drain effluents and street run-off might be the main sources of the river water contamination. Stations 4, 5, and 6 represent high levels of contamination, stations 2 and 7 areas with water quality recovery, and stations 1 and 3 relatively clean areas .

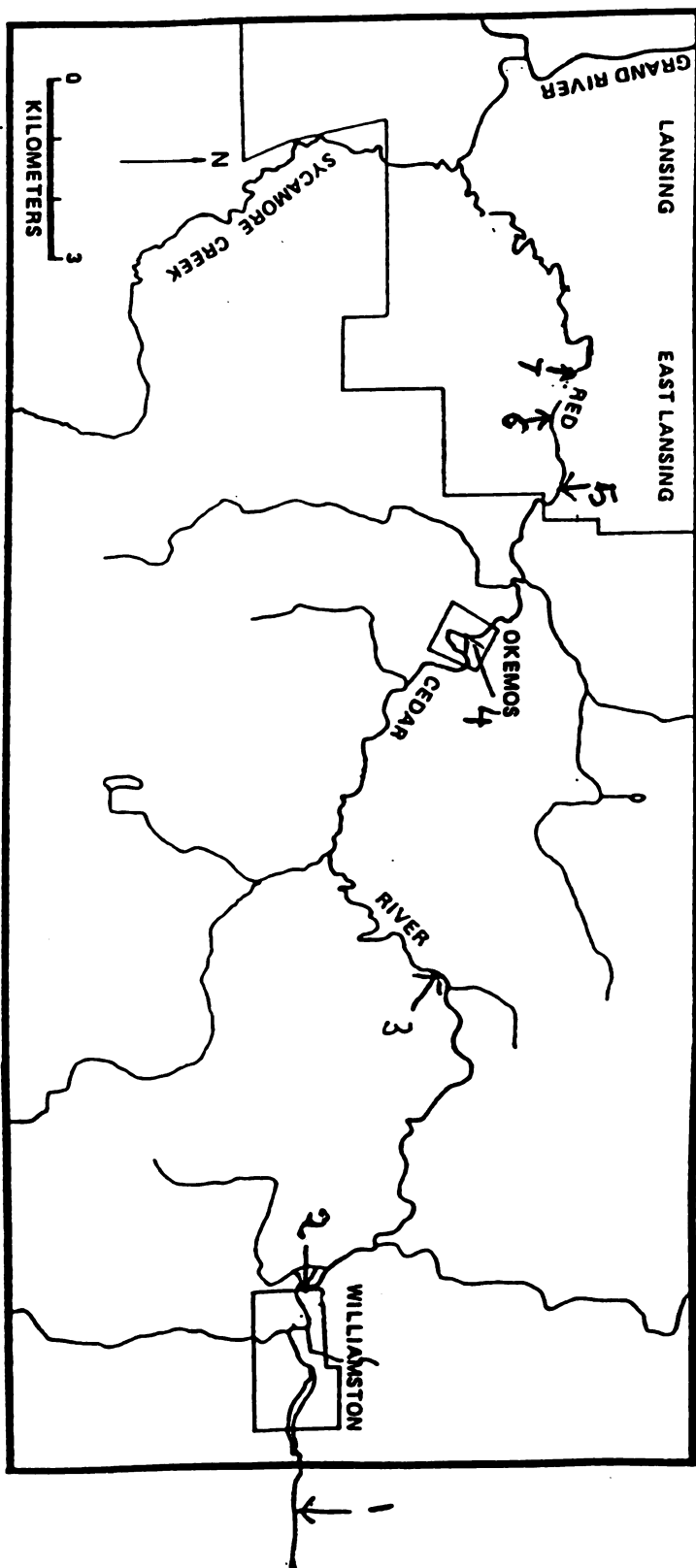


Figure 1: Map of the Red Cedar River with the study section
(adapted from Zabik et al., 1971)

IV- MATERIALS AND METHODS

A- Materials

1- Equipment

- Hewlett Packard Gas Chromatography model 5890 Series II with ^{43}Ni Electron Capture and Nitrogen Phosphorous Detectors

- Perkin-Elmer Gas Chromatography model 8500 with ^{43}Ni Electron Capture Detector

- Gas Chromatograph Mass Spectrometry Nermag R10-10C

- Zymark TurboVap Evaporator

- Buckler Rotary Evaporator

- Beckman pHmeter

- Mettler P₃ Analytical Balance

- Mettler H6T Analytical Balance

- EnviroGard Enzyme ImmunoAssay Kits

2- Reagents

a- Solvents

- Hexane, acetone, methylene chloride, methanol, Pesticide Quality

- Diethyl ether, reagent grade

b- Chemicals

- pesticide standards: Aldrin (98.7%), dieldrin (99.5%), lindane (98.5%), methoxychlor (99.0%), DDT-o,p' (99.5%), DDT-p,p' (99.0%), DDE-p,p' (99.0%), DDD-p,p' (99.0%), metolachlor (98.7%), endosulfan I (99.8%), endosulfan II (97.9%), heptachlor (99.5%), alachlor (98.7%), chlorpyrifos (99.7%), dyfonate (98.5%), terbufos (99.7%), methyl parathion (99.9%), phosmet (99.5%), monocrotophos (99.7%), glyphosate (99.9%), atrazine (99.0%), simazine (99.6%), metribuzin (99.0%), ametryne (99.0%), prometone (99.6%), 2,4-D methyl ester, silvex methyl ester, dicamba.

- other chemicals:

- * sodium sulfate anhydrous, granular, stored at 130 °C
- * florisil-PR grade, 60-100 mesh; activated at 135 °C
- * concentrated sulfuric acid. ACS grade; used as received
- * diazomethane; prepared as described by the EPA method 8150 (1986)
- * potassium hydroxide, ACS grade

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c- Miscellaneous items

- glass wool, pyrex
- glass rod
- filter papers

d- Glassware

- volumetric flasks: 5- 100 mL
- beakers: 100-500mL
- separatory funnels: 125-1000 mL
- graduated centrifuge tubes: 10-50 mL
- Zymark concentrating tubes: 200 mL
- chromatographic columns: 50-200 mL
- round bottom and reflux flasks: 50-500 mL

B- Methods**1- Sampling design and samples preservation**

Seven permanent sampling stations were set out in the Williamston-Okemos area, in a downstream direction, from above the M-52 bridge to below the East Lansing Wastewater Treatment Plant.

Samples collection was made according to a monthly schedule starting from May, 1992, to October, 1992, with an additional water sampling in April, 1993. Water samples were

collected as 5-liter grab samples. Sediment samples with a sediment corer. All samples were taken in duplicate, in the middle of the river or on the river edge during flood conditions. Water samples were held in a one gallon glass brown jugs sealed with teflon lined screw caps, preserved with sodium sulfate (3ml/gallon), and stored at 4 °C before analysis. Sediment samples were held in 8.oz widemouth glass containers with a teflon liner and stored at 4 C. Each sample was stored for no more than six months before anlalysis. The storage period was based on past unpublished research done by the Pesticide Chemistry Laboratory of the Michigan State University Pesticide Research Center.

2- Glassware preparation

Glassware was thoroughly washed with hot tap water and detergent, then rinsed with distilled water followed by acetone and hexane. It was finally stored in a 450 °C furnace for at least one day before use.

Glassware used to analyze the chlorinated acid herbicides was rinsed with a 1:1 sulfuric acid solution followed by a rinse with distilled water.

3- Residue survey scheme

The residue survey was performed according to a scheme comprising three major steps: preliminary analysis or background checking, actual residue analysis, and confirmation.

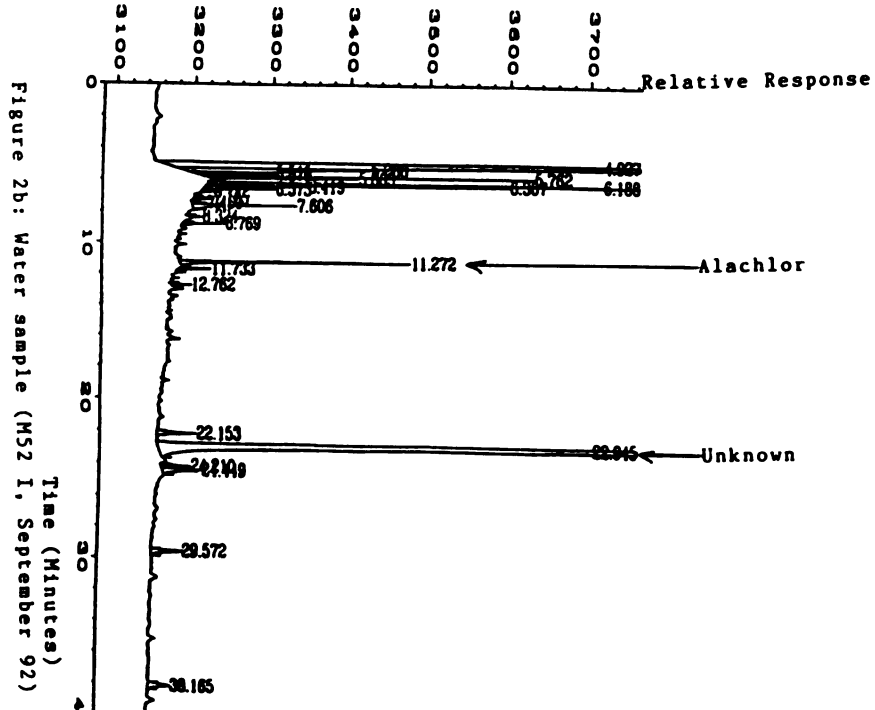
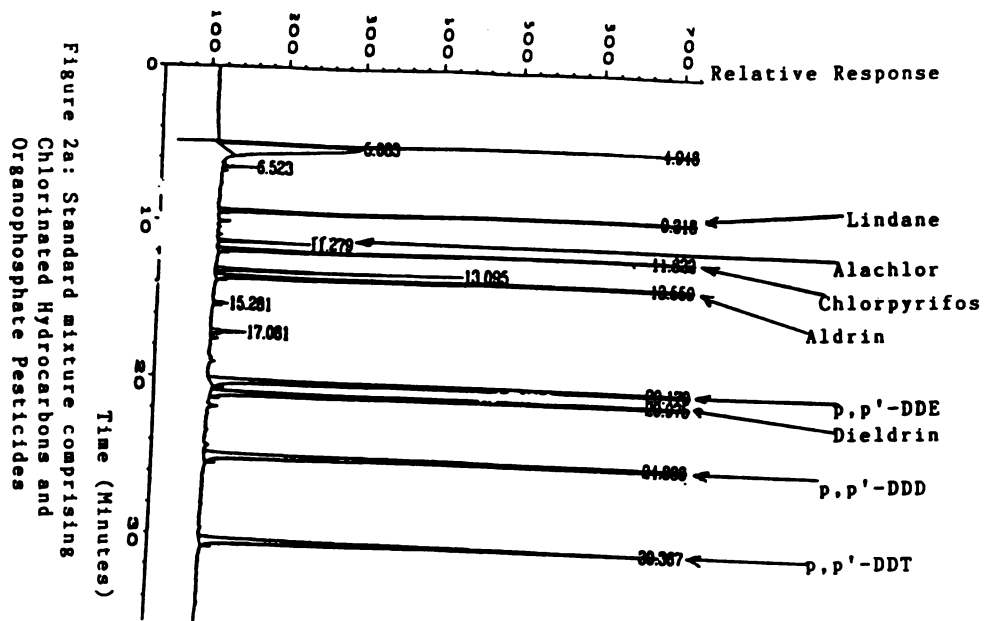
In the preliminary analysis step, a gas chromatographic procedure was set up for each class of pesticides. Recovery tests were then conducted to verify the applicability of the method to the corresponding group of compounds. According to whether the recoveries were in an acceptable range (our set range was 68-110%) or not, the method was validated or modified until acceptable recoveries were obtained. The recovery study was performed with pesticide standards belonging to the studied group of compounds and with three randomly selected samples. The validated procedure was then used to analyze seven randomly chosen samples representing the seven sampling stations. The extracts and selected pesticide standards were injected into a gas chromatograph under the same conditions. On the chromatograms, retention time was the parameter of interest; whenever an unknown peak matched the retention time of a given pesticide to plus or minus 0.03 min, we assumed this peak and the pesticide could possibly have the same identity. The plus or minus 0.03 min- retention time windows

was selected based on the EPA method 800 (1986). When applicable, a further qualitative study was performed using a different detector. Figures 2, 3, 4, and 5 are an illustration of this process. The results obtained from this preliminary analysis are shown in table 4 .

In step 2, actual residue analyses were undertaken for the suspected compounds. The extracts were then combined and concentrated for a gas chromatography/mass spectrometry-confirmation study in step 3.

Figure 2: Chromatograms of two different water samples and a standard mixture comprising chlorinated hydrocarbon compounds and organophosphate pesticides injected under the same G.C. conditions:

- 60 m DB-5 column
- Electron capture detector
- Oven temperature: 215 °C
- Inlet A temperature: 250 °C
- Inlet B temperature: 260 °C
- Detector A: 300 °C
- Detector B: 250 °C



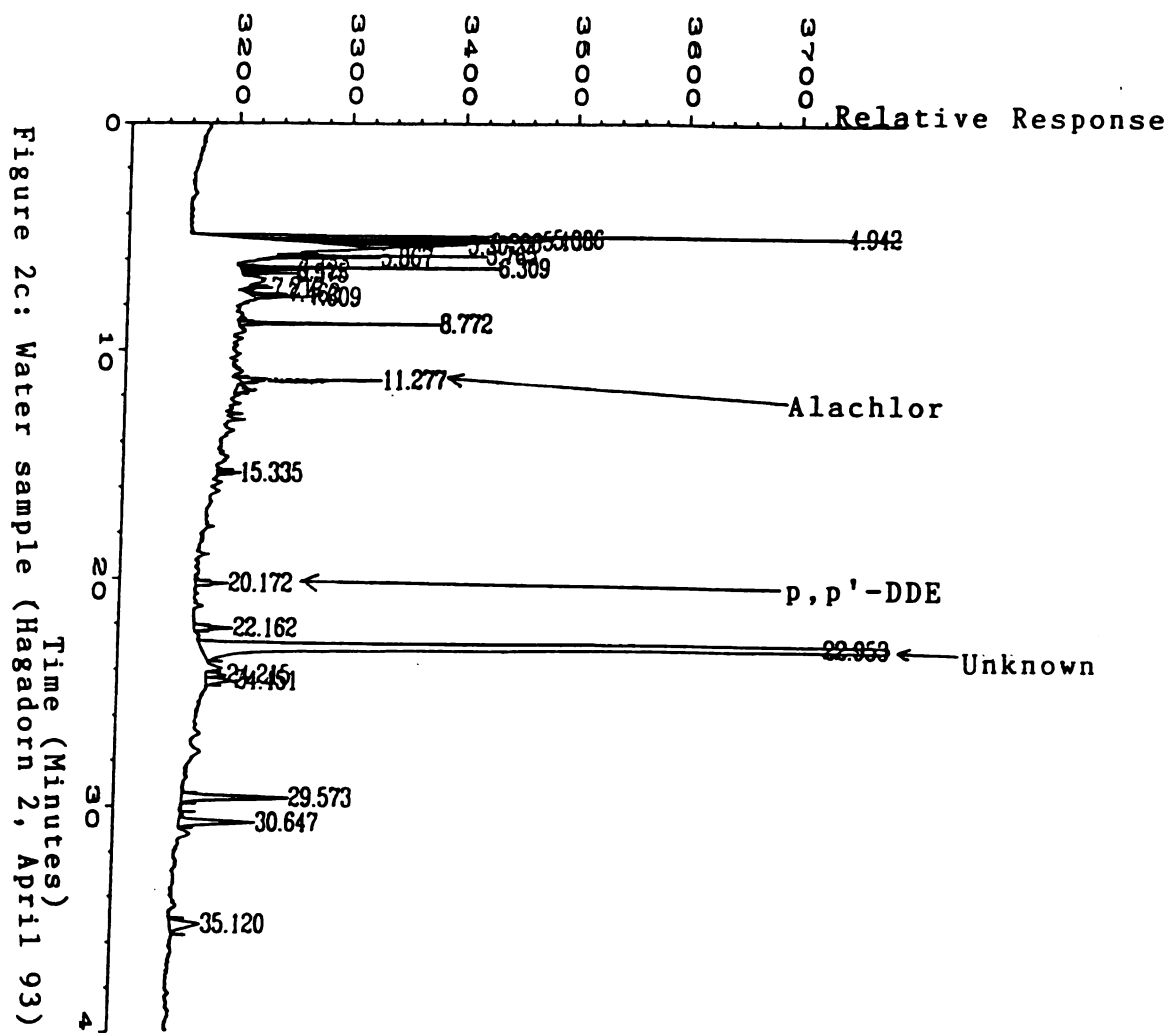


Figure 3: Chromatograms of a water sample and a standard mixture comprising chlorinated acid herbicides injected under the same G.C. conditions:

- 60 m DB-5 column
- Electron capture detector
- Oven temperature: 215 °C
- Inlet A temperature: 250 °C
- Inlet B temperature: 260 °C
- Detector A: 300 °C
- Detector B: 250 °C

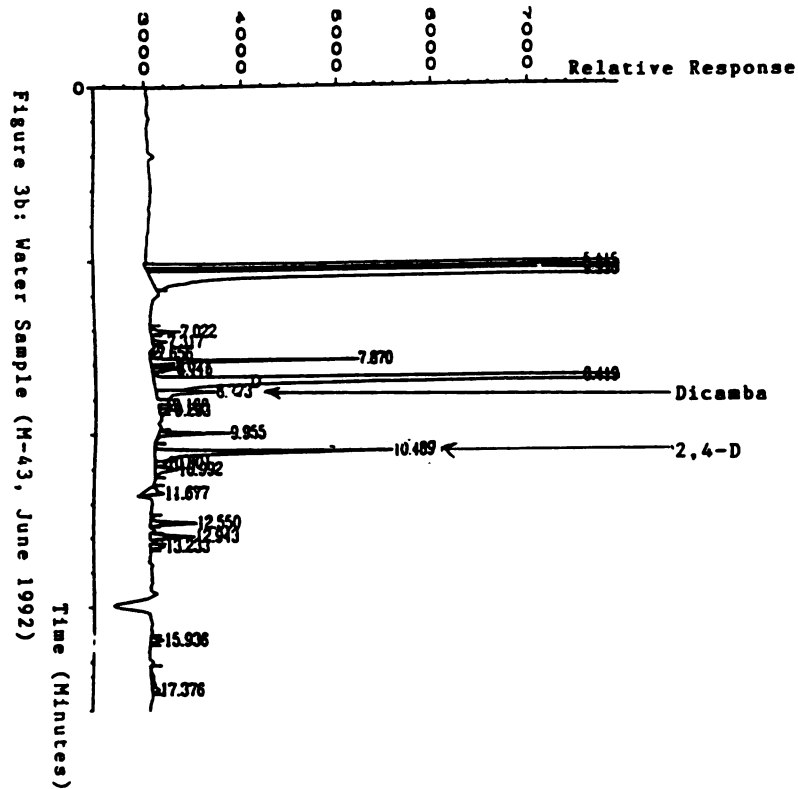
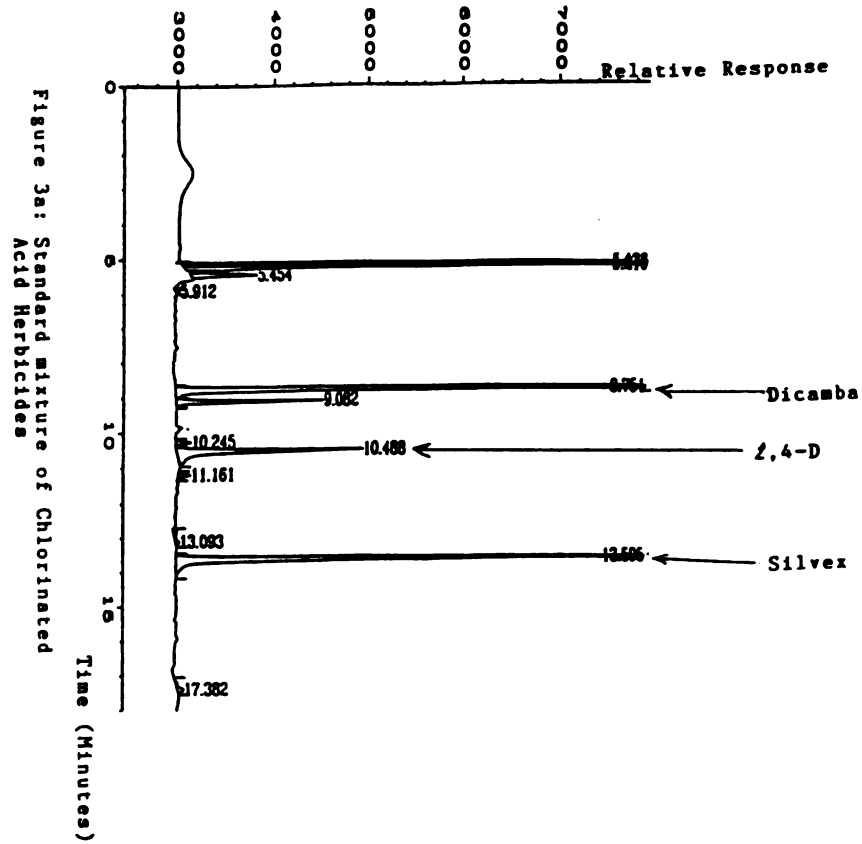


