

MONITORING HEAVY METALS AND PESTICIDES IN THE
CAPE FEAR RIVER BASIN OF NORTH CAROLINA

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ABSTRACT

A research effort to examine new methods for monitoring heavy metals and pesticides in natural waters of North Carolina was undertaken. The methods developed were applied to a monthly sampling of the Cape Fear River Basin for pesticides and heavy metals. The heavy metals (chromium, cadmium, copper, lead and zinc) monitoring technique was based upon the field application of cationic and anionic ion exchange resins to examine various species of the metals. Macroreticular XAD resins were used to concentrate the pesticides, atrazine, DDT (DDE, DDD) diuron, methyl parathion and trifluralin, from water. Both methods were incorporated into a field sampling procedure wherein the metals and pesticides were extracted from the water in the field and eluted at a later time in the laboratory. This method allows the collection and processing of samples to occur more rapidly and with less sample transport and handling than with most other methods. The procedures are shown to yield reproducible recovery of pollutants and could significantly reduce both the manpower and laboratory time required to carry out a monitoring program. Some additional research would be necessary before either system could be applied to a large scale monitoring effort. Monthly samples from 10 sites in the Cape Fear River Basin indicated that anionic chromium species were present at all sites except the farthest upstream, indicating anthropogenic inputs, that metal concentrations generally decrease as the water flows downstream, and that there were no evident correlations between metal concentrations and flow or rainfall. Cr, Cu and Cd appear to come principally from industrial and municipal sources, while Zn and Pb appear

to have non-point source origins. Only Pb values at two stations exceeded the EPA maximum values for public water supply. Zn, Cd, and Cr exceeded proposed minimal risk values. Pesticide concentrations were highly variable for different stations on any one date and for one station on different dates. The basin appears to be contaminated with low concentrations of several pesticides. Trifluralin was the most commonly observed compound present in 97% of the samples. Atrazine, although present in only 42% of the samples represents the pesticide present in highest concentration and transported in greatest quantity in the water. DDT, DDE and methyl parathion were also commonly detected, with diuron less frequently encountered. (No easily generalizable pattern of distribution was seen when pesticide concentrations, flow rates or frequencies of occurrence were compared to seasons.) It appears that some compounds, like DDT, which are tightly bound in soil and persistent, have their highest concentrations associated with periods of high rainfall (winter and spring). Other less tightly bound and more biodegradable compounds, like atrazine and diuron, show their high concentrations at the times when they are applied (spring and summer).

SUMMARY AND CONCLUSIONS

I. Continued industrial discharge of chromium is indicated in the Greensboro-Burlington area. Anionic chromium species were found at all stations except site 1 which suggest that this fraction comes from anthropogenic sources. Cr(VI) as $\text{CrO}_4^{=}$ at many of these sites is mixed with domestic sewage producing favorable conditions for reduction to Cr (III) and subsequent removal on particulates or complexation. Removal by precipitation is suggested since dissolved chromium concentration decreased with distance below likely sources of discharge.

II. Ion exchange techniques were found useful for separating dissolved ionic metal species. A significant amount of chromium was found as the anionic form, particularly near points of industrial and municipal discharges. Anionic species of copper and zinc were also found, anionic zinc being constant while anionic copper increased near industrial discharge points. Radio-tracer studies with Cr^{51} showed that 100% removal of Cr(III) and Cr(VI) was attained using ion exchange preconcentration. However, natural water spiked with Cr^{51} as Cr(III) indicated that about half the chromium was adsorbed by the particulate and the remainder partitioned between the cationic, non-ionic and anionic species with abundancies in that order.

III. In general, concentrations decreased downstream. No correlations between metal concentrations and flow were found.

IV. Although in some cases high concentrations could be associated with the incidence of rainfall on preceding days, no general trend was evident.

V. Cr, Cu and Cd appear to come principally from industrial and municipal sources near Greensboro and Burlington. Zn and Pb appear to have significant sources throughout the Cape Fear basin. These sources are likely from rainfall and urban runoff.

VI. Lead values exceeded maximum values recommended by EPA for a public water supply at two stations. No other metal concentrations exceeded maximum recommendations, but concentrations of Zn, Cd and Cr exceeded proposed minimal risk values.

VII. Ease of use of ion exchange for field preconcentration was demonstrated. High flow rates could be used and a 10 μ sample could be concentrated in 15-20 minutes. Preconcentration in the field reduced time and cost of sample transportation and workup, decreased possibility of contamination, assured that the species measured was the in situ species, and more efficiently utilized technician time.

VIII. The mechanism of removal of metals was inferred from this data to be adsorption on particulate followed by precipitation.

IX. A systematic monitoring program for low level toxic metal concentrations is necessary to assure continued safe use of the Cape Fear as a public water supply and to protect the estuarine areas it enters.

X. The macroreticular resin Amberlite XAD-2 adsorbs a broad spectrum of organic pesticides from aqueous solution. Elution of the resin by

diethyl ether in a batch type procedure with shaking removes the adsorbed particles.

XI. This XAD-2 procedure is suitable for field extraction of large water samples at high flow rates. The method is more convenient, more flexible in applications and cheaper than solvent extraction procedures for monitoring of pesticide contamination of natural waters. For a routine monitoring procedure the use of larger resin columns than employed in this study is recommended. Approximately 1 gram of resin for each 10 mg/l of TOC in the water to be sampled is recommended.

XII. The Cape Fear River Basin appears to be contaminated with low concentrations of several pesticides. Trifluralin, DDE and DDT were found in most samples of ng/l concentrations. Diuron, DDD and possibly methyl parathion were found in some samples. Atrazine was reported in a number of samples. DDT and DDE concentrations in most samples exceeded the recommended limits for protection of aquatic life.

XIII. Seasonal changes in flow and frequency distribution were noted but followed no easily generalizable pattern. For DDT the highest concentrations appear to be associated with periods of high rainfall, while for others, diuron and atrazine, the levels are highest at the time of application in spring and summer. Overall the frequency of occurrence of all pesticides studied shows a peak in winter and spring and lower frequencies during the summer.

XIV. Trifluralin was the most commonly observed compound followed by DDE, DDT, methyl parathion, atrazine and diuron.

RECOMMENDATIONS

1. Both sections of the study point to the need to institute some form of monitoring program for heavy metals and pesticides. The methods used and frequency of sampling would depend on the capability and resources of the agency conducting the monitoring, but methods developed in this study could be advantageously applied.
2. The site near Wilmington had a lower pH than sites upstream. The effect of lower pH could be the release of previously removed metals from river borne sediments as they entered coastal areas. This mechanism could be magnified during storms producing bottom scour and humic rich acid swamp wash-out. An investigation of metal release from particulates in the lower Cape Fear River is suggested.
3. A more systematic investigation of the fractionation of the total dissolved metal content should be carried out. This would add significantly to the knowledge of trace metal specification in the Cape Fear River.
4. Further procedure development is suggested to attain a smaller eluant volume which would allow smaller sample volumes to be taken and/or greater concentration of certain metals, such as cadmium, with subsequent improvement of accuracy.
5. Work on interfacing chemical technology as evidences in this report with the needs and capabilities of state water quality monitoring agencies.
6. More experiments or methods of eluting pesticides from XAD resins, as in underway in project A-087-NC. Also more research on the size of the

resin column to use in different applications would be helpful in application of method to actual monitoring program.

7. Areas in need of additional research include more information on pesticides in the sediments and how they are transported, an investigation of the changes in pesticide concentration over much shorter time intervals, hours and days, to provide perspective for less frequent sampling as will be part of any monitoring program.

8. Use resins to investigate a broader range of organics in real world water samples. Combined with GC/MS systems it could provide means to look at wider range of pesticides and other pollutionally generated organic compounds of environmental and health significance.

9. Investigate integration of XAD resins into a comprehensive continuous monitoring program for pesticides in natural waters.

INTRODUCTION

During the last 10 to 15 years we have been increasingly aware of problems that result from the contamination of our natural waters by agricultural and industrial pollutants. Many of these materials are hazardous to man through toxic, mutagenic and/or carcinogenic effects, while others have deleterious effects on natural ecosystems and their biological communities. Two of the major classes of water pollutants are pesticides and heavy metals. Specific compounds in both of these groups of materials have been implicated in detrimental effects either on man or the ecosystem. The effects of many others are, for the most part, unknown. Only a small percentage of all the pesticidal compounds and types of heavy metals studied have been shown to cause problems, the remainder being largely innocuous as a result of being nontoxic, rapidly biodegradable, nonmobile in the environment, or because they are used in very small quantities. The protection of man and the environment from exposure to hazardous compounds is based upon knowledge of which compounds pose a threat and an understanding of the occurrence and mobility of these compounds in the environment. Although a considerable amount of research has been directed toward gathering this type of information for a few compounds, relatively little is known about the total spectrum of pesticides and heavy metals that are used in agricultural and industrial applications. Much of this work is summarized in several publications (Water Quality Data Book, Vol. I, 1970; Vol. II, 1971); Pesticide Study Series-8, 1972).

The southeastern United States has undergone significant growth in population and industrialization over the last decade. Agriculture has always been, and continues to be, the use to which the majority of the land is applied. Agriculture and industry constitute the major sources of the pesticides and heavy metal pollutants that contaminate the waters of this region. Metal pollutants arise from a variety of urban and industrial sources which are summarized in Table 1. Each type of activity appears to have a rather characteristic metal discharge, based on the types of metals used in that industry. In the southeast, and especially in North Carolina, industry is of a very diverse nature, both in geographic distribution and materials produced. This diversity results in the specific sources of metal pollutants being rather widely dispersed. The wastes and effluents from these industries are added to the naturally occurring background concentrations of metals in the receiving waters, which in some instances makes specific point sources difficult or impossible to identify. If the health of both the population and the environment is to be protected, knowledge of the sources of metals, and especially the concentrations of heavy metals in water and waterways, must be available to health professionals and those agencies charged with environmental protection.

The southeast is an area with many different types of soil and a climatic gradation from temperate to subtropical. This great range of growing conditions has resulted in the production of tobacco, citrus, peanuts, pecans, cotton and vegetables amounting to approximately 85%, 65%, 61%, 28% and 12% respectively, of the total U.S. production (Agricultural Statistics, 1970). To optimize crop production and decrease labor involved in planting and harvesting, modern agriculture has come to depend on the use of herbicides and insecticides for the control of weeds and insect pests. For each crop

Table 1. Heavy metals associated with industrial wastes.

Industry	Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sb	Sn	Zn
Pulp, paper and wood products					X	X		X		X	X			
Organic chemicals, petrochemicals	X		X	X	X		X	X		X			X	X
Alkali, chlorine, inorganic chemicals	X		X	X	X		X	X		X			X	X
Fertilizers	X		X	X	X	X	X	X	X	X	X			X
Petroleum refining	X		X	X	X	X	X	X		X	X			X
Basic steel works, foundaries			X	X	X	X	X	X		X	X	X	X	X
Basic non-ferrous metals-works	X	X	X	X	X	X		X		X		X		X
Motor-vehicles, aircraft-plating	X	X		X	X	X		X			X			
Flat glass, cement, asbestos products														X
Textile mill products														X
Leather tanning, finishing														X
Steam generation power plants														X

Adapted from Dean, Bosqui and Lansuette (13).

and crop/soil combination there will be particular pests that require the use of specific pest control agents. Because of the great diversity of crops grown in the southeast and the variety of soil types, many different pesticides are needed. In a given geographic area there is usually a mixture of crops planted even though a particular crop may be predominant. Therefore, each area will see the use of a variety of pesticides. These compounds enter our waters and waterways by a number of routes, including leaching into ground water from the soil, pollution of surface waters via erosion and runoff from fields, rain out of volatilized pesticides from the atmosphere, washoff of pesticides from crops into soil and from there into the water. Due to the many pesticidal compounds available, the diverse crops on which they can be used and the variety of routes by which pesticides can enter water, it is usually impossible to determine the exact source of any pesticide found in water samples. To protect the public and the environment from those pesticides that constitute a hazard necessitates a program that gathers information on the distribution and concentrations of these compounds in specific water systems.

It seems readily apparent that population growth in the Southeast and especially the river basin of North Carolina has increased demands for water and also contaminated the source of a part of this water. Much of this water comes from surface supplies and after use is returned to the river as waste. Natural processes within the river are counted on to render the water safe for use at downstream municipal intakes. Trace metal contamination of the river from industrialization and urbanization as well as pesticides from agriculture and subsequent reuse of the river as a public water supply suggests that systematic monitoring programs to assess public health hazards are necessary as population in the basin increases and

distances between discharges and intakes for public use decrease. Monitoring is also necessary to provide the data on which to base decisions on the control of inputs, the degrees and type of treatment necessary before the water can be safely used, and evaluation of control costs versus potential benefits.

Metals in the Cape Fear River Basin

The Cape Fear River Basin is the largest in North Carolina (North Carolina Water Plan, 1972). Its major tributaries are the Haw, New Hope, Deep and Northeast Cape Fear Rivers. From its source above Greensboro to its mouth below Wilmington, the Cape Fear-Haw River system is about 300 miles in length. Part of all of 29 of North Carolina's 100 counties lie within the basin (27% of total North Carolina land area) and according to the 1970 census, 1,127,591 live within the basin (North Carolina Water Plan, 1972). North Carolina is primarily an agricultural state and the Cape Fear Basin is one of the most productive areas, although the upper part of the basin and area around Wilmington are becoming increasingly industrialized. The Greensboro-Burlington region is textile oriented, High Point has major furniture industries and Wilmington has textiles, agricultural chemicals and pulp and paper industries. Also within the basin are wood products, food processing and chemical industries. There are two major coal-fired power plants and a nuclear power plant along the river.

The Cape Fear-Haw Rivers are used for agricultural, industrial, recreational and public supply purposes. Of major concern from a public health viewpoint is the use of the Cape Fear-Haw Rivers for municipal water supplies. For example, approximately 30 miles below the Greensboro-Burlington area, the towns of Pittsboro and Bynum take their domestic water from the Haw. A number of larger municipalities, such as Fayetteville and Wilmington, also

use the Cape Fear for water supplies. The river has recreational value for bathing, boating and sport fishing. Below Wilmington are areas with salinities suitable for shellfish production. Modern agricultural practices have increased the use of the river for crop irrigation.

The Cape Fear basin has historically been the most rapidly growing area of North Carolina (North Carolina Water Plan, 1972). As a result, the region has attracted industry seeking an available work force. A convenient source of water of adequate quality and quantity is a consideration of industry locating in the Cape Fear Basin.

Table 1 has already presented the heavy metals most often associated with these industries. Not all of the industries in Table 1 are found within the Cape Fear Basin but are included for comparison. The major industry of the area is textiles which in Table 1 is shown to be a source of chromium wastes. The metals As, Cd, Co, Cu, Pb, Hg and Zn have also been reported as being present at $\mu\text{g}/\text{l}$ levels in raw textile waste as a result of dyes used during the finishing process (Dyes and the Environment, 1973). Chromium is used as an oxidant and is present in greater concentrations as hexavalent chromium (Dyes and the Environment, 1973). Aluminum and antimony are also found in textile waste as a result of application of flame retardant finishes. Previous studies of trace metal concentrations have been conducted on the Haw River in the Greensboro-Burlington area and the data from three of these studies is summarized in Table 2. The table indicates that contamination by chromium is important and that chromium concentration has remained constant over time.

Urban development of the upper regions of the basin has occurred along with industrial development. Lead concentrations in precipitation has been shown to correlate with amount of leaded gasoline consumed (Lazrus

Table 2. Trace metal concentrations in the Haw River, North Carolina.

A.

Metal	Total concentration range (mg/l)	Location where maximum occurred
Cr	<0.01 - 0.55	Burlington
Cu	<0.01 - 0.04	Swepsonville
Pb	<0.1	--
Zn	<0.01 - 0.12	Burlington

F.W.Q.A. (1969)

B.

Metal	Total concentration range (mg/l)	Dissolved concentration range (mg/l)
Cd	0.0001 - 0.0008	ND - 0.0008
Cr	0.0007 - 0.0742	ND - 0.0419
Pb	ND - 0.0056	ND
Zn	0.0025 - 0.0290	0.0004 - 0.0241

Sampling points at Saxapahaw and Pittsboro.

Maximums at Saxapahaw.

Minogue (1972)

C.

Metal	Total concentration range (mg/l)	Location where maximum occurred
Cr	N.D. - 0.714	Burlington

Haynie (1974)

et al., 1970) so that increased urbanization implies increased lead pollution and trace metals such as lead have been observed to increase in concentration following storms as a result of metals entering urban watersheds (Colston, 1974). The inputs from this source can be through the urban storm water collection system, or perhaps more importantly, it can come via surface runoff. This makes treatment for removal of all metal pollutants impractical if not impossible. In addition, trace metal contaminants of synthetic fertilizers and as components of pesticides and herbicides are added to soil to agricultural areas. The application rates are so low that negligible contributions are made to soil reserves (Bowen, 1966). However, the potential for leaching of these trace constituents exists and must be considered.

Trace metals can be classed into two nutritional classes based on whether they are essential or non-essential to man and animals. They can also be grouped according to their toxicity to man and animals. Unfortunately, the two classifications cannot be superimposed. For example, some trace metals such as copper and zinc are both essential in trace amounts and toxic in large amounts. Copper and zinc at high concentrations also become taste problems in potable water before reaching toxic concentrations (Water Quality Criteria, 1972). Additionally, chromium is essential as Cr(III) and toxic as Cr(VI) (Fox, 1972). Although drinking water standards are recommended based on total chromium, it is the soluble oxy-anion of Cr(VI) that is important to public health (Water Quality Criteria, 1972). Besides its oxidation states the chemical form of a metal is also important. Chemical reactions within the natural environment such as chelation or adsorption on particulates can provide decreased toxicity (Fox, 1972). Therefore, total metal may not be as important to toxicity as the concentration

of a particular chemical form. The classical itai-itai syndrome of Japan has been attributed to cadmium pollution (Fussett, 1972). Cadmium is considered non-essential and a no-effect level of intake has not been established (Water Quality Criteria, 1972). Lead is one of the most widely used non-ferrous metals and as a result has been distributed throughout the environment by man's activities (Goyer and Chisolm, 1972). The toxic effects of lead have been recognized for centuries and because of the narrow gap between normal everyday exposure and toxic quantities (Water Quality Criter, 1972), the toxicologic importance of lead is emphasized. Trace metals also affect aquatic life. In freshwater systems, the toxicities of trace metals depend on the presence of other metals and are also related to other water quality parameters such as hardness, complexation capacity and turbidity. Toxicity levels for aquatic organisms vary from species to species but concentrations considered safe for drinking supplies should not be exceeded if the water is to be considered safe for aquatic organisms.

Detailed information on trace metal concentrations in the Cape Fear-Haw River has been limited by the detection limits of the analytical techniques employed (see Table 2). The 1969 study in Table 2 shows detection limits of 0.01 mg/l Cr, Cu and Zn and 0.1 mg/l Pb. Using a freeze concentration technique followed by atomic absorption, Minogue (1972) improved these limits by approximately two orders of magnitude. This method of concentration requires the return of large volumes of water to the lab for the lengthy process of freeze concentrating. In the third study in Table 2 Haynie (1974) chose Neutron Activation Analysis (NAA) because of its sensitivity without sample pre-concentration (0.01 µg/l Cr). Thus NAA represents a detection method that is sensitive enough that pre-concentration

is not often required. However, the technique is not readily available to any laboratory, is expensive, is not sensitive to some metals such as lead and requires the storage of samples before delivery to the reactor facility.

Thus, it was the goal of this phase of the project to develop a procedure to pre-concentrate metals in the field for subsequent analysis by atomic absorption spectroscopy (AAS). AAS is readily available to many laboratories but pre-concentration is often necessary to give adequate sensitivity for many trace metals. Pre-concentration in the field also insures that loss or contamination from sample storage is minimized. Ion exchange chromatography was chosen for this pre-concentration step and its ability to differentiate between cationic and anionic solution species was considered as a first step toward monitoring specific chemical forms of trace metals in this river system.

Pesticides in the Aquatic Environment

Pesticides are a seemingly ubiquitous by-product of modern society. There are apparently no areas of the earth that are completely free of contamination by pesticidal chemicals. The problem is due primarily to the chlorinated hydrocarbons, a group of moderately toxic, but highly persistent compounds that includes not only insecticides such as DDT and dieldrin, but industrial compounds such as the polychlorinated biphenyls (PCB's). Table 3 lists some of the reports in the literature of the occurrence of pesticides and PCB's, and demonstrates the widespread occurrence of chlorinated hydrocarbons in natural waters. The environmental problems caused by these types of compounds have been reviewed by Risebrough (1971) and Wurster (1971).

The production and consumption of large quantities of pesticides in this country can be expected to continue for some time. In 1973 production

TABLE 3

Occurrence of Pesticides and Polychlorinated Biphenyls (PCB's) in Surface Waters and Rainfall

Pollutant	Type of Water	Location	Reference
DDT, Dieldrin	Surface	USA	Breidenbach and Lichtenberg, 1963
Chlorinated insecticides	Surface	USA	Hindin <u>et al.</u> , 1964
Chlorinated insecticides	Surface	USA	Nicholson <u>et al.</u> , 1964
Endrin	Surface	USA	Novak and Rao, 1965
Chlorinated insecticides	Rainfall	England	Wheatley and Hardman, 1965
DDT	Surface	USA	Warnick <u>et al.</u> , 1966
Chlorinated insecticides	Rainfall	USA	Weibel <u>et al.</u> , 1966
Chlorinated insecticides	Surface	USA	Schafer <u>et al.</u> , 1969
Chlorinated insecticides	Surface	USA	Barthel <u>et al.</u> , 1969
Chlorinated insecticides	Surface	Sweden	Ahling and Jensen, 1970
DDT, Dieldrin	Surface	USA	Sheets <u>et al.</u> , 1970
PCB's	Surface	USA	Veith and Lee, 1971
Chlorinated insecticides	Surface	USA	Johnson and Morris, 1971
Chlorinated insecticides	Surface	Canada	Miles and Harris, 1973
PCB's	Surface	North Atlantic Ocean	Harvey <u>et al.</u> , 1973, 1974

(continued)

TABLE 3 (continued)

Pollutant	Type of Water	Location	Reference
Chlorinated insecticides	Surface	USA	Richard and Fritz, 1974
BHC, DDT	Surface	Czechoslovakia	Uhnak <u>et al.</u> , 1974
PCB's	Surface	USA	Martell <u>et al.</u> , 1975
DDE, Dieldrin	Surface	North Atlantic Ocean	Jonas and Pfaender, 1976

of synthetic organic pesticides in the United States exceeded 600,000 metric tons (Environmental Quality, 1975). Of the total quantity of pesticides produced in this country, the proportion consisting of the persistent chlorinated insecticides has been declining. At the end of 1972 the United States Environmental Protection Agency suspended essentially all uses of DDT. Aldrin and dieldrin have since been similarly banned. As these persistent insecticides have been phased out, other insecticides have taken their place. However, these newer pesticides are generally more toxic, though much less persistent, than their predecessors. Methyl parathion, which has replaced DDT in many of its uses, is a much more toxic compound to warm-blooded animals and must be used with more caution. It is readily degraded in the environment so that it does not undergo biomagnification.

Some of the more important pesticides in use in the United States in 1972 are shown in Table 4 with production and use quantities. Most of these compounds are primarily used in agriculture. Many, however, have important industrial and household applications. This list includes four of the pesticides that were studied during this project. However, the others listed here should be considered for future monitoring.

Monitoring is a necessary part of our effort to clean-up and protect our environment by providing information on current conditions and trends (McNeilis, 1973). Important parameters in the environment such as DDT must be selected and then periodically and continually measured (Environmental Quality, 1970). The Environmental Protection Agency with other federal agencies has established a national water quality surveillance system to monitor a number of parameters including pesticides (Environmental Quality, 1976). However, this system is limited to a few and often only

TABLE 4

Production and Use of Selected Pesticides in the United States in 1972 in Thousands of Metric Tons^a

	Total Production	Total Use	Use by Category				Total Use Southeast
			Industrial and Commercial	Government	Home and Garden	Agricultural	
Insecticides							
Aldrin	5.9	5.8	0.8	small	small	5.0	0.3
Carbaryl	24.0	11.3	0.4	0.7	1.6	8.6	3.6
Chlordane	9.1	6.8	3.0	0.2	2.3	1.4	0.8
Methyl Parathion ^b	23.2	18.0	small	small	small	18.0	2.3
Toxaphene	34.5	26.3	0.4	small	small	25.9	9.2
Herbicides							
Atrazine ^b	43.1	34.0	0.8	0.1	0.4	32.7	2.5
2,4-D ^b	24.9	21.8	2.7	1.4	1.4	16.3	1.9
Diuron ^b	2.9	3.0	1.7	0.2	negligible	1.1	0.4
Trifluralin ^b	9.5	7.7	small	negligible	small	7.6	1.0
Fungicides							
Pentachlorophenol	22.5	22.2	21.5	negligible	0.7	negligible	3.4
Fumigants							
p-dichlorobenzene	32.7	24.9	6.4	0.9	17.7	negligible	4.2

^afrom von Rümker et al., 1975^bpesticides included in this study

one site in each river basin. Such a system can provide little information about specific areas of a basin, nor provide information on inputs, fates or seasonal fluctuations.

Current Methodology

Monitoring of pesticides in surface waters presents a number of difficulties. Of major importance is the generally very low concentrations of pesticides found in natural waters. Thus, large amounts of water must often be collected in order to obtain enough material for analysis. Frequently other organics are present that may interfere with the analytical procedure. Transportation, handling and storage of large water samples can be difficult, limits the number of samples and increases the chances for contamination. Most of the in situ sampling procedures, currently available, have other problems such as the requirement for expensive and elaborate apparatus or the problems associated with the carbon adsorption method as described below.

The most commonly used methods of extracting pesticides from water have been by solvent extraction and by adsorption into activated carbon. The carbon adsorption method (CAM) was widely used by the U.S. Public Health Service (Rosen and Middleton, 1959; Breidenbach et al., 1964) until its reliability was questioned (Burchfield and Johnson, 1965). For this procedure (Breidenbach et al., 1964), the water sample is pumped through a bed of activated carbon. The carbon is then dried and extracted with chloroform to remove the adsorbed organics. The extract is then concentrated and analyzed. The advantages and disadvantages of the CAM have been reviewed by Faust and Suffet (1966). The procedure takes a continuous sample and can handle large volumes. Its limitations include poor quantitation, adsorption of only part of the organic matter in water and biological

degradation of some organics on the carbon. Eichelberger and Lichtenberg (1971) reported poor recoveries for some pesticides. Brondtmann (1975) compared the method to a continuous solvent extraction procedure which he found to be somewhat more effective for removing pesticides from water and cheaper. In a newer version of the CAM Buelow et al. (1973a,b) simplified the procedure. This method is reported to be suitable for total organic material and not for identifying specific contaminants, however.

Solvent extractions or liquid-liquid extractions (LLE) are the most widely accepted methods of isolating pesticides, or any organic compound, from water. There are many variations of the basic method in use. Most procedures are batch extractions of water in a separatory funnel, flask or bottle with an organic solvent or mixture of solvents (Teasley and Cox, 1974; Ford et al., 1975). These methods vary in extraction solvent, in length of sample and in various other ways. Mestres et al. (1971) devised an all glass system for simultaneously extracting and concentrating pesticides from small water samples. Another type of system was used by Jonas and Pfaender (1976) in which the water sample was extracted by diffusing boiling ethyl ether in a continuous extraction chamber. A system for the continuous extraction of large samples of water for pesticides was developed by Kahn and Wayman (1964). This method was adapted by Ahnoff and Josefsson (1974) to on site extraction of the sample.