Figure 4: Chromatograms of two different water samples and a triazine standard mixture injected under the same G.C. conditions:

- 30 m DB-5 column
- Nitrogen-Phosphorus (NP) detector
- Oven temperature: 170 °C
- Inlet A temperature: 250 °C
- Inlet B temperature: 240 °C
- Detector A: 240 °C
- Detector B: 280 °C

Figure 4a: Triazine Herbicides
Standard mixture

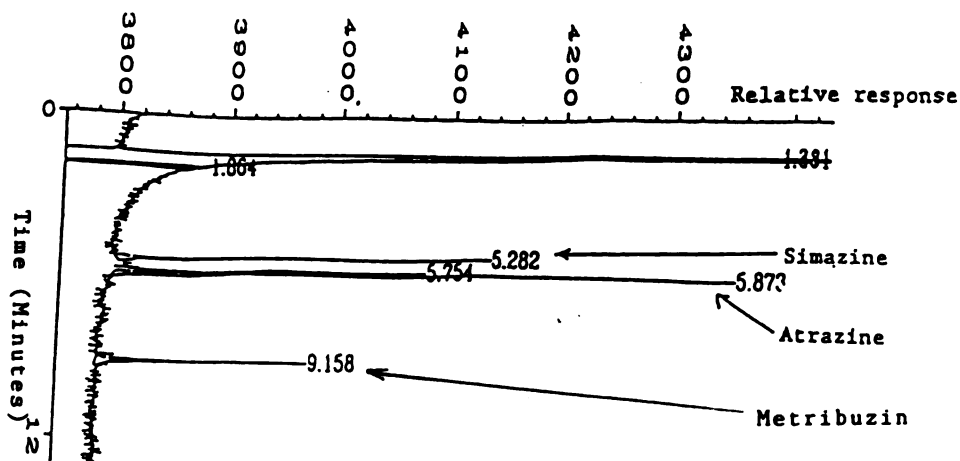


Figure 4b: Water sample
(MS2 I, May 92)

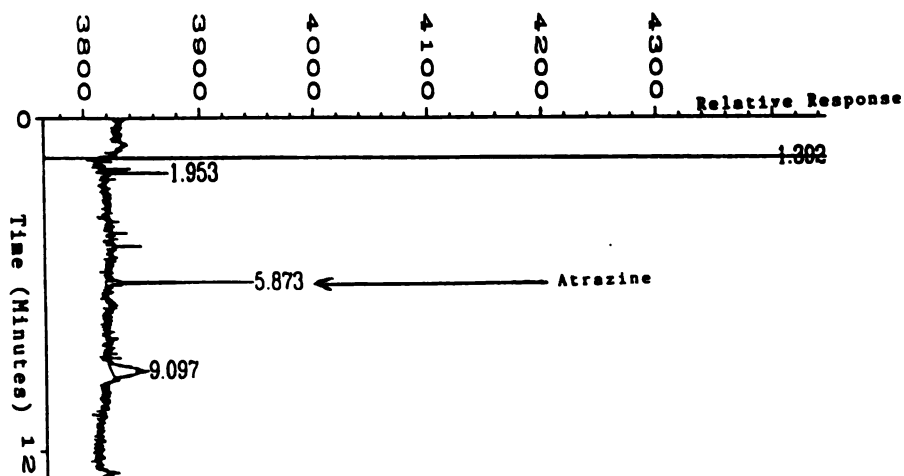


Figure 4c: Water sample
(Okemos I, June 92)

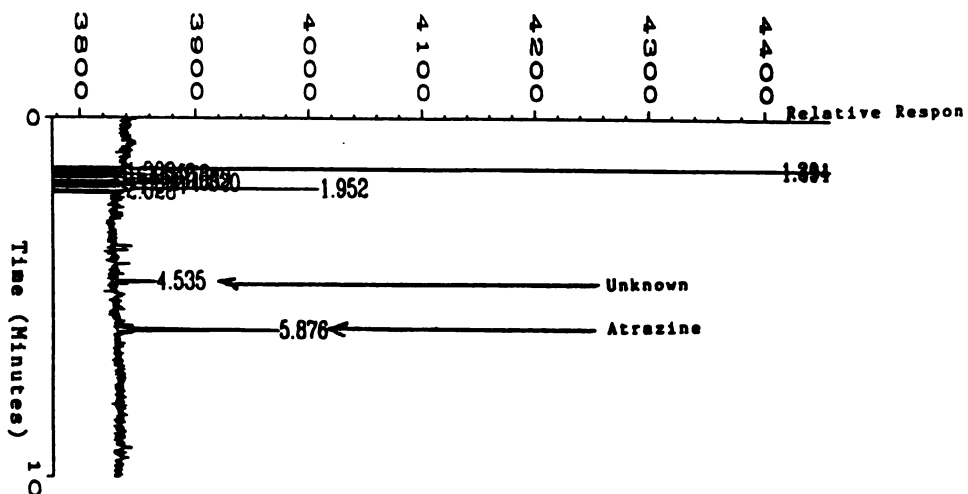


Figure 5: Chromatograms of a sediment sample and a standard mixture comprising chlorinated hydrocarbon compounds and organophosphate pesticides injected under the same G.C. conditions:

- 60 m DB-5 column
- Electron capture detector
- Oven temperature: 215 °C
- Inlet A temperature: 250 °C
- Inlet B temperature: 260 °C
- Detector A: 300 °C
- Detector B: 250 °C

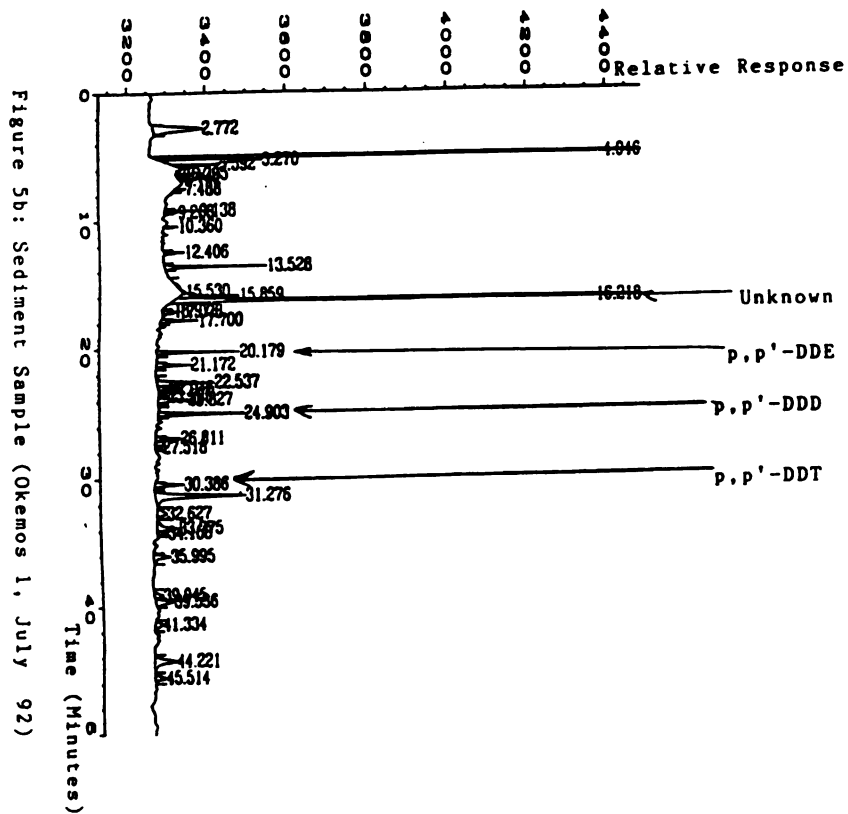
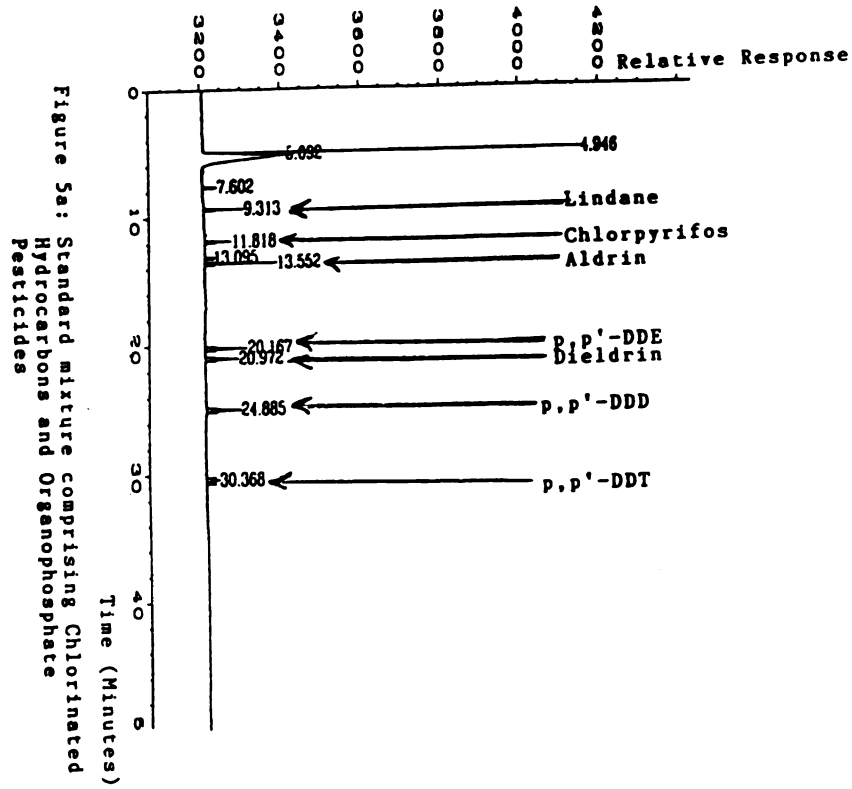


Table 4: Background of Water and Sediment Samples in Relation to the Assessed Pesticides

Class of Pesticide	Compounds	Water	Sediment
	aldrin	nd	nd
Chlorinated Hydrocarbons	dieldrin	nd	nd
	heptachlor	nd	nd
	metolachlor	nd	nd
	metoxychlor	nd	nd
	alchlor	suspected	nd
	lindane	nd	nd
	endosulfan I	nd	nd
	endosulfan II	nd	nd
	DDT-p,p'	nd	suspected
	DDE-p,p	suspected	suspected
	DDD-p,p'	suspected	suspected
	DDT-o,p'	nd	nd
Organophosphate Compounds	chlorpyrifos	nd	nd
	terbufos	nd	nd
	dyfonate	nd	nd
	methyl parathion	nd	nd
	phosmet	nd	nd
	monocrotofos	nd	nd
Triazines Herbicides	atrazine	suspected	nd
	simazine	nd	nd
	prometone	nd	nd
	ametryne	nd	nd
	metribuzin	nd	nd
Chlorinated Acid herbicides	2,4-D	suspected	nd
	dicamba	suspected	nd

nd = non detected

4- Organophosphate pesticides and chlorinated hydrocarbons

a- Extraction from water samples

An extraction procedure was set up to co-extract organophosphate pesticides and chlorinated hydrocarbons. This procedure was adapted from methods 8080 and 8140 of the EPA " Test Methods For Evaluating Solid Wastes" (1986), with some modifications.

A 50 ml volume of methylene chloride was added to a 500 ml of microfiltered water sample placed in a 1000 ml-separatory funnel. The funnel was then sealed, shaken for 1 to 2 min and left undisturbed for approximately 10 min to allow the partition of the pesticides from the aqueous fraction into the solvent. The organic layer was then collected into a 200 ml-beaker. This extraction procedure was performed two more times with 50 ml of fresh methylene chloride. The three solvent extracts were combined, dried over a drying column containing 10 cm of activated anhydrous sodium sulfate, collected into a 200 ml-concentrating tube, and concentrated almost to dryness on a Zymark TurboVap evaporator. Hexane (50 ml) was then added to the tube and concentrated to about 1 ml. Ultimately, the 1 ml extract was adjusted to 2 ml by rinsing the tube with hexane. This 2 ml extract was analyzed on a Hewlett Packard gas chromatograph, 5890 Series II, under the following

conditions:

- 60 m DB-5 column with a 0.25 μ m thickness
- Electron capture detector
- Detector A temperature: 250 °C
- Detector B temperature: 300 °C
- Inlet A temperature: 250 °C
- Inlet B temperature: 260 °C
- Oven temperature: 215 °C

The Method Quantification Limit (MQL), defined as the lowest concentration of a substance that can be measured and reported, was:

- Alachlor: 0.036 μ g/l
- p,p'-DDE: 0.0016 μ g/l
- p,p'-DDD: 0.002 μ g/l
- p,p'-DDT: 0.0026 μ g/l

b- Extraction and cleanup from sediment samples

The two classes of pesticides were co-extracted and cleaned up from sediment samples according to the procedure described by Zabik et al. (1971), with some minor modifications.

A 100 g sample of sediment was placed into a 500 ml-round bottom flask and thoroughly mixed with 200 ml of a (1:1) hexane-acetone mixture. The slurry was then shaken for 10 min and allowed to stand for 12-14 hr. After an

additional shaking of 10 min, the hexane portion was poured into a 100 ml-separatory funnel. The extraction procedure was performed two more times with two 100 ml portions of fresh hexane. The three hexane extracts were combined and treated exactly as described by the above authors, with the following exception. The concentrated 10 ml extract was eluted with 250 ml of hexane followed by 250 ml of a (1:1) hexane-acetone mixture. The collected eluate was reduced to 100 ml and analyzed on a Hewlett Packard gas chromatograph, 5890 Series II, under the conditions described in 4a. The MQL was 0.4 $\mu\text{g/Kg}$, 0.5 $\mu\text{g/Kg}$, and 0.65 $\mu\text{g/Kg}$ for p,p'-DDE, p,p'-DDD, and p,p'-DDT respectively.

c- Sediment samples organic matter content

Sediment samples percent organic matter was determined by the Michigan State University Soil Testing Laboratory using a Wet Digestion Method.

One gram of sediment was placed into a 50 ml-Erlenmeyer flask and 10 ml of $\text{Na}_2\text{Cr}_2\text{O}_7$ and 10 ml of concentrated sulfuric acid were added. The flask was then left undisturbed for 30 min after which the slurry was mixed with 15 ml distilled water and allowed to stand for at least 3 hr. Five milliliters of supernatant was then diluted in 5 ml of distilled water and the orange color intensity of the resulting solution was read on a colorimeter calibrated to

give 0 absorbance (100% transmittance) at 645 nm with appropriate blank samples and to read percent organic matter (or tons per acre) from a standard curve prepared from sediments of known organic matter contents. Table 5 shows the results obtained.

Table 5: Average percent organic matter of sediment samples per sampling station

sampling station	average organic matter (%)
M-52	0.8
Williamston WWTP	2.1
M-43 bridge	0.4
Okemos bridge	0.4
Hagadorn	3.7
MSU campus	0.7
East Lansing WWTP	1.9

note: WWTP: WasteWater Treatment Plant

d- Sediment samples moisture content

A sediment sample (5g) was placed in an aluminum dish and dried in a vacuum oven for at least 3 hr. The sample was then cooled in ambient temperature for about 1 hour and

reweighed to determine its dry weigh. The moisture content was obtained from the following equation:

$$\% \text{ moisture} = \frac{w_1 - w_2}{w_1} * 100$$

where:

- w_1 is the sample wet weigh
- w_2 is the sample dry weigh

Table 6 is a tabulation of the results.

Table 6: Sediment Samples Percent Moisture

	sample ID	w1 (g)	w2(g)	% moisture
May-92	M-52 I	5	4.8	4
	M-52 II	5	4.8	4
	WWWTP I	5	4.4	12
	WWWTP II	5	4.5	10
	M-43 I	5	4.9	2
	M-43 II	5	4.9	2
	OKEMOS I	5	4.9	2
	OKEMOS II	5	4.8	4
	HAGADORN I	5	3	40
	HAGADORN II	5	3.1	38
	MSU I	5	4.9	2
	MSU II	5	4.9	2
	ELWWTP I	5	4.5	10
	ELWWTP II	5	4.5	10
Jun-92	M-52 I	5	4.5	10
	M-52 II	5	4.4	12
	WWWTP I	5	4	20
	WWWTP II	5	4.2	18
	M-43 I	5	4.8	4
	M-43 II	5	4.7	6
	OKEMOS I	5	4.5	10
	OKEMOS II	5	4.6	8
	HAGADORN I	5	3.5	30
	HAGADORN II	5	3.5	30
	MSU I	5	4.5	10
	MSU II	5	4.4	12
	ELWWTP I	5	4	20
	ELWWTP II	5	4.2	18
Jul-92	M-52 I	5	4.3	14
	M-52 II	5	4.3	14
	WWWTP I	5	3.5	30
	WWWTP II	5	3.4	32
	M-43 I	5	4.8	4
	M-43 II	5	4.7	6
	OKEMOS I	5	4.6	8
	OKEMOS II	5	4.8	4
	HAGADORN I	5	3.5	30
	HAGADORN II	5	3.4	32
	MSU I	5	4.8	4
	MSU II	5	4.8	4
	ELWWTP I	5	3.5	30
	ELWWTP II	5	3.5	30

table 5 cont.

	sample ID	w1 (g)	w2(g)	% moisture
Aug. 92	M-52 I	5	4.8	4
	M-52 II	5	4.7	6
	WWWTP I	5	3.5	30
	WWWTP II	5	3.3	34
	M-43 I	5	4.8	4
	M-43 II	5	4.9	2
	OKEMOS I	5	4.7	6
	OKEMOS II	5	4.6	8
	HAGADORN I	5	3.8	24
	HAGADORN II	5	3.7	26
	MSU I	5	4.5	10
	MSU II	5	4.5	10
	ELWWTP I	5	3.5	30
	ELWWTP II	5	3.4	32
Sept. 92	M-52 I	5	4.8	4
	M-52 II	5	4.8	4
	WWWTP I	5	3.5	30
	WWWTP II	5	3.6	28
	M-43 I	5	4.8	4
	M-43 II	5	4.9	2
	OKEMOS I	5	4.7	6
	OKEMOS II	5	4.8	4
	HAGADORN I	5	3.4	32
	HAGADORN II	5	3.6	28
	MSU I	5	4.2	16
	MSU II	5	4.5	10
	ELWWTP I	5	3.5	30
	ELWWTP II	5	3.5	30
Oct. 92	M-52 I	5	4.8	4
	M-52 II	5	4.7	6
	WWWTP I	5	3.4	32
	WWWTP II	5	3.5	30
	M-43 I	5	4.9	2
	M-43 II	5	4.9	2
	OKEMOS I	5	4.8	4
	OKEMOS II	5	4.8	4
	HAGADORN I	5	3	40
	HAGADORN II	5	3.2	36
	MSU I	5	4.8	4
	MSU II	5	4.7	6
	ELWWTP I	5	3.5	30
	ELWWTP II	5	3.4	32

ELWWTP = East Lansing Wastewater Treatment Plant

WWWTP = Williamston wastewater Treatment Plant

5- Triazine Herbicides

a- Gas chromatographic (G.C.) procedure

Triazine herbicides were extracted using the procedure described in B4a with the exception that the final 2 ml extract was analyzed under the following conditions:

- 30 m DB-5 column with a 0.25 μ m thickness
- NP dectector
- Detector A temperature: 240 °C
- Detector B temperature: 280 °C
- Inlet A temperature: 240 °C
- Inlet B temperature: 250 °C
- Oven temperature: 170 °C

The MQL was 0.036 μ g/L for atrazine.

b- Enzyme-Linked-ImmunoAssay (ELISA) Procedure

Beside the above G.C. method, the triazine herbicides were also analyzed by ELISA according to the EnviroGard Triazine Test Kit.

Twenty antibody-coated test tubes were placed in a test tube rack. 160 μ l of negative control was added to tube 1, 160 μ l of a 0.1 ppb atrazine calibrator to tube 2, and 160 μ l of a 1.0 ppb atrazine calibrator to tube 3; each of the remaining tubes received 160 μ l of the corresponding sample. This step was immediately followed by an addition of

160 μ l of atrazine-enzyme conjugate to each tube. The tubes were then swirled for 2 to 3 sec, left undisturbed for 5 min, emptied, and washed three times with distilled water. After the washing step, 160 μ l of substrate was added to each tube followed by 160 μ l of chromogen. The tubes were gently mixed for a few sec, then a 40 μ l of stop solution was added to each of them. Finally, the absorbance of each test tube was read on a spectrophotometer calibrated to read 0 absorbance for a blank sample at 450 nm.

6-Chlorinated herbicides

A gas chromatographic procedure was adapted from method 8150 of the 1986 EPA "Test Methods For Evaluating Solid Waste" to extract chlorinated herbicides from the water samples. This method comprises four major steps: extraction, hydrolysis, cleanup, and esterification.

- Extraction: 500 ml of micro-filtered water (pore size of filter paper: 0.45μ) with a pH adjusted to less than 2 with sulfuric acid (1:1) was placed in a 1000 ml separatory funnel. Diethyl ether (100 ml) was added to the funnel which was then sealed, shaken for 1 to 2 min, and left undisturbed for at least 10 min. The organic layer was collected in a 300 ml-reflux flask containing 2 ml of 37% KOH. The extraction was repeated two more times with 50 ml of fresh diethyl ether and the three extracts combined.

- Hydrolysis: Since the compounds of interest may occur in water as the salt, ester, or acid form of the herbicide, it was required that the solvent extracts be hydrolyzed in order to determine the active part of these compounds. In this procedure, 15 ml of distilled water was added to the combined extracts and the resulting mixture was concentrated for 60 min on a Zymark TurboVap evaporator. The hydrolyzed ether extracts were let stand for about 10 min and transferred into a 60 ml-separatory funnel using 10 ml of distilled water. The basic solution was then washed twice with two 20 ml-portions of diethyl ether for 1 min. The organic layer was discarded and the aqueous layer kept for subsequent analysis.

- Solvent cleanup: the content of the funnel was acidified with 2 ml of cold sulfuric acid (1:3), mixed with 20 ml ethyl ether, and shaken for 2 min. The solvent layer was then collected into a 150 ml-beaker containing 0.5 g of acidified Na_2SO_4 . This extraction process was performed two more times with 10 ml aliquots of ethyl ether. The extracts were combined, kept in contact with the Na_2SO_4 for approximately 2 hr, and then concentrated on a Zymark TurboVap evaporator to about 0.5 ml. Next, 0.1 ml of methanol was added to the concentrated extract and the volume adjusted to 2 ml with diethyl ether.

- Esterification: 2 ml of diazomethane was added to the tube and the extract was let stand until the yellow

color persisted. The colored extract was reduced to less than 1 ml by vaporization under ambient conditions, adjusted to 2 ml with hexane, and analyzed on a Hewlett Packard G.C., 5890 Series II, under the conditions described in B4a, except the oven temperature was 190 °C. The method quantification limit was 0.022 µg/l and 0.0115 µg/l for dicamba and 2,4-D respectively.

7- Recovery study

a- Water samples

Recovery tests were performed for alachlor, atrazine p,p'-DDE, 2,4-D methyl ester, and dicamba in the water samples. Three different samples were randomly selected and two sub-samples of 500 ml were taken from each sample. One duplicate was spiked with 1 ml of a 0.5 ppm spike solution comprising the compounds of interest whereas the other was left unspiked. The samples were then left undisturbed for approximately 12 hr and extracted according to the appropriate procedure. The results are tabulated in Table 7.

Table 7: Percent recoveries from water samples of alachlor, p,p'-DDE, atrazine, 2,4-D methyl ester, and dicamba

compound	recovery range (%)	average recovery (%)	Std Dev (%)
alachlor	82.86 - 93.43	88.38	5.30
p,p'-DDE	87.73 -106.28	94.37	10.33
atrazine	90.80 -104.18	97.67	7.00
2,4-D ME	70.87 - 75.51	72.83	2.40
dicamba	69.27 - 73.44	71.36	2.94

b- Sediment samples

- Sample recovery

The recovery study for sediment samples was similar to that of the water samples with the following exceptions. Each of the three samples was divided into two duplicates of 100 g. One duplicate was spiked with 1 ml of a 5 ppm standard mixture comprised by aldrin, p,p'-DDE, p,p'-DDD, p,p'-DDT, lindane, heptachlor, dieldrin, chlorpyrifos, and alachlor; the other duplicate was left non-spiked. The samples were then kept undisturbed for approximately 24 hr after which they were extracted according to the procedure described in IV 4b. Table 8 shows the recoveries of p,p'-DDE, p,p'-DDD, and p,p'-DDT from the sediment samples.

Table 8: Percent recoveries of p,p'-DDE, p,p'-DDD, and p,p'-DDT from sediment samples

compound	recovery range (%)	average recovery (%)	Std Dev (%)
p,p'-DDE	83.35 -104.29	91.54	11.19
p,p'-DDD	82.07 - 95.13	88.57	6.53
p,p'-DDT	85.70 -109.22	98.58	11.92

- Column recovery

A recovery test was also conducted to evaluate the suitability of the cleanup column for the analyzed compounds. In this perspective, 1 ml of a 5 ppm pesticide mixture was added to the column, eluted, and concentrated as described in IV 4b. The recoveries obtained for DDT and its metabolites are tabulated in Table 9.

Table 9: Florisil-celite (5:1)-column recoveries for DDT complex

compound	recovery range (%)	average recovery (%)	Std Dev (%)
p,p-DDE	89.23 -102.12	95.52	6.45
p,p'-DDD	88.55 - 98.41	93.04	4.99
p,p'-DDT	93.78 -110.34	103.25	8.53

8- Quantification

a- Water samples

A standard curve was constructed for each pesticide of interest to determine its concentration in the final extract based on its peak area. This concentration and the volume of water extracted were the basis for the pesticide quantification. The amount computed from these parameters was then corrected to compensate for the amount lost during the extraction. The calculations were performed with the following equation:

$$\text{amount (ug/ml)} = \frac{c * v_f}{v} * 100/R$$

where:

- c is the concentration in ppm of the pesticide obtained from its standard curve
- v_f is the final extract volume in ml
- v is the volume in ml of sample extracted
- R is the percent recovery of the pesticide

b- Sediment samples

The quantification of the compounds extracted from sediment samples was performed as in the water samples with the exception that other parameters were taken into account

in the calculations. The amount of pesticide extracted was computed using the following formula:

$$\text{amount } (\mu\text{g/g}) = \frac{c * v_f}{DW} * 100/R_s * 100/R_c$$

where:

- c = concentration in ppm obtained from a standard curve
- v_f = extract final volume (ml)
- DW = sample Dry Weigh (g)
- R_s and R_c = sample recovery and column recovery respectively

9- Mass Spectrometry and confirmation

A confirmation study was performed for the previously analyzed compounds using a Nermag R10-10C gas chromatograph-mass spectrometer system under the following conditions:

- Capillary column: DB-1 30 m with 0.25mm diameter
- Column pressure: 20 psi
- Carrier gas: Helium
- Moderating gas: methane
- Oven temperature program: 180 to 250 °C at 5 °C per min
- Quadrupoles scan range: 60 to 500 u

For each compound of interest, the combined and concentrated extracts and the corresponding pesticide standard were injected into the confirmation system, under

the same conditions. Confirmation was based on the comparison and interpretation of the resulting molecular ions. Overall, each of the seven suspected pesticides (alachlor, atazine, 2,4-D, dicamba, p,p'-DDE, p,p'-DDD, p,p-DDT) was confirmed.

10- Results and Discussion

a-Results

The residues data for alachlor, p,p'-DDT complex, atrazine, 2,4-D, and dicamba are shown in the following Tables and Figures:

Table 10: Results for Duplicate G.C. Analyses of Water Samples for Atrazine

	station ID	atrazine concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	MS2	0.70	0.67	0.69	0.02
	WWWTP	0.92	0.88	0.90	0.03
	MERIDIAN	1.68	1.63	1.66	0.04
	OKEMOS	0.61	0.67	0.64	0.04
	HAGADORN	1.65	1.63	1.64	0.01
	MSU	0.30	0.27	0.29	0.02
	ELWWTP	0.27	0.25	0.25	0.01
	average May			0.67	0.03
Jun-92	MS2	1.01	0.98	1.00	0.02
	WWWTP	0.53	0.52	0.53	0.01
	MERIDIAN	0.55	0.51	0.53	0.03
	OKEMOS	0.56	0.67	0.72	0.22
	HAGADORN	0.80	0.63	0.72	0.12
	MSU	0.68	0.75	0.72	0.05
	ELWWTP	0.73	0.55	0.64	0.13
	average June			0.69	0.08
Jul-92	MS2	0.37	0.40	0.39	0.02
	WWWTP	0.47	0.40	0.44	0.05
	MERIDIAN	0.77	0.57	0.67	0.14
	OKEMOS	0.61	0.81	0.71	0.14
	HAGADORN	0.44	0.53	0.49	0.06
	MSU	0.55	0.55	0.55	0.00
	ELWWTP	0.57	0.42	0.50	0.11
	average July			0.53	0.06
Aug. 92	MS2	0.45	0.21	0.33	0.17
	WWWTP	0.34	0.29	0.32	0.04
	MERIDIAN	0.27	0.19	0.23	0.06
	OKEMOS	0.29	0.16	0.23	0.09
	HAGADORN	0.33	0.23	0.28	0.07
	MSU	0.23	0.17	0.20	0.04
	ELWWTP	0.41	0.21	0.31	0.14
	average Aug.			0.27	0.05
Sept. 92	MS2	0.27	0.17	0.22	0.07
	WWWTP	0.18	0.19	0.19	0.01
	MERIDIAN	0.28	0.40	0.34	0.08
	OKEMOS	0.43	0.22	0.33	0.15
	HAGADORN	0.47	0.36	0.42	0.08
	MSU	0.34	0.33	0.34	0.01
	ELWWTP	0.25	0.33	0.29	0.06
	Sept. average			0.30	0.05
Oct. 92	MS2	0.039	0.048	0.04	0.01
	WWTP	0.037	0.051	0.04	0.01
	MERIDIAN	0.045	0.043	0.04	0.00
	OKEMOS	0.065	0.073	0.07	0.01
	HAGADORN	0.078	0.061	0.07	0.01
	MSU	0.072	0.39	0.23	0.22
	ELWWT	0.043	0.049	0.05	0.00
	Oct. average			0.08	0.08
Apr-93	MS2	0	0	0.00	0.00
	WWTP	0	0	0.00	0.00
	MERIDIAN	0.042	0.037	0.04	0.00
	OKEMOS	0.045	0.051	0.05	0.00
	HAGADORN	0.055	0.072	0.06	0.01
	MSU	0.038	0.067	0.05	0.02
	ELWWT	0.044	0.055	0.05	0.01
	April average			0.04	0.01

Table 11: Atrazine Concentration (ppb) in relation to Sampling Month and Station According to GC Data

Month	Sampling Station									average
	MS2	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP			
May-92	0.69	0.90	1.66	0.64	1.64	0.29	0.25			0.87
Jun-92	1.00	0.53	0.53	0.72	0.72	0.72	0.64			0.69
Jul-92	0.39	0.44	0.67	0.71	0.49	0.55	0.50			0.54
Aug-92	0.33	0.32	0.23	0.23	0.28	0.20	0.31			0.27
Sep-92	0.22	0.19	0.34	0.33	0.42	0.34	0.29			0.30
Oct- 92	0.04	0.04	0.04	0.07	0.07	0.23	0.05			0.08
Apr-93	0.00	0.00	0.04	0.05	0.06	0.05	0.05			0.04
average	0.38	0.35	0.50	0.39	0.53	0.34	0.30			

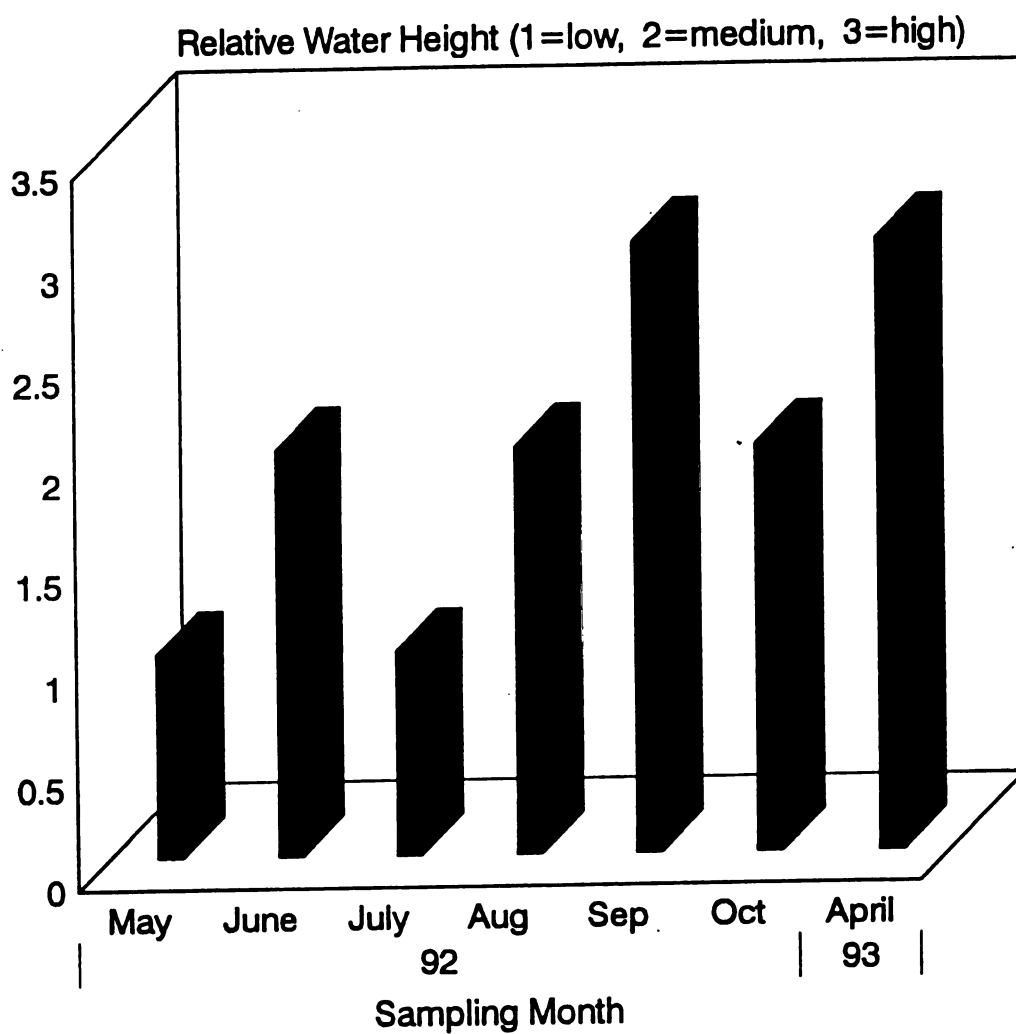


Figure 6: Water Level by Sampling Month

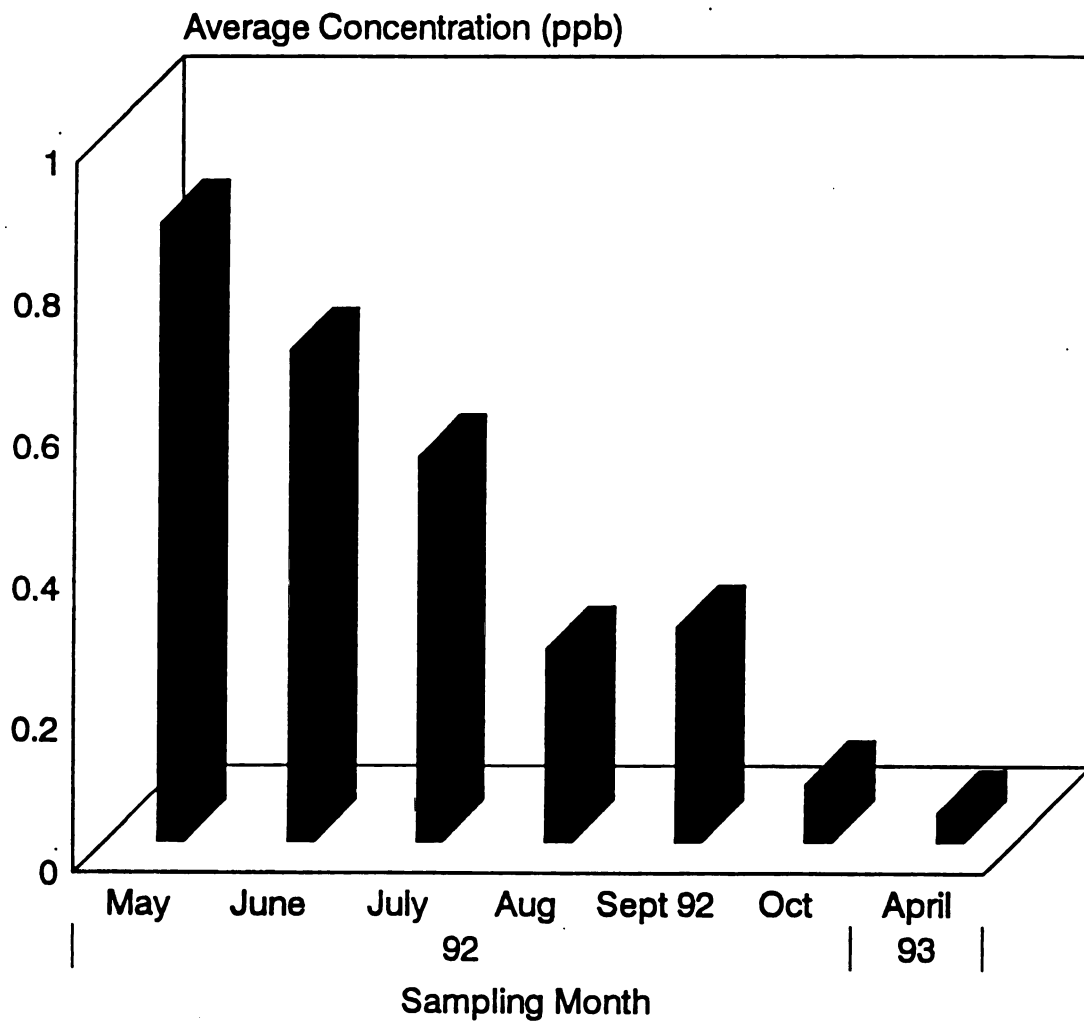


Figure 7: Atrazine Concentration (ppb) by Sampling Month
According to G.C. Data

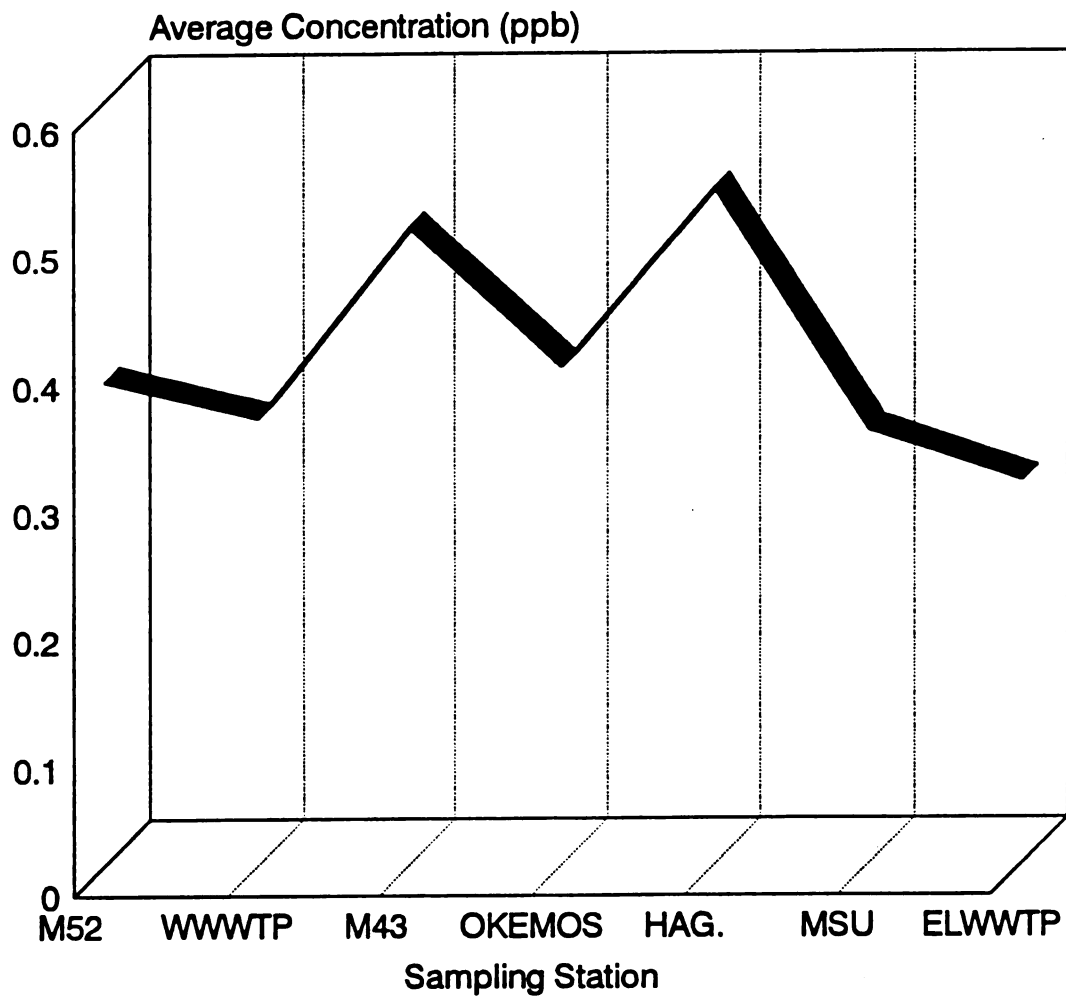


Figure 8: Atrazine Concentration (ppb) by Sampling Station
According to G.C. Data