Standard Methods (APHA, 1976) recommends batch extraction procedures for analysis of pesticides in water. This type of procedure is also recommended for pesticide analysis by the U.S. Geological Survey (Goerlitz and Brown, 1972) and by an EPA laboratory (Thompson, 1972). LLE methods were reviewed by Faust and Suffet (1966). The major advantages are their quantitative recovery efficiencies (generally more than 85%) and their

shorter processing times relative to the carbon adsorption method. Limitations of solvent extraction include the need for very pure solvents and for clean-up of the extract of interferences. The ratio of sample to solvent is relatively low so that impurities in the solvent are necessarily concentrated. Large samples can be handled only with much tedium, except with the use of procedures such as Ahnoff and Josefsson, which is not adapted to processing many samples such as would be required in a monitoring program. An earlier monitoring program in North Carolina pointed up these limitations (Sheets et al., 1970). To overcome these limitations the number of samples must be reduced or costs will increase.

The existence of these problems has motivated various workers to propose new methods for pesticide extraction from water. Researchers have experimented with a variety of methods. Ito (1971) unsuccessfully attempted to extract pesticides from water with chlorosilanes bonded to Celite. A similar method was reported by Aue et al. (1972) in which silicone polymers were bonded to Chromosorb W. No quantitative data were provided. Several workers have experimented with polyurethane foams, uncoated and coated with silicone polymers, as extractants of organo-chloride insecticides and PCB's from water (Geser et al., 1971; Uthe et al., 1972; Musty and Nickless, 1974b, 1976). These procedures are simple and can be carried out in the field. Webb (1975) verified the effectiveness of the foam for extracting PCB's from water, but found them to be ineffective at extracting a variety of industrial organics from water. They may be quite useful as semi-quantitative, in situ monitors of PCB and chlorinated insecticide pollution in water (Uthe et al., 1974).

Another procedure of use in particular applications of pesticide analysis is the method of reversed liquid-liquid partitioning (Ahling and Jensen,

1970) in which the water sample is pumped through a column of Carbowax 4000 monostearate and undecane on Chromosorb W. This column is then eluted with petroleum ether to recover the extracted pesticides or PCB's. Quantitative recoveries of a number of chlorinated insecticides from distilled water were obtained.

A more promising extraction procedure for pesticides in water has been adsorption by macroreticular resins. Riley and Taylor (1969) demonstrated that the macroreticular resin XAD-1 was effective in isolating a variety of non-polar organic compounds at trace levels from seawater. Pesticides and other non-polar organics were trapped, while amino acids, carbohydrates and inorganic ions passed through the resins. Burnham et al. (1972) showed that XAD-2 and XAD-7 effectively removed neutral organics from water, particularly aromatics. Elution of the sorbed material from the resin was apparently less effective. Harvey (1973) was able to extract and elute, quantitatively, several chlorinated hydrocarbons in water with XAD-2 resin. In this procedure, designed for shipboard use, water is pumped through a column of XAD-2 at a rate of 5 bed volumes per minute. The column was then eluted with boiling acetonitrile or ethanol. Recovery efficiencies of 100% were reported for several chlorinated pesticides and PCB's. Samples of as large as 80 liters were handled. High sample to elution solvent ratios were maintained. No clean-up of extracts was needed. By a similar procedure Richard and Tritz (1974) detected several pesticides in a stream in Iowa. Osterroht (1974) designed a more elaborate apparatus for in situ extraction of large volumes of seawater with XAD-2. Elution is by Soxhlet extraction of the resin for eight hours with methanol. Junk et al. (1974) reported a procedure that quantitatively, quickly and easily isolated a wide range of organic compounds from water. The sample is allowed to percolate through a

small column of resin (XAD-2 or XAD-4). Elution is effected by a small amount of diethyl ether. Schnare (1976) was unable to duplicate Junk's work without modification. Other workers have found XAD resins to be effective for isolating pesticides from water (Niederschulte and Ballschmitter, 1974; Musty and Nickles, 1974a). Tenax, a synthetic, porous polymer resin composed of 2,6-diphenyl-p-phenylene oxide, was found by Leoni et al. (1975) to be useful for isolating pesticides from water.

The literature suggests that macroreticular resins, particularly XAD-2 and XAD-4, are effective means of isolating pesticides and other non-polar organic pollutants from natural waters. In particular, these resins seem well suited to the routine monitoring of pesticides in natural waters where numerous, large samples must be collected.

XAD-2 Resins

The macroreticular resin XAD-2 is one of a series of polymeric adsorbents produced by the Rohm and Haas Company of Philadelphia. This material is in the form of hard, white porous beads. It is composed of cross-linked co-polymers of styrene and divinyl benzene. The physical characteristics of the resin are presented in Table 5. The resin has a large surface area making it an excellent adsorbent. XAD-2 and the chemically identical XAD-4 (smaller pore size and larger surface area) have very non-polar, hydrophobic molecules from aqueous solutions. The bonding that holds the adsorbents to the surface are primarily Van der Waals forces. These bonds are weak, so that the adsorption step is reversible. During the extraction step the hydrophobic organic molecules preferentially adsorb to the resin surface. During elution the adsorbed molecules are dissolved by the non-polar solvent, for which the sorbed molecules have a strong affinity.

TABLE 5

XAD-2 Characteristics*

Appearance	Hard, spherical, opaque beads
Porosity	0.40-0.45 ml pore/ml bead, dry basis
Surface Area	330 m ² /g, dry basis
Effective Size	0.30-0.45 mm
Harmonic Mean Particle Size	0.45-0.60 mm
Average Pore Diameter	90 Å, dry basis
True Wet Density	1.02 g/ml in distilled water
Skeletal Density	1.07 g/ml
Bulk Density	0.64-0.70 g/ml
Dipole Moment of Functional Group	0.3

*from "Amberlite XAD-2", Rohm and Haas Co., Philadelphia.

Because of these characteristics XAD-2 resin is well suited to concentrating compounds such as pesticides from water. Pesticidal chemicals are readily trapped by the resin as the water passes through the resin bed. A small volume of an appropriate solvent then elutes the pesticides. Because of the non-polar characteristics of the resin, other more polar compounds and ionic species will pass through the resin. This effect can be enhanced by use of moderate flow rates, so that the need for cleaning up the extract can be eliminated (Harvey, 1973).

This phase of the study had two objectives: first, to develop a better method of sampling natural waters for pesticides that was suitable for a routine monitoring program; second, to apply this procedure to a survey of the Cape Fear River Basin of North Carolina. This procedure would offer a more rapid, efficient and cheaper method of monitoring pesticides in natural waters than is currently available. Water samples were to be collected, with extraction by XAD-2 resin in the field so that no water would be transported back to the laboratory or stored. The amount of water to be extracted would be under the control of the investigator. Large samples could be handled if needed. The application of the procedure to an actual monitoring program would allow for better evaluation of its advantages and limitations; and in addition provide data on the Cape Fear River.

Little pesticide data is available on the Cape Fear Basin. A 1969 survey of the Haw River reported the finding of a trace amount of DDE only, at one site (Water Quality Survey -- Haw River Sub-Basin, 1969). No details of the methods used were given.

MATERIALS AND METHODS

Sample Sites

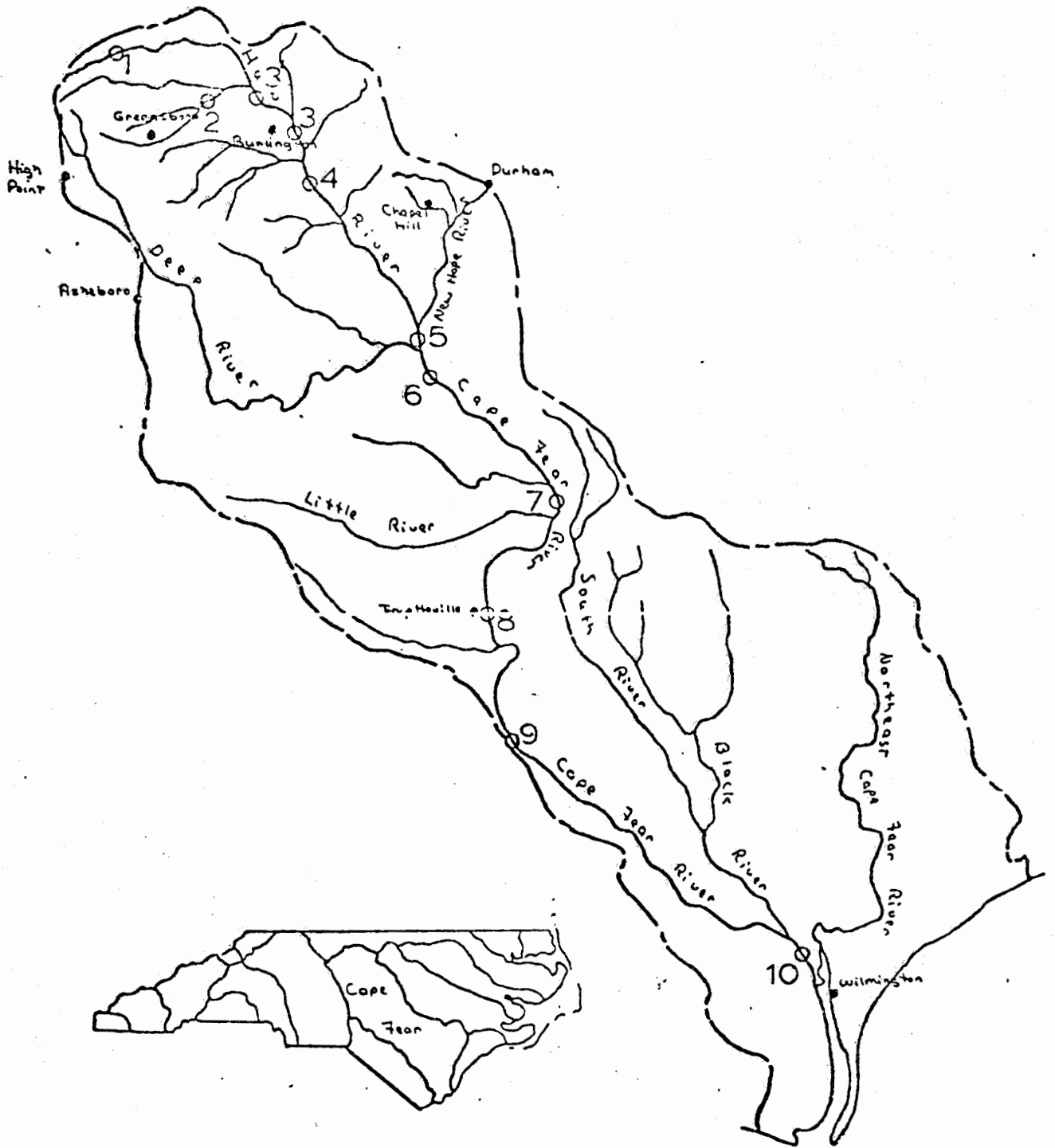
Samples were collected from ten sites in the Cape Fear River Basin of North Carolina. These sites are listed in Table 6. A map of the basin with sampling stations marked is shown in Figure 1. Samples were taken monthly from July 1974 through June 1975 except in October. Samples were initially taken at stations 3' and 10' but later were taken from stations 3 and 10, beginning in November and August respectively. A U.S. Geological Survey gauging station was located at station 3. Station 10 was more accessible than the site of 10'.

At most stations water samples were drawn from the stream in a Nalgene bucket and transferred into a Nalgene jerrican. At all times at station 6 and on occasion at stations 4 and 7, the sample was collected directly with the jerrican from the bank. Generally a sample of 21 to 22 liters was collected of which 10 liters were extracted for pesticides.

Stations 1 through 6 were collected on one day; and 7 through 10 usually the following day. A list of actual sampling dates is provided in the appendix (Table A-1).

Water temperature, pH, flow conditions and approximate time were noted for each station on each sampling trip. Mean monthly flow rates for several stations were obtained from U.S. Geological Survey publications (Water Resource Data for North Carolina, 1975, 1976) and are provided in the appendix (Table A-2). Stations 3 and 9 were located at U.S.G.S. gauging

Figure 1. Cape Fear River Basin with Sampling Stations



stations. Stations 5 and 7 were near U.S.G.S. gauging stations. Table 6 lists the U.S.G.S. station numbers for the corresponding station used in this study.

Metals Study

Materials. All reagents were prepared from reagent grade chemicals. Standards were prepared according to Perkin Elmer Atomic Adsorption instruction manual. The cation exchange resin used was AG-50W x 8, 100-200 mesh particle size (Analytical Grade) purchased from Bio-Rad Laboratories in the hydrogen form. In early developmental work AG-50W x 16, 20-50 mesh obtained from Sigma Chemical Co. in the hydrogen form and Chelex 100, 100-200 mesh from Bio-Rad Laboratories were used. The anion exchange resin used was reagent grade AG-1 x 8, 50-100 mesh and was purchased from J. T. Baker Chemical Co. in the chloride form. The manganese oxide-dioxide impregnated acrylic fibers used as an inorganic exchanger were supplied by Moore and Reid (1973). All buffers used for standardization of the pH meter were Fisher certified (± 0.02 pH units).

Borosilicate glass was used throughout with the exception of tubing. Soda-lime soft glass or Tygon brand polyvinyl chloride were used for tubing. Pre-filters were constructed of 3/4 in. by 4 in. (or 6 in.) polyethylene gas drying tubes with borosilicate glass wool plugs. The main filter was a 0.2 μ m Gelman double open-end Accroflow-II filter cartridge housed in a Filterite talc reinforced polypropylene housing with connections made through polyvinyl chloride and nylon fittings.

Ten liter polyethylene buckets and 10 and 20 l polyethylene jerricans from Nalge were used to collect and transport samples for both parts of the study to the pumping apparatus in the field. Polypropylene and polyethylene

TABLE 6

Location of Sampling Stations

Station	Description
1	Haw River near Oak Ridge at S.R. 2109. Near source of stream. Sample from north bank of stream.
2	Buffalo Creek near McLeansville at S.R. 2795. Below sewage outfall from Greensboro. Sample from downstream side of bridge.
3'	Haw River near Ossipee at S.R. 1530. Sample from bridge.
3	Haw River at town of Haw River at U.S. 70. U.S.G.S. station # 02096500. Sample from bridge.
4	Haw River at Saxapahaw at S.R. 2171. Sample from bridge or underneath bridge.
5	Haw River near Moncure at U.S. 1. U.S.G.S. station # 02098200. Sample from bridge.
6	Cape Fear River near Corinth at N.C. 42. Below confluence of Haw and Deep Rivers. Sample from dock at boat landing.
7	Cape Fear River near Erwin at N.C. 217. U.S.G.S. station # 02102500 several kilometers upstream. Sample from west bank below bridge.
8	Cape Fear River at Fayetteville at N.C. 24-210. Sample from bridge.
9	Cape Fear River near Tar Heel at Lock and Dam #3. U.S.G.S. station # 02105500. Sample from lockwall upstream from dam.
10'	Cape Fear River near Phoenix at Strawberry Hill Landing. Sample from boat tied to bank.
10	Cape Fear River near Wilmington at I.V. Sutton Power Plant (Carolina Power and Light Company). Sample from bank below tug slip.

bottles were used for storage of eluates and standards in the laboratory.

Borosilicate glass columns with Teflon fittings, purchased from Bio-Rad Laboratories were used for laboratory developmental work. Field columns were constructed of polyvinyl chloride with nylon fittings and a borosilicate glass fritted disc. Teflon tape was used to prevent binding and insure proper seals. Whatman No. 1 filter paper was used to separate resin and eluate.

The Cr^{51} was purchased from ICN Life Science Group. Five mCi each of CrCl_3 and Na_2CrO_4 were obtained with initial specific activities of 550 ci/g Cr.

Metal analysis was accomplished with a Perkin-Elmer Model 303 atomic absorption spectrophotometer with a Fisher Recordall Series 5000 recorder. The Cr^{51} was counted using a well type Beckman Gamma 310 Radiation Counter. A Fisher Model 150 portable pH meter with a combination glass electrode was used to determine pH in the field.

Method Development. A sample size of 10 l and a pumping rate of 500 ml to 1 l per minute was selected. This gave a sampling time of 15 to 30 minutes per sample site and adequate concentration for atomic absorption analysis by direct aspiration into the flame. Instrument availability and the success of other investigators using ion exchange techniques in combination with atomic absorption spectrometry (Biechler, 1965; Riley and Taylor, 1968; Zlatkin et al., 1971) were the based for the choice of methods.

A series of comparative studies were carried out to select the most appropriate exchanger for incorporation into the field sampling unit. The utility of chelating resins in the analytical separation of trace metals from solutions of high ionic strength has been demonstrated using Dowex A-1

resins (Biechler, 1965; Schmuckler, 1965; Turse and Rieman, 1961). Chelex 100 (purified form of Dowex A-1) was used by Riley and Taylor (1968) to concentrate various metal ions from sea water, including cadmium, chromium (Cr(III)), copper, lead and zinc followed by analysis by atomic absorption. Similarly, Chelex 100 was used by Biechler (1965), in conjunction with atomic absorption, to analyze industrial waste water for Cu, Zn, Cd, Ni and Fe (4). Both investigators used a flow rate of less than $15 \text{ ml-min}^{-1}\text{-cm}^{-2}$. Riley and Taylor (1968) used this flow rate because of the slow rate of exchange of the resin. Schmuckler (1965) suggests that the exchange process of chelating resins is controlled either by particle diffusion or by a second order chemical reaction. To use this resin at a flow rate of 500 ml per min total would require a column diameter of 6.5 cm to obtain a flow of $15 \text{ ml-min}^{-1}\text{-cm}^{-2}$. This diameter column was considered impractical.

In addition to low flow rates, Riley and Taylor (1968) found that with Chelex 100 it was necessary to buffer the sample to an "optimum" pH which depended upon the metal of interest. It was also noted that while 100% retention of Cr(III) could be accomplished, 100% elution was never observed. Although early experiments carried out in this study using cadmium spiked distilled water samples showed good retention on Chelex 100 resin, its use was abandoned because of flow rate considerations.

Moore and Reid (1973) described a technique by which acrylic fibers were impregnated with manganese oxide-dioxide and subsequently used as ion exchangers to quantitatively removed radium from seawater. In column experiments, 90% removal of radium was observed at flow rates of $198 \text{ ml-min}^{-1}\text{-cm}^{-2}$ (Moore and Reid, 1973).

Synthetic cationic and anionic resin exchangers, while not as selective as chelating exchangers, have a more rapid exchange process (Schmuckler,

1965). The utility of cationic and anionic exchangers for the analysis of natural waters has been demonstrated (Standard Methods, 1975, Colmon, 1954; Nydahl, 1951). Flow rates used range from $3 \text{ ml-min}^{-1}\text{-cm}^{-2}$ (1) to $55 \text{ ml-min}^{-1}\text{-cm}^{-2}$ (Nydahl, 1951).

Both the AG-50W resin and the manganese fibers showed nearly 100% retention of cadmium, zinc, lead and copper at flow rates examined (see Appendix B). Using a column elution technique, down flow mode, the manganese fiber column could be eluted with smaller volumes than could the cation exchange resin columns (see Appendix B). This has obvious advantages since greater concentration can be achieved. The manganese fiber eluate also produced lower noise levels when analyzed by atomic absorption. However, it was observed that over time, the manganese fiber column lost its ability to completely remove dissolved metal ions from solutions of distilled water. This apparent loss of exchange sites may have been caused by some deactivation mechanism or by simple wash off of the manganese oxides observed by Moore and Reid (1973). A color change of the fiber column was observed with aging. Therefore, while manganese oxide-dioxide impregnated acrylic fibers show promise as ion exchangers for the concentration of dissolved metal ions, the loss of exchange capacity led to abandoning them as a column material.

The AG-50W ion exchange resin was adopted for the work described here. The resin has been used to extract and separate dissolved metal ions by a number of researchers (Fritz and Abbink, 1965; McCallum and Woodward, 1966; Strewlow, 1968). To calculate the exchange capacity necessary for extraction of metals from a 10μ sample, expected concentrations had to be estimated. These are given in the Introduction section (Table 2). From this data and the manufacturers specifications for exchange capacity

it was determined that less than 0.1 ml of resin would provide the maximum number of exchange sites needed for the five metals of interest in a 10 ℓ sample.

Preliminary work using a 1.0 x 20 cm column (16 ml resin) showed that sub ppm quantities of Cd, Zn and Pb could be extracted and eluted using the gravity controlled down flow mode. Maximum flow rate in this unpressurized system was 20 ml-min⁻¹ total or 25 ml-min⁻¹-cm⁻². Retentions of approximately 100% were observed at this rate. Greater than 90% elution was obtained with 200 ml of 1.5 N HCl. Based on this eluant volume and a sample size of 10 ℓ, a concentration by a factor of 50 was achieved. To extract a 10 ℓ sample at this flow rate would take over eight hours, so that faster flow rates were necessary to be practical. This was accomplished with an increase in column cross-section. A 2.5 cm column with a 40 ml resin bed increased the cross-sectional area and therefore, the total flow rate by a factor of 6.25. However, to attain greater than 90% elution now required 700 ml of eluant.

Another approach, other than column elution, is a batch technique which is simple, based on equilibrium conditions (Dorfner, 1972) and offers the advantage of working with smaller volumes (Helfferich, 1962). Strewlow (1960) used a batch technique to determine a selectivity scale of cations for Dowex 50W x 8 in solutions of various hydrochloric acid normalities. Its utility as an elution procedure was examined in the present study in order to decrease elution volume. The resin with metals absorbed was transferred to a flask with 50 ml of 3 N HCl and allowed to equilibrate with occasional mixing for a minimum of 24 hours. Resin and eluant were separated by filtration and the resin washed with approximately 50 ml of 3 N HCl bring final volume to 100 ml. Recoveries from distilled water spikes are

shown in Table 7. It should be pointed out, as shown in Appendix 3, that the data in Table 7 was obtained by using sub mg/l spikes into 10 l of distilled water and flow rates of from 40 to 126 ml-min⁻¹-cm⁻² for extraction. Ten liter water blanks were run in each case and the data in Table 7 reflects the adjustments made for background.

A second column of AG-1 x 8, 50-100 mesh anion exchange resin was included to collect anionic metal species after the procedure suggested by Pankow et al. (1973). Radioactive tracers have been used to evaluate ion exchange systems (Moore and Reid, 1973; Szabo and Joensau, 1967) and Pankow et al. used Cr⁵¹ (a weak gamma emitter) as a tracer in their speciation studies. Cr⁵¹ was also used in the present study to evaluate a dual column cationic-anionic exchange system. Table 6 shows recovery of Cr⁵¹ when the batch elution technique was used. Less than 100% recovery of Cr⁵¹ was due to the inefficiency of the batch elution technique. The resin extraction efficiency was shown to be near 100% for both Cr(III) and CrO₄⁼.

Natural water samples spiked with known amounts of metal, concentrated by the ion exchange technique and quantified by atomic absorption gave erratic results because of the inability of the procedure to differentiate between naturally occurring metal and spiked metal and the lack of control over the speciation of the metal once the spike was introduced. Speciation was studied by using spikes of Cr⁵¹ (both Cr(III) and Cr(VI)) as a tracer. Two natural samples (from two locations) were collected and returned to the lab. One liter aliquots were spiked with Cr⁵¹, equilibrated for 1 hour, pumped through 0.22 µm membrane filters and the ion exchange collection system. The resins were eluted by the batch technique and the fractions of Cr⁵¹ as particulate, cationic, anionic and dissolved non-ionic were determined. The results tabulated in Table 8 show that the CrO₄⁻²

Table 7. Recoveries with batch elution method.

Metal	% Recovery							Mean	Media	Range
Cd	90	88	98	96	100	97	97	95	97	88 - 100
Cu	66	62	85	89	88	81	79	79	81	62 - 89
Zn	158	80	86	130	103	120	195	125	120	80 - 195
Pb	90	89	100	94	100	91	87	93	91	87 - 100
*Cr(III)	86	85	71	78				80	82	71 - 86
*CrO ₄ ⁼	97	97	89	96				93	96	86 - 97

* Studies with Cr⁵¹ tracer.

Table 8. Chromium speciation in natural waters spiked with Cr⁵¹.

Experiment	System component	Sample fraction	Sample source % of spike		Form of spike
			Saxapahaw	Morgan Creek	
1	Filter	particulate	1	3	Na ₂ CrO ₄
	Cation column	dissolved cationic	1	4	
	Anion column	dissolved anionic	88	73	
	waste	dissolved nonionic	ND	-	
2	Filter	particulate	63	56	CrCl ₃
	Cation column	dissolved cationic	6	23	
	Anion column	dissolved anionic	4	2	
	waste	dissolved nonionic	9	-	
3.	Filter	particulate	51*	52*	Na ₂ CrO ₄ and CrCl ₃
	Cation column	dissolved cationic	8*	22*	
	Anion column	dissolved anionic	92**	82**	
	waste	dissolved nonionic	26*	-	
4	Filter	particulate	1	distilled water	
	Filter	particulate	1.3		

* % of CrCl₃ spike

** % of Na₂CrO₄ spike

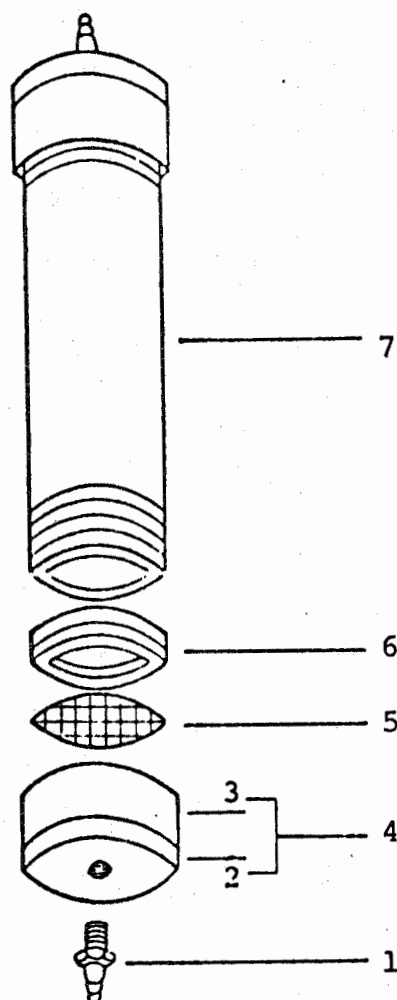
was collected almost entirely as an anionic species. Cr(III), in contrast to Cr(VI), was found mainly as particulate, but significant amounts were found in other forms. In contrast to the natural water samples, spikes into distilled water showed that Cr(III) is not trapped by the filter. The results in Table 8 indicate that a large fraction of Cr(III) introduced to natural water comes out of solution and the remainder partitions between the other three fractions.

Apparatus Development: Adaptations of laboratory separation techniques for field use required consideration of ruggedness, low weight, compactness and portability. As discussed above, maximization of flow rates was the controlling factor in final column size. The columns were similar to a design of Buelow, Carswell and Symons (1973) who used them to concentrate organics from natural water using granular activated carbon. Figure 2 gives the column design. The columns were constructed of PVC with nylon fittings and with a borosilicate glass frit. The column was suitable for a pressurized system and included a head space to trap air before the sample contacted the resin.

Since many commercially available filtration units are either too small to filter 10 l samples at high flow rates or too large and costly to be destroyed for particulate analysis, a non-disposable membrane filter manufactured by Gelman was used and the particulate fraction was not analyzed. A 0.2 μm filter cartridge with a filtration area of six square feet was placed in line before the ion exchange columns. A glass wool-gas drying tube pre-filter was included to extend the life of the main filter. The system is shown schematically in Figure 3.

The system was mounted on a metal chassis for portability. The entire field unit fitted conveniently into the rear seat area (with seat removed) of a Plymouth Valiant and could be handled by one man.

Figure 2. Field ion exchange column design.



1. $\frac{1}{8}$ in. M.P.T. to $\frac{1}{8}$ in. tube nylon fitting.
2. $\frac{1}{8}$ in. PVC sheet machined for correct fit and for $\frac{1}{8}$ in. F.P.T.
3. One half of $1\frac{1}{2}$ in. schedule 80 PVC coupling.
4. End cap consists of 2 and 3 solvent welded together.
5. 40 mm borosilicate glass fritted disc.
6. Frit retainer ring.
7. 6 in. schedule 80 PVC nipple.

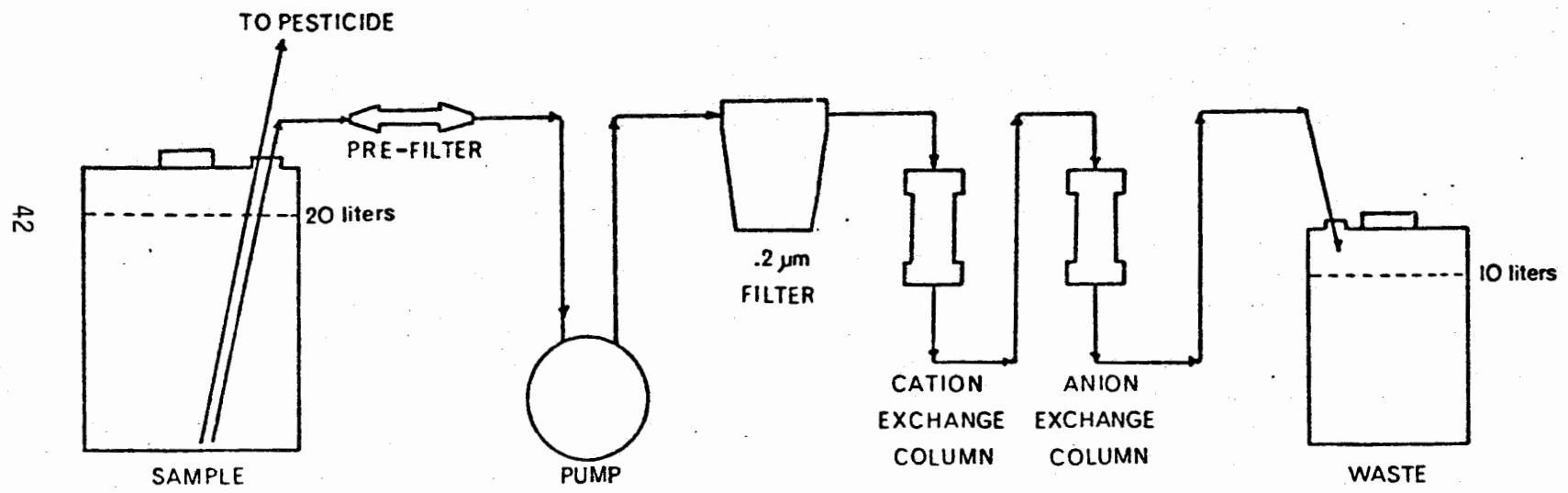


Figure 3. Schematic of trace metal sampling apparatus.

Methods Used: Columns, fritted disc and retainer rings were washed using tap water and brush followed by a 24 hour immersion in 1:2 HNO₃. Since the nylon fittings were attacked by strong acid, they could not be leached in acid solution and were simply rinsed with 1:2 HNO₃. (However, before the first use, new end caps themselves were leached in 1:2 HNO₃ before attaching the nylon fittings.) A distilled water rinse and air drying completed the cleaning procedure. Reassembly was made with Teflon tape to insure a water tight seal and to prevent binding of the threaded connections. Columns were stored with fittings capped.

Spent resin was regenerated in bulk using a 5.0 cm x 50 cm glass column. The resin was backwashed with distilled water to remove accumulated debris and allow packing by size distribution. Two liters of 1.5 N HCl was used to regenerate the resin by down flow through the column at approximately 10 ml/min, followed by 4 l of distilled water. Resin was transferred to a stoppered 500 ml flask and stored under water. Initial resin preparation was preceded by an overnight equilibration under distilled water to hydrate the resin. Regeneration was the same for both cation and anion resin.

The field columns were packed in the laboratory and transported to the field. Pre-wash of the empty column in the down flow mode under vacuum with distilled water insured the removal of air trapped beneath the fritted glass disc. After transferring and allowing the resin to settle, packing was completed by washing with distilled water under vacuum in the down flow mode. The column was then filled with distilled water, the end cap attached with rubber bulb covering inlet and stored in an upright position.

Field and Laboratory Procedure: An approximately 22 ℓ surface sample was collected using a 10 ℓ bucket. The temperature and pH were determined using a mercury thermometer and a portable pH meter. Air was displaced from the filter and housing followed by a minimum one liter flush of the complete system with sample water. The ion exchange columns were then connected and the system was checked for leaks. While in route to the next sampling station, a 10 ℓ sample was pumped through the system at a flow rate of approximately $600 \text{ ml}\cdot\text{min}^{-1}$ total. The columns were removed and stored upright for transportation back to the lab.

Columns were drained and the resin transferred to an Erlenmeyer flask with 50 ml of 3 N HCl. The resin slurry was allowed to equilibrate with occasional mixing for a minimum of 24 hours. The resin was then separated by gravity filtration through Whatman No. 1 filter paper (pre-washed with 3 N HCl). Complete transfer and washing of the resin and flask was with aliquots of 3 N HCl. The filtrate was collected for regeneration. Elution was the same for both resins.

Analysis was by atomic absorption. Using Eppendorf micro-pipetes, a suitable range of working standards were prepared from 1000 mg/l stock standards. Working standards were diluted with 3 N HCl and a 3 N HCl blank was used. A standard curve was prepared and sample concentration determined from it. A three slot burner and standard conditions from the instrument instruction manual were used.

Pesticide Study

Method Development

As stated in the introduction the development of a new sampling and extraction procedure for pesticides in water was a major goal of this study.

A series of developmental experiments was carried out with XAD-2 resin prior to the collection of samples. From this preliminary work a new procedure was designed that could be utilized in the actual field sampling program.

The initial series of experiments was designed to investigate the ability of XAD-2 resin to extract pesticides from water and the ability of several solvents to elute them from the resin. In these experiments XAD-2 resin was placed in glass columns (62 cm long by 1.5 cm ID) to a height of about 10 cm (volume of 17.5 cc; length to diameter ratio of 6.7). Distilled water, to which a known amount of pesticide had been added, was pumped through the column at a rate of 200 milliliters per minute with a Cole-Parmer Master-Flex peristaltic pump. The effluent from the column was collected. A fraction of the pesticide spiked water that had not been through the column was also saved. The column was then eluted by a single solvent or by a series of solvents. The water fractions were extracted in a separatory funnel with diethyl ether. The solvent extracts from both water and resin were then dried with sodium sulfate and concentrated by reduced pressure rotary evaporation. The extracts were analyzed by electron capture gas chromatography. Pesticides, concentrations, solvents and the results of these experiments were presented in Table 14 in the Results chapter.

Subsequent columns and a sampling apparatus were made for collection of environmental samples. Polyethylene and polypropylene drying tubes (Bel-Art Products) were used to make resin columns and filter tubes. Shortened rubber policemen were used to cap the columns. The sampling apparatus (outlined as in Figure 2), consisting of a frame on which two peristaltic pumps, brackets for the resin and filter tubes and holders for

two jerricans were mounted, was built by the School of Public Health shop. Tygon and glass tubing served as conduit for the sample between the pump, jerricans and tubes. Nalgene jerricans were used as reservoirs to hold the samples. An inverter was installed on the vehicle to be used on sampling trips to provide AC power. During sampling trips the sampling apparatus was placed in the back of an automobile where it could easily be operated.

Several experiments were performed to establish the efficiency and reliability of this new method. Two ten-liter samples of distilled water were placed in jerricans and a standard containing the seven pesticides, in known amounts, added. After shaking for two minutes, the samples were pumped through a glass wool filter and an XAD-2 resin column at about 300 milliliters per minute. The filters and columns were processed and analyzed in the same manner as the field samples. The empty jerricans were rinsed with diethyl ether which was concentrated and analyzed. In a similar manner samples of Haw River water were spiked and processed during the May and June sampling trips. These two experiments were carried out under field conditions with environmental samples from stations 4 and 1. The pesticides added, amounts and results are given in Tables 15, 16 and 17 in the Results chapter.

Tests of the variability of the new procedure were made by collecting environmental samples in triplicate at two stations. In January at station 2 and in March at station 4, three replicate samples were collected. These samples were also treated in the same manner as all other samples. Results of these samples are given in Table 18 in the Results chapter.

A list of pesticides with chemical names and suppliers is given in Table 9. Solvents were either pesticide quality or reagent grade and redistilled in an all glass still, unless otherwise stated. Sodium sulfate was

TABLE 9

List of Studied Pesticides with Suppliers

Pesticide		Source
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethyl-urea	EPA*
Trifluralin	a,a,a-trifluoro-2,6-dinitro-N-N-di-n-propyl-p-toluidine	EPA
Atrazine	2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine	EPA
Methyl parathion	0,0-dimethyl-0-p-nitrophenyl phosphorothioate	EPA
DDE	1,1-dichloro-2,2-bis-(p-chlorophenyl) ethylene	Aldrich
DDD	1,1-dichloro-2,2-bis-(p-chlorophenyl) ethane	Geigy
DDT	1,1,1-trichloro-2,2-bis-(p-chloro-phenyl) ethane	Aldrich
Toxaphene	Octachlorocamphene	EPA

*Quality Assurance Section
Pesticides and Toxic Substances Effects Laboratory
EPA Environmental Research Center
Research Triangle Park, N.C. 27711

of reagent grade and washed with ether to eliminate any possible PCB contamination. All glassware was carefully washed with a detergent, rinsed sequentially with tap water, distilled water and commercial grade acetone. The glassware was then dried in a 200°C oven to combust or drive off any remaining organic contaminants. No contamination from glassware was noted during this project.

Field Sampling

Prior to each sampling trip resin columns and glass wool filters were prepared. The columns were prepared from drying tubes, with small plugs of glass wool at each end and contained approximately 10 cc of XAD-2 resin. On the basis of the work of Harvey (1973), this amount of resin added should have the capacity for at least 700 µg of total pesticides. The columns were rinsed with distilled water to remove the methanol and wet the resin and then were capped with rubber policemen. Filters were made by placing large plugs of glass wool in drying tubes. The filters were rinsed with pesticide quality acetone and distilled water. The jerricans and tubing were washed with detergent and rinsed, sequentially, with tap water, distilled water and acetone.

Upon reaching the sampling site, the water sample was collected and transferred to a jerrican. Since it was impossible to completely seal the tubes, the above negative pressure mode of operation was chosen because any leaks in the pumping train would result in air coming in rather than water leaking out. The pumping rate varied depending upon engine speed (the current output of the DC/AC converted nullified the pump controls), but averaged approximately 300 milliliters per minute. On most occasions 10 liters of water was sampled, though for several samples smaller volumes were extracted, due to clogging of the filters and columns or insufficient

sample. The water was then discarded; and the filters and columns stored on ice. The samples were refrigerated upon return to the laboratory.

Extraction and Concentration

The filter and resin columns were eluted and analyzed separately in the laboratory. The XAD-2 resin was extracted in a batch-type operation in 125 ml separatory funnels. The resin was washed out of the drying tube with a 25 ml portion of diethyl ether into the separatory funnel and allowed to stand for an hour to enable the ether to thoroughly contact the resin beads. The mixture was shaken for ten minutes on a wrist-action shaker. The ether was drained into a glass-stoppered Erlenmeyer flask. The elution was repeated with another 25 ml portion of ether and ten minutes of shaking. The ether fractions were combined and stored under refrigeration for later cleaning.

The glass wool used as filters and as plugs for the resin columns was combined for each sample and placed in glass-stoppered flasks. A 25 ml portion of ether was added to each, the glass wool compressed with a glass rod to remove bubbles and to submerge the glass wool in the ether. The filter was then allowed to soak in ether for at least 24 hours in the refrigerator. The ether was then poured off, using a glass rod to squeeze out as much as possible. The glass wool was then soaked with a second 25 ml portion of ether for several minutes. This ether fraction was then poured off and combined with the first fraction and refrigerated until time for concentration.

All samples, both filter and resin extracts, were concentrated in the same manner. The extracts were placed in a -70°C freezer to freeze water out of the ether. The ether was then poured off into the chamber of a Kuderna-Danish evaporator. Four milliliters of hexanes were added and a

three-ball Synder column attached to the Kuderna-Danish flask. The solution was fluxed over a steam bath until the volume was reduced to about four milliliters. The volume was adjusted to four milliliters and the extract decanted into screw cap tubes with Teflon liners and refrigerated.

Analysis

Electron capture gas-liquid chromatography was the method of analysis. A Perkin-Elmer Model 900 gas chromatograph equipped with a Ni⁶³ detector was used for all analyses. An Infotronics Model CRS-208 electronic digital integrator and printer provided retention times and relative peak areas. A Westronics strip chart recorder produced traces of the sample chromatograms. Table 10 lists the gas chromatographic (GC) parameters that were used in this study. Experimentation with several GC columns determined that 3% OV-1 liquid packing provided separation of all seven pesticides that were to be monitored. Temperature programming of the GC oven improved peak resolution and shortened the analysis time. Because of the great difference in temperatures at which dieldrin and DDT were eluted from the column, this factor was very important. Jonas (1974) found the use of nitrogen as the carrier gas with the electron capture detector in the pulse mode to produce excellent results.

Calibration curves for each compound were prepared using both peak height and peak area (integrator counts) by least squares regression. In this study peak area proved to be very unreliable due to the limited response characteristics of the integrator. The integrator tended to choose as the baseline the low point of the depression following the solvent peak, so that peak area counts were erroneous. A more stable baseline might have made the integrator useable. All quantifications of pesticides were based on peak height. Janik (1975) reported peak height

TABLE 10

Analytical Gas Chromatographic Parameters

Gas Chromatograph	Perkin Elmer Model 900
Integrator	Infotronics Model CRS-208
Recorder	Westronics: 1 mv
Column Temperature Program	Initial 130°C (1 minute) Increase at 12°C/minute Final 190°C (10 minutes)
Injector Temperature	225°C
Detector Temperature	250°C
Carrier Gas	Nitrogen (zero gas grade)
Detector	Electron capture (Nickel 63)
Detector Voltage	Pulse mode, C Channel (50 volts, 1 μ second duration)
Solid Support	60-80 mesh Gas-Chrom-Q ^R
Stationary Phase	3% OV-1 ^R
Column Dimensions	Length 180 cm Outside Diameter .635 cm Inside Diameter .2 cm
Column Material	Glass
Amplifier	x 100
Attenuation	x 1

to be as precise and cheaper and easier to determine than peak area. Grant and Clarke (1974) found electronic integration most precise where peaks are completely separated and the baseline stable. They report peak height to be of comparable precision and less affected by long term variations. The calibration curves prepared from peak height are found in Appendix A (Figures A-1 to A-7).

At the beginning of each day's analyses an injection of hexanes was made to check for proper operation of the gas chromatograph. Several injections of standards were made to measure the sensitivity of the detector. These injections were used to obtain a correction factor for the sensitivity for that day to be used in calculating pesticide quantities. A single injection of each sample was made except when there appeared to be contamination of the system. At the end of the day's analyses another injection of standards was made to determine if detector sensitivity had changed.

Using the calibration curves, the quantity of each pesticide, identified on the basis of retention time, was calculated from the peak height, after correction for sensitivity. The quantity of pesticide injection was incorporated into a calculation including sample size, extract volume, injection volume and the correction factor for the efficiency of the extraction procedure to determine the actual pesticide concentration in the initial water sample. A sample calculation is presented in Figure 4. The actual data of the environmental monitoring work is given in the Appendix and summarized in the Results chapter.

An attempt was made to verify the pesticide identifications by use of a gas chromatograph coupled to a mass spectrometer. For this purpose a number of sample extracts with similar chromatograms were combined into two composite samples and further concentrated. These two samples were then

Figure 4. Sample Calculation Showing Calculation of Dissolved DDT in Station 5 in April 1975.

Peak at 606 seconds (DDT retention time - 607 seconds)

Peak height measured at 21 mm

Sensitivity correction factor 1.3

Injection volume 1 ml

Extract volume 3 ml

Water sample volume 10 l

Extraction coefficient for DDT 5

Corrected peak height $21 \text{ mm} \times 1.3 = 27.3 \text{ mm}$

Amount in injection 64 pg
(from calibration curve)

Amount in original water sample $64 \text{ pg/ml} \times 3 \text{ ml} \div 10 \text{ l} = 19 \text{ ng/l}$
(assuming 100% recovery)

Amount in original water sample $19 \text{ ng/l} \times 5 = 95 \text{ ng/l}$

taken to a laboratory at the National Institute of Environmental Health Sciences for the analysis. No pesticides were identified by this analysis due to insufficient concentrations to be detected by the mass spectrometer.

Resin Cleaning and Handling Procedure

The procedure for cleaning and handling the resin was found to be of great importance. The procedure initially used to clean XAD resin was found to be ineffective. This procedure was a sequential Soxhlet extraction of the resin by diethyl ether, acetonitrile and methanol for two hours each. This method is similar to that used by Junk et al. (1974). Some of the resin may have dried out, a condition Junk notes can lead to contamination because the fragile beads tend to break up exposing new surfaces.

Experimentation with the XAD resin cleaning procedure revealed that shaking resin that had been used to extract environmental samples with 1 N NaOH and 1 N HCl before the Soxhlet extractions improved the effectiveness of the cleaning. The NaOH noticeably removed yellow color from the used resin. These findings were incorporated into a new resin cleaning procedure along with longer extraction times. This procedure is given in Table 11.

TABLE 11

Cleaning Procedure for XAD-2 Resin

Wash in 1 N NaOH.

Rinse with high quality distilled water.

Wash in 1 N HCl.

Rinse twice with high quality distilled water.

Extract with methanol in Soxhlet for at least eight hours.

Extract with acetonitrile in Soxhlet for at least eight hours.

Extract with diethyl ether in Soxhlet for at least eight hours.

Store in methanol.

RESULTS

Metals

The dissolved metals analyzed were classified as anionic or cationic depending upon the column on which they were collected. Cationic species of all five metals were observed. Anionic species were observed only for chromium, zinc and copper. Mean dissolved metal concentrations and ranges are shown in Tables 12 and 13 by sample station. Figure 5 shows these mean concentrations plotted vs. mileage upstream from the mouth of the Cape Fear River (concentration units in Figure 5 have been adjusted so as to maximize variations from site to site).

In all cases, the mean cationic species concentration at site 10 is less than the mean concentration at site 1. Anionic species of copper and zinc were rather constant with only copper showing a very slight increase at sites 2-7 (range of none detected to 1.8 $\mu\text{g}/\text{l}$ throughout river system). Anionic chromium was increased sharply around Greensboro and Burlington and gradually dropped off at sites downstream. Anionic chromium was detected at all sites except site 1 and ranged in concentration from none detected at site 1 to 21.5 $\mu\text{g}/\text{l}$ at site 2. Cationic chromium ranged from none detected at site 10 at 16.4 $\mu\text{g}/\text{l}$ at site 4. Lead had the broadest concentration range (1.1 $\mu\text{g}/\text{l}$ to 74.0 $\mu\text{g}/\text{l}$), followed by Zn, Cr, Cu and Cd in that order.

At sites 1-5, the general order of abundance of the five metals based on the mean of all samples is $\text{Zn} > \text{Pb} > \text{Cu}$ or $\text{Cr} > \text{Cd}$. Cu is greater at

Table 12. Means and ranges of dissolved cationic metal species.

Site #	Metal				
	Cd	Cr	Cu	Pb	Zn
	Mean ($\mu\text{g/l}$)				
	Range ($\mu\text{g/l}$)				
1	0.28 0.13-0.55	2.1 0.3-3.8	1.6 0.9-4.1	7.3 1.1-39.0	13.2 3.9-55.0
2	0.77 0.29-1.22	6.3 3.0-15.0	4.6 2.4-9.1	11.9 4.0-37.2	52.6 37.8-74.0
3	0.36 0.16-0.65	2.8 1.6-5.9	3.9 2.5-6.5	8.3 3.5-37.9	15.1 7.0-30.0
4	0.31 0.16-0.40	5.1 1.5-16.4	2.9 1.8-4.7	5.6 2.4-9.5	13.2 5.7-21.5
5	0.29 0.14-0.40	2.7 1.5-5.7	2.5 2.0-3.3	5.3 2.4-9.8	10.4 4.3-17.7
6	0.31 0.12-0.55	2.0 0.5-3.3	2.2 1.6-3.7	7.5 1.4-38.9	7.1 4.0-16.2
7	0.28 0.14-0.68	1.5 0.3-4.1	2.0 1.4-2.9	10.0 1.2-59.0	8.0 2.9-15.5
8	0.29 0.14-0.85	1.6 0.3-3.0	1.7 1.4-2.4	5.7 1.8-24.4	7.7 4.6-12.8
9	0.29 0.10-1.12	0.9 ND-1.4	1.5 1.2-2.3	12.7 1.4-74.0	7.1 3.8-15.1
10	0.18 ND-0.35	0.8 ND-1.7	1.5 1.0-2.5	3.9 1.4-15.8	7.3 3.7-12.0

ND = None detected.

Table 13. Means and ranges of dissolved anionic metal species.

Site #	Metal		
	Cr	Cu	Zn
	Mean ($\mu\text{g/l}$)		
	Range ($\mu\text{g/l}$)		
1	ND	0.5 ND-0.7	0.2 0.1-0.2
2	7.9 2.2-21.5	0.8 ND-1.3	0.2 0.1-0.2
3	1.5 ND-5.0	0.8 ND-1.3	0.2 0.1-0.3
4	2.0 ND-5.0	0.8 ND-1.1	0.2 0.1-0.2
5	1.9 ND-7.0	0.8 ND-1.8	0.2 0.1-0.3
6	0.7 ND-2.4	0.6 ND-1.0	0.1 0.1-0.2
7	0.5 ND-2.0	0.7 ND-1.0	0.2 0.1-0.3
8	0.4 ND-1.0	0.6 ND-0.9	0.2 0.1-0.3
9	0.1 0.1-0.2	0.4 ND-0.8	0.1 0.1-0.2
10	0.1 ND-0.6	0.5 ND-0.9	0.1 0.1-0.2

ND = none detected.

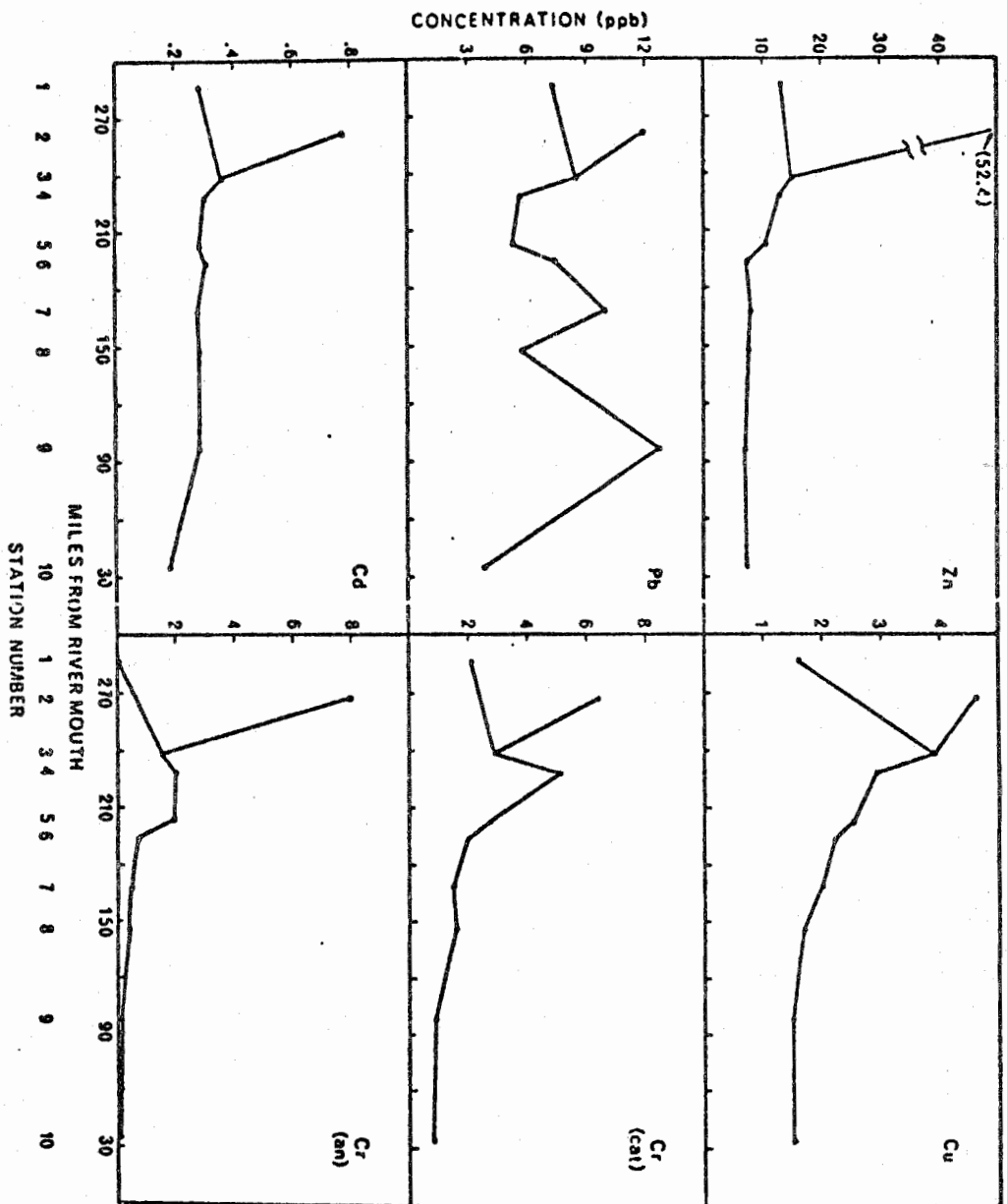


Figure 5. Mean metal concentration vs. distance from mouth of Cape Fear River.

site 3 while Cr is greater at 1, 2, 4 and 5. The order for sites 6-10 is Pb or Zn > Cu > Cr > Cd showing the importance of the chromium removal mechanism. At sites 6, 7 and 9 lead is greater than zinc > while zinc is greater at sites 8 and 10.

Temperature and pH were monitored and this data is included in Appendix C. In general, temperature was a function of season and was elevated at sites 2 and 6 possibly due to Greensboro's waste at site 2 and cooling water discharge from the power plant and/or industrial discharge above site 6. The lowest temperature recorded was 2°C at site 1 and the highest was 33°C at site 6. The pH was generally slightly acidic and tended to be higher downstream of the Greensboro-Burlington area relative to site 1. Station 10 was observed to be more acidic than upstream areas perhaps reflecting the effect of the highly colored drainage from the surrounding swampy areas. The highest observed pH was 7.9 at site 7 and the lowest was 5.8 at site 10. The importance of pH as a trace metal control mechanism, particularly in poorly buffered natural systems, has been indicated (Gadde and Kartinen, 1974).

Pesticides

XAD-2 Extraction and Elution Data

Results of the initial series of experiments, conducted to investigate the usefulness of XAD-2 resin for the isolation of pesticides from water, are presented in Table 14. Both the efficiency of the resin in removing pesticides from water and the effectiveness of several solvents in eluting these adsorbed pesticides from the resin were measured. The trapping efficiency of the resin for all pesticides tested was at least 90%. Elution percentages were more variable and in general less than the trapping efficiencies. The elution efficiency of toxaphene was particularly poor -- 17%.

TABLE 14

Efficiencies of Extraction and Elution of Pesticides
in Water by XAD-2 Resin

		% Trapped	Solvents	% Eluted
Diuron	100 µg/l	90	Acidic methanol	100
Trifluralin	10 µg/l	95	Diethyl ether	85
Atrazine	100 µg/l	99+	Diethyl ether	98
Methyl Parathion	100 µg/l	99	Methanol, diethyl ether	74
DDT	10 µg/l	94	Methanol, propanol, acetone	98
Toxaphene	10 µg/l	100	Diethyl ether, methanol, diethyl ether	17

This preliminary work established the usefulness of XAD-2 resin as a tool for the isolation of organic pesticides from water. The XAD-2 resin was then incorporated into a procedure for the monitoring of pesticides from natural waters. Tables 15 to 18 provide data from several experiments evaluating the effectiveness and variability of this method.