Table 12: Results for Duplicate ELISA Analyses of Water Samples for Atrazine

	station ID	atrazine concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	M52	0.66	0.76	0.66	0.14
	WWWTP	0.27	0.48	0.38	0.15
	MERIDIAN	1.20	0.98	1.09	0.16
	OKEMOS	1.19	0.79	0.99	0.28
	HAGADORN	1.21	1.37	1.29	0.11
	MSU	0.85	0.79	0.87	0.11
	ELWWTP	1.01	1.06	0.25	0.04
	average May			0.79	0.14
Jun-92	M52	1.00	1.03	1.02	0.02
	WWWTP	0.95	1.21	1.08	0.18
	MERIDIAN	1.28	1.15	1.22	0.09
	OKEMOS	1.08	1.02	1.05	0.04
	HAGADORN	1.35	1.21	1.28	0.10
	MSU	1.28	1.21	1.25	0.06
	ELWWTP	1.21	1.13	1.17	0.06
	average June			1.15	0.08
Jul-92	M52	0.85	1.07	0.96	0.16
	WWWTP	1.12	1.11	1.12	0.01
	MERIDIAN	1.06	1.34	1.20	0.20
	OKEMOS	1.17	1.13	1.15	0.03
	HAGADORN	1.27	1.22	1.25	0.04
	MSU	1.08	1.30	1.19	0.16
	ELWWTP	1.27	1.33	1.30	0.04
	average July			1.17	0.08
Aug. 92	M52	0.34	1.02	0.68	0.48
	WWWTP	0.92	1.12	1.02	0.14
	MERIDIAN	1.12	1.13	1.13	0.01
	OKEMOS	1.17	1.36	1.27	0.13
	HAGADORN	1.11	1.12	1.12	0.01
	MSU	0.91	1.17	1.04	0.18
	ELWWTP	1.11	1.08	1.10	0.02
	average Aug.			1.06	0.18
Sept. 92	M52	1.09	1.08	1.09	0.01
	WWWTP	1.08	1.23	1.16	0.11
	MERIDIAN	1.28	1.18	1.24	0.06
	OKEMOS	1.18	1.17	1.18	0.01
	HAGADORN	0.86	0.85	0.86	0.01
	MSU	0.90	0.89	0.90	0.01
	ELWWTP	1.03	1.08	1.06	0.04
	Sept. average			1.07	0.04
Oct. 92	M52	0.55	0.58	0.57	0.02
	WWTP	0.4	0.41	0.41	0.01
	MERIDIAN	0.48	0.47	0.48	0.01
	OKEMOS	0.51	0.49	0.50	0.01
	HAGADORN	0.52	0.49	0.51	0.02
	MSU	0.46	0.47	0.47	0.01
	ELWWT	0.47	0.49	0.48	0.01
	Oct. average			0.49	0.01
Apr-93	M52	0.52	0.49	0.51	0.02
	WWTP	0.6	0.61	0.61	0.01
	MERIDIAN	0.68	0.66	0.67	0.01
	OKEMOS	0.64	0.65	0.65	0.01
	HAGADORN	0.78	0.74	0.76	0.03
	MSU	0.72	0.71	0.72	0.01
	ELWWT	0.72	0.73	0.73	0.01
	April average			0.66	0.01

Table 13: Atrazine Concentration (ppb) in relation to Sampling Month and Station According to ELISA Data

Month	Sampling Station								average
	MS2	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP		
May-92	0.66	0.38	1.09	0.99	1.29	0.87	0.25		0.79
Jun-92	1.02	1.08	1.22	1.05	1.28	1.25	1.17		1.15
Jul-92	0.96	1.12	1.20	1.15	1.25	1.19	1.30		1.17
Aug-92	0.68	1.02	1.13	1.27	1.12	1.04	1.10		1.05
Sep-92	1.09	1.16	1.24	1.18	0.86	0.80	1.06		1.07
Oct-92	0.57	0.41	0.48	0.50	0.51	0.47	0.48		0.49
Apr-93	0.51	0.61	0.67	0.65	0.76	0.72	0.73		0.66
average	0.78	0.83	1.00	0.97	1.01	0.92	0.87		

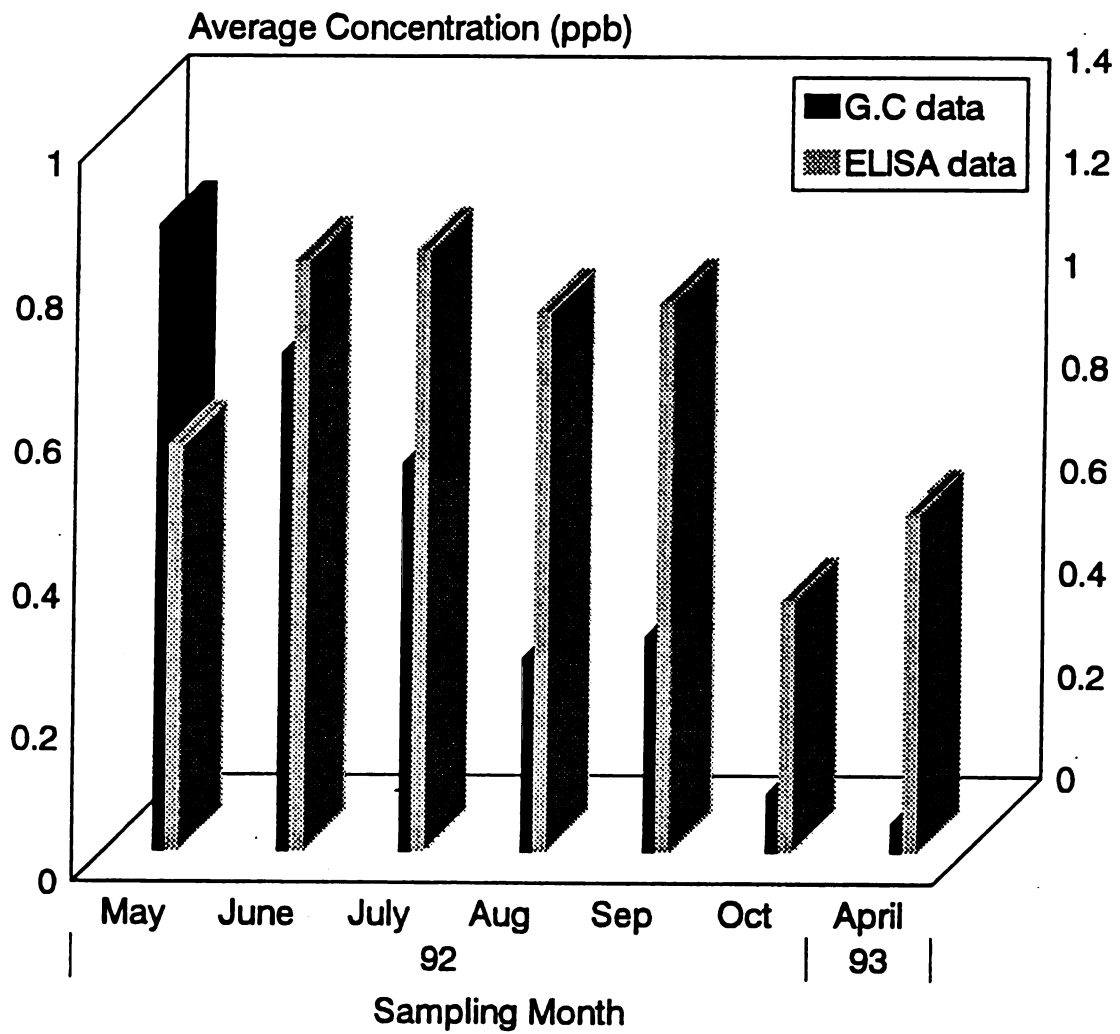


Figure 9: Atrazine Concentration (ppb) by Sampling Month
According to G.C. and ELISA Data

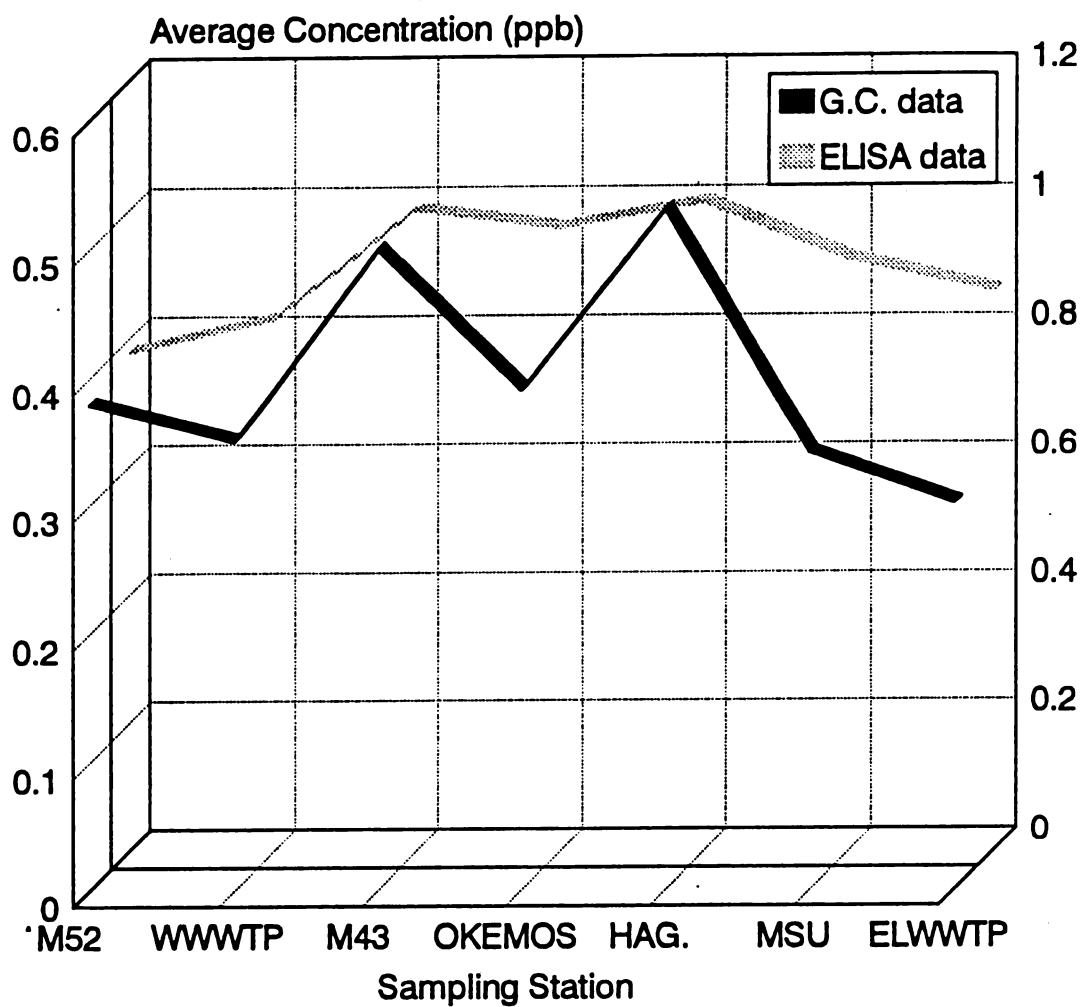


Figure 10: Atrazine Concentration (ppb) by Sampling Station According to G.C. and ELISA Data

Table 14: Results for Duplicate Analyses of Water Samples for Alachlor

	station ID	alachlor concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	M52	0.16	0.15	0.16	0.01
	WWWTP	0.12	0.13	0.12	0.01
	MERIDIAN	0.33	0.32	0.33	0.01
	OKEMOS	0.17	0.27	0.22	0.07
	HAGADORN	0.21	0.22	0.21	0.00
	MSU	0.12	0.14	0.13	0.01
	ELWWTP	0.11	0.11	0.11	0.01
	average May			0.18	0.02
Jun-92	M52	0.63	0.54	0.59	0.06
	WWWTP	0.18	0.24	0.21	0.04
	MERIDIAN	0.37	0.42	0.40	0.04
	OKEMOS	0.23	0.30	0.27	0.05
	HAGADORN	1.06	0.60	0.83	0.33
	MSU	0.15	0.18	0.17	0.02
	ELWWTP	0.10	0.04	0.07	0.04
	average June			0.36	0.08
Jul-92	M52	0.04	0.05	0.05	0.01
	WWWTP	0.09	0.22	0.16	0.09
	MERIDIAN	0.19	0.19	0.19	0.00
	OKEMOS	0.11	0.09	0.10	0.01
	HAGADORN	0.21	0.83	0.52	0.44
	MSU	0.07	0.09	0.08	0.02
	ELWWTP	0.06	0.06	0.06	0.00
	average July			0.16	0.16
Aug. 92	M52	0.13	0.15	0.14	0.01
	WWWTP	0.20	0.20	0.20	0.00
	MERIDIAN	0.17	0.15	0.16	0.01
	OKEMOS	0.11	0.16	0.13	0.03
	HAGADORN	0.11	0.09	0.10	0.02
	MSU	0.10	0.09	0.09	0.01
	ELWWTP	0.09	0.09	0.09	0.00
	average Aug.			0.13	0.04
Sept. 92	M52	0.63	0.59	0.61	0.03
	WWWTP	1.00	0.63	0.82	0.26
	MERIDIAN	0.77	1.22	1.00	0.32
	OKEMOS	0.72	1.00	0.86	0.20
	HAGADORN	0.81	0.91	0.86	0.07
	MSU	0.68	0.91	0.80	0.16
	ELWWTP	0.81	1.09	0.95	0.20
	Sept. average			0.84	0.10
Oct. 92	M52	0.05	0.06	0.06	0.01
	WWTP	0.15	0.15	0.15	0.00
	MERIDIAN	0.15	0.11	0.13	0.03
	OKEMOS	0.19	0.13	0.16	0.04
	HAGADORN	0.07	0.06	0.06	0.01
	MSU	0.06	0.04	0.05	0.02
	ELWWT	0.07	0.06	0.07	0.01
	Oct. average			0.10	0.01
Apr-93	M52	1.67	1.72	1.70	0.04
	WWTP	1.36	1.36	1.36	0.00
	MERIDIAN	1.18	1.32	1.25	0.10
	OKEMOS	1.40	1.49	1.45	0.06
	HAGADORN	1.72	1.86	1.79	0.10
	MSU	1.13	1.18	1.16	0.04
	ELWWT	2.04	1.86	1.95	0.13
	April average			1.52	0.05

Table 15: Alachlor Water Concentration (ppb) in relation to Sampling Month and Station

Month	Sampling Station								average
	MS2	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP		
May-92	0.16	0.12	0.33	0.22	0.21	0.13	0.11		0.18
Jun-92	0.59	0.21	0.40	0.27	0.83	0.17	0.07		0.36
Jul-92	0.06	0.15	0.19	0.10	0.55	0.08	0.06		0.17
Aug-92	0.14	0.20	0.16	0.13	0.10	0.09	0.09		0.13
Sep-92	0.61	0.82	1.00	0.86	0.86	0.80	0.95		0.84
Oct-92	0.06	0.15	0.13	0.16	0.06	0.05	0.07		0.10
Apr-93	1.70	1.36	1.25	1.45	1.79	1.16	1.95		1.52
average	0.47	0.43	0.49	0.45	0.63	0.35	0.47		