The efficiency of the procedure for the recovery of pesticides from water was measured by the addition of a known quantity of a mixture of pesticides to a water sample. Table 15 gives the results of an addition of the seven pesticides to duplicate 10 liter samples of distilled water. This experiment was performed in the laboratory where flow rate could be more easily controlled than in the field. The table lists the amount of each pesticide added to each sample, the amount recovered for each replicate and the average recovery for the two replicates expressed as a percentage. The overall average recovery is about 40%. Agreement between replicates is good with the exception of diuron and DDT. This large variability shown by diuron is repeated throughout this study. DDT, however, usually gives good repeatability of quantitation. If the zero DDT replicate is neglected, the 38% recovery for DDT is consistent with the recovery efficiencies of the other pesticides. No significant amount of these pesticides was found in the glass wool filter extracts or in an diethyl ether rinse of the jerricans used to make up the pesticide solutions.

Results of a similar pesticide addition to water collected at station 1 near the head of the Haw River are given in Table 16. Data is presented as in the previous table. In this case the recoveries for DDT and its metabolites and trifluralin are significantly different from the previous experiment. Trifluralin is recovered at a slightly lower efficiency; DDT, DDD, DDE are recovered at about half the efficiency in the distilled water

TABLE 15

Recovery Efficiencies for Pesticides
from Spiked Distilled Water

Pesticide	Amount Added	Amount Recovered		Average % Recovered
		S1	S2	
Diuron	1000	400	160	28
Trifluralin	25	12.1	12.4	49
Atrazine	20	7.0	7.6	36
Methyl Parathion	500	202	222	42
DDE	50	18	21.4	40
DDD	50	14.4	19.6	39
DDT	50	18.6	ND	19

Pesticide concentrations are reported in ng/l except for atrazine which is in $\mu\text{g/l}$.

TABLE 16

Recovery Efficiencies for Pesticides
from Haw River Water from Station #1

Pesticide	Amount Added	Amount Recovered A	Amount Recovered B	Average % Recovered	Correction Coefficient
Diuron	1000	310	180	24.5	4
Trifluralin	25	9.4	9.3	37.4	3
Atrazine	20	10	7.9	44.8	2.5
Methyl Parathion	500	243	173	41.6	2.5
DDE	50	9.9	6.8	16.7	5
DDD	50	11.5	7.8	19.3	5
DDT	50	10.8	7.0	17.8	5

Pesticide concentrations are reported in ng/l except for atrazine which is in $\mu\text{g/l}$.

TABLE 17

Recovery Efficiencies of Pesticides
from Haw River Water from Station #4

Pesticide ¹	Amount Added		Amount Recovered		Average % Recovered	
	A	B	A	B	A	B
Diuron	1000	10,000	146	492	15	4.9
Trifluralin ²	100	1000	8.9	36	0	3.6
Atrazine ³	1	10	5.9	4.4	170	2
Methyl Parathion	500	5000	129	641	26	13
DDE	100	1000	9.9	61	9.9	6.1
DDD	100	500	4	38	4	7.6
DDT	50	500	ND	36	0	7.2

¹Pesticide concentrations are in ng/l except for atrazine which is in µg/l.

²Concentration of 10 ng/l in raw water.

³Concentration of 4.2 µg/l in raw water.

TABLE 18

Repeatability Study for Sampling Procedure

Pesticide	Dissolved			Mean and Standard Deviation	Particulate			Mean and Standard Deviation
	A	B	C		A	B	C	
Station 2 January 1975								
Diuron	ND	ND	ND		ND	ND	ND	
Trifluralin	9.7	ND	ND		9.2	9.2	7.5	8.6±1.0
Atrazine	ND	ND	ND		ND	ND	ND	
Methyl parathion	8.8	ND	ND		ND	ND	ND	
DDE	ND	2.2	0.9	1.0±1.1	1.1	1.7	0.7	1.2±0.5
DDD	ND	ND	ND		0.6	0.4	0.6	0.5±0.1
DDT	8.6	ND	ND		6.2	4.2	3.9	4.8±1.2
Station 4 March 1975								
Diuron	ND	ND	ND		ND	ND	ND	
Trifluralin	12.7	9.6	10.1	10.8±1.7	2.7	1.5	1.4	1.9±0.7
Atrazine	2.5	2.5	2.2	2.4±0.2	ND	ND	ND	
Methyl parathion	2.2	ND	ND		0.1	ND	ND	
DDE	1.5	0.2	0.9	0.9±0.7	0.1	0.2	0.2	0.2±0.06
DDD	ND	ND	ND		ND	ND	ND	
DDT	31.4	22.8	29.2	27.8±4.5	6.8	10.0	4.2	7.0±2.9

Pesticide concentrations are in ng/l except for atrazine which is in µg/l.

ND--none detected.

experiment. Again, excluding diuron, the replicates show good agreement. Also included in this table is the correction factors derived from this experiment that were used to calculate pesticide concentrations in the environmental samples.

Table 17 gives the results of another experiment conducted as before, but with water from station 4, a point on the Haw River downstream from a number of municipal and industrial sewage outfalls. In this experiment the pesticide additions were not duplicates. The amounts added were somewhat larger than in the previous additions for most pesticides. The recovery percentages found in this experiment were almost invariably less and usually much less than the other experiments, in most cases well below 40%. The sample with the smaller amount of added pesticide had the higher recovery percentage for four pesticides. The other sample with larger pesticide additions had the higher recovery for the other three pesticides.

Two further tests of the reliability of this new procedure were made by collecting triplicate environmental samples (Table 18). These samples were collected as a part of the regular monitoring program at station 2 in January and station 4 in March. Concentrations of reported pesticides are given for each sample for the dissolved and the particulate fractions. These values were not adjusted with the correction factor for the efficiency of the extraction procedure. The mean and standard deviation is provided where at least two values are given. The repeatability of the replicates is good, except where the reported concentrations are very small. At low levels the particulate replicates are more consistent than are the dissolved replicates. Some of the resin that was used during the late fall and early winter was found to be of questionable cleanliness, so that thereafter only clean, fresh resin was used. This may explain the smaller variation in the March samples than in the January samples.

Gas Chromatographic Data

Identification and quantification of pesticides was by electron capture gas chromatography, which is both a sensitive and rapid analytical method. All seven pesticides could be identified and quantified from a single injection of sample. This is an important consideration in a monitoring program with many samples to analyze.

A chromatogram of a 1 μ l injection of a standard containing all seven pesticides (amounts are given in Table 19) is shown in Figure 6. Separation between peaks is generally good, though the closeness of the diuron peak to the solvent peak can be seen. The tendency of the baseline to drop below its initial level following a peak is illustrated here. This effect prevented use of the automatic digital integrator which requires a steady baseline. Figures 7 and 8 are chromatograms of actual sample extracts. The former is from station 1, the latter from station 4. The first sample contains no identified pesticides, though there are a number of unidentified peaks present. The latter sample contains a much larger amount of unidentified material and two pesticides, trifluralin and DDT. This chromatogram illustrates the difficulty in ascertaining the baseline for purposes of quantitation as well as the difficulty in isolating pesticide peaks from the others.

The electron capture detector varies in response to different compounds. The presence of atoms or functional groups that have an affinity for electrons is the most important determinant. Compounds containing halogens thus generally have the greatest sensitivity. Of the compounds included in this study, trifluralin, which has a trifluoro group and two nitro groups bound to a ring, was detectable with greatest sensitivity. Atrazine, with a single chlorine and two alkyl groups bound to a ring, had the poorest

sensitivity. The other pesticides were of intermediate sensitivity as can be seen from Table 19, which lists smallest mass detectable under the given gas chromatographic conditions.

The retention times for a number of pesticides, given the gas chromatographic conditions cited in Table 10, are listed in Table 20. This list includes five chlorinated insecticides that were not monitored in this study. These insecticides have been widely used and are persistent. The table shows that three of these compounds have retention times close to those of some of the monitored pesticides: lindane and atrazine, dieldrin and DDE, toxaphene and DDD and DDT. This finding suggests that caution has to be used in the identification of these four pesticides.

Minimum detection limits for these seven pesticides are also given in Table 20. These detection limits are not absolute; they are calculated values based on the following assumptions: an initial sample size of 10 liters, a final extract volume of 4 mls, an injection volume of 1 μ l, and a recovery efficiency of 40%. These limits can be lowered by decreasing the final extract volume, increasing the initial sample size of the injection volume, or by improving the extraction efficiency.

Cape Fear River Pesticide Data

Data collected in the monthly monitoring program of the Cape Fear River is given in Figures 9 through 15 in graphic form and Tables B-3 through B-9 in the appendix in tabular form. In the figures the letters at the top indicate the month during which the sample was collected, beginning in July 1974 and ending in June 1975. No sample was collected in October. Solid bars represent dissolved pesticide concentrations (resin extracts); striped bars represent particulate-associated pesticide concentrations (glass wool extracts). For all samples the striped bars are to the left and solid bars

Figure 6. Chromatogram of Pesticide Standard Mixture

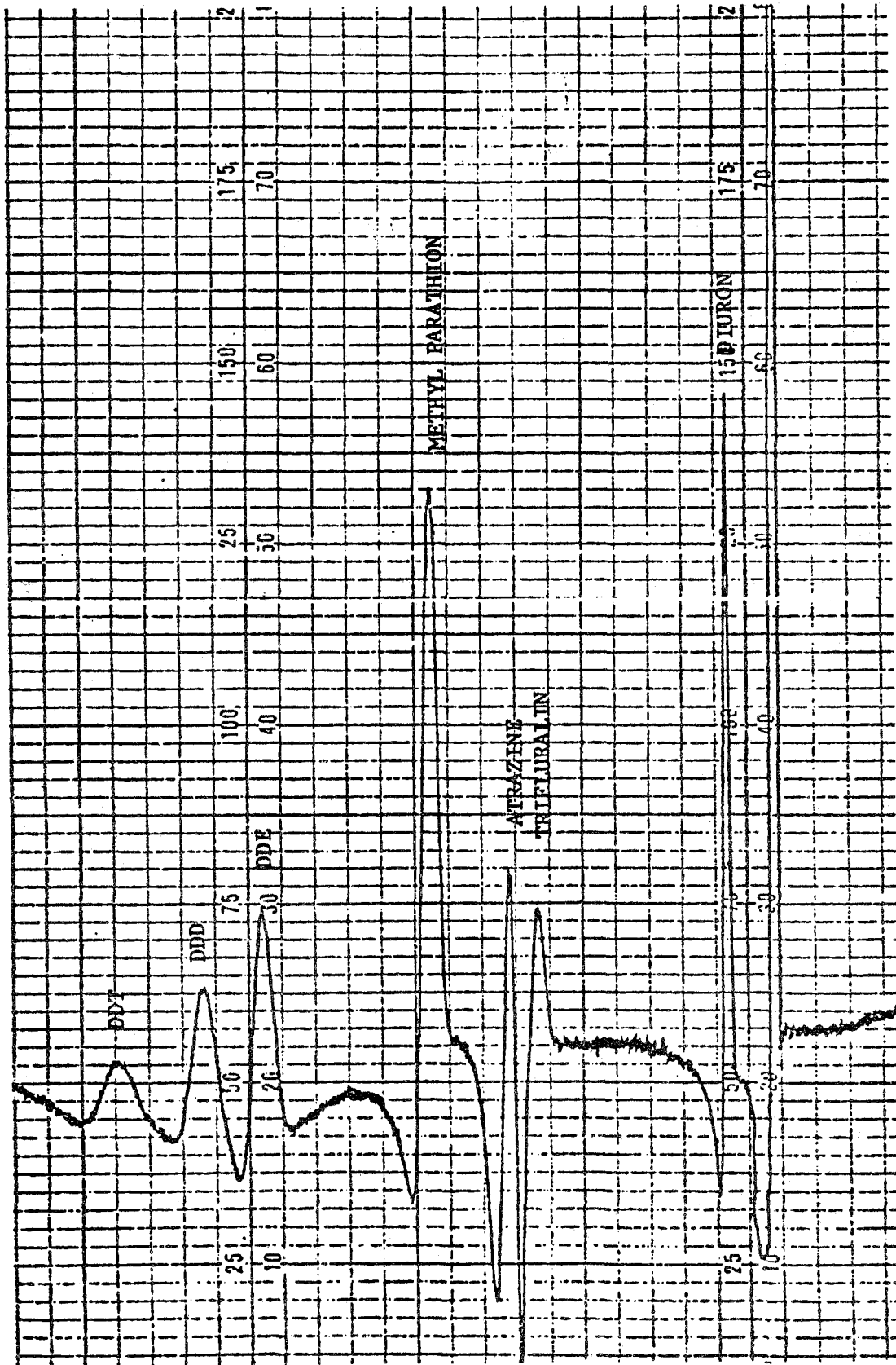


Figure 7. Chromatogram of Resin Extract from Station 1, June 1975

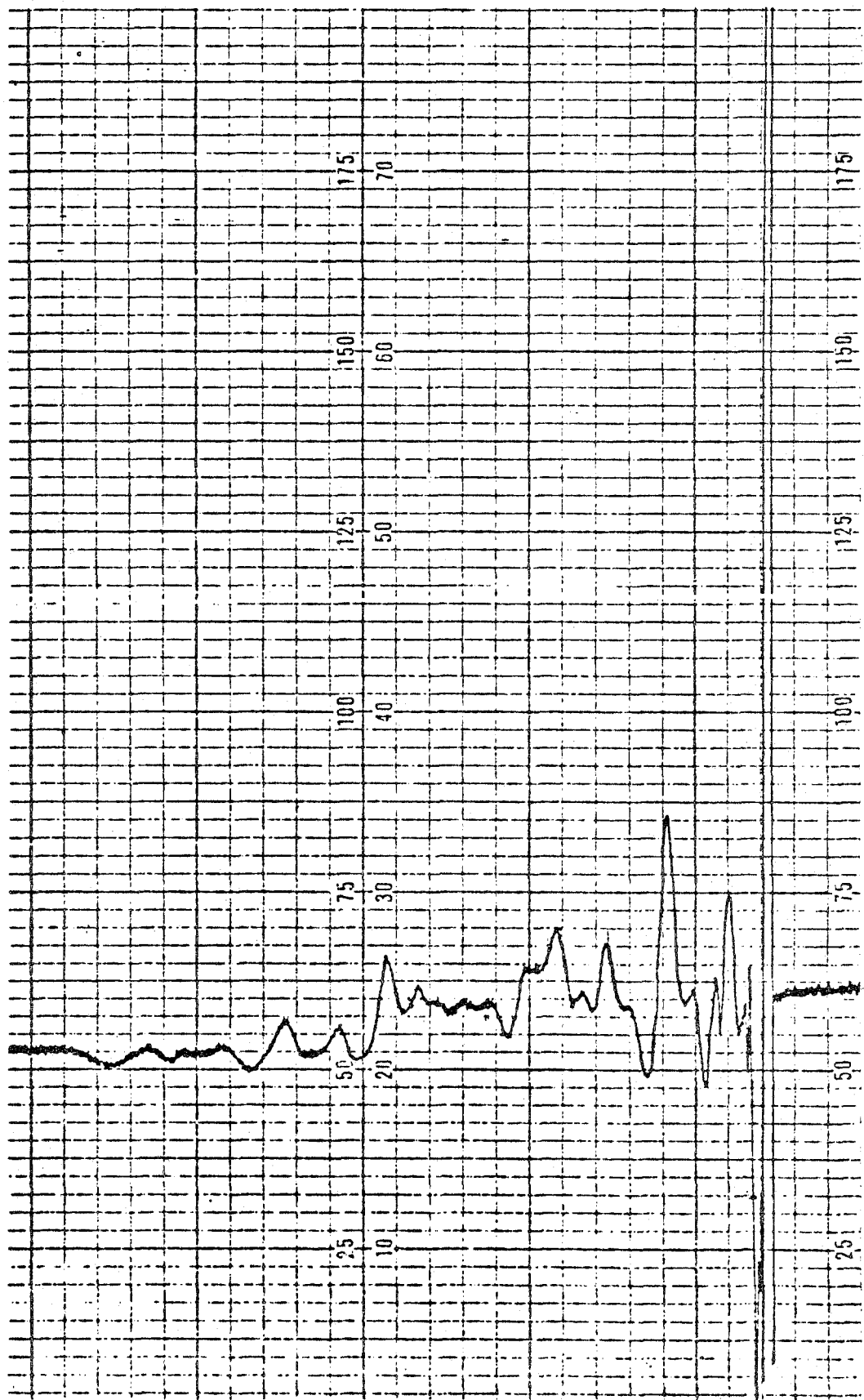


Figure 8. Chromatogram of Resin Extract from Station 4, April 1975

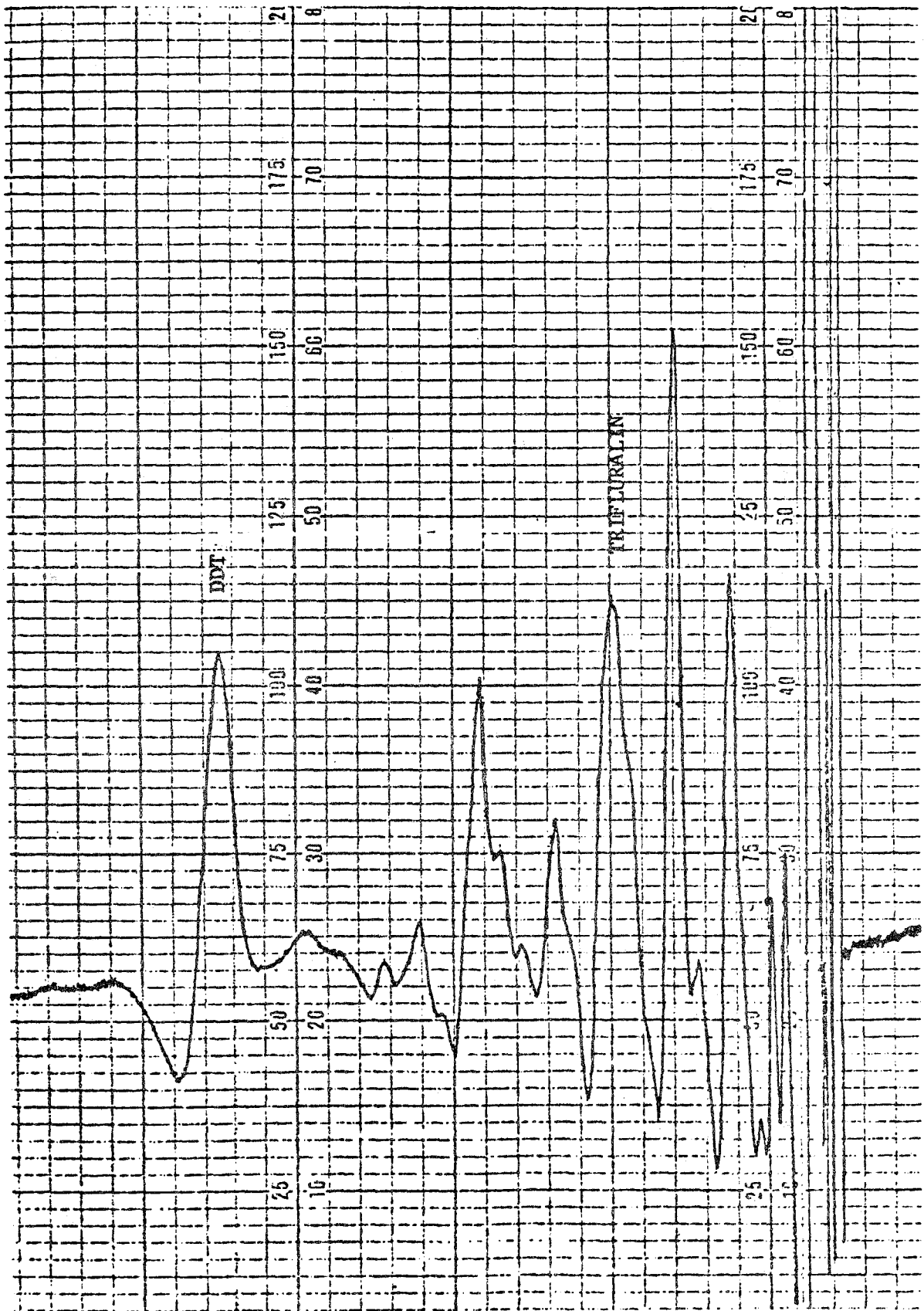


TABLE 19

Electron Capture Detector Sensitivity of Pesticides

	Minimum Detectable Mass	Mass in 1 μ l Pesticide Standard
Diuron	20 pg	1 ng
Trifluralin	1 pg	25 pg
Atrazine	5 ng	20 ng
Methyl Parathion	10 pg	500 pg
DDE	2 pg	50 pg
DDD	10 pg	50 pg
DDT	20 pg	50 pg

TABLE 20

Pesticide Retention Times and Minimum Detectable Limits

Pesticide	Retention Time (seconds)	Minimum Detectable Limits ¹
Diuron	55	20 ng/l
Trifluralin	227	1 ng/l
Lindane	248	---
Atrazine	255	5 µg/l
Methyl parathion	322	10 ng/l
Aldrin	370	---
Chlordane	425 ²	---
Dieldrin	477	---
DDE	490	2 ng/l
Toxaphene	514, 594 ²	---
DDD	530	10 ng/l
DDT	600	20 ng/l

¹See text for method of determination.

²Principal peaks of compounds producing several peaks.

Figure 9. Diuron Concentrations in Cape Fear River

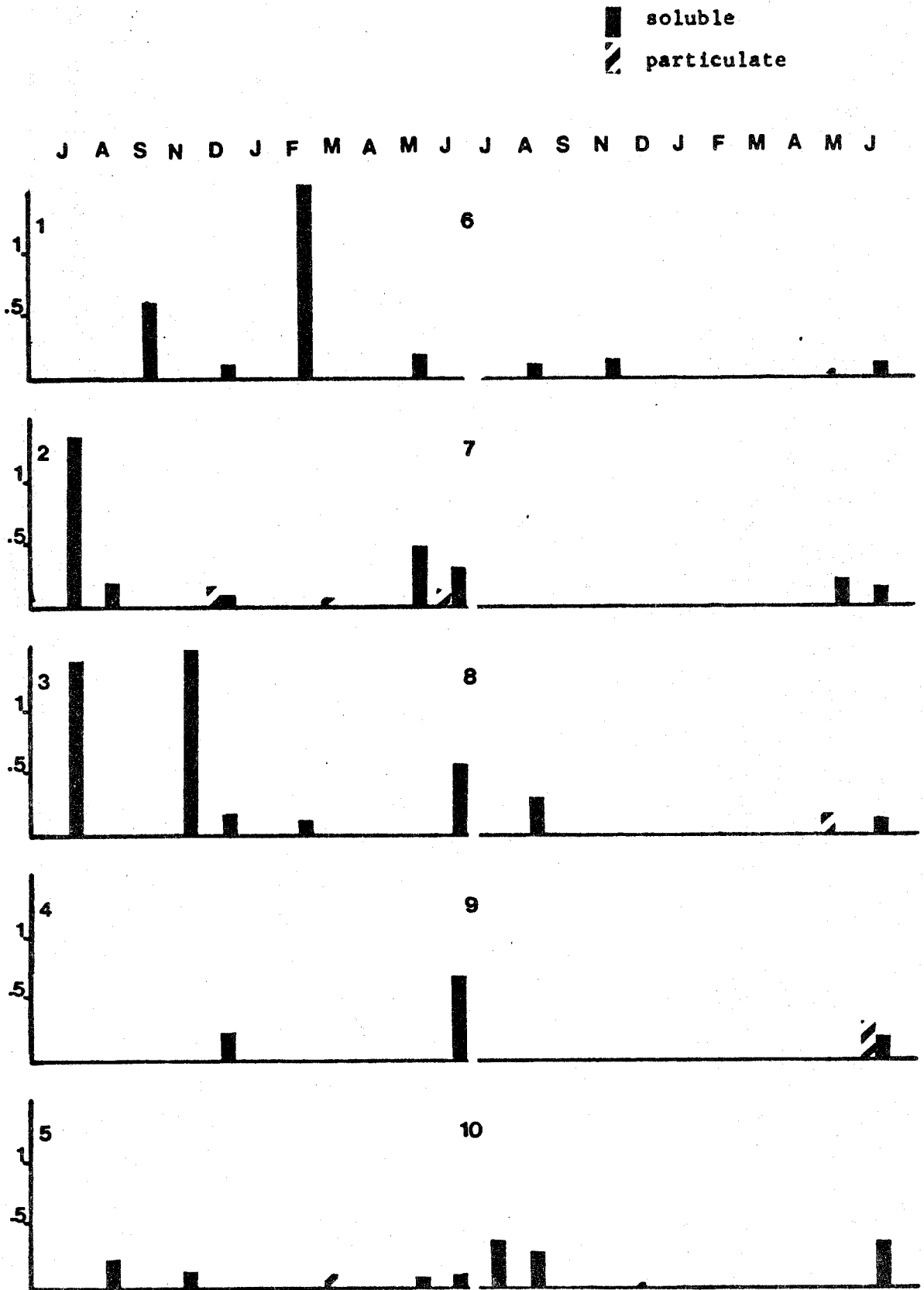


Figure 10. Trifluralin Concentrations in Cape Fear River

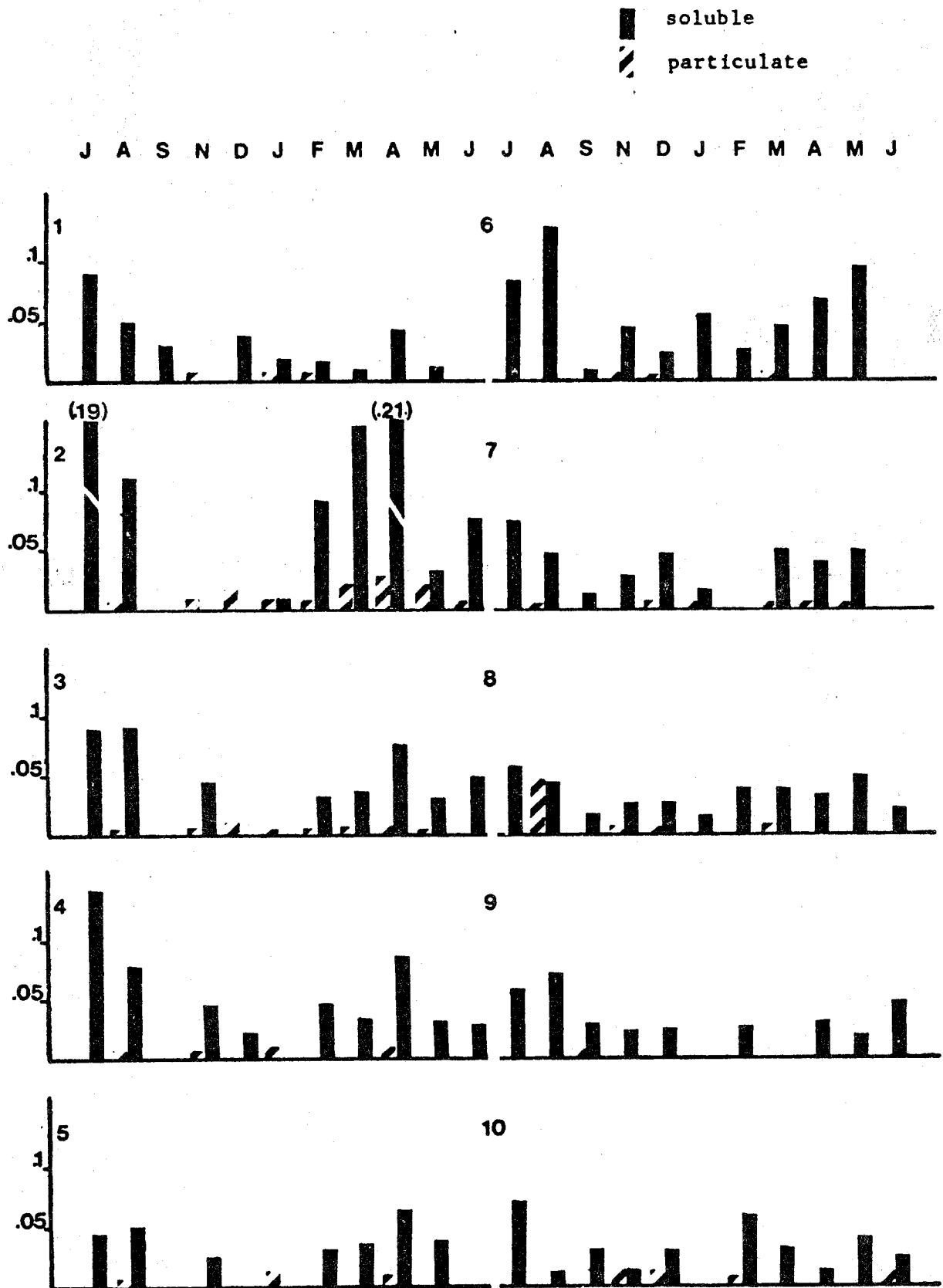


Figure 11. Atrazine Concentrations in Cape Fear River

soluble
 particulate

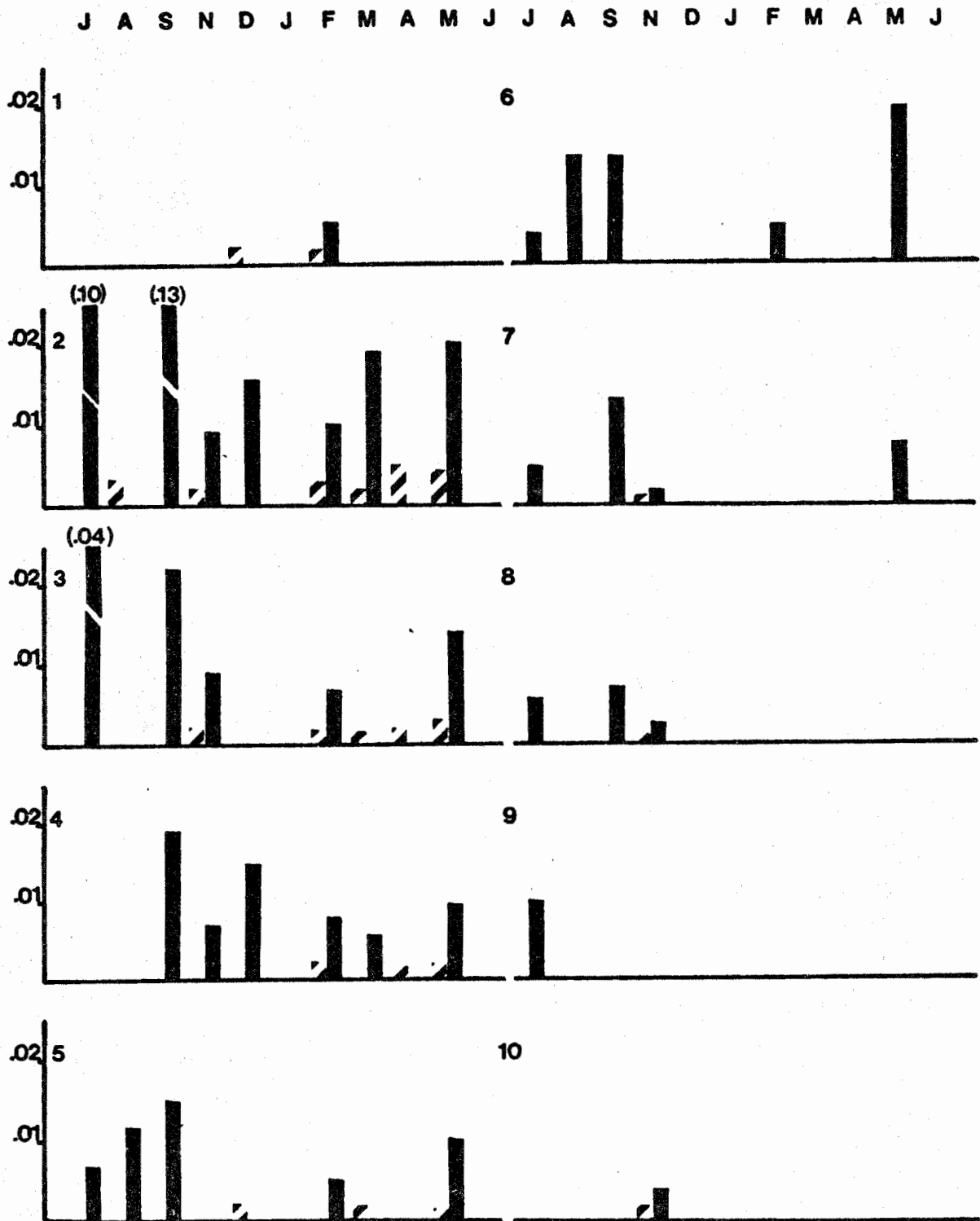


Figure 12. Methyl Parathion Concentrations in Cape Fear River

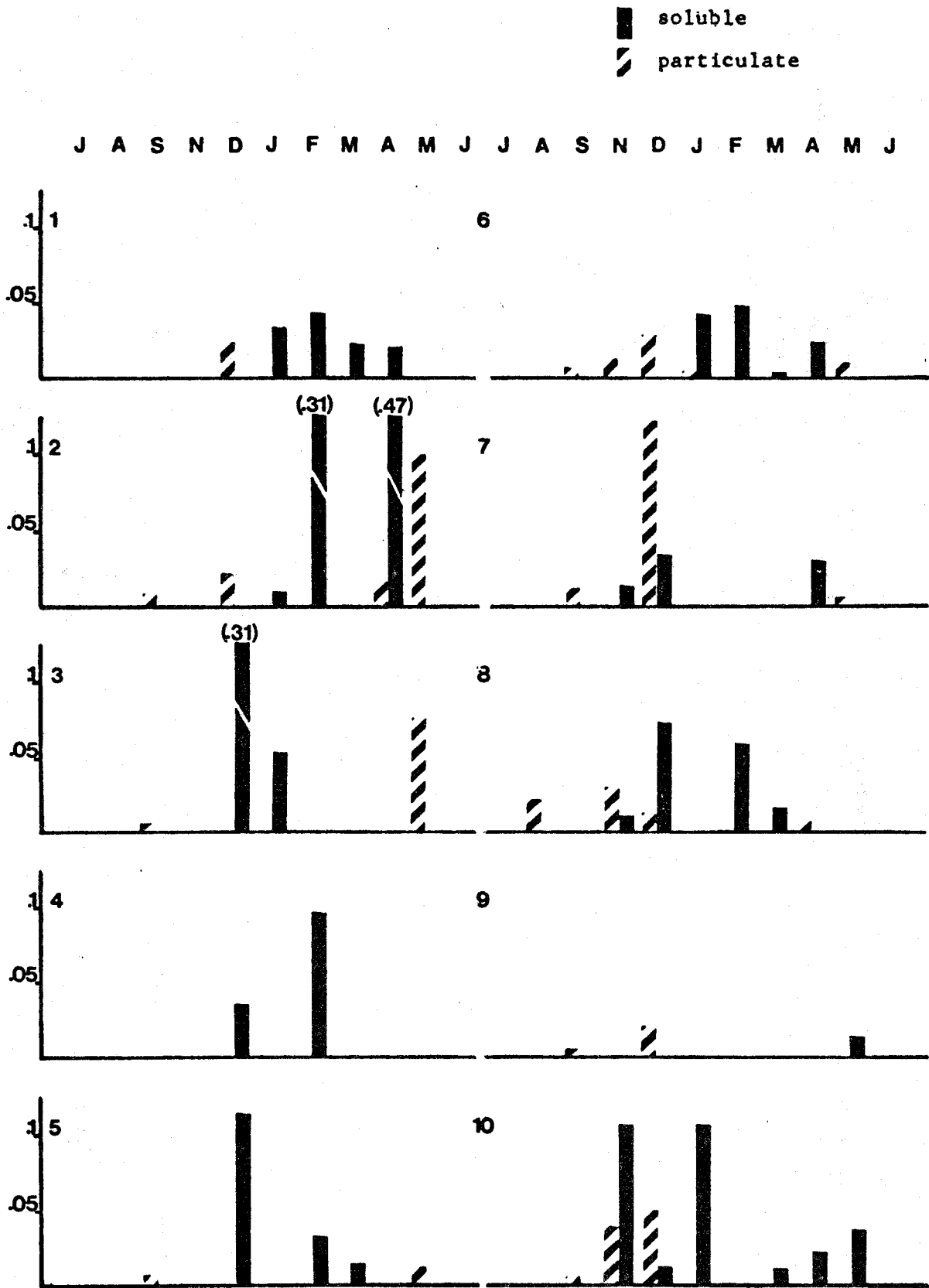


Figure 13. DDE Concentrations in Cape Fear River

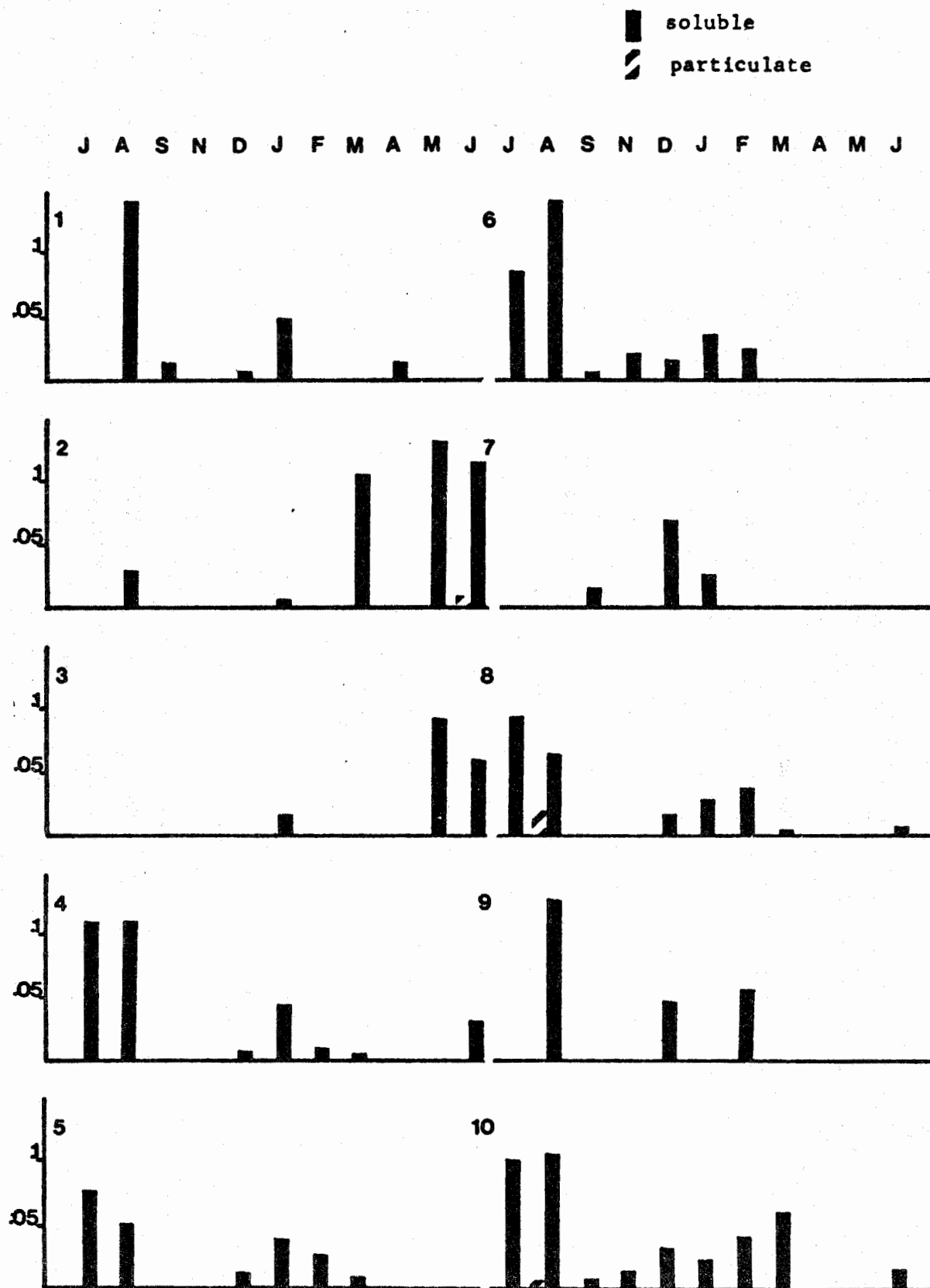


Figure 14. DDD Concentrations in Cape Fear River

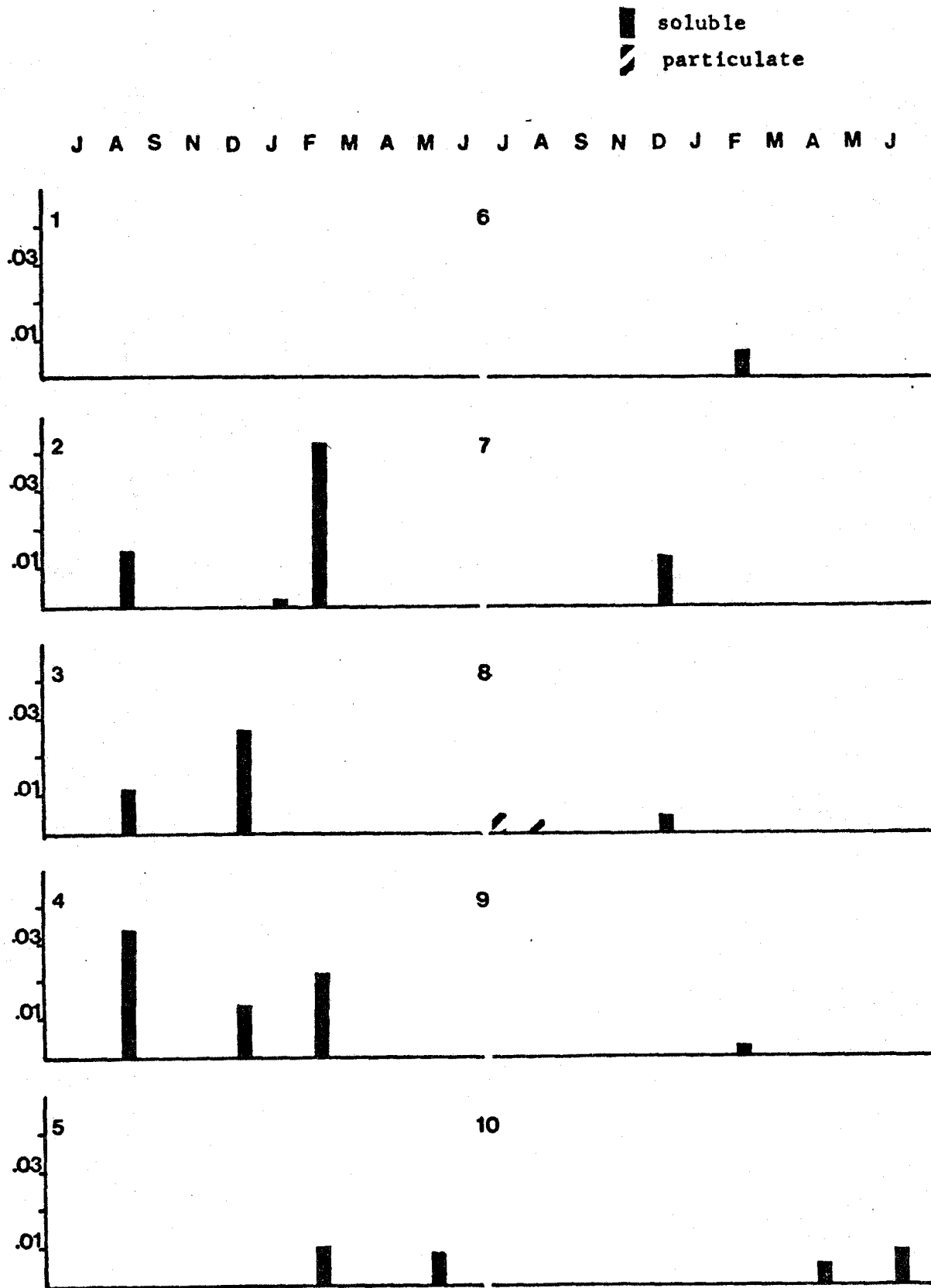
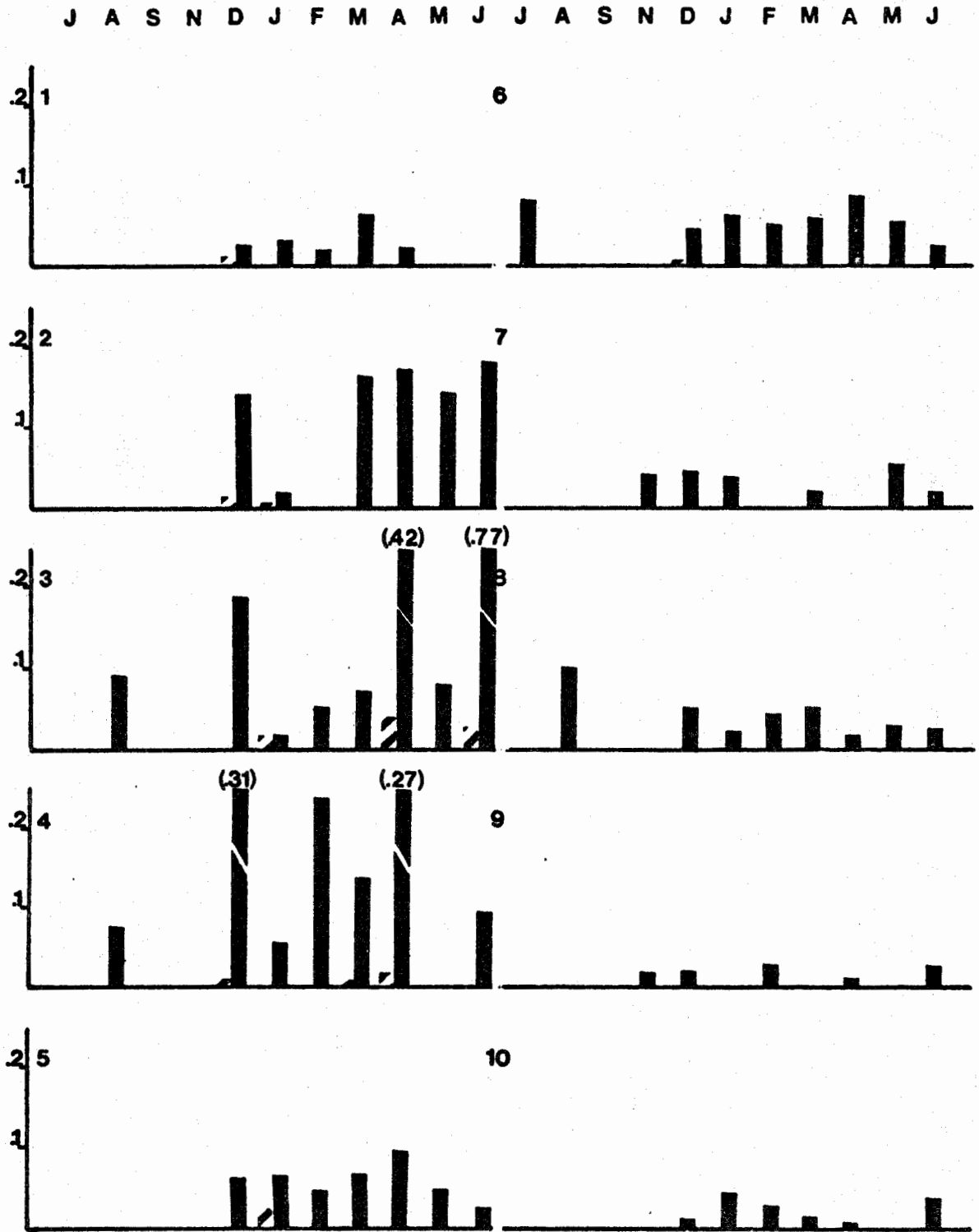


Figure 15. DDT Concentrations in Cape Fear River

soluble
 particulate



to the right. For example in Figure 10 the trifluralin concentrations for station 3 in November are approximately 0.01 $\mu\text{g}/\text{l}$ for the particulate-associated fraction and approximately 0.05 $\mu\text{g}/\text{l}$ for the soluble fraction. The data is presented similarly in the tables. The letter T indicates a trace amount of pesticide, too little to quantify. The letters ND indicate no pesticide was detected in the sample.

In general dissolved pesticide concentrations were larger than the particulate associated concentrations. The dissolved pesticide concentrations exhibited a greater range of values than the particulate-associated. Atrazine had the largest concentrations while DDD had the smallest overall. While there was much variation between sampling stations and sampling times, station 1 had the lowest overall concentration and station 2 the highest. Downstream of station 2, pesticide concentrations generally declined.

From these concentrations and stream flow rates, estimated monthly pesticide transport rates were calculated (Table 21). Mean monthly flow rates were obtained for four stations on the Cape Fear River from U.S. Geological Survey publications (see Table B-2 in appendix). From these data and the total pesticide concentrations for each sample (dissolved and particulate fractions added together), an estimated total quantity of each pesticide that would pass that station in a month was calculated. These monthly values were then grouped according to season: summer consisted of June, July, August and September; winter, November, December, January and February; and spring, March, April and May; and then averaged. A yearly average was also calculated. These data show some of the same characteristics of the calculated. These data show some of the same characteristics of the concentration data upon which they are based. Certain other trends, however, are shown here; for example, the increase in quantity of trifluration

and DDE as one goes downstream.

The frequency with which each pesticide was found in the Cape Fear Basin is given in Table 22. Seasonal groupings are as in Table 21. This percentage represents the number of samples (resin and filter considered as one) in which the pesticide was found. A value of 1.00 indicates the pesticide was identified in all samples (in either dissolved or particulate fraction or both). Trifluralin was found in nearly all samples, DDD and diuron in a few, the others in an intermediate percentage of samples. Several different patterns of seasonal occurrence are shown. These data from the environmental sampling work will be discussed in the following chapter.

TABLE 21

Pesticide Transport Rates in Kilograms per Month

Station	Pesticide	Summer	Winter	Spring	Year
3	Diuron	7.6	9.0	<.1	6.0
5	Diuron	6.4	0.8	14	6.4
7	Diuron	5.0	<.1	17	7.0
9	Diuron	22	<.1	<.1	9.9
3	Trifluralin	1.6	1.1	4.5	2.2
5	Trifluralin	1.8	3.1	11	4.9
7	Trifluralin	4.3	11	25	12.7
9	Trifluralin	14	13	12	13.3
3	Atrazine	596	194	406	398
5	Atrazine	1059	377	679	707
7	Atrazine	1085	58	583	626
9	Atrazine	113	<1	<1	50
3	Methyl parathion	0.1	5.9	1.2	2.5
5	Methyl parathion	0.3	6.3	2.9	3.2
7	Methyl parathion	1.0	17	3.3	6.4
9	Methyl parathion	0.3	2.6	2.1	1.5
3	DDE	0.5	0.5	1.6	0.8
5	DDE	1.8	6.3	1.5	3.4
7	DDE	1.2	15	0.6	5.7
9	DDE	14	15	0.4	11.3
3	DDD	0.1	0.4	<.1	0.2
5	DDD	<.1	0.6	0.3	0.3
7	DDD	<.1	1.3	<.1	0.4
9	DDD	<.1	0.8	<.1	0.3
3	DDT	7.0	4.4	13	7.7
5	DDT	0.5	15	20	11.2
7	DDT	0.7	18	10.9	8.8
9	DDT	2.3	13	3.9	6.2

TABLE 22

Frequency of Pesticide Occurrence in the Cape Fear River

Pesticide	Summer	Winter	Spring	Year
Diuron	.48	.26	.28	.34
Trifluralin	.92	1.00	1.00	.97
Atrazine	.42	.41	.41	.42
Methyl parathion	.22	.64	.72	.51
DDE	.82	.72	.90	.81
DDD	.20	.33	.07	.21
DDT	.42	.77	.86	.67

DISCUSSION

Metals

A 1969 survey of water quality of the Haw River in the area around Greensboro and Burlington indicated significant inputs of Cr, Zn and Cu into the tributaries that feed Buffalo Creek (Water Quality Survey - Haw River Sub-Basin, 1969). Chromium concentrations ranged from 0.01 to 0.16 mg/l. Haynie in a 1974 study found a range of chromium concentrations from none detectable to 0.062 mg/l (mean of 0.021) for water taken from Reedy Fork Creek downstream from the confluence with Buffalo Creek (approximately 15 miles below site 2) (Haynie, 1974). Both of the above sets of data were for unfiltered water. Data in this report shows a range for total dissolved ionic chromium of 0.0062 mg/l to 0.0260 mg/l with a mean of 0.0132 mg/l. The 0.0132 mg/l value is 63% of Haynie's 0.021 mg/l value from 1974. In the Materials and Method section, a preliminary experiment was discussed in which $\text{Cr}^{51}(\text{III})$ was introduced into a natural water sample. Results indicated that 51% to 63% of the Cr(III) spike was subsequently separated with the particulate fraction and 9% to 26% passed through without collection by either column (soluble non-ionic). Curl, Cutshall and Osterbert (1975) reported that Cr^{51} from the Hanford Laboratory Reactor introduced into the Columbia River as $\text{CrO}_4^{=}$ could be removed from river water by cation, anion and chelating resins and membrane filters and that the fraction associated with the particulate gradually increased with distance downstream. They attribute this to the reduction to Cr(III) and adsorption of

Cr(III) on particulates. Combining Cr(VI) industrial waste with domestic sewage could cause the reduction of Cr(VI) to Cr(III) with subsequent adsorption on particulate, or possibly complexation by soluble organics. Although the anionic fraction as indicated by chromium collected by the anionic resin is probably Cr(VI), it is possible that anionic Cr(III) species are also collected. Complexes of Cr(III) in environments of domestic wastes could include chloro-amine complexes which vary in charge from cationic to non-ionic to anionic (Cotton and Wilkinson, 1962). Of the total chromium from the Reedy Fork station (about 15 miles downstream of site 2), Haynie found no sizable soluble chromium fraction (Haynie, 1974). She found detectable soluble chromium on only one occasion on Reedy Fork with a concentration of 7.7 $\mu\text{g/l}$ Cr. This is within the range observed in this report for site 2. Gibbs (1973) found only 10.4% and 12.6% of the total chromium transported by the Amazon and Yukon Rivers was in soluble forms. Soluble ionic chromium concentration decreases between sites 4 and 5. Therefore, it appears that chromium introduced into the stream is rapidly associated with species that are either not soluble or non-ionic and therefore escape detection with the ion exchange technique. The value of the ion exchange technique is to study soluble chromium speciation (anionic and cationic of both Cr(III) and Cr(VI)). It is not as useful for monitoring total chromium since the researcher has no control over chromium speciation in the natural environment (particulate could be measured but the soluble non-ionic species will not be detected).

Chromium pollution is indicated by this data as continuing to exist in the area studied and is most likely related to the textile industry. It was assumed that site 1 received no local point source pollutants. It is also the only site at which no anionic chromium was detected. All other

sites had detectable concentrations of anionic chromium at some time and were subject to chromium inputs from human activity. Thus the presence of detectable quantities of anionic chromium species in this river system suggests anthropogenic sources.