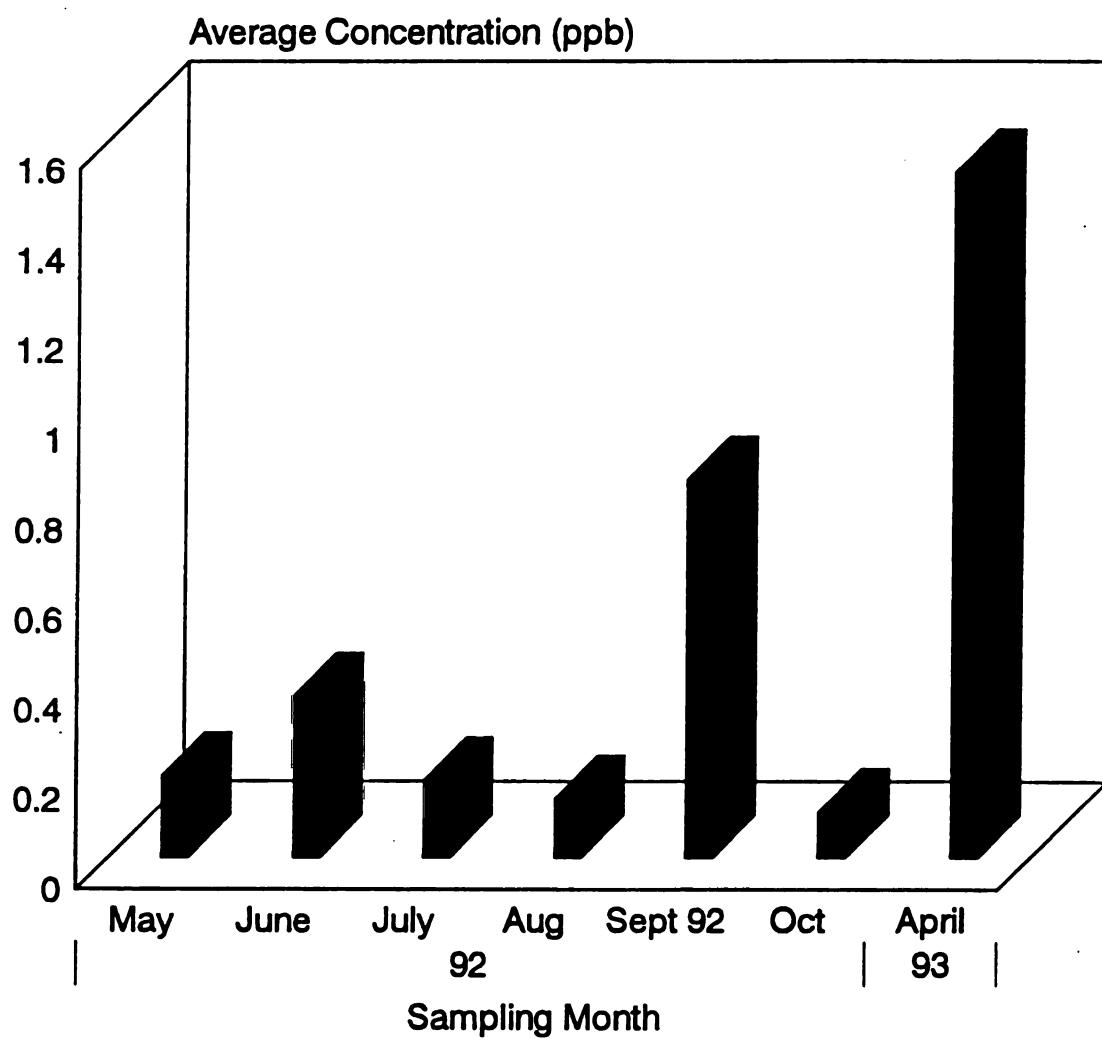


Figure 11: Alachlor Water Concentration by Sampling Month

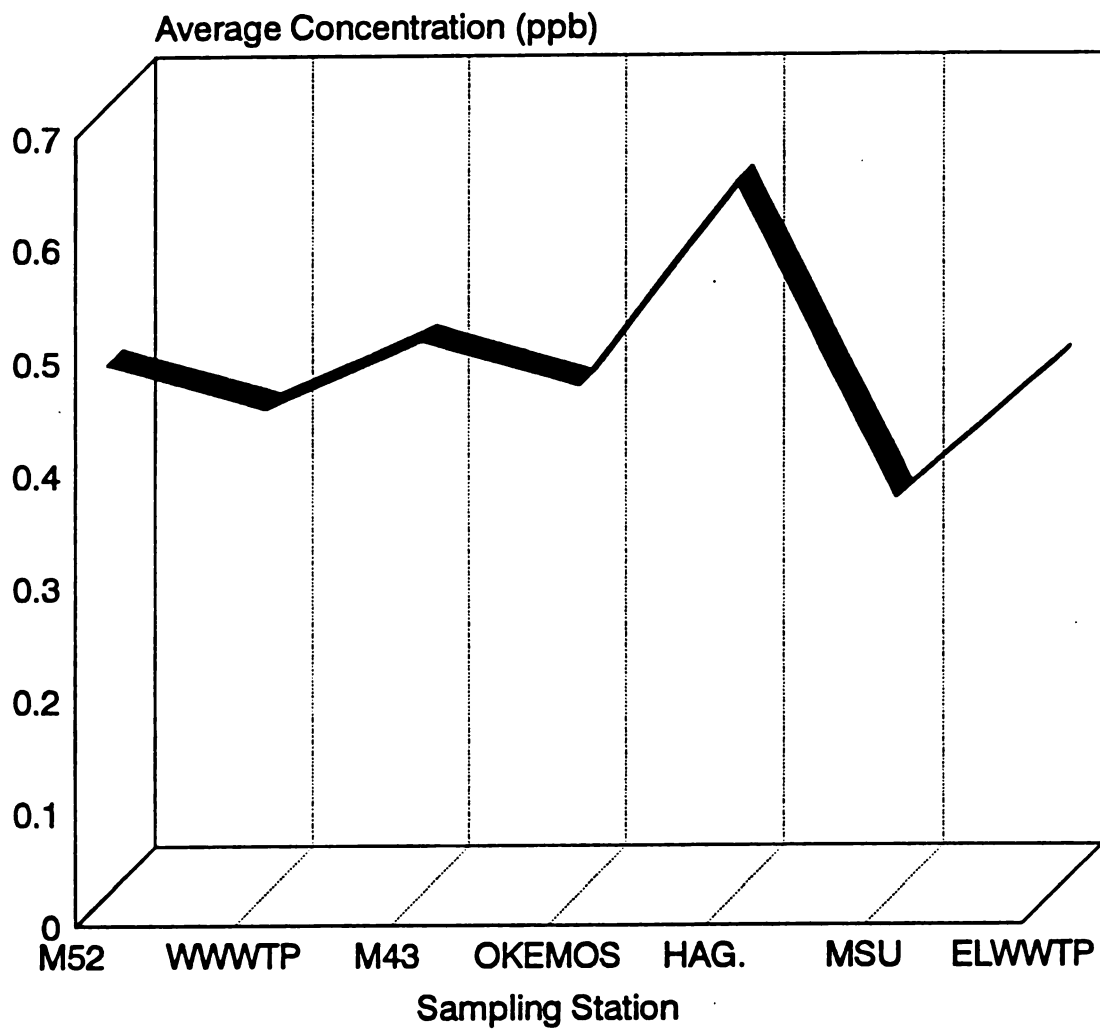


Figure 12: Alachlor Water Concentration (ppb) by Sampling Station

Table 16: Results for Duplicate Water Analyses of Water Samples for p,p'-DDE

	station ID	2,4-D concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	M52	0.72	0.69	0.71	0.02
	WWWTP	1.13	1.38	1.26	0.18
	MERIDIAN	0.70	0.74	0.72	0.03
	OKEMOS	2.00	2.08	2.04	0.08
	HAGADORN	1.04	0.74	0.89	0.21
	MSU	0.95	0.42	0.44	0.37
	ELWWTP	1.01	1.09	1.16	0.06
	average May			1.03	0.13
Jun-92	M52	0.81	0.90	0.86	0.06
	WWWTP	1.38	1.28	1.33	0.07
	MERIDIAN	1.32	1.32	1.32	0.00
	OKEMOS	1.31	1.69	1.46	0.20
	HAGADORN	0.71	0.95	0.83	0.17
	MSU	0.93	0.33	0.63	0.42
	ELWWTP	1.19	1.24	1.22	0.04
	average June			1.09	0.14
Jul-92	M52	0.69	1.04	0.87	0.25
	WWWTP	0.93	0.92	0.93	0.01
	MERIDIAN	1.82	2.17	2.00	0.25
	OKEMOS	2.09	2.64	2.37	0.39
	HAGADORN	2.02	1.88	1.95	0.10
	MSU	0.62	0.62	0.67	0.07
	ELWWTP	0.82	0.63	0.68	0.21
	average July			1.34	0.13
Aug. 92	M52	0.34	0.49	0.42	0.11
	WWWTP	0.74	0.53	0.64	0.16
	MERIDIAN	0.90	0.71	0.81	0.13
	OKEMOS	1.33	1.24	1.29	0.08
	HAGADORN	1.29	1.27	1.28	0.01
	MSU	0.61	0.97	0.79	0.26
	ELWWTP	1.05	0.53	0.79	0.37
	average Aug.			0.86	0.32
Sept. 92	M52	0.45	0.34	0.40	0.08
	WWWTP	0.43	0.60	0.47	0.06
	MERIDIAN	0.71	0.41	0.66	0.21
	OKEMOS	0.97	0.67	0.82	0.21
	HAGADORN	0.43	0.45	0.44	0.01
	MSU	0.28	0.19	0.23	0.05
	ELWWTP	0.16	0.09	0.13	0.05
	Sept. average			0.43	0.08
Oct. 92	M52	0.25	0.21	0.23	0.03
	WWTP	0.39	0.34	0.37	0.04
	MERIDIAN	0.69	0.75	0.72	0.04
	OKEMOS	0.4	0.6	0.46	0.07
	HAGADORN	0.3	0.66	0.48	0.26
	MSU	0.1	0.16	0.13	0.04
	ELWWT	0.26	0.33	0.30	0.05
	Oct. average			0.38	0.08
Apr-93	M52	0.2	0.28	0.23	0.04
	WWTP	0.34	0.32	0.33	0.01
	MERIDIAN	0.36	0.35	0.36	0.01
	OKEMOS	0.31	0.51	0.41	0.14
	HAGADORN	0.36	0.35	0.36	0.01
	MSU	0.21	0.17	0.19	0.03
	ELWWT	0.26	0.08	0.17	0.13
	April average			0.29	0.06

Table 17: p,p'-DDE Water Concentration (ppt) in relation to Sampling Month and Station

Month	Sampling Station									average
	MS2	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP			
May-92	<MDL	<MDL	1.50	<MDL	<MDL	1.30	2.10			0.70
Jun-92	<MDL	<MDL	<MDL	1.35	2.15	<MDL	<MDL			0.50
Jul-92	<MDL	<MDL	1.45	<MDL	<MDL	<MDL	<MDL			0.21
Aug-92	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL			<MDL
Sep-92	<MDL	1.55	1.23	<MDL	<MDL	<MDL	<MDL			0.40
Oct-92	<MDL	<MDL	0.82	<MDL	<MDL	<MDL	<MDL			0.12
Apr-93	<MDL	<MDL	0.70	<MDL	1.62	1.98	<MDL			0.76
average	0.00	0.22	0.81	0.19	0.54	0.47	0.30			

MDL : Method Detection Limit

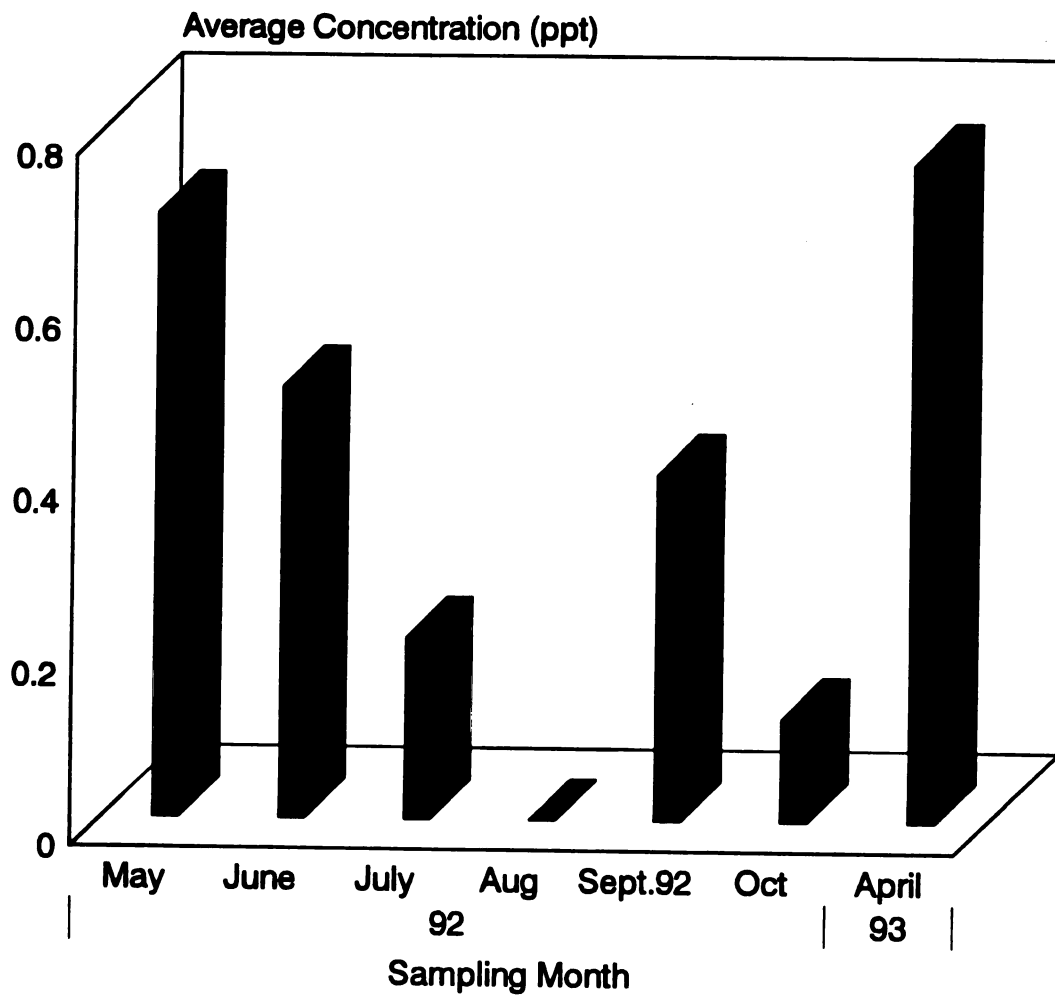


Figure 13: p,p'-DDE Water Concentration (ppt) by Sampling Month

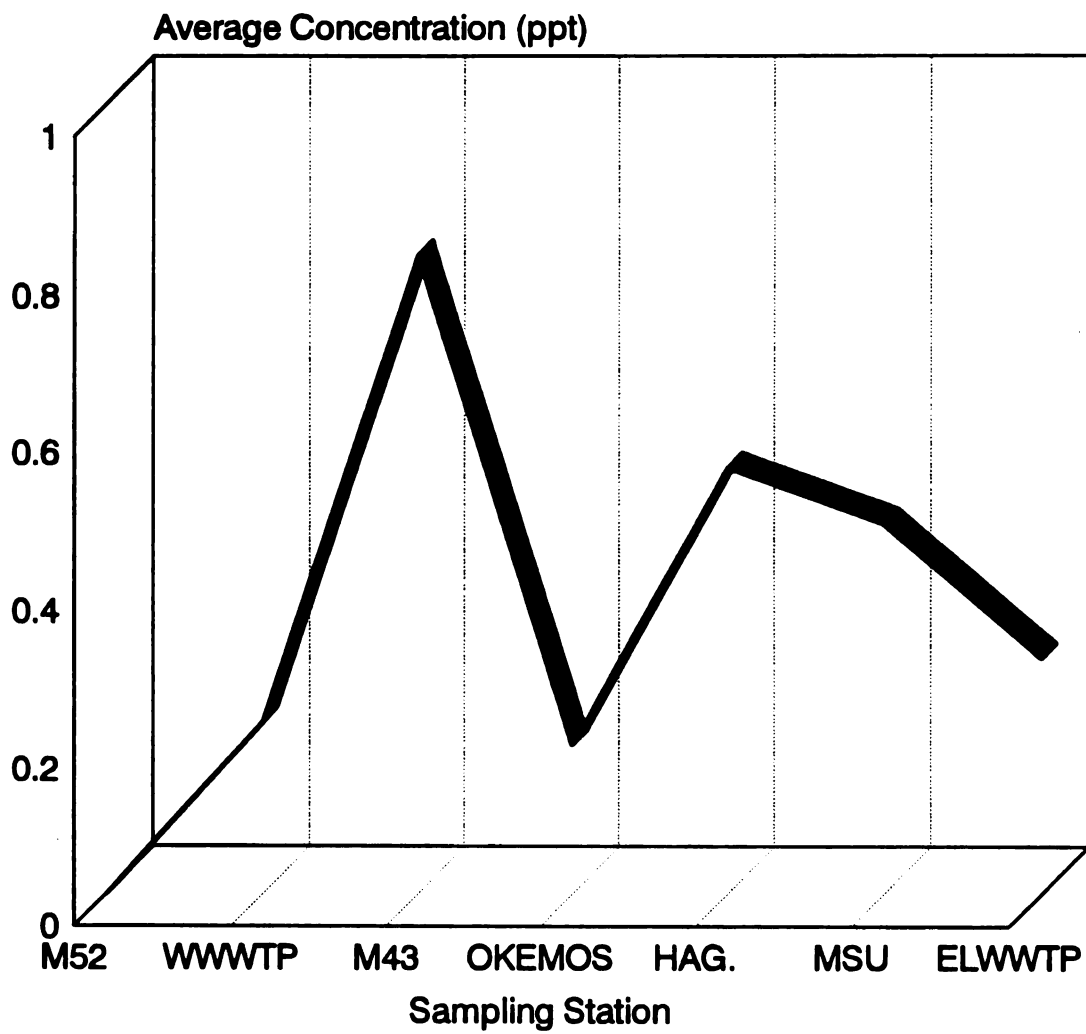


Figure 14: p,p'-DDE Water Concentration (ppt) by Sampling Station

Table 18: Results for Duplicate Analyses of Water Samples
for 2,4-D

	station ID	2,4-D concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	M52	0.72	0.69	0.71	0.02
	WWWTP	1.13	1.38	1.26	0.18
	MERIDIAN	0.70	0.74	0.72	0.03
	OKEMOS	2.00	2.08	2.04	0.06
	HAGADORN	1.04	0.74	0.89	0.21
	MSU	0.95	0.42	0.44	0.37
	ELWWTP	1.01	1.09	1.16	0.08
	average May			1.03	0.13
Jun-92	M52	0.81	0.90	0.86	0.06
	WWWTP	1.38	1.28	1.33	0.07
	MERIDIAN	1.32	1.32	1.32	0.00
	OKEMOS	1.31	1.59	1.46	0.20
	HAGADORN	0.71	0.95	0.83	0.17
	MSU	0.93	0.33	0.63	0.42
	ELWWTP	1.18	1.24	1.22	0.04
	average June			1.09	0.14
Jul-92	M52	0.69	1.04	0.87	0.25
	WWWTP	0.93	0.92	0.93	0.01
	MERIDIAN	1.82	2.17	2.00	0.26
	OKEMOS	2.09	2.64	2.37	0.39
	HAGADORN	2.02	1.88	1.95	0.10
	MSU	0.62	0.52	0.67	0.07
	ELWWTP	0.82	0.53	0.68	0.21
	average July			1.34	0.13
Aug. 92	M52	0.34	0.49	0.42	0.11
	WWWTP	0.74	0.53	0.64	0.16
	MERIDIAN	0.90	0.71	0.81	0.13
	OKEMOS	1.33	1.24	1.29	0.06
	HAGADORN	1.29	1.27	1.28	0.01
	MSU	0.61	0.97	0.79	0.26
	ELWWTP	1.05	0.53	0.79	0.37
	average Aug.			0.86	0.32
Sept. 92	M52	0.45	0.34	0.40	0.08
	WWWTP	0.43	0.50	0.47	0.06
	MERIDIAN	0.71	0.41	0.66	0.21
	OKEMOS	0.97	0.67	0.82	0.21
	HAGADORN	0.43	0.45	0.44	0.01
	MSU	0.26	0.19	0.23	0.06
	ELWWTP	0.16	0.09	0.13	0.06
	Sept. average			0.43	0.08
Oct. 92	M52	0.25	0.21	0.23	0.03
	WWWTP	0.39	0.34	0.37	0.04
	MERIDIAN	0.69	0.75	0.72	0.04
	OKEMOS	0.4	0.5	0.45	0.07
	HAGADORN	0.3	0.66	0.48	0.25
	MSU	0.1	0.16	0.13	0.04
	ELWWT	0.26	0.33	0.30	0.05
	Oct. average			0.38	0.08
Apr-93	M52	0.2	0.26	0.23	0.04
	WWWTP	0.34	0.32	0.33	0.01
	MERIDIAN	0.36	0.35	0.36	0.01
	OKEMOS	0.31	0.51	0.41	0.14
	HAGADORN	0.36	0.35	0.36	0.01
	MSU	0.21	0.17	0.19	0.03
	ELWWT	0.26	0.08	0.17	0.13
	April average			0.29	0.06

Table 19: 2,4-D Concentration (ppb) in relation to Sampling Month and Station

Month									average
	MS2	WWWTP	MER	OKECOS	HAGAD.	MSU	ELWWTP		
May-92	0.71	1.26	0.70	2.04	0.89	0.44	1.16		1.03
Jun-92	0.86	1.33	1.32	1.45	0.83	0.63	1.22		1.09
Jul-92	0.87	0.93	2.00	2.37	1.95	0.57	0.68		1.34
Aug-92	0.42	0.64	0.81	1.29	1.28	0.79	0.79		0.86
Sep-92	0.40	0.47	0.56	0.82	0.44	0.23	0.13		0.44
Oct-92	0.23	0.37	0.72	0.45	0.48	0.13	0.30		0.38
Apr-93	0.23	0.33	0.36	0.41	0.36	0.19	0.17		0.29
average	0.53	0.76	0.92	1.26	0.89	0.43	0.64		