The 1969 survey of the Haw River reported ranges for total metals of 0.03-0.06 mg/l Cu, 0.04-0.24 mg/l Zn and less than 0.1 mg/l Pb for the small creeks that feed into site 2. Gibbs (1973) reported 6.9% and 3.3% of the copper in the Amazon and Yukon Rivers was transported by what he referred to as solution and/or organic complex mechanisms. The range of copper observed in this study, 2.6 $\mu\text{g/l}$ to 10.7 $\mu\text{g/l}$ is 4.3% to 35.6% of the total load range reported in the 1969 survey. Stiff (1971) reported from 11.8% to 57.4% of total copper as soluble in English environmental samples. Using 800 $\mu\text{g/l}$ spikes into filtered polluted fresh water, Stiff (1971) found that less than 2% remained as simple ionic copper and that the remainder partitioned between CuCO_3 , amino acid complexes, inert humic complexes, hexanol extractable and other complexes. Spiking before filtration resulted in a loss of 59.3% of the spike to the particulate fraction. Figure 5 shows elevated copper concentrations near Greensboro and Burlington and subsequent decrease in concentration downstream. This suggests copper reactions similar to those observed by Stiff (1971), either precipitation or complexation. Helz, Huggett and Hill (1975) in a study of Me, Fe, Cu, Zn, Cd and Pb discharged with domestic waste into an estuarine environment found that decreased concentrations, observed with distance from discharge point, could not be accounted for by dilution. The observation was that increasing percentages of the total metal content were associated with the particulate fraction as distance from the outfall increased and it was postulated that adsorption was the removal mechanism (Helz *et al.*, 1975). Gadde and Kaitinen

(1974) studied the adsorption of Pb, Zn, Cd and Tl by hydrous iron and manganese oxides in synthetic solutions and suggested this as an important control mechanism in natural systems. If dilution effects are important in the Cape Fear - Haw River system, it would seem that a negative correlation with flow would be observed. Flow data was obtained from the U.S. Geological Survey and plots of flow vs. concentration did not indicate a correlation between concentration and flow. Pita and Hyne (1975) postulated that the important transport mechanism for zinc and lead was as soluble organo-metallic complexes or ionic solutions with subsequent removal by adsorption on settling particulates during long residence times in a reservoir. Sites 5, 6, 8 and 9 are located in reservoirs on the Cape Fear - Haw River system so the decrease in concentrations through these sites may be due to removal on solids. Therefore, the fate of zinc, lead and cadmium is suggested to be similar to that of copper and chromium. That is, the decrease of concentration with distance as shown in Figure 5 is the result of removal rather than dilution effects.

Minogue (1972) in a 1972-72 study of the Haw River below the Burlington area reported dissolved metal concentrations at site 4 of 22.4 $\mu\text{g/l}$ Cr, 0.4 $\mu\text{g/l}$ Cd, no detectable Pb and 13.5 $\mu\text{g/l}$ Zn. These compare with means of 7.1 $\mu\text{g/l}$ Cr, 0.31 $\mu\text{g/l}$ Cd, 5.6 $\mu\text{g/l}$ Pb and 13.4 $\mu\text{g/l}$ Zn found in this study. Ranges reported that Cd and Zn were approximately equal to those reported here. A higher mean and a broader range of Cr was reported by Minogue (1972), perhaps indicating the importance of the non-ionic soluble species to chromium transport or the improvement of treatment of the textile waste discharged upstream.

Kopp and Kroner (1976) in a study of U.S. rivers report mean dissolved concentrations of 15 $\mu\text{g/l}$ Zn, 7 $\mu\text{g/l}$ Cr and 10 $\mu\text{g/l}$ Cu at the Kerr Dam on

the Roanoke River. Kerr Dan is located in Virginia near the North Carolina state line some 65 miles northeast of Chapel Hill. These values are higher than those reported here for the lower stretches of the Cape Fear and may indicate either a different geochemistry for the area or the importance of non-ionic dissolved species. Assuming that at site 1 the dissolved metal content was due to leaching from the surrounding natural sources, it follows that metal concentrations would remain relatively constant. Examination of Figure 16 shows that this is not the case. With zinc and lead, higher concentrations were often associated with the higher flows although no discernible pattern is evident. As discussed above, Figure 16 does indicate that dilution is not necessarily an important factor in control of metal concentrations. This area has known copper deposits in the head water area of Buffalo Creek (Conley, 1971) and Figure 16 shows that copper does remain relatively constant regardless of flow rate with the exception of one sampling date. Thus, the importance of local geochemistry is shown in the case of copper but the large variations in the concentrations of lead and zinc suggests control on the metal concentration other than local geochemistry. Andelman (1974) has pointed out that concentrations in rain water and surface water are strikingly similar which indicates that they may be related and supports the case for local geochemistry control.

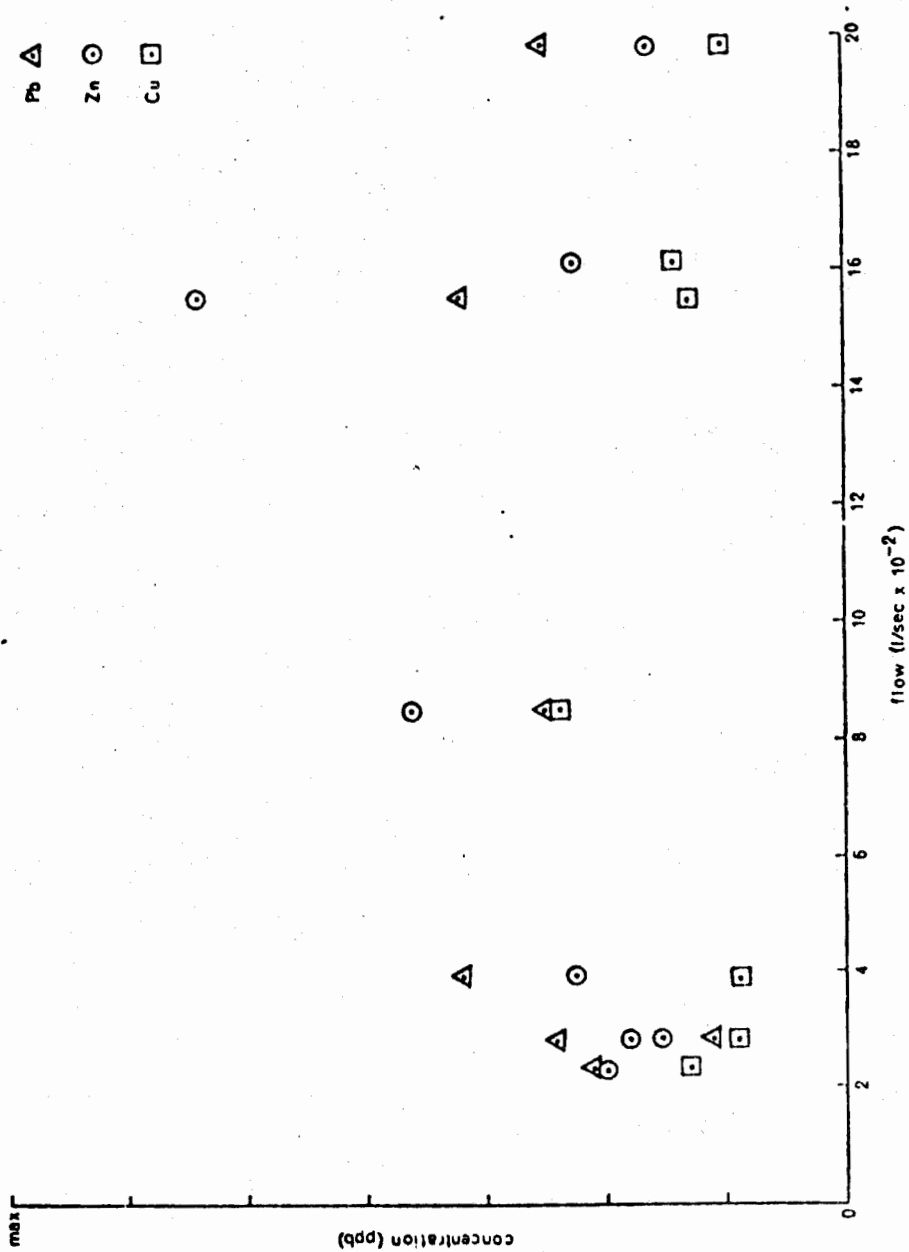
The concentrations of Cd, Pb and Zn in roadside soils have been observed to vary with distance from roadbeds (Lagerwerff and Specht, 1970). Pb in snow and rain has been attributed to the combustion of leaded gasoline (Chow and Johnstone, 1975; LaBarre et al., 1973). Lagerwerff and Specht (1970) attribute Zn and Cd to tires, motor oil and other parts of the automobile. Lazrus, Lorange and Lodge (1970) showed that the pattern of Pb, Zn, and Cu concentrations in rainfall in the U.S. indicated that the source

of these metals was human activity. Koenigshofer (1975) used Zn, Cd, Pb and Cu in rainfall, after 15 min. initial washout of local effects, as a tracer to analyze long range transport and showed that the metal concentrations depending upon the source region of pollution. Ranges observed at a sampling station near Pittsboro, N.C. were less than 5 to 120 g/l Zn, 0.2 to 18.0 $\mu\text{g/l}$ Cd, 12 to 81 $\mu\text{g/l}$ Pb and 3 to 91 $\mu\text{g/l}$ Cu in rainfall from 8 storms (Koenigshofer, 1975). The high Cd, Cu and Pb were all associated with two storms from over an area that has a copper smelter. Colston (1974) in a study of urban runoff found increased metal concentrations as the storm water mixed with the receiving stream followed by a decrease with time indicating a first flush effect. The stream studied was small and the source of the pollutants could be attributed to small areas within the drainage basin. Thus, the high values obtained in the present study may actually result from inputs from urban runoff or storm systems that contain significant metals from sources at great distances from the sample site.

Precipitation data for the region was obtained from the National Oceanic and Atmospheric Administration in an effort to correlate rainfall with high concentrations of lead, zinc and cadmium. No correlations were found. The problem was similar to the attempts to correlate with flow, that is, while in most cases high concentrations occurred following the incidence of rainfall within three to four days previous to sampling dates, low concentrations were also observed after significant rainfall. Colston (1974) plotted metal concentrations and flow against time following the initiation of rainfall. Flow increased with time but metal concentration was observed to first increase, then peak, then decrease even though flow continued to increase in the same time range. Lack of correlation between metal concentrations and amount of rainfall is undoubtedly due to the randomness of

sampling during or following rainfall so that metals were sampled on both sides of their concentration peak.

The broad ranges of concentrations reported here point to the necessity for a monitoring program that will give a more accurate picture than that available by monthly grab samples. The Cape Fear - Haw Rivers are the source of drinking water for some of the municipalities along the system and they feed a small shellfish area around the mouth of the Cape Fear. A 1972 report funded by the Environmental Protection Agency sought to establish criteria for water quality based on recommended characteristics of water for specific uses. From these criteria, a standard was to be recommended based on feasibility of monitoring and/or identification (Water Quality Criteria, 1972). The recommendations for public water supplies and marine aquatic life as relevant to the Cape Fear - Haw River system were 10 $\mu\text{g}/\text{l}$ Cd, 50 $\mu\text{g}/\text{l}$ Cr, 1,000 $\mu\text{g}/\text{l}$ Cu, 50 $\mu\text{g}/\text{l}$ Pb and 5,000 $\mu\text{g}/\text{l}$ Zn for public water supply and 0.2 $\mu\text{g}/\text{l}$ Cd, 50 $\mu\text{g}/\text{l}$ Cr, 10 $\mu\text{g}/\text{l}$ Cu, 10 $\mu\text{g}/\text{l}$ Pb and 20 $\mu\text{g}/\text{l}$ Zn for "minimal risk of deleterious effects." It was further recommended that due to synergistic effects, the presence of copper and/or zinc at 1,000 $\mu\text{g}/\text{l}$ should result in lowering of Cd standard and that levels of less than 10 $\mu\text{g}/\text{l}$ chromium should be maintained in shellfish areas. The data obtained in this study indicates that the maximum recommended concentrations for public water supply are not exceeded except by lead and then only on two occasions. However, this data does not represent total dissolved metal which may be higher. With regard to the minimal risk recommendation, all except copper exceeded these recommendations at one or more points within the area of study. Since the minimal risk recommendations are exceeded by Pb, Zn, Cd and Cr and the recommended public water supply standards are exceeded by Pb, it would appear that a systematic



Max = 7.0 $\mu\text{g/l}$ Pb, 7.0 $\mu\text{g/l}$ Cu, and 28 $\mu\text{g/l}$ Zn

Figure 16. Metal concentrations as a function of flow at site 1.

monitoring program for low level metal concentrations is necessary to assure intelligent use of the Cape Fear River for public water supply and to protect shellfish industry.

Pesticides

XAD-2 Pesticide Procedure

The initial experiments with XAD-2 resin (Table 14) indicate that the resin is a useful tool for isolating organic pesticides from water. This procedure of isolating pesticides with a macroreticular resin is a two step operation. First, the pesticide is adsorbed by the resin from aqueous solution. Secondly, the adsorbed pesticides are desorbed with an appropriate solvent. The first step, trapping of the pesticides by XAD-2, was essentially complete in these six trials. A fast flow rate (approximately 11 bed volumes per minute) was used for this step to decrease sampling time. Elution was generally somewhat less efficient and for toxaphene was very poor. A problem with the elution procedure in which the solvent was poured over the wet resin sometimes developed which may have contributed to the poor elution efficiencies. Elution with a non-polar solvent such as ether following water was a problem because of the immiscibility of the two liquids.

As described previously, a procedure, utilizing XAD-2 as the extractant, followed by elution with diethyl ether, was devised. This method was designed for field extraction of the samples and elution in the laboratory. To facilitate handling and storage, plastic drying tubes were used to make resin columns and glass wool filters. No problem with contamination of the samples from the plastic adsorption of pesticides onto the plastic was observed. Because of the imperfect fit of the drying tube parts, air bubbles

entered the sampling system around the tubes during the extraction operation. Batch-type elution of the resin provided better contact between resin and solvent than was possible with in column elution, eliminating the problem of nonmiscible solvents. Diethyl ether was found by Junk et al. (1974) to elute quantitatively organics from XAD-2 resin. The volatility of ether makes concentration of the elutant easier.

The pesticide recovery rates for this new sampling procedure were lower than those found in the initial experiments. The recovery efficiency averaged 40% overall for the pesticides, as shown in Table 16. This experiment was on extraction of pesticides added to distilled water. This lower efficiency is probably due to the use of a much faster flow rate than in the earlier work -- about 30 bed volumes per minute for this experiment. Flow rates of 5 bed volumes per minute were found to be optimum for extraction of PCB's and DDT (Harvey, 1973) and several chlorophenoxy herbicides (Niederschute and Ballschmiter, 1974) from water by XAD-2 resin. Though the recovery efficiencies for this method are much less than 100%, they are consistent. This is indicated by the generally good agreement between duplicate recovery values and the overall agreement between pesticides. The relatively large variability indicated by diuron is probably due to analytical problems resulting from the short retention time of diuron, causing variability in peak height. If the zero recovery value for DDT in this experiment is neglected, the recovery efficiency for DDT would be 38%. This value is more consistent with the recovery rates of the other pesticides.

The generally lower recovery rates from an environmental water sample, indicated in Table 16, can be best explained as an effect of the presence of colloidal materials in the water. Colloids, such as clay, and particulates

can adsorb pesticides from solution (Hague and Freed, 1974). Adsorbed organics would not be adsorbed by the resin and would pass through the resin. The pesticides with lowest solubilities in water, trifluralin, DDT, DDE and DDD, show this effect more strongly. Humic and fulvic acids found in neutral waters are capable of adsorbing or reacting with pesticides (Wershaw and Goldberg, 1972). The effect of such events would probably be to make the pesticide unavailable to adsorption by a macro-reticular resin.

Another environmental sample to which pesticide additions were made produced even lower recovery efficiencies (Table 17). This water was from station 4 which is downstream of several municipal and industrial effluent outfalls. The water from the river at this site contains many unidentified organic compounds, as indicated in Figure 8, which is a chromatogram of an extract from this site. An analysis of the river by the Federal Water Quality Administration reported 69 mg/l of organic chloride compounds near this site (Water Quality Survey, 1969). The presence of this large amount of organic material may have overloaded the resin so that most of the pesticides were not adsorbed by the resin. Larger bed volumes of resin may be required to overcome this problem. Many of these unidentified compounds may be of interest because of possible deleterious effects to river life or human health.

Repeatability of the field extraction procedure was demonstrated by the agreement between triplicate samples collected at two stations (Table 18). Both filter extract concentrations and resin extract concentrations and resin extract concentrations show good agreement in the March sampling. The January dissolved concentrations are more variable, as a result probably of difficulties with cleaning and handling of the resin noted previously.

A pesticide extraction procedure such as this one reduced or eliminates many of the problems associated with other methods, as noted in the introduction. Since the water sample is extracted in the field, there is no need to transport and store large quantities of water. The risk of contamination or change in the sample is reduced. The small resin columns are easily handled and stored. A larger column than that used in this study is recommended to eliminate the possibility that the resin bed becomes overloaded and adsorption declines. This procedure can relatively easily handle large samples of water. Because of the selectiveness of the resin the need for sample clean-up is reduced. The amount of solvent needed for elution of the resin is small. Thus, less concentration of the solvent will be needed, reducing the time required for this step and the chance of concentrating interferences or contaminants in the solvent. An XAD resin extraction procedure is flexible. The type of resin, the quantity of resin, or the sampling mode can be varied to suit the needs of the investigator. For instance the resin extraction could be adapted to a continuous or composite in situ sampling scheme. These advantages should allow the collection of more samples than would be possible at the same cost with solvent extraction methods.

The proposed method does have problems that must be overcome. The primary problem is the low recovery rates. The reason for this problem needs to be discerned. Poor recovery efficiency may be due to overloading of the resin with organic matter, to poor adsorption of pesticide by the resin due to a high flow rate or some other reason, or to losses during handling, concentration or analysis. With this knowledge steps can be taken to improve efficiency. Additionally, a more effective filtering system needs to be devised.

In summary a monitoring system for pesticides and other organic pollutants utilizing macro-reticular resins, such as XAD-2, has been shown to be useful. Such a method is capable of handling many samples. Further research is needed to increase the recovery efficiency.

Gas Chromatographic Analysis

Electron capture gas chromatography, the method for identification and quantitation of pesticides, is a very sensitive and rapid analytical tool. As a quantitative method it is excellent; however, for qualitative uses it has limitations. Confirmation of pesticide identifications by other methods in addition to chromatographic retention times is essential (McGully, 1971; Guidelines on Analytical Methodology for Pesticide Residue Monitoring, 1975). Because of the very low levels (generally ng/l) of pesticides in these samples, chemical methods such as thin layer chromatography, or paper chromatography were not applicable. The analysis of two composite samples by gas chromatography-mass spectrometry revealed no pesticides. However, this instrument was not equipped with a computerized data base for identification of contaminants and was less sensitive than electron capture gas chromatography.

Further indication of the need for confirmation of pesticide identifications was provided in Table 20. Because of the similar retention times of these other persistent pesticides and the presence of many organic contaminants in the environmental samples, retention time alone is not a sufficient identification method. Particularly with the pesticides eluting before DDE -- diuron, trifluralin, atrazine, and methyl parathion -- the misidentification with other organic contaminants is a possibility.

For monitoring programs such as this in which many samples must be collected and analyzed for a variety of pesticides or other organic contaminants,

gas chromatography-mass spectrometry with a computerized listing of possible contaminants is a powerful method (McGuire et al., 1973). Gas chromatography separates the constituents of the sample and provides quantitative data; the mass spectrometry provides compositional and structural information about the constituents (Roboz, 1973). However, the cost of this capability is quite large for equipment requisition, maintenance is high and highly trained personnel are required.

Cape Fear River Basin Pesticide Survey

The data presented previously (Figures 9 through 15) indicate the presence of pesticides in the Cape Fear River. Pesticide concentrations were generally in the ng/l range, except for atrazine which was in $\mu\text{g/l}$. The concentrations of DDT and its analog, DDE, exceeded Water Quality Criteria 1972 recommended levels for protection of aquatic life in most samples. Recommended criteria for DDT were not exceeded for water supply.

The frequency of pesticide occurrences varied with season (Table 22). Spring and winter were the seasons when pesticides were most often found. Summer had the lowest frequency of occurrence. The transport rates for the various pesticides, which is an estimate of the total amount of pesticide in the river at a given station and time, also tended to be larger in spring and winter (Table 21).

The major pathways by which pesticides enter streams are by rainout of volatilized pesticides, by wind erosion, by application-associated losses, from contaminated ground water and from runoff and soil erosion. (von Rümker et al., 1975). Even though pesticide use is negligible in winter, significant quantities of persistent pesticides may be encountered then, because of the input by erosion and runoff.

Several different seasonal patterns are shown by the data for the different pesticides. DDT was reported in more samples and in greater quantities in spring and winter. This correlates well with runoff, as would be expected because DDT has not been in use in this state since 1972, but is very persistent. Of the two principal degradation products of DDT--DDE and DDD--only DDE was reported in sufficient amounts to discuss seasonal patterns. DDE should have a similar seasonal pattern to DDT because it is derived from DDT, but does not. Diuron and atrazine indicate largest inputs into the river in summer and spring. These herbicides are fairly persistent, but much less so than DDT, about 8 to 10 months in soils (Kearney et al., 1969). Thus diuron and atrazine are found in the largest amounts in spring after application and in summer while large amounts are still found in the soil. Trifluralin is less persistent, disappearing from soils in about 6 months (Kearney et al., 1969). The data indicate significant levels of trifluralin in all seasons, but greatest in spring when its use is heaviest. Because of the strong bonding of trifluralin to soil particles, it apparently can persist into the winter. The data for methyl parathion is probably in error because of identification of an unknown compound with a similar retention time as the insecticide. This pesticide is very rapidly degraded in the environment (von Rümker et al., 1975). In consequence there should be little chance of isolating it in natural water, particularly in winter.

In addition to the seasonal patterns found in the data, there were station-associated patterns. Pesticide concentrations were generally low at Station 1, peaked at Station 2, declined through Station 5 and were fairly low but variable for the remaining stations. The upper portion of the Cape Fear River is in the Piedmont, which is characterized by fairly steep

slopes, clay soils and small streams. The lower part of the Basin is flatter, has sandy soils and larger streams. The concentration of pesticides tends to be higher in the upper Cape Fear samples because there is less water for dilution and erosion is a bigger problem (Pesticide Usage and Its Impact on the Aquatic Environment in the Southeast, 1972). In the lower reaches of the river concentration declines because of dilution and through loss by volatilization or deposition (Gerakis and Sficas, 1974), even though the total quantity of pesticide in the stream is greater.

Station 2, on Buffalo Creek, is downstream of Greensboro's wastewater outfalls. The identification of large amounts of pesticides in samples from this site indicates that Greensboro is a significant source of pesticide contamination or that other contaminants in these highly contaminated waters were identified as pesticides. The input into the river systems from this tributary was gradually diluted in Stations 3, 4 and 5.

The data in Table 21 indicate that the total mass of pesticide in the river generally increased downstream as the flow of the river increases. Trifluralin and DDE exhibit this trend best indicating inputs along the river. Atrazine shows a sharp drop in quantity at Station 9. The major source of atrazine is apparently above Station 7. Below this point atrazine is apparently lost through the processes of volatilization or deposition. Diuron, DDD and DDT are roughly constant in total mass of pesticide at all four sites. Most input of these compounds must be at the upper end of the basin with little loss downstream. Or perhaps losses along the river are equal to inputs so that the total amount of the pesticide in the stream at any point remains essentially the same.

In essentially all samples the concentration of pesticide in the dissolved fraction (resin extract) was much greater than the particulate-associated

fraction (glass wool filter extract). The effectiveness of the glass wool filters at trapping particulates was not known, nor the efficiency of the extraction procedure. Because the filters clearly did not trap all of the particulate matter, the concentrations reported for the particulate-associated fraction are certainly conservative. No correction was applied to these numbers. Many pesticides strongly adhere to particulate and colloidal material in water so that a larger percentage of the pesticides in water may be in this form. For a better understanding of the movement and impact of pesticides in the aquatic environment, more data on this fraction of pesticides is needed.

Recommended limits for diuron (1.6 $\mu\text{g}/\text{l}$) and DDT (2 ng/l) in water were established for protection of aquatic life (Water Quality Criteria 1972). Diuron concentrations in four samples approached the limit, but did not exceed it. Most samples contained no detectable quantity of diuron. The concentration of DDT as well as DDE were usually in excess of the recommended limit. As DDT is no longer in use in this country in significant quantities these concentrations should gradually decline. No criteria were given for the other pesticides studied. The concentrations of all of these except atrazine were low -- a maximum of 210 ng/l of trifluralin and 470 ng/l of methyl parathion. In view of these findings the Cape Fear River should be monitored for the presence of pesticides and other organic contaminants.

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APPENDIX A

TABLE A-1
Sampling Dates

Date	Stations 1-6	Stations 7-10
July 1974	19	20
August 1974	19	20
September 1974	21	22
November 1974	22	24
December 1974	17	18
January 1975	25	26
February 1975	22	23
March 1975	21	22
April 1975	11	12
May 1975	12	13
June 1975	13	14

TABLE A-2

Mean Monthly Flow Rates for Cape Fear River
(liters per second)

		Stations			
		3	5	7	9
1974	July	4,021	11,583	23,676	44,831
	August	16,539	37,609	64,343	158,649
	September	34,862	72,811	120,587	171,138
	November	4,956	12,687	19,088	50,551
	December	21,098	60,776	114,243	165,332
1975	January	47,861	169,014	348,336	444,907
	February	28,575	92,068	195,946	317,750
	March	78,276	194,558	390,533	479,458
	April	16,992	69,696	116,650	186,034
	May	18,380	47,578	90,029	119,454
	June	11,583	28,801	52,165	81,505

Stations	U.S.G.S. Station Numbers
3	02096500
5	02098200
7	02102500
9	02105500

Source: Water Resources Data for North Carolina, Part I, Surface Water Records, Water Year 1974, U.S.G.S., Raleigh, N.C., 1975, and Water Resources Data for North Carolina, Water Year 1975, U.S.G.S., Raleigh, N.C., 1976.

TABLE A-3
Diuron Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fraction</u>											
1	ND	ND	591	ND	96	ND	1530	ND	ND	165	ND
2	1350	180	ND	ND	99	ND	ND	↓	↓	444	294
3	1365	ND	↓	1482	177	ND	99	↓	↓	ND	540
4	ND	ND	↓	ND	225	↓	ND	↓	↓	ND	693
5	↓	192	↓	90	ND	↓	↓	↓	↓	66	90
6	↓	105	↓	153	↓	↓	↓	↓	↓	ND	108
7	↓	ND	↓	ND	↓	↓	--	↓	↓	213	147
8	↓	282	↓	↓	↓	↓	ND	↓	↓	ND	99
9	↓	ND	↓	↓	↓	--	↓	--	↓	↓	168
10	327	270	↓	↓	↓	ND	↓	ND	↓	↓	348
<u>Particulate-Associated Fraction</u>											
1	ND	--	--	ND	ND	ND	ND	ND	ND	ND	19
2	↓	ND	ND	↓	152	↓	↓	59	↓	26	107
3	↓	↓	↓	↓	ND	↓	↓	ND	↓	ND	ND
4	↓	↓	↓	↓	↓	↓	↓	ND	↓	ND	ND
5	↓	↓	↓	↓	↓	↓	↓	67	↓	↓	↓
6	↓	↓	↓	↓	↓	↓	↓	ND	↓	35	↓
7	↓	↓	↓	↓	↓	↓	↓	↓	↓	ND	↓
8	↓	↓	↓	↓	↓	↓	↓	↓	↓	127	↓
9	↓	↓	↓	↓	↓	--	↓	--	↓	ND	252
10	↓	↓	↓	↓	24	ND	↓	ND	↓	ND	ND

116

ND--none detected
-- no sample

TABLE A-4
Trifluralin Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fraction</u>											
1	85	46	25	ND	34	20	19	8.1	40	19	ND
2	193	103	ND	↓	ND	9.6*	85	146	206	28	68
3	85	88	↓	40	↓	ND	29	34	71	29	46
4	140	76	↓	43	23	↓	46	32*	83	30	28
5	45	49	↓	28	ND	↓	28	34	61	36	ND
6	82	122	11	44	25	53	27	42	66	91	↓
7	69	44	11	27	43	13	--	45	37	46	↓
8	56	42	16	26	28	16	38	39	33	48	23
9	56	67	28	22	22	--	26	--	31	19	47
10	67	12	31	21	30	ND	58	31	14	38	23
<u>Particulate-Associated Fraction</u>											
1	2.6	--	--	4.0	2.3	7.1	2.3	1.3	2.3	2.2	T
2	2.4	4.8	ND	11	15	8.6*	9.6	21	26	20	8.0
3	ND	4.8	1.2	6.4	11	5.4	5.4	7.8	8.3	5.1	3.8
4	↓	7.2	3.0	6.7	4.6	9.7	4.7	1.9*	11	1.7	2.5
5	2.4	7.0	ND	ND	1.9	9.0	2.0	T	7.5	4.1	1.5
6	2.0	2.9	↓	6.4	7.2	4.7	1.2	6.2	4.9	3.4	2.5
7	3.0	4.8	3.0	4.4	7.6	5.6	2.6	5.7	6.0	5.0	2.0
8	ND	46	1.5	5.1	7.9	2.3	4.3	7.9	5.5	4.0	2.6
9	↓	ND	1.8	5.5	4.3	--	3.7	--	1.1	5.5	2.0
10	1.2	4.3	3.8	12	14	1.7	8.5	3.3	3.8	3.5	10

ND--none detected

T--trace

*average of three samples

-- no sample

TABLE A-5

Atrazine Concentrations (µg/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fraction</u>											
1	ND	ND	ND	ND	ND	ND	5.5	ND	ND	ND	ND
2	99	↓	131	9	16	↓	10	19	↓	20	↓
3	38	↓	22	8.8	ND	↓	7.0	ND	↓	14	↓
4	ND	↓	19	6.8	15	↓	7.8	6.0*	↓	10	↓
5	7.8	12	15	ND	ND	↓	5.0	ND	↓	9.8	↓
6	4.5	14	14	ND	ND	↓	4.8	ND	↓	20	↓
7	4.5	ND	13	2.2	↓	↓	--	↓	↓	7.5	↓
8	5.8	↓	7	2.8	↓	↓	ND	↓	↓	ND	↓
9	9.8	↓	ND	ND	↓	↓	↓	↓	↓	↓	↓
10	ND	↓	↓	3.8	↓	ND	↓	ND	↓	↓	↓
<u>Particulate-Associated Fraction</u>											
1	ND	--	--	ND	2.1	ND	1.8	ND	ND	ND	ND
2	↓	2.8	ND	1.7	ND	↓	2.5	1.4	5.2	4.8	↓
3	↓	ND	↓	1.9	↓	↓	1.6	1.6	2.1	2.8	↓
4	↓	↓	↓	ND	↓	↓	1.6	ND	1.4	2.0	↓
5	↓	↓	↓	↓	2.0	↓	ND	1.4	ND	1.0	↓
6	↓	↓	↓	↓	ND	↓	↓	ND	↓	ND	↓
7	↓	↓	↓	1.3	↓	↓	↓	↓	↓	T	↓
8	↓	↓	↓	1.4	↓	↓	↓	↓	↓	ND	↓
9	↓	↓	↓	ND	↓	↓	↓	↓	↓	↓	↓
10	↓	↓	↓	1.3	↓	ND	↓	ND	↓	↓	↓

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ND--none detected
 T--trace
 *average of three samples
 -- no sample

TABLE A-6

Methyl Parathion Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fractions</u>											
1	ND	ND	ND	ND	ND	32	42	21	19	ND	ND
2	↓	↓	↓	↓	↓	7.2*	312	ND	468	↓	↓
3	↓	↓	↓	↓	312	52	ND	ND	ND	↓	↓
4	↓	↓	↓	↓	32	ND	95	T	↓	↓	↓
5	↓	↓	↓	↓	112	↓	32	14	↓	↓	↓
6	↓	↓	↓	↓	ND	41	48	T	24	↓	↓
7	↓	↓	↓	12	42	ND	—	ND	30	↓	↓
8	↓	↓	↓	9.2	72	↓	58	16	ND	↓	↓
9	↓	↓	↓	ND	ND	↓	ND	↓	↓	12	↓
10	↓	↓	↓	105	12	105	↓	9.2	22	35	↓
<u>Particulate-Associated Fractions</u>											
1	ND	--	--	ND	22	ND	T	ND	ND	T	ND
2	↓	ND	ND	↓	19	↓	ND	↓	13	97	↓
3	↓	↓	6.0	↓	ND	↓	↓	↓	ND	75	↓
4	↓	↓	ND	↓	↓	↓	↓	↓	↓	ND	↓
5	↓	↓	6.5	↓	↓	↓	↓	↓	↓	12	↓
6	↓	T	4.7	11	29	3.7	↓	↓	↓	9.4	↓
7	↓	T	12	T	123	ND	↓	↓	↓	3.2	↓
8	↓	22	ND	31	12	↓	↓	↓	6.4	ND	↓
9	↓	ND	2.6	ND	18	—	↓	—	T	↓	↓
10	↓	↓	3.8	37	48	ND	↓	ND	ND	↓	↓

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ND--none detected
 T--trace
 *average of three samples
 -- no sample

TABLE A-7
DDE Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fraction</u>											
1	ND	140	11	ND	8.5	46	3.5	ND	14	3.5	ND
2	↓	28	1.0	↓	ND	5.0*	ND	100	ND	130	115
3	↓	5.0	ND	↓	↓	16	↓	ND	↓	95	60
4	110	110	↓	↓	8.5	45	10	4.5*	↓	ND	32
5	75	50	↓	↓	11	38	23	8.5	↓	↓	ND
6	85	140	6.0	20	16	36	26	ND	↓	↓	↓
7	ND	ND	15	ND	70	26	--	1.0	↓	↓	1.0
8	95	65	2.0	↓	20	29	40	4.0	↓	↓	7.5
9	ND	130	3.5	↓	50	--	28	--	↓	↓	ND
10	100	105	7.5	15	34	24	41	60	↓	↓	16
<u>Particulate-Associated Fraction</u>											
1	ND	--	--	ND	2	1.1	ND	ND	0.8	T	ND
2	↓	ND	ND	↓	ND	1.2*	↓	0.7	1.3	ND	3.6
3	↓	ND	ND	↓	ND	1.1	T	0.7	4.2	↓	3.7
4	↓		ND	↓	↓	0.9	ND	T	T	↓	0.6
5	1.1		T	↓	1.2	2.3	0.9	T	0.6	T	0.9
6	0.7	2.4	ND	↓	ND	1.6	ND	0.6	1.5	0.5	ND
7	ND	0.7	↓	↓	T	T	↓	T	1.0	0.9	↓
8	ND	22	↓	2.2	ND	1.2	↓	T	1.4	1.0	0.5
9	T	1.2	T	ND	1.1	--	↓	--	1.0	0.5	2.4
10	ND	3.6	ND	↓	T	0.5	↓	T	ND	T	1.8

ND--none detected

T--trace

*--average of three samples

-- no sample

TABLE A-8
DDD Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J	
	<u>Dissolved Fraction</u>											
1	ND	ND	ND	ND	T	ND	ND	ND	ND	ND	ND	ND
2		14			ND	T	43					
3		11			27	ND	ND					
4		3.4			13		22			8.5		
5		ND			ND		10			ND		
6					↓ 13		6.5					
7					T		--					
8					ND		ND					
9					↓		T					
10							ND					8.5
	<u>Particulate-Associated Fraction</u>											
1	ND	--	--	ND	T	ND	ND	ND	ND	ND	ND	ND
2		ND	ND		T	T	ND					T
3					ND	ND						ND
4												
5												
6												
7					↓							
8		4.2			T							
9		ND			T							
10		T			ND							T

ND--none detectable
T--trace
-- no sample

TABLE A-9
DDT Concentrations (ng/l)

Station	J	A	S	N	D	J	F	M	A	M	J
<u>Dissolved Fraction</u>											
1	ND	ND	ND	ND	24	30	22	60	20	ND	ND
2	↓	↓	↓	↓	140	14*	ND	160	170	140	180
3	↓	90	↓	↓	185	14	50	70	415	80	770
4	↓	75	↓	↓	310	55	240	140*	270	ND	95
5	↓	ND	↓	↓	60	65	48	70	95	48	27
6	80	↓	↓	↓	43	60	47	60	85	55	24
7	ND	↓	↓	↓	38	38	--	20	ND	55	21
8	↓	100	↓	↓	ND	21	43	50	18	29	26
9	↓	ND	↓	↓	18	--	31	--	15	ND	28
10	↓	↓	↓	↓	ND	45	32	18	5.5	↓	39
<u>Particulate-Associated Fraction</u>											
1	ND	--	--	ND	9.9	ND	ND	3.8	T	T	ND
2	↓	ND	T	↓	9.9	T	↓	ND	ND	ND	↓
3	↓	↓	ND	↓	5.6	13	↓	6.5	36	↓	26
4	↓	↓	↓	↓	9.5	ND	↓	7.0*	18	↓	ND
5	↓	↓	↓	↓	5.2	26	↓	ND	6.2	T	↓
6	↓	T	↓	↓	7.8	6.0	T	T	T	ND	↓
7	↓	ND	↓	↓	T	T	ND	ND	ND	↓	↓
8	↓	↓	↓	↓	5.6	ND	↓	↓	ND	↓	↓
9	↓	5.9	↓	↓	T	--	↓	--	T	↓	T
10	↓	T	↓	T	6.1	ND	↓	T	ND	↓	6.7

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ND--none detected
T--trace
*average of three samples
-- no sample