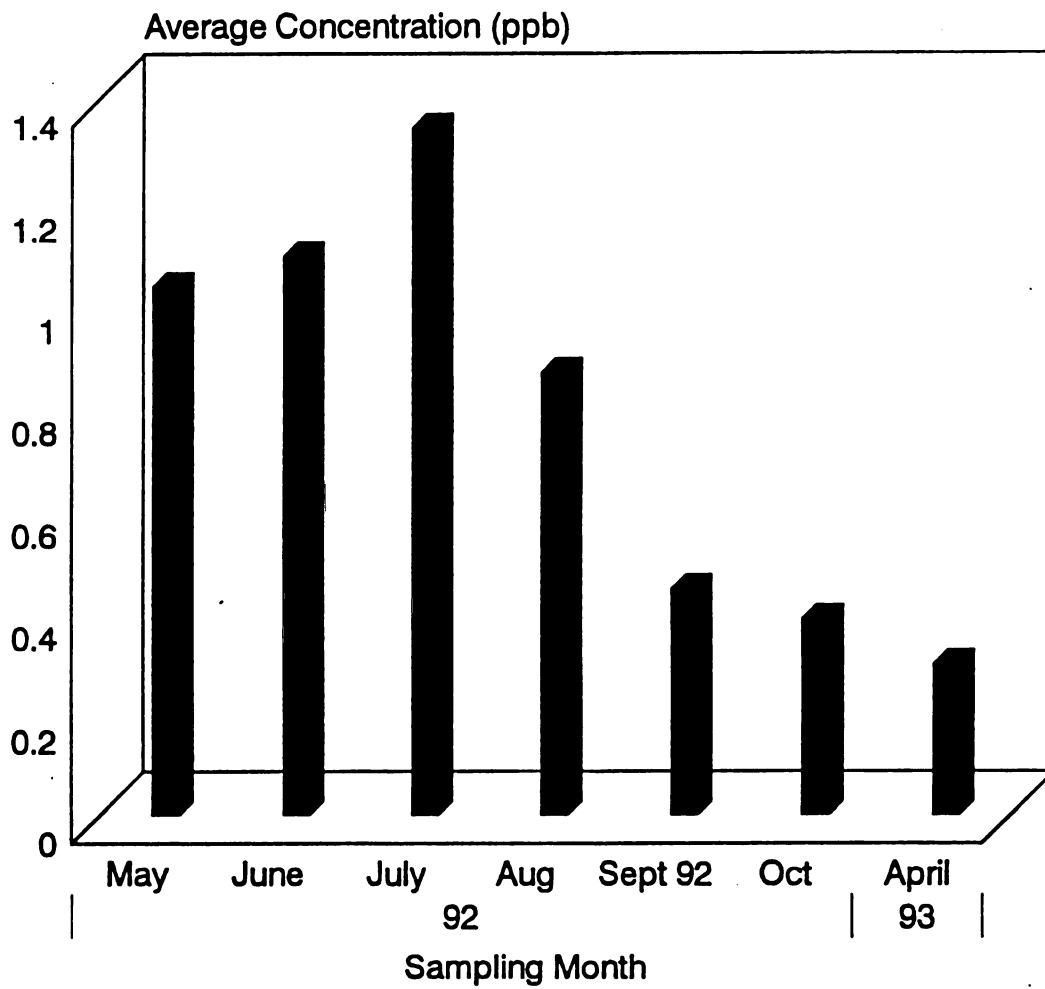


Figure 15: 2,4-D Water Concentration (ppb) by Sampling Month

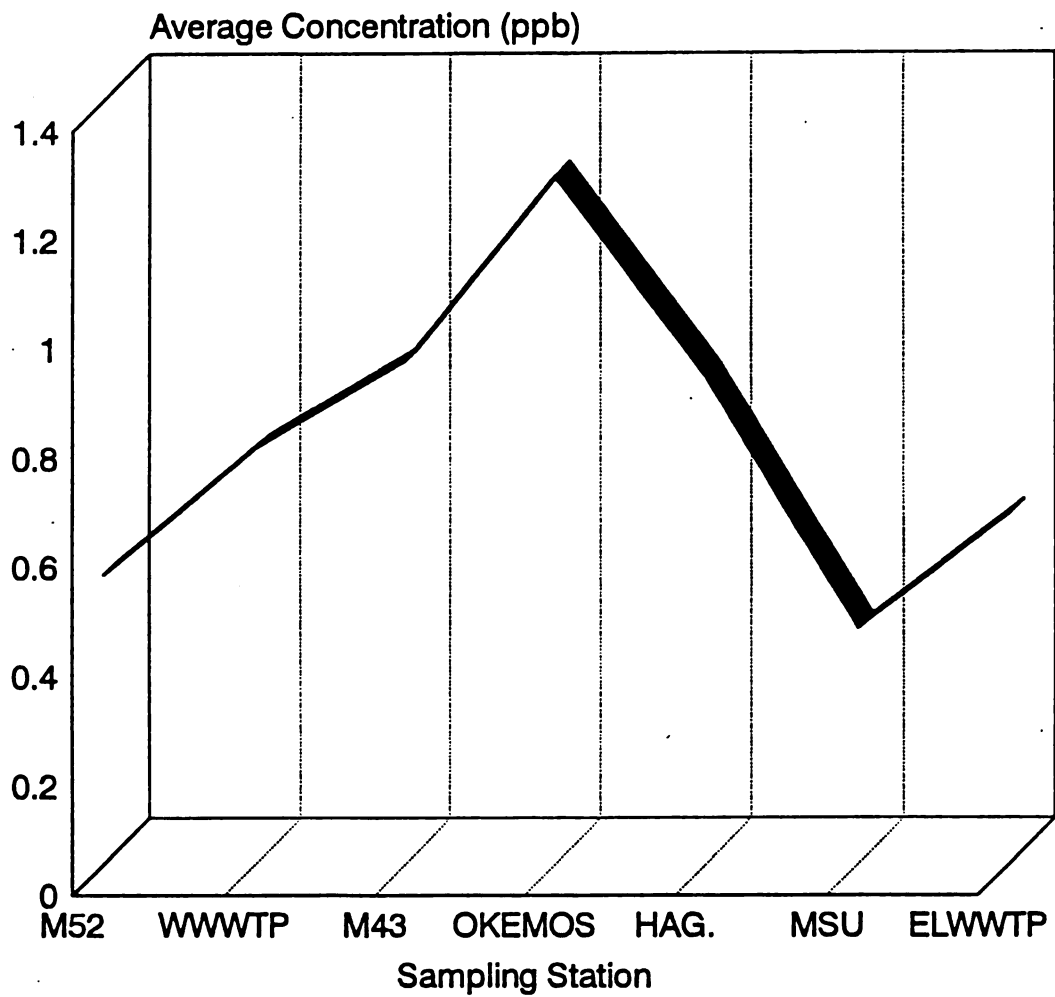


Figure 16: 2,4-D Water Concentration (ppb) by Sampling Station

Table 20: Results for Duplicate Analyses of Water Samples for Dicamba

	station ID	Dicamba concentration (ng/ml)			
		duplicate 1	duplicate 2	mean	Std
May-92	MS2	0.28	0.25	0.27	0.02
	WWWTP	0.29	0.32	0.31	0.02
	MERIDIAN	0.23	0.16	0.20	0.05
	OKEMOS	0.26	0.26	0.26	0.00
	HAGADORN	0.31	0.44	0.38	0.09
	MSU	0.18	0.28	0.44	0.07
	ELWWTP	0.15	0.23	1.16	0.06
	average May			0.43	0.04
Jun-92	MS2	0.22	0.15	0.19	0.05
	WWWTP	0.29	0.27	0.28	0.01
	MERIDIAN	0.24	0.33	0.29	0.06
	OKEMOS	0.18	0.23	0.21	0.04
	HAGADORN	0.24	0.25	0.25	0.01
	MSU	0.12	0.16	0.14	0.03
	ELWWTP	0.19	0.23	0.21	0.03
	average June			0.22	0.03
Jul-92	MS2	0.10	0.13	0.12	0.02
	WWWTP	0.11	0.09	0.10	0.01
	MERIDIAN	0.23	0.34	0.29	0.08
	OKEMOS	0.26	0.25	0.26	0.01
	HAGADORN	0.28	0.29	0.29	0.01
	MSU	0.10	0.09	0.10	0.01
	ELWWTP	0.15	0.13	0.14	0.01
	average July			0.18	0.03
Aug. 92	MS2	0.13	0.19	0.16	0.04
	WWWTP	0.34	0.21	0.28	0.09
	MERIDIAN	0.20	0.29	0.25	0.06
	OKEMOS	0.30	0.28	0.29	0.01
	HAGADORN	0.10	0.15	0.13	0.04
	MSU	0.09	0.08	0.09	0.01
	ELWWTP	0.11	0.14	0.13	0.02
	average Aug.			0.19	0.08
Sept. 92	MS2	0.11	0.16	0.14	0.04
	WWWTP	0.10	0.13	0.12	0.02
	MERIDIAN	0.11	0.09	0.10	0.01
	OKEMOS	0.10	0.12	0.11	0.01
	HAGADORN	0.09	0.16	0.13	0.05
	MSU	0.14	0.12	0.13	0.01
	ELWWTP	0.11	0.18	0.15	0.05
	Sept. average			0.12	0.02
Oct. 92	MS2	0.11	0.13	0.12	0.01
	WWTP	0.16	0.14	0.15	0.01
	MERIDIAN	0.12	0.15	0.14	0.02
	OKEMOS	0.13	0.09	0.11	0.03
	HAGADORN	0.11	0.17	0.14	0.04
	MSU	0.1	0.16	0.13	0.04
	ELWWT	0.19	0.14	0.17	0.04
	Oct. average			0.14	0.01
Apr-93	MS2	0.08	0.13	0.11	0.04
	WWTP	0.09	0.11	0.10	0.01
	MERIDIAN	0.09	0.12	0.11	0.02
	OKEMOS	0.23	0.17	0.20	0.04
	HAGADORN	0.25	0.18	0.22	0.05
	MSU	0.1	0.1	0.10	0.00
	ELWWT	0.08	0.14	0.11	0.04
	Apr9 average			0.13	0.02

Table 21: Dicamba Concentration (ppb) in relation to Sampling Month and Station

Month	Sampling Station								
	M52	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP		average
May-92	0.27	0.31	0.20	0.26	0.38	0.44	1.16		0.43
Jun-92	0.19	0.28	0.29	0.21	0.25	0.14	0.21		0.22
Jul-92	0.12	0.10	0.29	0.26	0.29	0.10	0.14		0.19
Aug-92	0.16	0.28	0.25	0.29	0.13	0.09	0.13		0.19
Sep-92	0.14	0.12	0.10	0.11	0.13	0.13	0.15		0.13
Oct-92	0.12	0.15	0.14	0.11	0.14	0.13	0.17		0.14
Apr-93	0.11	0.10	0.11	0.20	0.22	0.10	0.11		0.14
average	0.16	0.19	0.20	0.21	0.22	0.16	0.30		

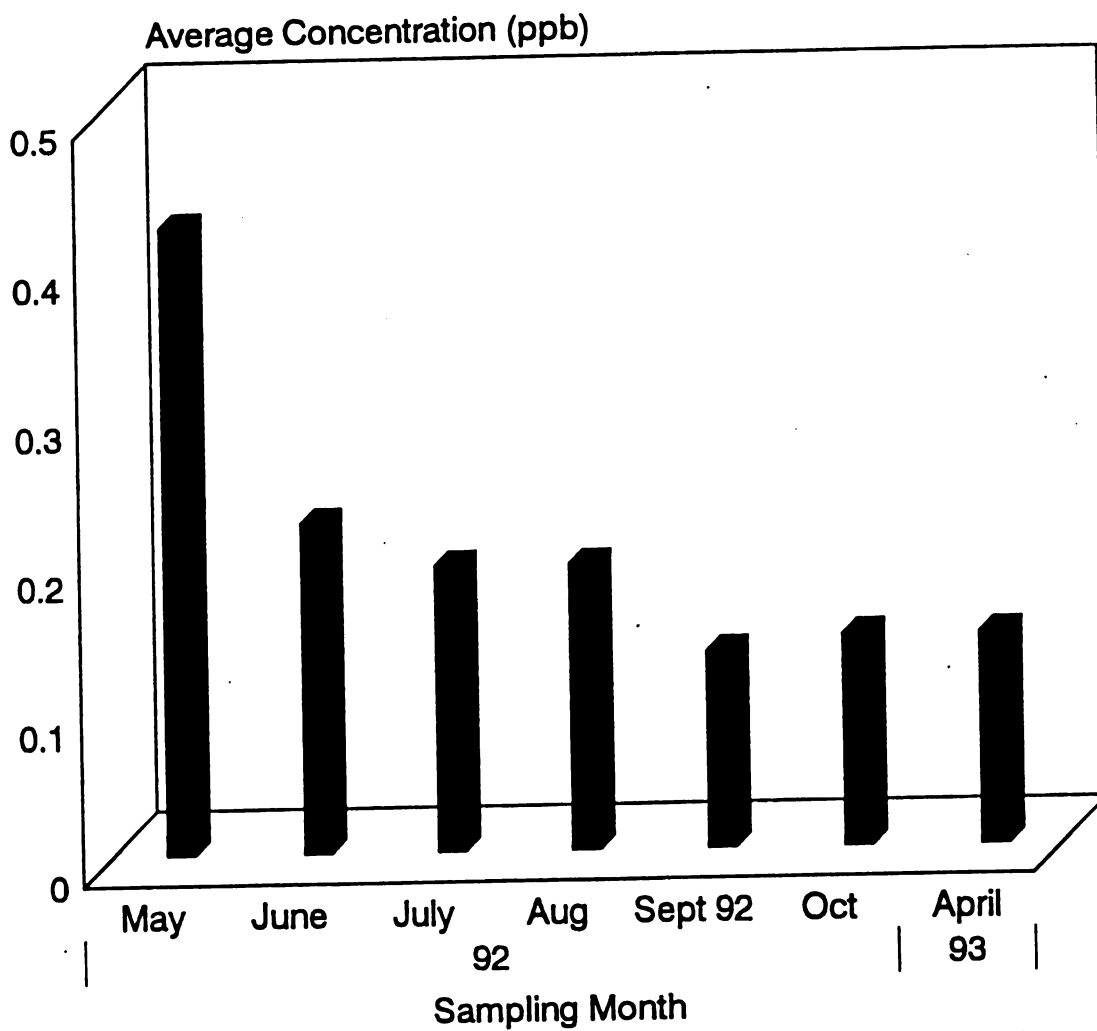


Figure 17: Dicamba Water Concentration (ppb) by Sampling Month

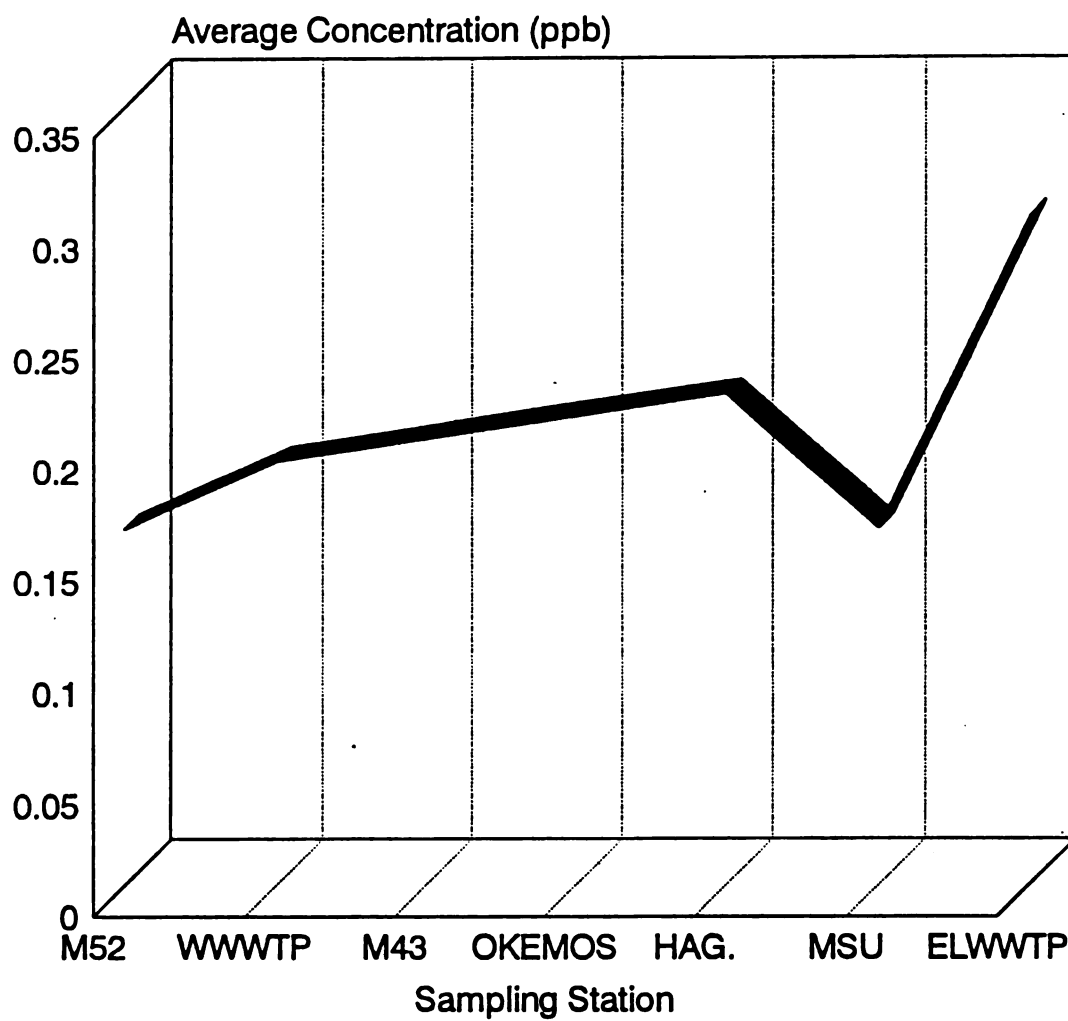


Figure 18: Dicamba Water Concentration (ppb) by Sampling Station

Table 22: Results for Duplicate Analyses of Sediment Samples for p,p'-DDE

	station ID	p,p'-DDE concentration (ng/g)			
		duplicate 1	duplicate 2	mean	Std
May-92	M52	0.48	0.61	0.55	0.09
	WWWTP	5.72	3.59	4.66	1.51
	MERIDIAN	2.65	3.02	2.84	0.26
	OKEMOS	1.90	2.52	2.21	0.44
	HAGADORN	11.02	12.16	11.59	0.81
	MSU	2.33	2.11	2.22	0.16
	ELWWTP	5.09	5.71	5.40	0.44
	average May			4.21	
Jun-92	M52	0.00	0.00	0	0.00
	WWWTP	18.21	2.56	10.39	11.07
	MERIDIAN	1.18	1.81	1.40	0.30
	OKEMOS	4.12	3.05	3.59	0.78
	HAGADORN	8.63	7.31	7.97	0.93
	MSU	3.18	3.01	3.10	0.12
	ELWWTP	8.39	5.93	7.16	1.74
	average June			4.80	
Jul-92	M52	0.00	0.00	0.00	0.00
	WWWTP	18.37	14.50	16.44	2.74
	MERIDIAN	0.73	0.88	0.81	0.11
	OKEMOS	1.41	1.34	1.38	0.05
	HAGADORN	7.49	8.16	7.83	0.47
	MSU	5.32	6.58	5.95	0.89
	ELWWTP	34.10	37.79	35.95	2.61
	average July			9.76	
Aug.	M52	0.54	0.55	0.55	0.01
	WWWTP	25.14	31.65	28.40	4.60
	MERIDIAN	0.88	0.82	0.85	0.04
	OKEMOS	2.28	2.24	2.26	0.03
	HAGADORN	7.68	6.69	7.19	0.70
	MSU	6.38	5.71	6.05	0.47
	ELWWTP	23.78	20.39	22.09	2.40
	average Aug.			9.62	
Se	M52	0.53	0.75	0.64	0.16
	WWWTP	12.94	11.04	11.99	1.34
	MERIDIAN	0.80	0.66	0.73	0.10
	OKEMOS	2.86	1.93	2.40	0.66
	HAGADORN	7.34	6.35	6.85	0.70
	MSU	2.67	3.46	3.07	0.56
	ELWWTP	25.91	19.23	22.57	4.72
	Sept. average			6.89	
Oct-92	M52	0.59	1.34	0.97	0.53
	WWTP	8.67	10.11	9.39	1.02
	MERIDIAN	1.07	0.67	0.87	0.28
	OKEMOS	1.85	2.18	2.02	0.23
	HAGADORN	13.45	13.20	13.33	0.18
	MSU	6.01	7.12	6.57	0.78
	ELWWT	16.34	21.53	18.94	3.67
	Oct. average			7.44	

Table 23: p,p'-DDE Sediment Concentration (ppb) in relation to Sampling Month and Station

Month	Sampling Station							
	MS2	WWWTP	MER	OKEMOS	HAGAD.	MSU	ELWWTP	Average
May-92	0.55	4.66	2.84	2.21	11.59	2.22	5.40	4.21
Jun-92	0.00	10.39	1.40	3.59	7.97	3.10	7.16	4.80
Jul-92	0.00	16.44	0.81	1.38	7.83	5.95	35.95	9.77
Aug-92	0.55	28.40	0.85	2.26	7.19	6.05	22.09	9.63
Sep-92	0.64	11.99	0.73	2.40	6.85	3.07	22.57	6.89
Oct-92	0.97	9.39	0.87	2.02	13.33	6.57	18.94	7.44
average	0.45	13.55	1.25	2.31	9.13	4.49	18.69	

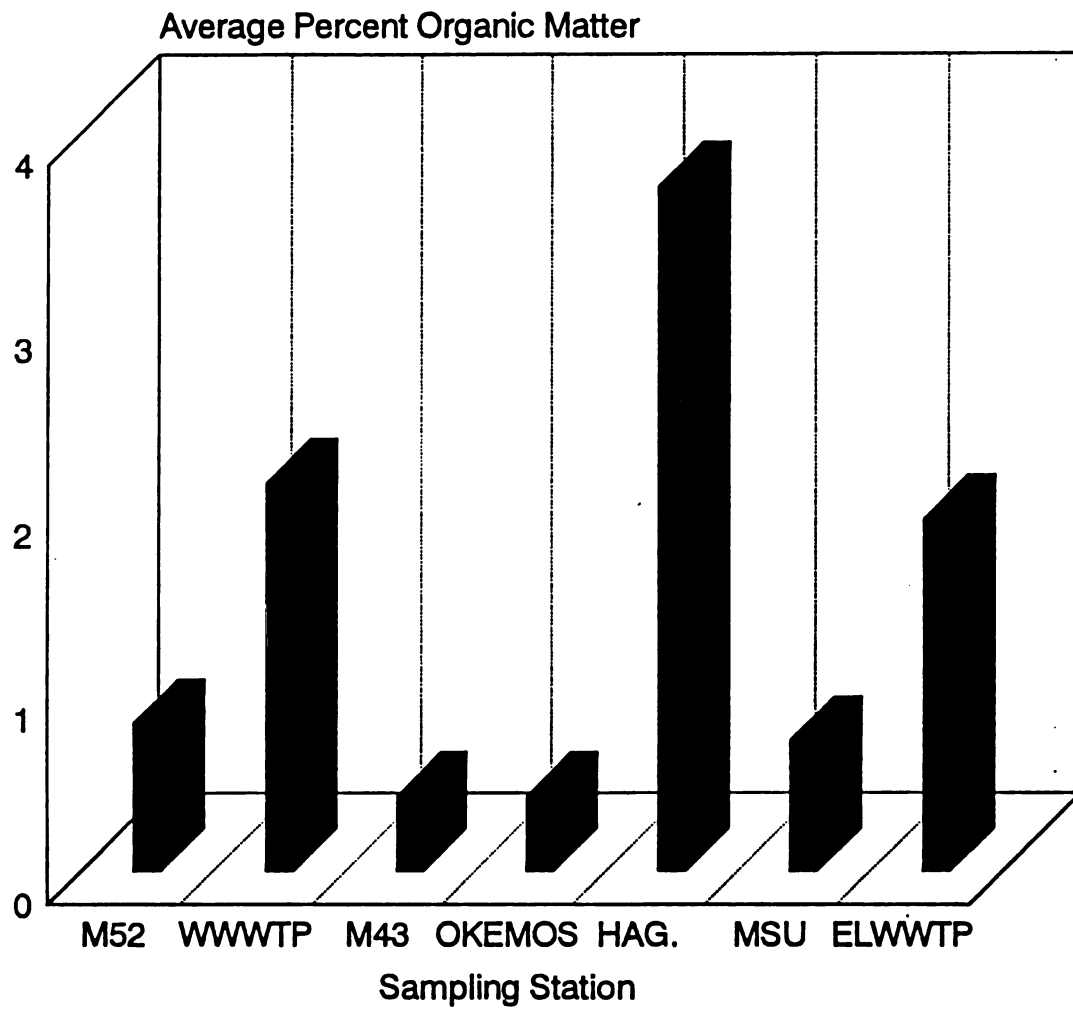


Figure 19; Average Percent Organic Matter by Sampling Station

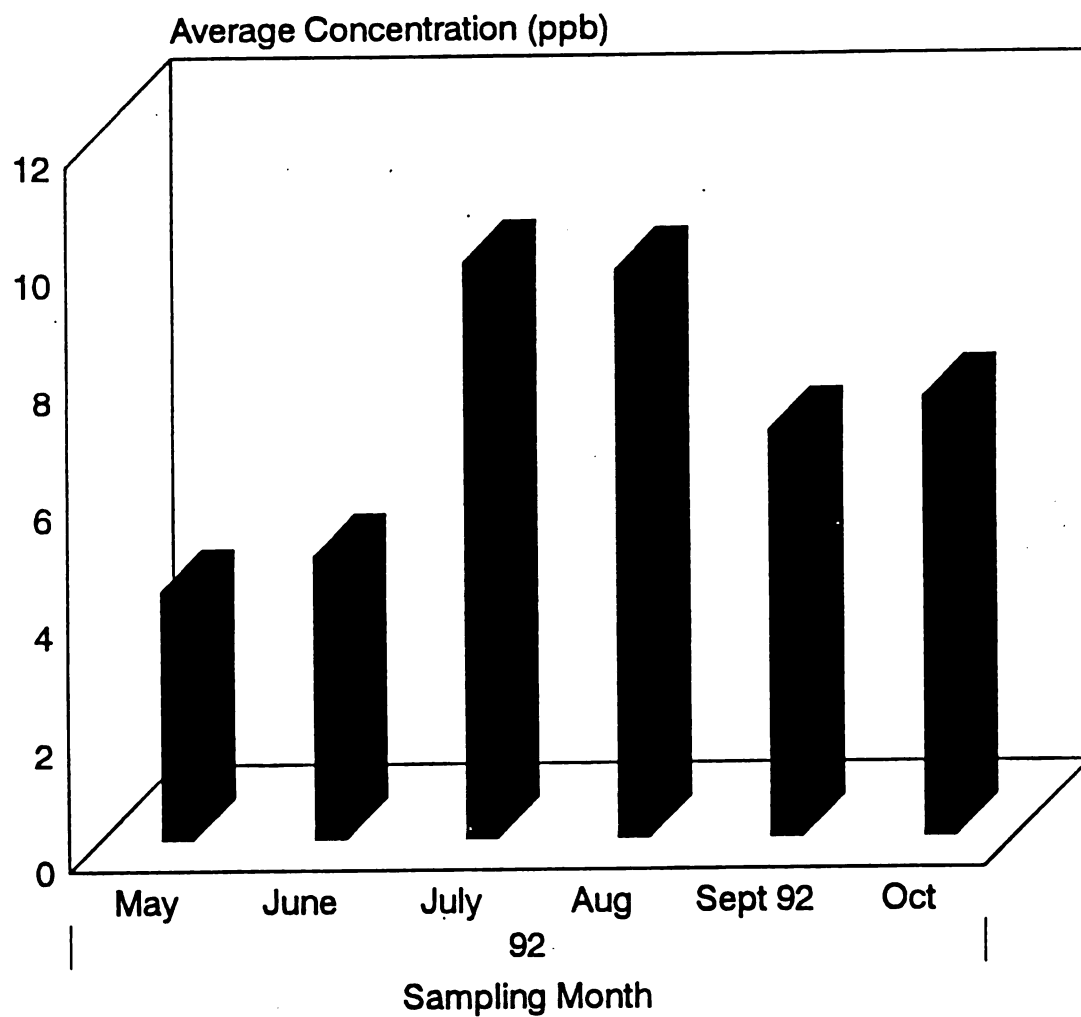


Figure 20: p,p'-DDE Sediment Concentration (ppb) by Sampling Month

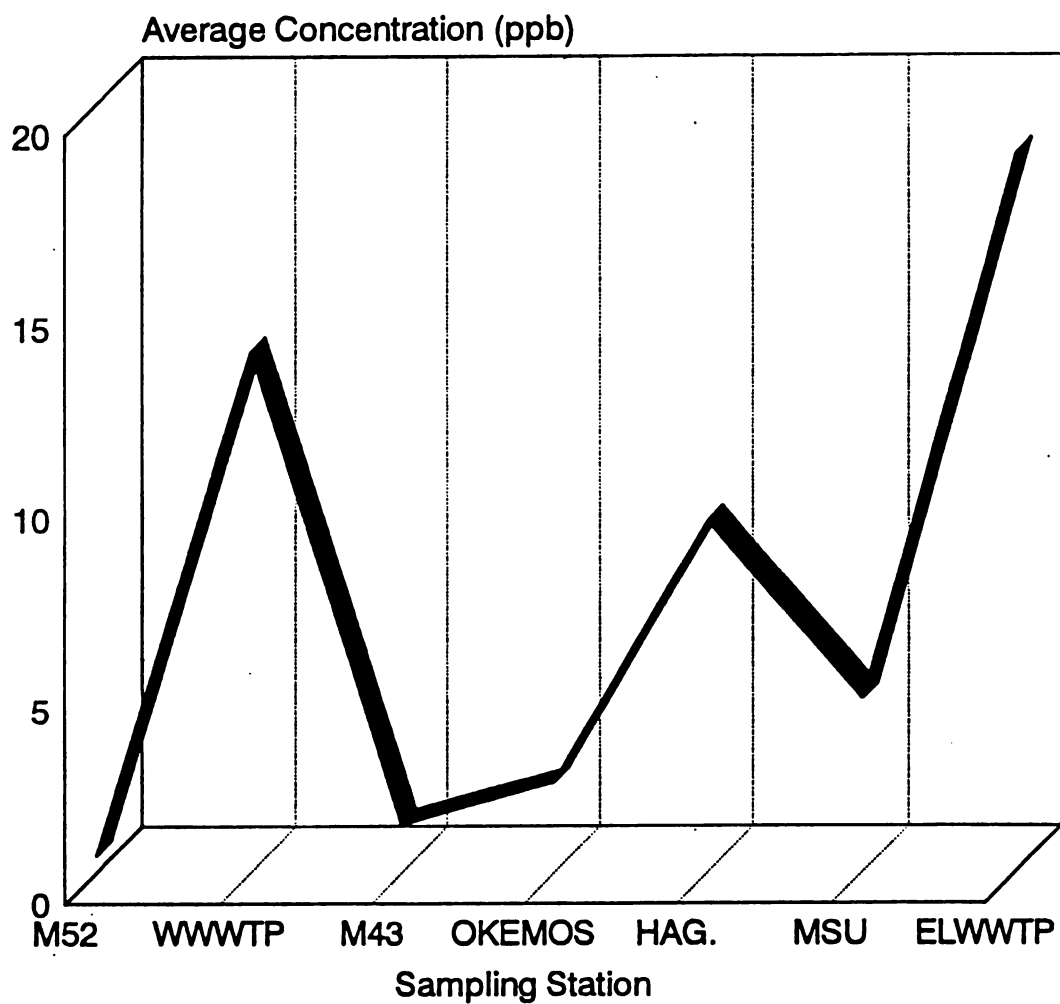


Figure 21: p,p'-DDE Sediment Concentration (ppb) by Sampling Station

Table 24: Results for Duplicate Analyses of Sediment Samples for p,p'-DDD

	p,p'-DDD concentration (ng/g)			
station ID	duplicate 1	duplicate 2	mean	Std
M52	0.16	0.47	0.32	0.22
WWWTP	4.92	4.67	4.80	0.18
MERIDIAN	0.68	0.79	0.74	0.08
OKEMOS	0.00	0.00	0.00	0.00
HAGADORN	6.97	7.29	7.13	0.23
MSU	4.70	5.01	4.86	0.22
ELWWTP	10.80	8.70	9.75	1.48
average May			3.94	
M52	0.00	0.00	0.00	0.00
WWWTP	3.60	3.90	3.75	0.21
MERIDIAN	1.20	1.30	1.25	0.07
OKEMOS	0.00	0.00	0.00	0.00
HAGADORN	5.79	6.84	6.32	0.74
MSU	3.80	2.90	3.35	0.64
ELWWTP	8.39	8.02	8.21	0.26
average June			3.27	
M52	0.00	0.00	0.00	0.00
WWWTP	1.69	2.41	2.05	0.51
MERIDIAN	1.12	1.46	1.29	0.24
OKEMOS	0.99	0.75	0.87	0.17
HAGADORN	6.93	5.90	6.42	0.73
MSU	4.68	3.51	4.10	0.83
ELWWTP	16.31	12.29	14.30	2.84
average July			4.15	
M52	0.04	0.05	0.05	0.01
WWWTP	3.12	1.25	2.19	1.32
MERIDIAN	0.01	0.08	0.05	0.05
OKEMOS	0.12	0.05	0.09	0.05
HAGADORN	2.27	3.13	2.70	0.61
MSU	1.66	3.01	2.34	0.95
ELWWTP	2.19	2.65	2.42	0.33
average Aug.			1.40	
M52	0.00	0.00	0.00	0.00
WWWTP	2.42	2.54	2.48	0.08
MERIDIAN	0.65	0.57	0.61	0.06
OKEMOS	1.53	1.65	1.59	0.08
HAGADORN	9.22	5.08	7.15	2.93
MSU	3.67	2.45	3.06	0.86
ELWWTP	8.34	6.53	7.44	1.28
Sept. average			3.19	
M52	1.34	0.98	1.16	0.25
WWTP	4.25	5.03	4.64	0.55
MERIDIAN	0.00	0.00	0.00	0.00
OKEMOS	0.07	0.05	0.06	0.01
HAGADORN	6.45	12.13	9.29	4.02
MSU	3.40	4.21	3.81	0.57
ELWWT	9.56	13.89	11.73	3.06
Oct. average			4.38	

Table 25: p,p'-DDD Sediment Concentration (ppb) in relation to Sampling Month and Station

Month	Sampling Station									
	MS2	WWWTP	MER	OKECOS	HAGAD.	MSU	ELWWTP			average
May-92	0.32	4.80	0.74	<MDL	7.13	4.86	9.75			3.94
Jun-92	<MDL	3.75	1.25	<MDL	6.32	3.25	8.21			3.25
Jul-92	<MDL	2.05	1.29	0.87	6.42	4.10	14.30			4.15
Aug-92	<MDL	2.19	0.05	0.09	2.70	2.34	2.42			1.40
Sep-92	<MDL	2.48	0.61	1.59	7.15	3.06	7.44			3.19
Oct-92	1.16	4.64	<MDL	0.06	9.29	3.87	11.73			4.39
average	0.25	3.32	0.66	0.44	6.50	3.58	8.98			

MDL = Method Detection Limit

MDL = Method Detection Limit

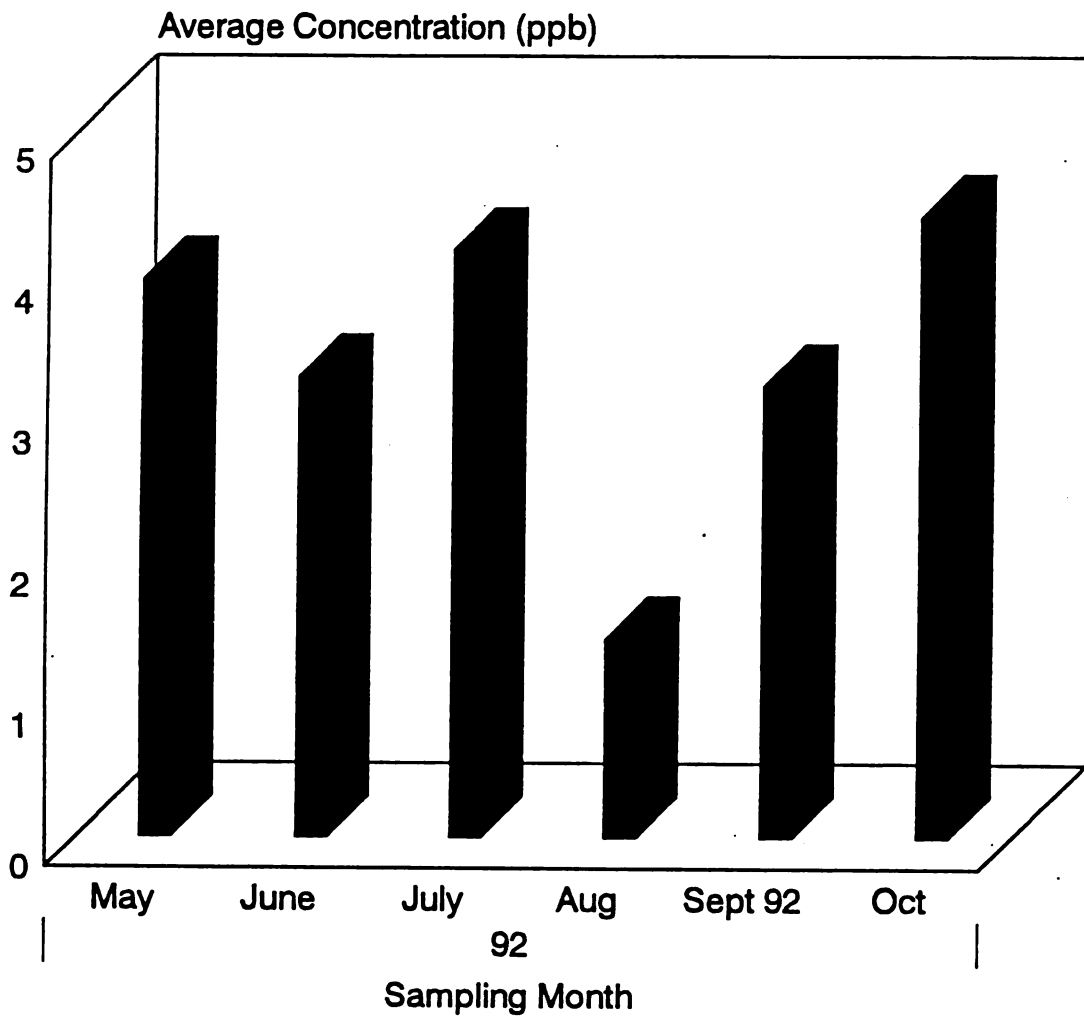


Figure 22: p,p'-DDD Sediment Concentration by Sampling Month

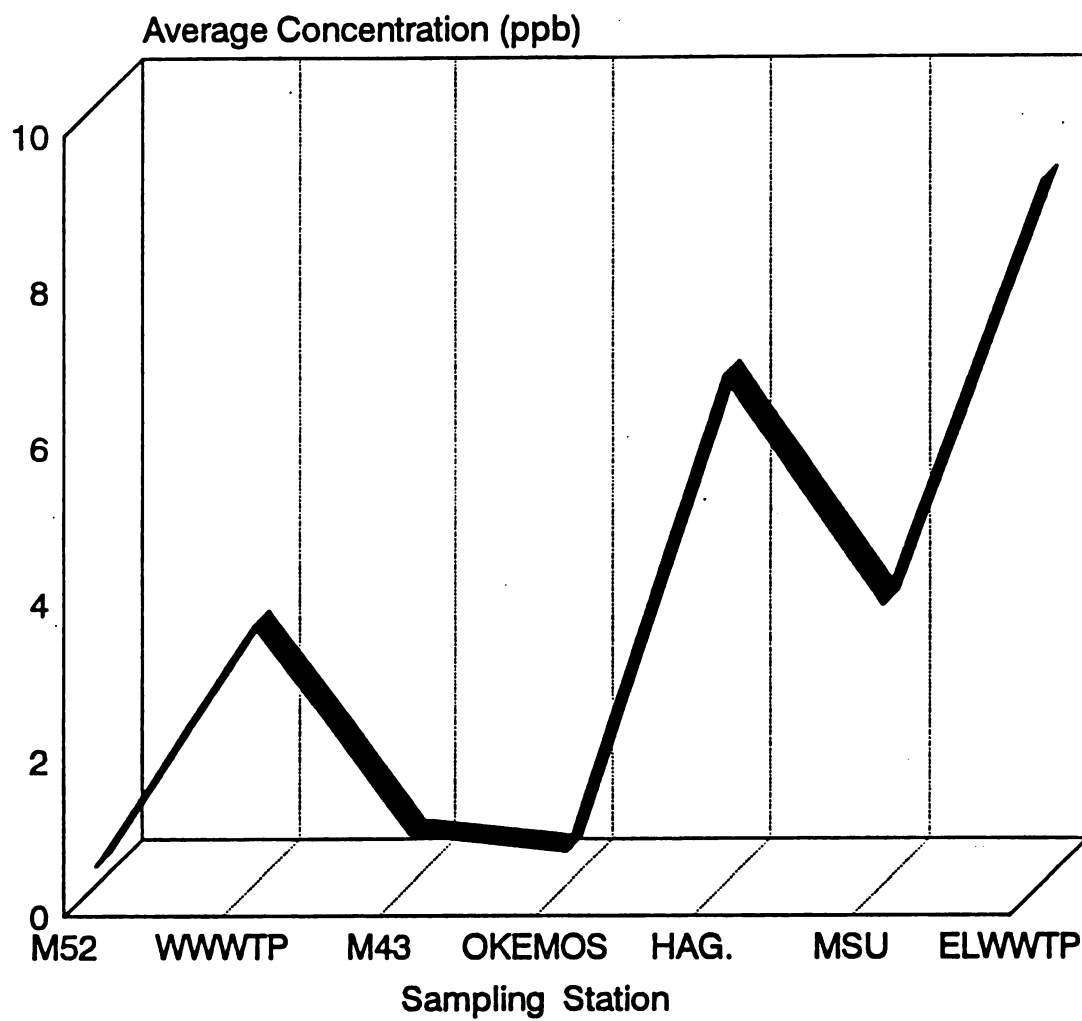


Figure 23: p,p'-DDD Sediment Concentration by Sampling Station

Table 26: Results for Duplicate Analyses of Sediment Samples for p,p-DDT

	station ID	p,p'-DDT concentration (ng/g)			
		duplicate 1	duplicate 2	mean	Std
May-92	M62	0.73	0.91	0.82	0.13
	WWWTP	8.66	10.32	9.49	1.17
	MERIDIAN	1.22	0.69	0.96	0.37
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	3.98	5.90	4.94	1.36
	MSU	0.84	0.98	0.91	0.10
	ELWWTP	10.34	9.43	9.89	0.64
	average May			3.86	
Jun-92	M62	0.00	0.00	0.00	0.00
	WWWTP	10.63	9.26	9.95	0.97
	MERIDIAN	0.00	0.00	0.00	0.00
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	4.67	2.30	3.49	1.68
	MSU	1.20	0.93	1.07	0.19
	ELWWTP	5.70	6.92	6.31	0.86
	average June			3.27	
Jul-92	M62	0.00	0.00	0.00	0.00
	WWWTP	4.13	4.04	4.09	0.06
	MERIDIAN	0.00	0.00	0.00	0.00
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	9.53	6.71	8.12	1.99
	MSU	2.31	1.30	1.81	0.71
	ELWWTP	6.21	8.91	7.56	1.91
	average July			3.08	
Aug-92	M62	0.00	0.00	0.00	0.00
	WWWTP	9.61	8.91	9.26	0.49
	MERIDIAN	0.00	0.00	0.00	0.00
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	5.98	7.53	6.76	1.10
	MSU	2.43	3.90	3.17	1.04
	ELWWTP	10.34	15.02	12.68	3.31
	average Aug.			4.55	
Sept-92	M62	0.00	0.00	0.00	0.00
	WWWTP	2.78	1.65	2.22	0.80
	MERIDIAN	0.00	0.00	0.00	0.00
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	7.54	11.32	9.43	2.67
	MSU	3.11	4.32	3.72	0.86
	ELWWTP	9.23	12.83	11.03	2.55
	Sept. average			3.77	
Oct-92	M62	0.00	0.00	0.00	0.00
	WWTP	3.02	1.99	2.51	0.73
	MERIDIAN	0.00	0.00	0.00	0.00
	OKEMOS	0.00	0.00	0.00	0.00
	HAGADORN	3.87	6.32	5.10	1.73
	MSU	2.78	2.23	2.51	0.39
	ELWWT	5.19	4.18	4.69	0.71
	Oct. average			2.11	

Table 27: p,p'-DDT Sediment Concentration (ppb) in relation to Sampling Month and Station

Month	Sampling Station									
	MS2	WWTP	MER	OKEMOS	HAGAD.	MSU	ELWWT		average	
May-92	0.82	9.49	0.96	<MDL	4.94	0.91	9.89		3.86	
Jun-92	<MDL	9.95	<MDL	<MDL	3.49	1.07	6.31		3.27	
Jul-92	<MDL	4.09	<MDL	<MDL	8.12	1.81	7.56		3.08	
Aug-92	<MDL	9.26	<MDL	<MDL	6.76	3.17	12.68		4.55	
Sep-92	<MDL	2.22	<MDL	<MDL	9.43	3.72	11.03		3.77	
Oct- 92	0.11	2.51	<MDL	<MDL	5.10	2.51	4.69		2.11	
average	0.16	6.25	0.16	<MDL	6.31	2.20	8.69			