Figure A-1. Duxon Calibration Curve

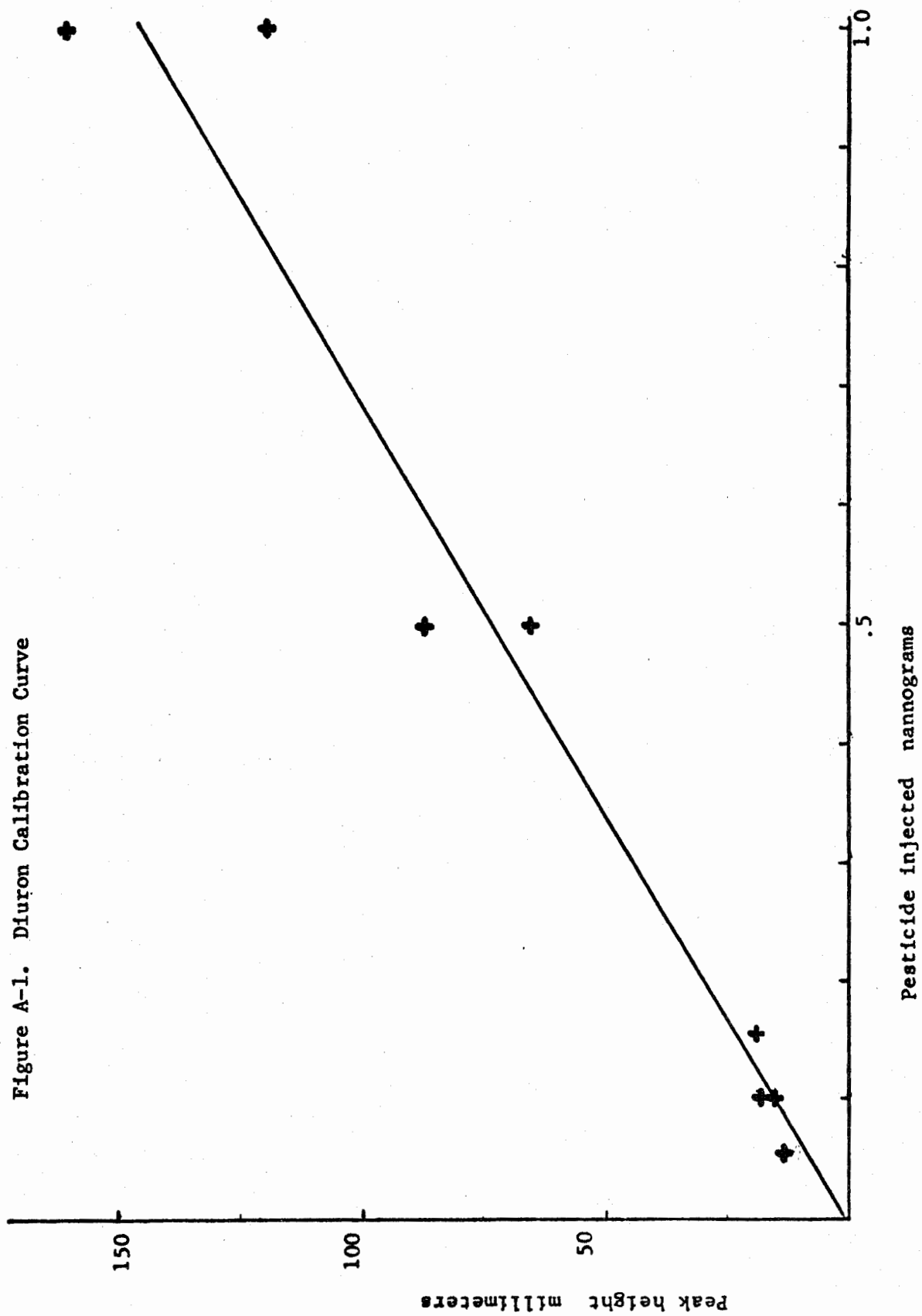


Figure A-2. Trifluralin Calibration Curve

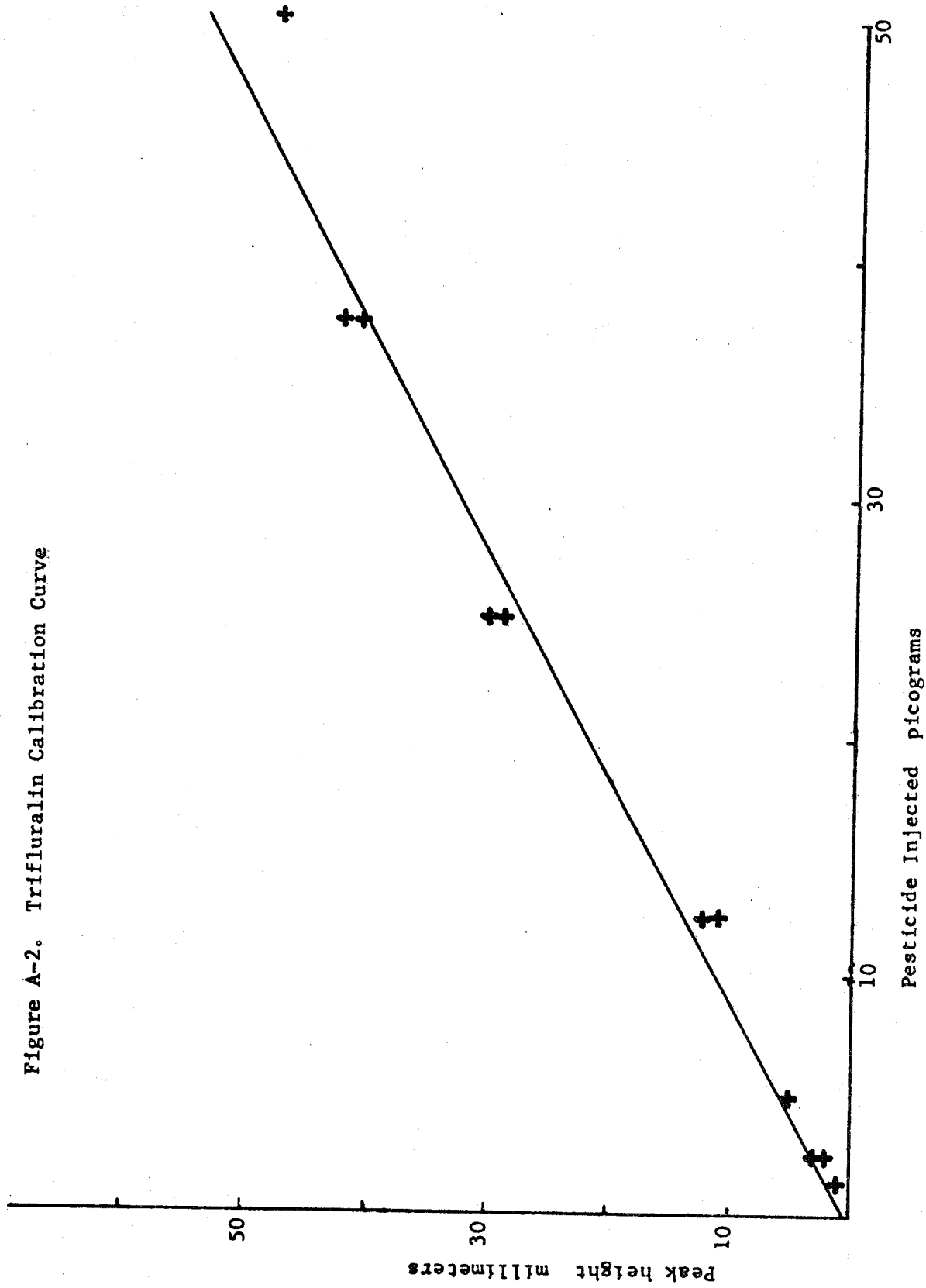


Figure A-3. Atrazine Calibration Curve

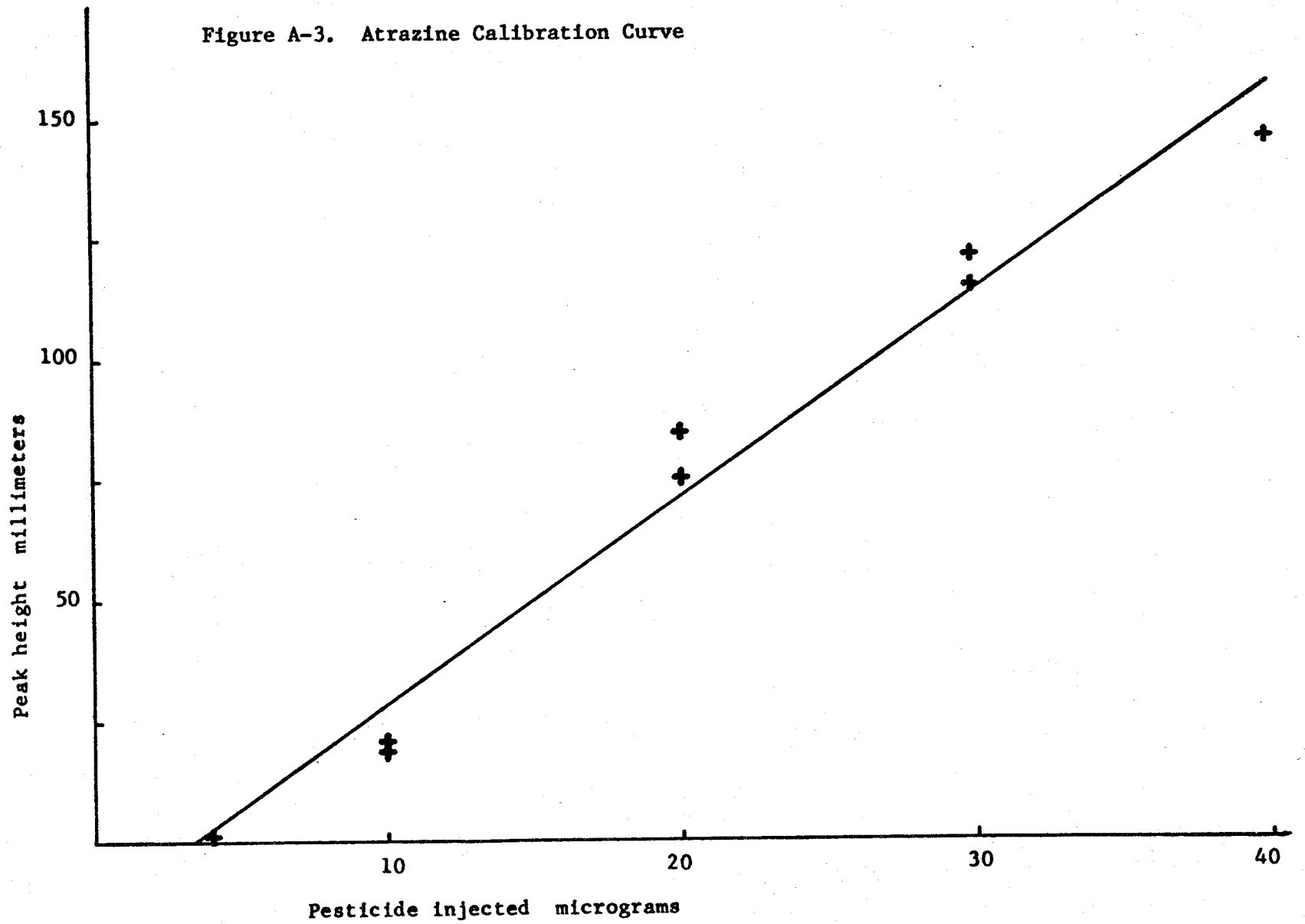


Figure A-4. Methyl Parathion Calibration Curve

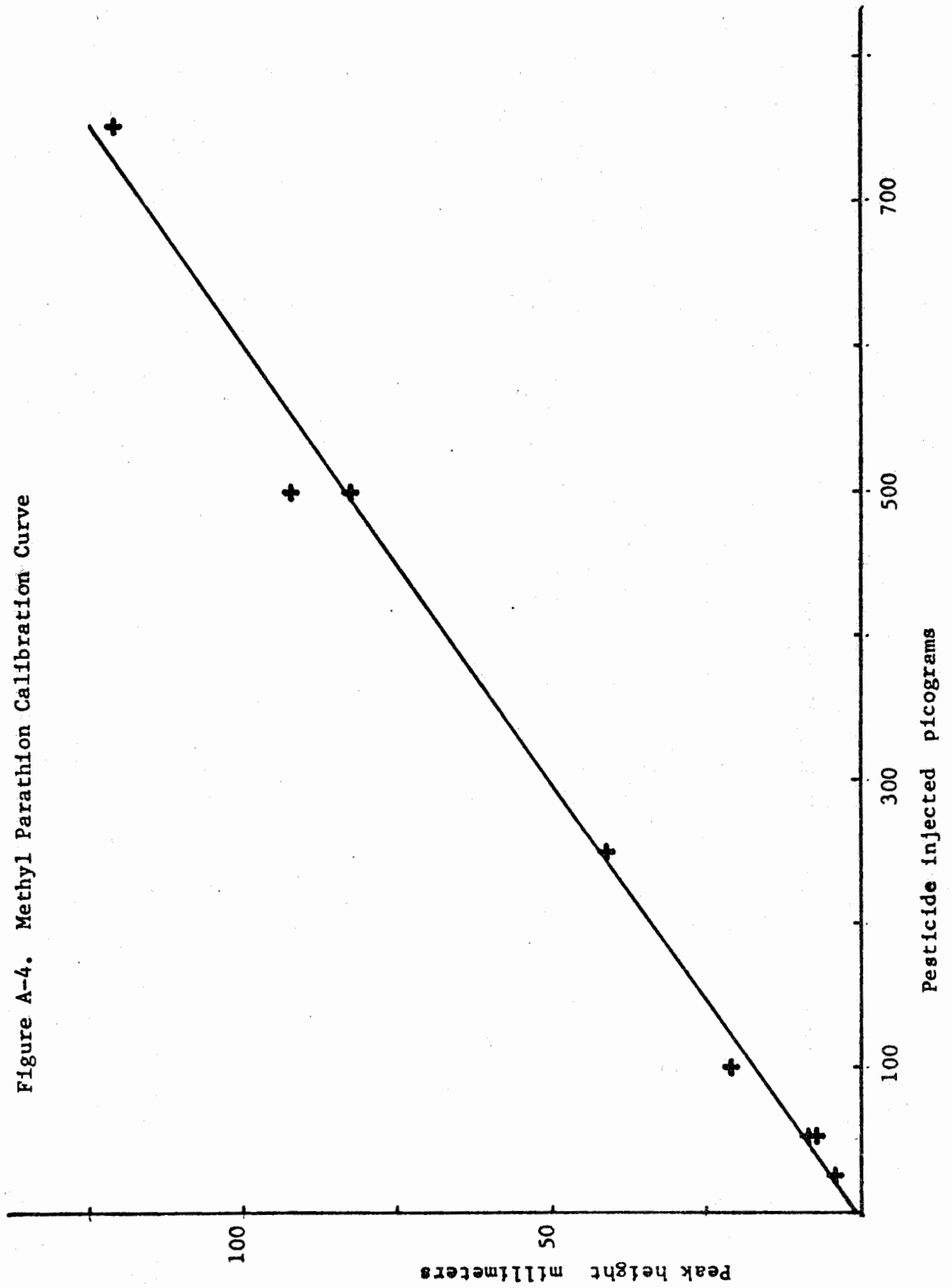


Figure A-5. DDE Calibration Curve

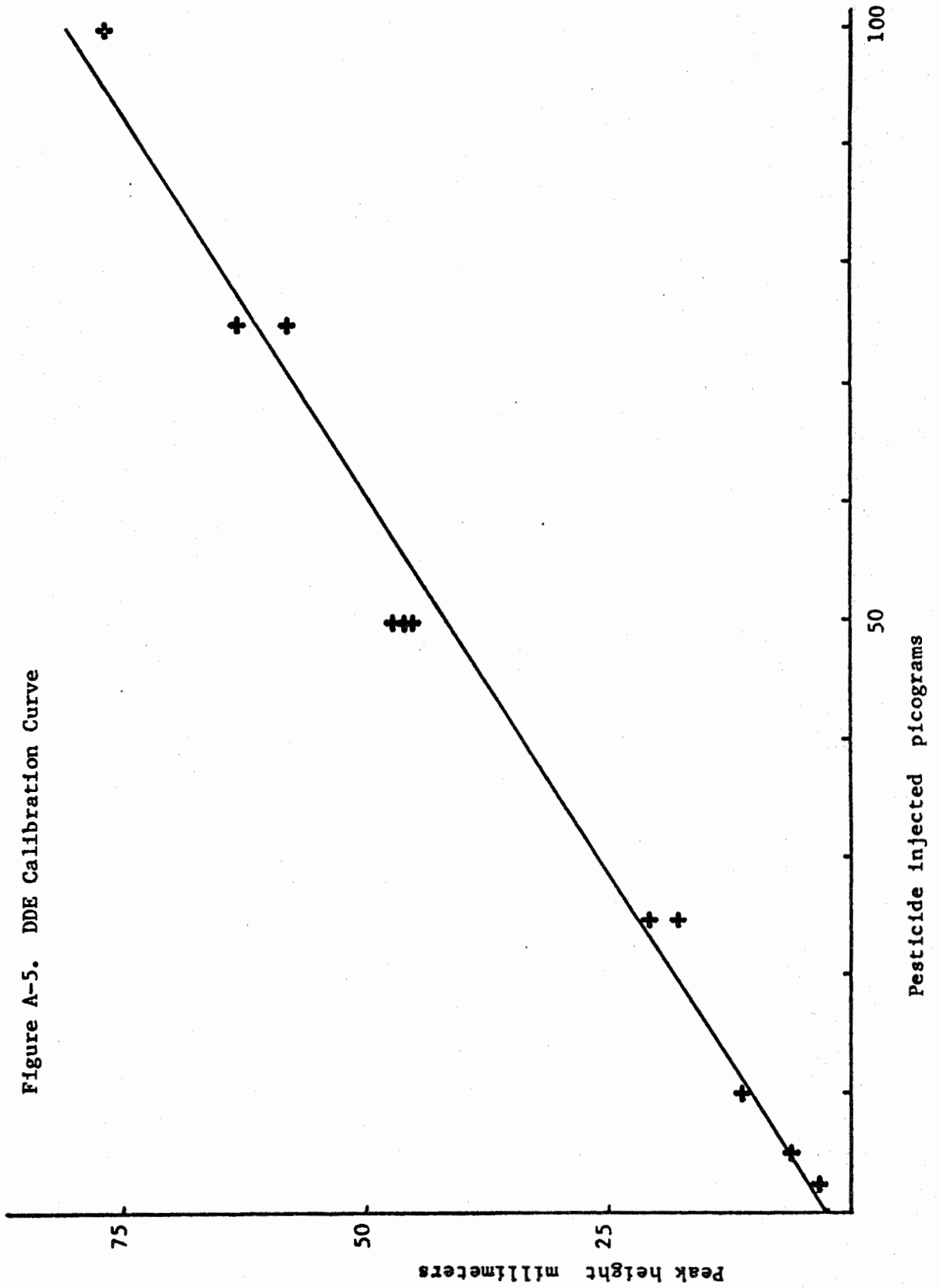
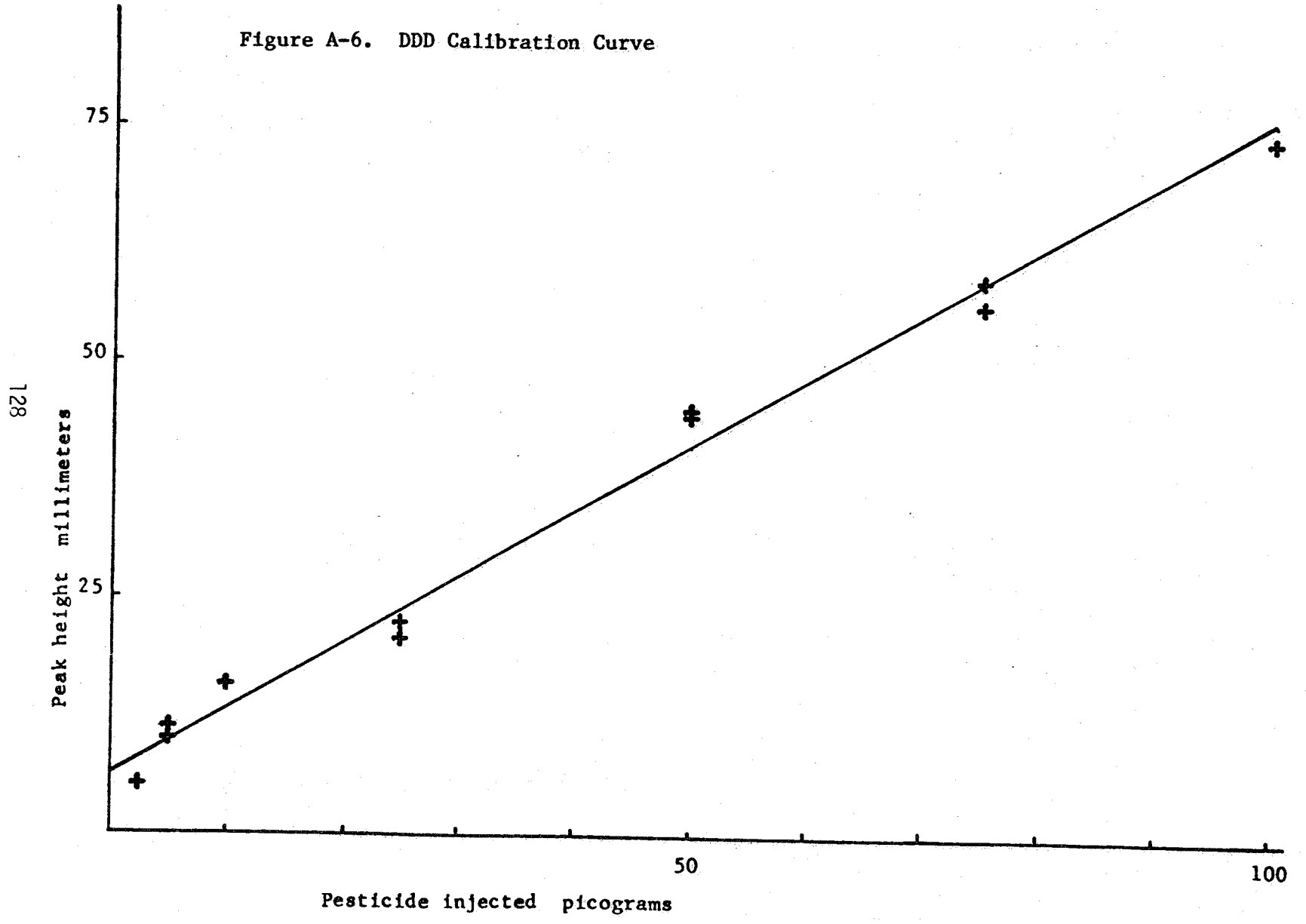
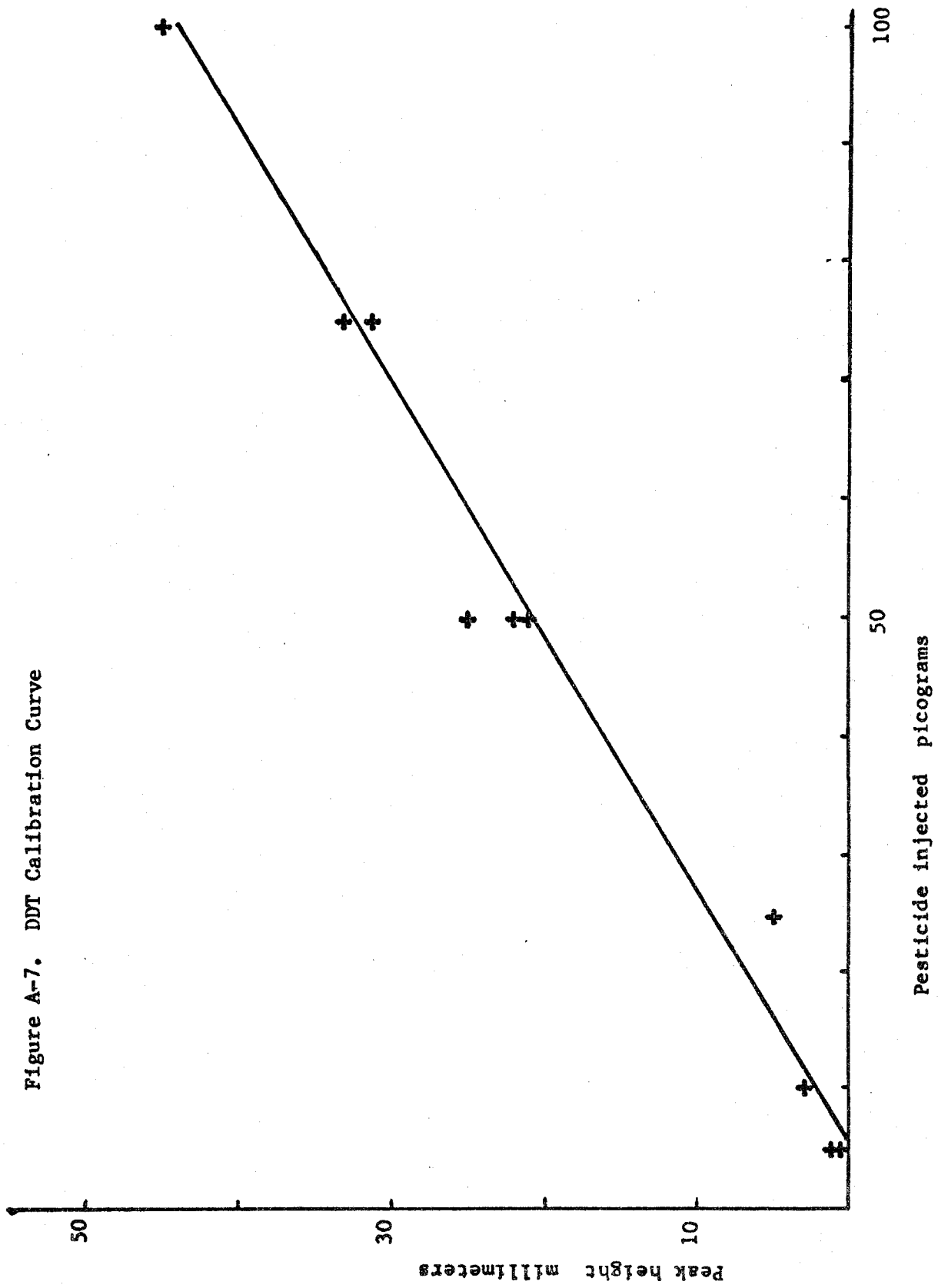


Figure A-6. DDD Calibration Curve



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Figure A-7. DDT Calibration Curve



APPENDIX B

TABLE B-1

Recovery of Metal Spikes

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
Chelex 100					
100 ml DH ₂ O	2.5	1.0	1.5 N HCl	20	4
Manganese oxide-dioxide impregnated acrylic fibers					
Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
100 ml DH ₂ O	2.5	1.0	1.5 N HCl	20	80
100 ml DH ₂ O	3.8	1.0	1.5 N HCl	60	84
100 ml DH ₂ O	7.6	1.0	1.5 N HCl	60	98
100 ml DH ₂ O	12.7	1.0	1.5 N HCl	50	99
100 ml DH ₂ O	25	1.0	1.5 N HCl	50	95
100 ml DH ₂ O	38	1.0	1.5 N HCl	60	96
100 ml DH ₂ O	51	1.0	1.5 N HCl	60	96
100 ml DH ₂ O	85	1.0	1.5 N HCl	50	100
1 l DH ₂ O	85	1.0	1.5 N HCl	50	99
500 ml DH ₂ O	85	1.0	1.5 N HCl	50	86

Manganese oxide-dioxide impregnated acrylic fibers

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
100 ml DH ₂ O	85	1.0	1.5 N HCl	50	99
400 ppb Zn					
100 ml DH ₂ O	85	1.0	1.5 N HCl	50	78
400 ppb Zn					
100 ml DH ₂ O	85	1.0	1.5 N HCl	50	83
400 ppb Zn					
100 ml DH ₂ O	108	1.0	1.5 N HCl	50	95
400 ppb Zn					
100 ml DH ₂ O	108	1.0	1.5 N HCl	100	95
10 ppm Pb					
100 ml DH ₂ O	12	2.5	1.5 N HCl	200	67
10 ppm Pb					
200 ml DH ₂ O	41	2.5	1.5 N HCl	200	77
10 ppm Pb					
100 ml DH ₂ O	35	2.5	1.5 N HCl	400	99
10 ppm Pb					
1 l DH ₂ O	42	2.5	1.5 N HCl	400	
1 ppm Cu					
1 l DH ₂ O	35	2.5	1.5 N HCl	500	105
1 ppm Cu					

New Column

Reuse of fiber apparently decreasing extraction efficiency, monitor of column effluent gave 100% and 95% accounting

Manganese oxide-dioxide impregnated acrylic fibers

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
10 l DH ₂ O 1 ppb Cd 10 ppb Pb 1 ppb Zn 1 ppb Cu					(eluants gave absorptions near or below sensitivity of instrument)
10 l DH ₂ O 60 ppb Cd 80 ppb Cu 500 ppb Pb 30 ppb Zn	39	2.5	2.0 N HCl	500	Cd 108 Cu 100 Pb 98 Zn 100
10 l University Lake 30 ppb Cd 20 ppb Zn 400 ppb Pb 50 ppb Cu (no filter)	30	2.5	2.0 N HNO ₃	700	Cd 102 Zn 108 Pb 75 Cu 82
10 l University Lake .30 ppb Cd 20 ppb Zn 400 ppb Pb 50 ppb Cu (glass wool filter)	25 (avg.)	2.5	2.0 N HNO ₃	700	Cd 95 Cu 70 Zn 109 Pb 32

Dowex 50w x 16

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
100 ml DH ₂ O .2 ppm Cd	2.5	1.0	1.5 N HCl	20	69
100 ml DH ₂ O 1 ppm Cd	3.8	1.0	1.5 N HCl	50	116
100 ml DH ₂ O 1 ppm Cd	7.6	1.0	1.5 N HCl	80	79
100 ml DH ₂ O 1 ppm Cd	12.7	1.0	1.5 N HCl	100	98
100 ml DH ₂ O 1 ppm Cd	25	1.0	1.5 N HCl	120	82
100 ml DH ₂ O 1 ppm Cd	25	1.0	1.5 N HCl	130	90
100 ml DH ₂ O 1 ppm Cd	25	1.0	1.5 N HCl	200	103
1 l DH ₂ O 100 ppb Cd	25	1.0	1.5 N HCl	150	101
500 ml DH ₂ O 100 ppb Zn	25	1.0	1.5 N HCl	150	91
100 ml DH ₂ O 400 ppb Zn	25	1.0	1.5 N HCl	150	112
100 ml DH ₂ O 400 ppb Zn	25	1.0	1.5 N HCl	200	93
100 ml DH ₂ O 10 ppm Pb	25	1.0	1.5 N HCl	200	92
100 ml DH ₂ O 10 ppm Pb	12	2.5*	1.5 N HCl	200	67 [†]

† eluant volume not large enough

* 50 ml of exchanger

Dowex 50w x 16

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
200 ml DH ₂ O	38	2.5	1.5 N HCl	350	95
100 ml DH ₂ O	31	2.5	1.5 N HCl	400	98
1 l DH ₂ O	36	2.5	1.5 N HCl	400	80 [†]
1 l DH ₂ O	30	2.5	1.5 N HCl	500	133*
10 l DH ₂ O	(eluants gave absorptions near or below sensitivity of instrument)				
10 l DH ₂ O	60	2.5	2 N HCl	600**	Cd 88 Cu 89 Pb 90 Zn 93
10 l University Lake	34	2.5	2 N HNO ₃	700	Cd 100 Cu 71 Zn 102 Pb 90
(no filter)					

† eluant volume not large enough

* standards in water - remade in 1.5 N HCl

** resin reduced to 39 ml

Dowex 50w x 16

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
10 1 DH ₂ O 20 ppb Cu 100 ppb Pb 5 ppb Zn 5 ppb Cd	64	2.5	3.0 N HCl	100	Cu 66 Pb 90 Zn 158 Cd 90
10 1 DH ₂ O 20 ppb Cu 100 ppb Pb 5 ppb Zn 5 ppb Cd	49	2.5	3.0 N HCl	100*	Cu 62 Pb 89 Zn 80 Cd 88
+10 1 DH ₂ O 20 ppb Cu 100 ppb Pb 5 ppb Zn 5 ppb Cd	40	2.5	3.0 N HCl	100 *	Cu 85 Pb 100 Zn 86 Cd 98
10 1 DH ₂ O 20 ppb Cu 100 ppb Pb 4 ppb Zn 5 ppb Cd			3.0 N HCl	100	Cu 89/88 Pb 94/100 Zn 130/103 Cd 96/100

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* elution by equilibration method

+ exchanger Dowex 50W x 8 100-200 mesh

Dowex 50w x 8 100-200 mesh

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery %
10 l DH ₂ O					
10 ppb Cu					81/79
50 ppb Pb					91/87
2 ppb Zn	80	2.5	3 N HCl	100	120/195
3 ppb Cd					97/97
10 l University Lake					
10 ppb Cu					59
50 ppb Pb					40
2 ppb Zn	--	2.5	3 N HCl	100	0
3 ppb Cd					33

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Dowex 1 x 8

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery/ Elution, %*
10 l DH O with 2μCi of Cr ⁵¹ as Na ₂ CrO ₄					
	95	2.5	3 N HCl	100	10/97
	100	2.5	3 N HCl	100	101/97
	~100	2.5	3 N HCl	100	39
	~100	2.5	3 N HCl	100	96

* Recovery = amount of spike extracted (extraction efficiency of resin).

Elution = amount eluted by batch technique.

Dowex 1 x 8

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery/ Elution, %
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10 l DH ₂ O with 1 μCi of Cr ⁵¹ as Na ₂ CrO ₄	126	2.5	3 N HCl	100	86
--	-----	-----	---------	-----	----

Dowex 50W x 8 100-200 mesh

Sample	Flow rate ml-min ⁻¹ -cm ⁻²	Col. dia. cm	Eluant	Vol. ml	Recovery/ Elution, %*
--------	---	-----------------	--------	------------	--------------------------

10 l DH ₂ O with 2 μCi of Cr ⁵¹ as CrCl ₃	94	2.5	3 N HCl	100	100/86
	103	2.5	3 N HCl	100	98/85
	105	2.5	3 N HCl	100	77/57**
	118	2.5	3 N HCl	100	97/71
	126	2.5	3 N HCl	100	78

* Recovery = amount of spike extracted (extraction efficiency of resin)

Elution = amount elated by batch technique

** Normal sequence of resin columns reversed

TABLE B-2 Temperature

Temperature (°C)

Date Mo/Yr	1	2	3	4	5	6	7	8	9	10
7/74	22	26	25	29	28	33	29	29	29	--
8/74	22	25	25	28	27	28	26	26	27	25
9/74	18	23	22	23	24	24	24	23	23	23
11/74	5	9	10	10	9	10	9	10	11	14
12/74	2	7	6	7	6	7	5	7	7	8
1/75	8	10	8	9	8	8	8	8	-	9
2/75	4	10	10	10	10	11	12	12	13	14
3/75	8	11	11	12	12	12	12	12	12	12
4/75	11	15	12	14	13	14	13	13	14	17
5/75	16	20	18	21	21	24	21	21	23	23
6/75	19	23	23	25	25	27	26	25	26	26

TABLE B-3 - pH

pH

Date Mo/Yr	1	2	3	4	5	6	7	8	9	10
7/74	6.9	7.3	7.1	7.2	7.4	7.6	7.9	7.6	7.6	6.4
8/74	6.5	7.2	7.0	7.3	6.9	6.6	6.5	6.6	6.3	5.9
9/74	6.2	7.0	6.9	7.2	7.1	6.9	6.4	6.5	6.3	6.4
11/74	6.4	6.5	6.6	6.7	6.7	6.5	6.7	6.6	7.6	6.4
12/74	-	-	-	-	-	-	6.8	6.9	6.8	6.7
1/75	6.7	7.3	6.7	7.0	6.8	6.5	6.8	7.0	-	6.8
2/75	6.6	6.8	6.8	6.6	6.5	6.4	6.5	6.4	6.2	5.8
3/75	6.4	6.7	6.7	6.8	6.5	6.3	6.3	6.2	-	6.3
4/75	6.6	6.9	6.7	6.9	6.7	6.7	6.7	6.5	6.2	6.1
5/75	6.4	6.8	7.0	7.0	6.9	7.0	6.9	6.7	6.5	6.2
6/75	6.5	7.3	6.8	7.2	7.1	7.1	6.7	6.5	6.4	6.2

TABLE B-4 Flow

Flow

Date: Mo/Yr	7/74	8/74	9/74	11/74	12/74	1/75
Site #	Flow, l/sec					
1				1,982	850	1,558
2					6,514	
3	3,115	9,119	7,986	7,080	18,776	54,941
5	6,513	22,572	17,245	30,865	65,129	158,574
7	7,362	56,634	31,118	31,998	128,841	726,326
9	29,453	88,358	67,402	94,872	163,123	665,520

Date: Mo/Yr	2/75	3/75	4/75	5/75	6/75
Site #	Flow, l/sec				
1	232	1,614	397	283	283
2	2,832	19,992	4,248	6,514	6,514
3	12,263	103,085	17,898	10,733	7,731
5	49,838	359,623	39,927	31,715	
7	93,162	557,841	70,226	40,210	
9	235,339	790,128	130,555		

TABLE B-5 Dissolved Ionic Trace Metal Concentrations

By Sample Site and Date

Lead

Date:	Mo/Yr	7/74	8/74	9/74	11/74	12/74	1/75
No anionic species observed							
Site		Cation (µg/l)					
1		6.0	39.0	11.1	2.5	2.5	3.2
2		14.5	9.1	22.7	4.0	7.5	37.2
3		3.5	37.9	8.4	-	3.5	4.0
4		9.5	5.5	7.3	5.0	7.5	7.0
5		5.0	9.8	5.1	5.0	9.0	5.4
6		5.0	38.9	12.9	4.0	2.5	3.2
7		2.0	59.0	16.3	2.5	2.5	4.0
8		3.0	12.2	24.4	2.0	2.9	2.4
9		3.0	74.0	3.8	HW	2.0	HW
10		3.0	15.8	6.1	3.5	1.5	2.4

HW = high water

Note--Column used on 7/74 sample trip was 25 x 60 mm borosilicate glass. Field column was not yet complete. Filtration on 7/74 and 8/74 was by glass wool only and ion exchange columns were preceded by a resin column for collection of pesticides.

Lead (continued)

Date:	Mo/Yr	2/75	3/75	4/75	5/75	6/75
No anionic species observed						
Site	Cationic (µg/l)					
1	2.1	-	3.2	1.1	2.4	
2	6.0	-	5.7	7.0/6.8	5.8/5.8	
3	3.6	-	4.3	6.0	3.8	
4	6.0	-	3.2/3.2	2.8	2.4	
5	2.8	-	6.0	2.8	2.4	
6	2.1	-	2.8	1.4	1.8	
7	2.1	-	2.5	7.5	1.2	
8	1.8	-	3.6	2.8	2.0	
9	1.8	-	2.2	1.4	13.5	
10	2.1	-	1.8	1.4	1.8	

Cadmium

Date:	Mo/Yr	7/74	8/74	9/74	11/74	12/74	1/75	2/75	3/75	4/75	5/75	6/75
Site #						Cationic (µg/l)						
1		.13	.55	.39	.27	.40	.20	.29	.14	.19	.23	.29
2		1.22	.70	.74	1.08	.70	.29	1.04	.48	.86	.59/.49	.82
3		.55	.65	.28	--	.35	.23	.29	.16	.31	.44	.38
4		.40	.40	.34	.40	.35	.29	.32	.16	.23/.26	.23	.32
5		.40	.40	.28	.37	.37	.24	.22	.14	.26	.26	.30
6		.40	.55	.37	.45	.23	.12	.22	.20	.26	.23	.33
7		.28	.68	.33	.27	.16	.36	.18	.14	.19	.23	.28
8		.28	.85	.31	.23	.27	.18	.14	.14	.19	.26	.30
9		.10	1.12	.16	--	.23	HW	.18	HW	.12	.13	.29
10		.35	.30	.16	.27	.20	ND	.14	.09	.12	.15	.19

No anionic species observed

HW - high water

ND - none detected

Chromium

Date: Mo/Yr	1/75	2/75	3/75	4/75	5/75	6/75
Site #	Anionic ($\mu\text{g}/\text{l}$)					
1	ND	ND	ND	ND	ND	ND
2	2.4	7.1	3.2	4.3	2.3/2.2	20.0/21.5
3	ND	1.0	ND	0.9	2.0	5.0
4	2.9	0.5	ND	1.6/1.4	0.7	5.0
5	7.0	0.5	ND	2.4	1.3	ND
6	2.4	ND	ND	1.2	0.8	ND
7	2.0	ND	ND	0.4	0.7	ND
8	1.0	ND	ND	0.7	0.4	ND
9	HW	ND	HW	0.2	0.1	ND
10	ND	ND	ND	ND	0.6	ND
Site #	Cationic ($\mu\text{g}/\text{l}$)					
1	1.4	1.7	0.3	2.3	3.1	3.8
2	15.0	4.3	3.0	5.4	7.3/4.7	5.3/5.1
3	3.3	1.7	1.6	2.5	5.9	2.0
4	16.4	1.9	1.5	5.9/5.9	2.0	2.0
5	1.5	1.6	1.9	5.7	3.8	1.5
6	2.0	0.5	2.0	3.3	2.1	2.0
7	4.1	0.3	1.4	1.9	0.8	0.4
8	3.0	0.3	2.0	1.7	1.0	1.7
9	HW	ND	HW	1.3	1.0	1.4
10	1.7	ND	0.3	1.2	0.8	0.9

HW - high water

ND - none detected

Copper

	11/74	12/74	1/75	2/75	3/75	4/75	5/75	6/75
Date: Mo/Yr								
Site #	Anionic (µg/l)							
1	0.5	0.7	0.7	0.7	0.7	0.3	0.2	ND
2	0.7	1.1	1.6	1.2	1.3	0.5	0.3-0.3	ND
3	1.0	0.9	1.0	1.1	1.3	0.6	0.6	ND
4	0.6	0.9	1.1	1.1	1.1	0.9/0.7	0.6	ND
5	0.5	0.9	1.8	1.0	1.0	0.6	0.6	ND
6	ND	0.7	0.8	1.0	0.9	0.6	0.6	ND
7	0.4	0.7	1.0	1.0	1.0	0.5	0.6	ND
8	0.5	0.7	0.8	0.9	0.9	0.5	0.5	ND
9	HW	0.6	HW	0.8	HW	0.3	0.7	ND
10	0.3	0.7	0.7	0.8	0.9	0.2	0.3	ND

HW - high water

ND - none detected

Copper (continued)

	7/74	8/74	9/74	11/74	12/74	1/75	2/75	3/75	4/75	5/75	6/75
Date: Mo/Yr											
Site #	Cationic (µg/l)										
1	1.0	2.0	4.1	1.0	2.4	1.4	1.3	1.3	0.9	0.9	0.9
2	5.5	4.5	2.4	6.1	5.5	9.1	4.7	4.3	3.2	3.4/2.7	2.5/2.6
3	2.8	6.5	6.0	-	3.5	3.2	3.9	3.1	3.7	3.5	2.5
4	2.5	3.4	3.6	2.2	2.5	4.7	3.1	2.4	2.7/2.9	1.8	3.0
5	2.0	3.0	3.3	2.4	2.2	3.0	2.3	2.0	3.0	2.5	2.3
6	2.3	2.2	2.0	2.8	1.9	1.6	3.7	2.2	2.0	1.7	2.0
7	1.5	2.0	1.9	2.1	1.8	2.8	2.9	1.7	1.4	1.6	1.5
8	1.5	1.7	1.4	1.6	1.6	2.0	2.4	2.1	1.4	1.6	1.5
9	1.2	2.0	1.4	-	1.6	HW	2.3	HW	1.1	1.1	1.6
10	1.4	1.3	1.4	1.7	1.6	1.6	2.5	1.5	1.1	1.0	1.2

HW - high water

ND - none detected

Zinc

Date: Mo/Yr 1/75 2/75 3/75 4/75 5/75 6/75

Site #	Anionic (µg/l)					
1	0.2	0.2	0.2	0.1	0.1	0.1
2	0.2	0.2	0.2	0.2	0.1/0.1	0.1/0.1
3	0.3	0.1	0.2	0.1	0.2	0.2
4	0.2	0.2	0.2	0.1/0.2	0.1	0.1
5	0.3	0.2	0.2	0.1	0.2	0.2
6	0.2	0.1	0.2	0.1	0.1	0.1
7	0.3	0.2	0.2	0.2	0.1	0.1
8	0.2	0.1	0.2	0.1	0.2	0.1
9	HW	0.2	HW	0.1	0.1	0.1
10	0.2	0.1	0.2	0.1	0.1	0.1

HW - high water

Zinc (continued)

Date: Mo/Yr	7/74	8/74	9/74	11/74	12/74	1/75	2/75	3/75	4/75	5/75	6/75
Site #	Cationic (µg/l)										
1	4.1	3.9	55.0	6.5	14.5	21.5	8.0	9.0	9.1	7.2	6.1
2	63.0	49.0	43.0	74.0	54.0	73.0	74.0	45.0	43.0	42.2/37.8	43.0/43.0
3	14.5	7.0	16.0	-	30.0	14.3	17.0	8.5	12.3	19.2	12.2
4	12.0	12.7	20.0	21.5	14.8	19.3	13.5	7.8	9.5/9.5	5.7	11.8
5	4.3	16.2	14.3	17.7	8.9	12.8	7.6	7.3	12.2	7.5	6.0
6	4.2	6.4	7.9	16.2	6.5	7.4	4.3	11.6	5.4	4.3	4.0
7	2.9	7.0	7.8	12.0	7.0	15.5	9.9	7.8	5.0	4.9	8.2
8	4.9	12.8	6.8	9.1	6.0	11.2	9.1	9.8	6.0	4.6	4.6
9	3.8	15.1	7.1	-	6.5	HW	8.6	HW	4.2	4.2	7.1
10	3.7	10.2	12.0	6.4	7.7	8.3	10.2	6.6	5.6	4.1	4.9

HW - high water

TABLE B-6 Detection Limits

Metal	Detection Limits
Cd	0.09 µg/l
Cr	0.1 µg/l
Cu	0.2 µg/l
Pb	1.0 µg/l
Zn	0.1 µg/l

Detection limits shown represent limits for technique (i.e., ion exchange preconcentration followed by atomic absorption).

TABLE B-7 Standard Conditions of Analysis
By Atomic Absorption

Metal	Wavelength (nm)	Flame type
Cd	228.8	Oxidizing
Cr	357.9	Reducing
Cu	324.7	Oxidizing
Pb	283.3	Oxidizing
Zn	213.9	Oxidizing

A three slot Belling burner and air-acetylene flame were used for all five metals.