MDL = Method Detection Limit

MDL = Method Detection Limit

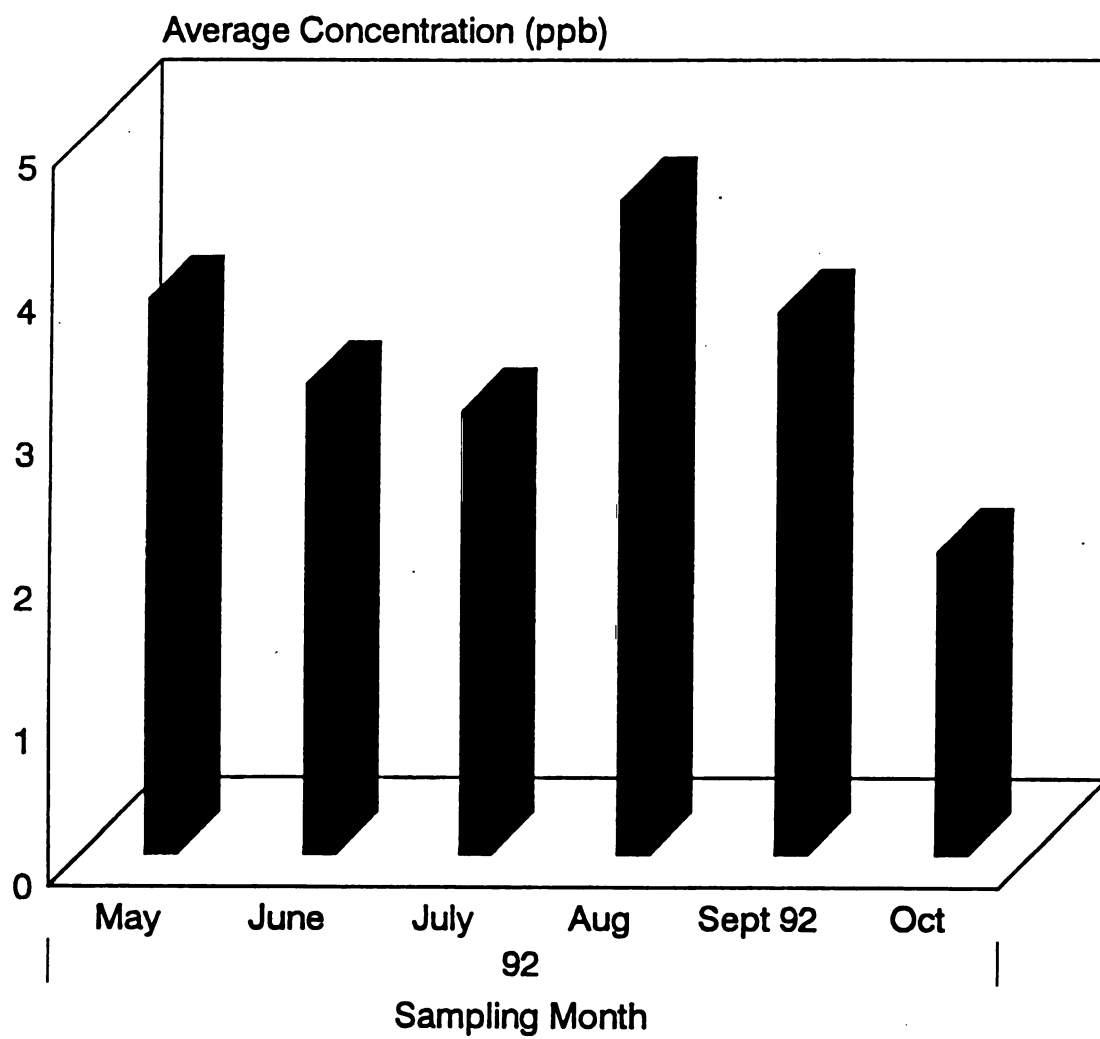


Figure 24: p,p'-DDT Sediment Concentration by Sampling Month

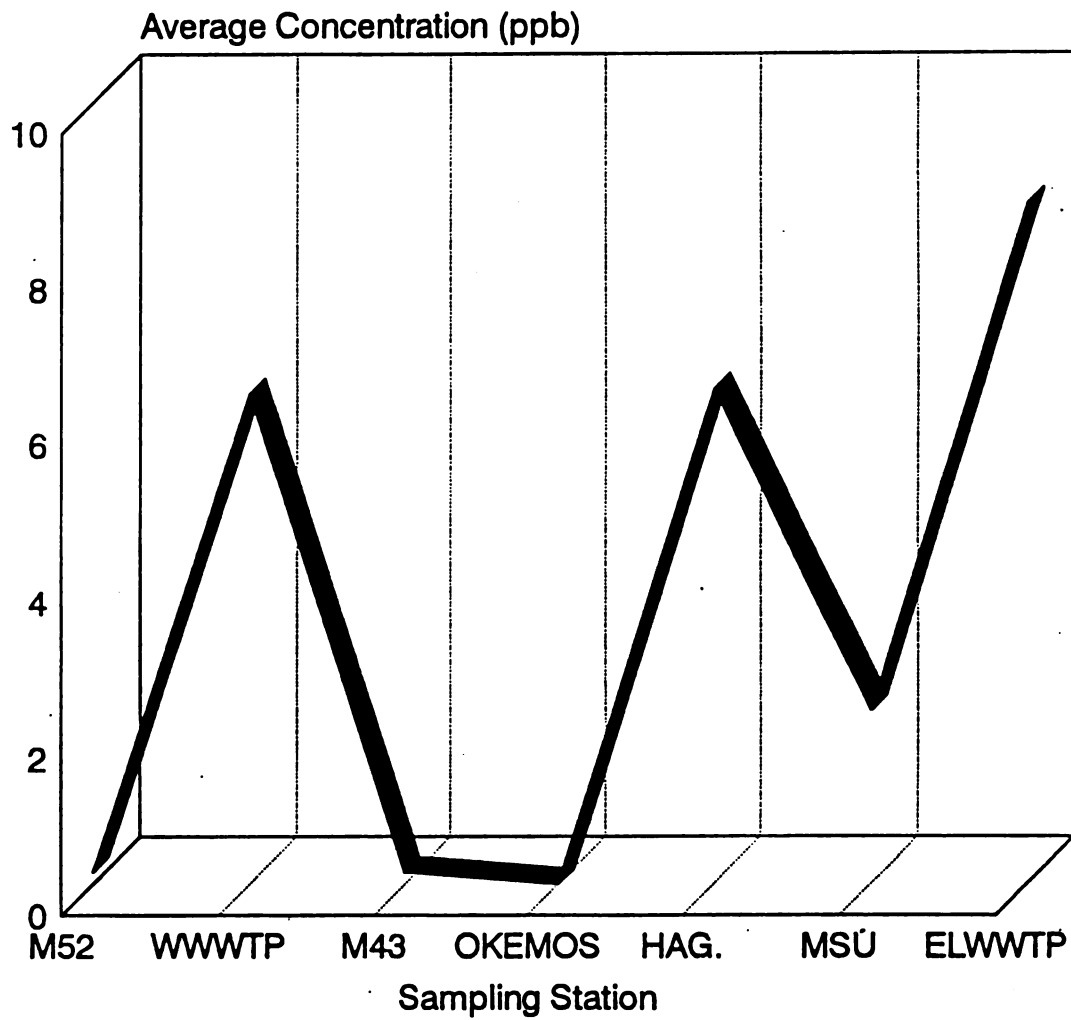


Figure 25: p,p'-DDT Sediment Concentration by Sampling Station

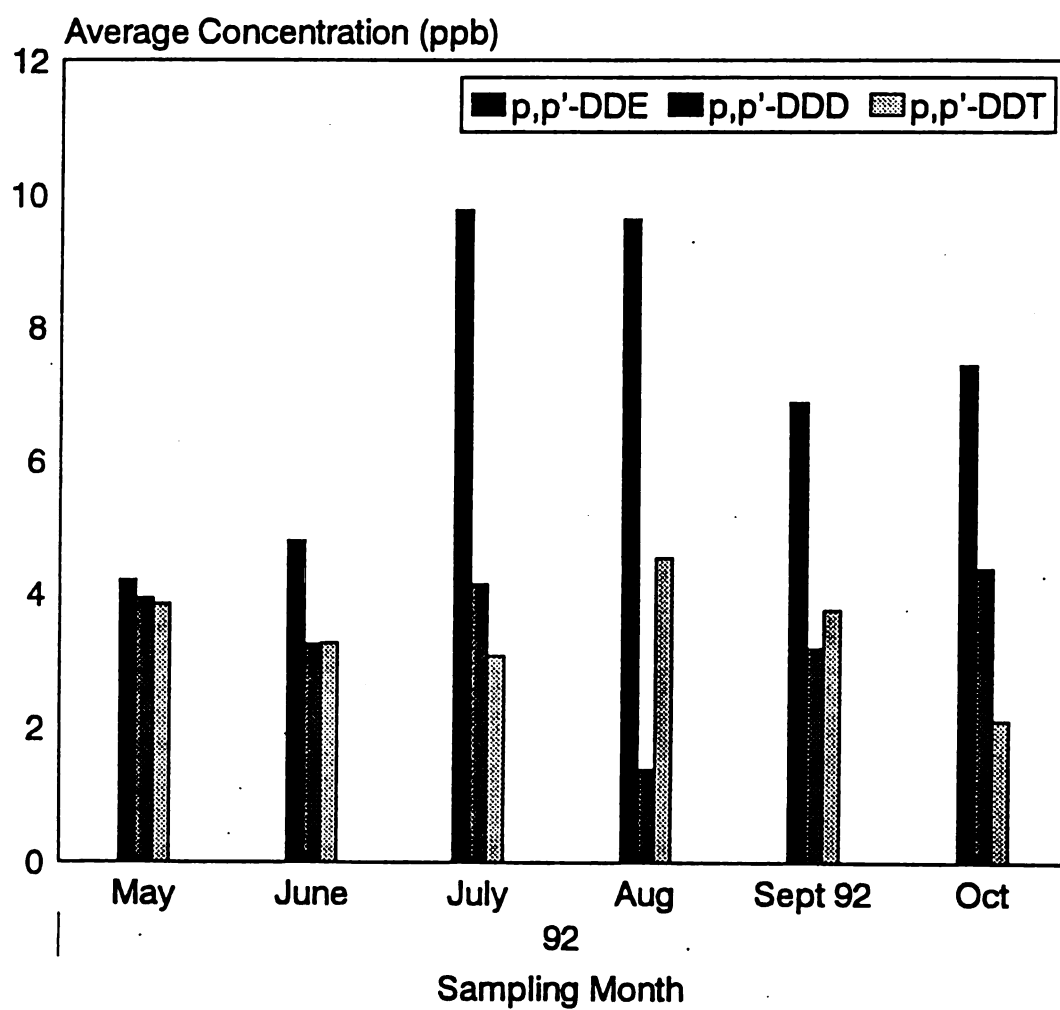


Figure 26: DDT Complex Sediment Concentration by Sampling Month

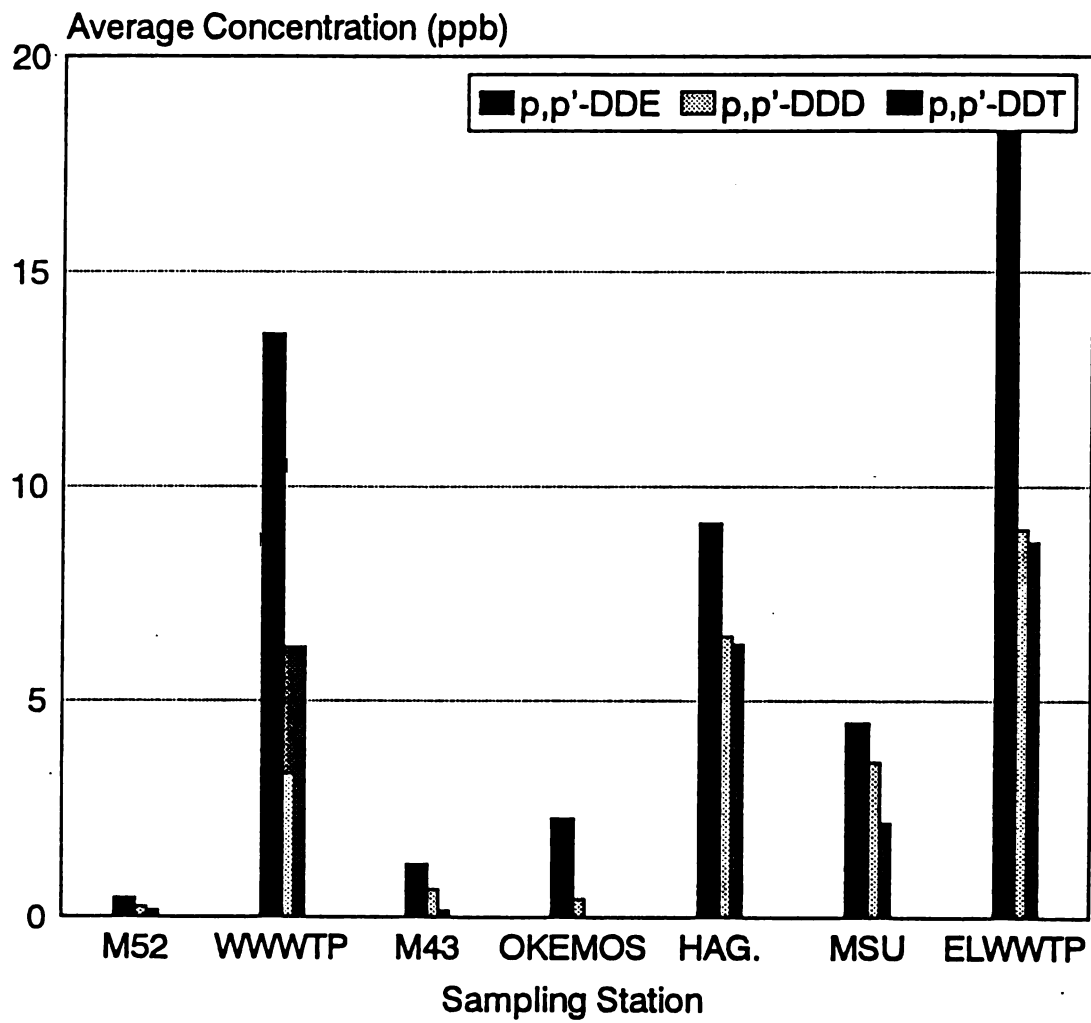


Figure 27: DDT Complex Sediment Concentration by Sampling Station

b- Discussion

The results for the preliminary analysis (samples background checking) are shown in Table 4. Seven of the 26 compounds studied: atrazine, 2,4-D methyl ester, dicamba, alachlor, P,P'-DDT, p,p'-DDE, and p,p'-DDD were found in the water and/or sediment samples.

In the water samples, residues of atrazine, 2,4-D methyl ester, dicamba, alachlor, and DDE-p,p' were found. The residue levels ranged from 0.039 to 1.36 ppb for atrazine (based on both G.C. and ELISA data), 0.04 to 2.04 ppb for alachlor, 0.08 to 2.64 ppb for 2,4-D methyl ester, and 0.08 to 0.44 ppb for dicamba. The residue level was below the Maximum Contaminant Level (maximum permissible level of a contaminant in water which is delivered to any user of a public water system) set by the EPA (1994) for drinking water. The Maximum Contaminant Level (MCL) being 3.00 ppb, 2.00 ppb, and 70 ppb for atrazine, alachlor, and 2,4-D respectively.

Two data sets were obtained for atrazine using two different analytical techniques: the gas chromatography technique (G.C.) and the ELISA technique. The Wilcoxon rank-sum test carried out on the two data sets showed that the residue levels obtained by ELISA were higher than those obtained by G.C. at 99 percent confidence level. The difference in concentrations could be explained by the

difference in specificity between the two techniques. While the amount of atrazine obtained by G.C. was based on the detection of only atrazine, the residue level given by the ELISA kit was actually based on all triazines present in the samples. Consequently, the concentrations computed by the ELISA procedure were higher than those of the G.C. method. This result is not surprising because as illustrated in Figure 4b, atrazine was not the only compound detected under the conditions described in Figure 4. The NP detector (which is specific to nitrogen and/or phosphorus-containing organic molecules) indicated the presence of other nitrogen and/or phosphorus-containing compounds that might belong to the triazine group. The ELISA procedure seems to be more suitable for qualitative studies than for quantitative analyses.

In general, the concentrations of atrazine, 2,4-D methyl ester, and dicamba decreased over the sampling period (Figures 7, 15, and 17), May, June, July, and August being the major period of input. On the other hand, the highest concentrations of alachlor were obtained during flood conditions, that is, June, September, and April. Hence, the run-off pattern of alachlor during the sampling period was different from the other detected herbicides. This finding is in partial agreement with the study by Baker (1987) who observed that cyanazine, atrazine, alachlor, and metolachlor had similar Spring runoff patterns and were

primarily carried to the watershed between May and July. Why did alachlor behave differently in our study? The water solubility and leaching and run-off potentials of these compounds are listed in Table 1 (page 11). The sorption coefficient is 190, 163, and 2 for alachlor, atrazine, and dicamba respectively (Farm Chemicals Handbook, 1990). A possible explanation of the difference in pattern between alachlor and the other three compounds could be based on the ways these chemicals are applied. Under the assumption that alachlor has been more incorporated in the soil by farmers than the other herbicides, higher levels of alachlor could be expected with stronger surface run-off leading to higher water levels. On the other hand, atrazine, 2,4-D methyl ester, and dicamba would not need any strong surface run-off to reach the water. The first run-off following their application would do the job. Consequently, their highest concentrations in the water would correspond to their major period of application, that is, May to June.

The residue levels over the study section are shown in Figures 8, 12, 16, and 18 for atrazine, alachlor, 2,4-D methyl ester, and dicamba respectively. Generally, the residue level tends to increase at the M-43 and Hagadorn bridges for atrazine and alachlor. The concentration of 2,4-D methyl ester increases from the M-52 bridge to Okemos and decreases from Okemos to the MSU campus before increasing again. As far as dicamba is concerned, its

concentration tends to increase in a downstream direction. Overall, the downstream pollution pattern indicated by Zabik et al. (1971) and Talsma (1972) is only observed with dicamba. The variation of the concentrations could best be explained based on more complete and accurate information about the use of these herbicides in the vicinity of the study area and about the locations of drain effluents. However, in the absence of such information, one could attempt to explain the differences in variation pattern under the assumption that these four chemicals have not been equally used at the same locations. That is, while some might be heavily used at a given location around our study area, others might rather be used at higher rates at another location.

p,p'-DDE was detected in 28 percent of the 98 water samples. The residue level ranged from 0.21 to 2.54 ppt, which is approximately 1,000 times less than the concentration of p,p'-DDT metabolites found by Zabik et al. in 1971 (about 4 to 28 ppb). The variation of p,p'-DDE over the sampling zone did not show any particular pattern. Neither did its variation over the sampling period.

In the sediment samples, only p,p'-DDT and its metabolites (p,p'-DDE and p,p'-DDD) were detected. The residue level was between 0.48 and 37.79 ppb for p,p,p'-DDE, 0.01 and 16.31 ppb for p,p'-DDD, and 0.69 and 15.02 ppb for p,p'-DDT. These numbers suggest a quality recovery in the

bottom material of the river as far as contamination by DDT is concerned. Indeed, the residue level found by Zabik et al. in 1971 ranged approximately from 4 to 65 ppm for DDT and from 1 to 44 ppm for DDT metabolites. An explanation of the levels founds in the present study could be the lack of further input of DDT since the cancellation of the use of this compound in the 1970's. Also, volatilization, leaching, and degradation might have contributed to the disappearance of DDT-complex from the river water. These facts could explained why the downstream pollution pattern reported by the 1971 study was not observed in this research for DDT and its metabolites.

The amount of p,p'-DDE detected at each sampling station was generally higher than that of p,p'-DDD which was in turn greater than that of p,p'-DDT (Figures 26 and 27), contrary to the 1971 study by Zabik et al. (in 1971, the amount of DDT was much greater than that of its metabolites). Figure 19 is a plot of the percent organic matter by sampling station. The variation of the concentration over the study section is shown in Figures 21, 23, and 25 for p,p'-DDE, p,p'-DDD, and p,p'-DDT respectively. The variation of the residue levels over the sampling period is shown in Figures 20, 22, and 24. In the whole, the concentrations seem to be more related to the organic matter content than to any other parameter.

All these findings suggest that p,p'-DDT has not been

used in the vicinity of East Lansing, Michigan for a long time.

11- Summary

Analysis of 98 water samples and 74 sediment samples collected monthly at seven different points led to the following results:

- Of aldrin, methoxychlor, and DDT and its metabolites previously reported to be present in the Red Cedar river, only p,p'-DDT, p,p'-DDD and p,p'-DDE were detected in the river.

- While all three compounds were detected in the sediment samples, only p,p'-DDE was found in the water samples.

- Overall, the content of DDT and its metabolites was approximately 1,000 times less than that found by Zabik et al. in 1971.

- The concentration of p,p'-DDT and its metabolites in the bottom material appeared to be more related to the samples organic matter content than to any other parameter.

- These results indicate a quality recovery of the river water as far as contamination by DDT and DDT analogues is concerned.

- Beside DDT and its metabolites, atrazine, alachlor, 2,4-D methyl ester, and dicamba (which were not studied in

1971) were also detected in the river water. The residue levels ranged from 0.037 to 1.37 ppb for atrazine, 0.04 to 2.04 ppb for alachlor, 0.08 to 2.64 ppb for 2,4-methyl ester, and 0.08 to 0.44 ppb for dicamba.

- While the concentrations of atrazine, 2,4-D, and dicamba showed a relation with the major periods of application (May-June) for these pesticides, the residue level of alachlor was rather more related to the water height due to release to the river in run-off.

- Overall, the downstream pollution pattern indicated in 1971 by Zabik et al. was not observed.

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