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for organochlorine pesticides and
polychlorinated biphenyls"

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Kraidt Adjobi Nicolas

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RESIDUE ANALYSIS OF MUNICIPAL SLUDGES
FOR ORGANOCHLORINE PESTICIDES
AND POLYCHLORINATED BIPHENYLS

By

Kraidt Adjobi Nicolas

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ABSTRACT

RESIDUE ANALYSIS OF MUNICIPAL SLUDGES
FOR ORGANOCHLORINE PESTICIDES
AND POLYCHLORINATED BIPHENYLS

By

Kraidt Adjabi Nicolas

Municipal sewage sludges from several Michigan communities were analyzed for the presence of DDT analogs, lindane, aldrin, dieldrin, endrin and PCBs.

The samples were extracted with methylene chloride via liquid/liquid extraction. The cleanup was achieved through acid/base partitioning and activated florisil columns. Following separation using activated silica gel, samples were injected into a gas liquid chromatography equipped with Ni^{63} electron capture detector.

Residue concentrations of PCBs present in sludge varied from traces to 1960 ug/kg. Pesticides concentrations were lower. DDT showed the highest concentration among the pesticides at 17.50 ug/kg. Endrin and methoxychlor were not detected.

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INTRODUCTION

Sewage sludge is obtained from the processing of waste waters from domestic and/or industrial areas. It may be liquid, semi-liquid or solid, according to the extent of water removal. Considering its sources, sewage may contain any kinds of contaminants, and a significant number of bacteria, fungi and microbes as well.

The value of sludge as fertilizer is as old as agricultural practices. Application of human wastes to the soil is an integral part of the traditional agriculture. In the Orient, human wastes had been collected and used for crop fertilization for centuries. The most extensive and successful operations were begun around 1850, but the most sophisticated system seemed to be the one at Wassmannsforf, Germany (1930) where sewage was treated in anaerobic digester before both the liquid effluent and the sludge were distributed to farms (Allen, Jonathan, 1973).

In the United States, the use of sewage effluent for crop irrigation on a large scale started in the early twentieth century. The most successful experiment seems to be that of the Waste Water Renovation and Conservation Project of Pennsylvania State University which monitors the effects of secondary sewage effluents on forests and croplands. Throughout the country, several other interesting projects were undertaken. They include: the Metropolitan Sanitary District of Greater Chicago; Muskegon, Michigan; Santee, California; East San Francisco Bay; University of Michigan. A number of facts have led to the beneficial management of sewage products (Hays, Barbara D., 1977):

1. The discharging and dumping of raw and/or treated sewage into our surface waters and the incineration of dried sludges has led to unacceptable levels of pollution.
2. Critical water shortages have encouraged consideration of the use of sewage effluent as a source of irrigation water
3. Increasing costs of maintaining soil nutrients and soil structure suggest that a valuable fertilizer and soil amendement are being wasted by disposing sewage effluent and sludge into the ocean, burying it, or incinerating it.
4. The increasing cost of energy has led some planners to consider sewage as a source of energy, as methane gas produced during the anaerobic digestion of sewage sludge can be captured and used for heating purposes
5. The high cost of alternative technologies make sewage land application attractive
6. Sludges have been recognized for centuries as soil conditioner and fertilizer.

On the other hand, a number of environmental and health questions have been raised as to whether or not land application of sewage plant products can cause unreasonable risks. Some of the problems associated with the disposal of sludge to agricultural land may be the following (Hays, 1977):

1. Public acceptance of the beneficial use of sewage

sludge or effluent on land

2. Diseases, bacterial, viral and parasitic may be transmitted through the man - sewage - soil crop - man cycle
3. Toxic ions (particularly nitrates), and toxic heavy metals, such as cadmium, mercury, lead, copper, nickel, zinc, arsenic, etc., as well as persistent organic chemicals may accumulate in the ground water, soil or crops, making the water unsafe for drinking, the soil unable to support future plant growth, or crop products too risky to eat.

Due to mismanagement or lack of proper management monitoring of some sludge disposal systems, there has been a history of soil, plant and ground water contamination from heavy metals, toxic organics and pathogenic bacteria. With the increased input of household chemicals and industrial effluents into municipal sewage systems, the problem of waste disposal has come into the forefront for federal, state and local agencies. Passage of the Federal Water Pollution Control Act in 1972 has caused a huge increase in the amount of sewage sludge requiring disposal. Under Michigan's Act 64, the "Hazardous Waste Management Act", sludges which contain hazardous organic materials present at concentrations from 1 to 1,000 ppm are designated "notification waste" and may subsequently be designated "hazardous waste". This designation tags the sludge as a potential environmental pollutant and must be disposed of properly and continually monitored by the waste-

water treatment facility affected. Ultimately, the Michigan Department of Natural Resources must enforce and regulate the management of such wastes.

In order to manage wastes properly it is important to know if they contain hazardous materials and if so, in what levels, in order that they may be used safely, detoxified or disposed of via incineration or an approved landfill. For this reason the Michigan Department of Natural Resources and the United States Environmental Protection Agency contracted researchers from Michigan State University to characterize 250 sewage treatment plant sludge (Figure 1). These sludges came from throughout the state and were analyzed for the following toxic substances or potential xenobiotics.

PHENOLS

o-Chlorophenol
m-Chlorophenol
p-Chlorophenol
o-Cresol
m-Cresol
p-Cresol
2,3-Dichlorophenol
2,4-Dichlorophenol
2,5-Dichlorophenol
2,6-Dichlorophenol
3,4-Dichlorophenol
3,5-Dichlorophenol
2,3-Dimethylphenol
2,4-Dimethylphenol
2,5-Dimethylphenol
2,6-Dimethylphenol
3,4-Dimethylphenol
3,5-Dimethylphenol
4,6-Dinitro-o-cresol
2,4-Dinitrophenol
Hydroquinone
Pentachlorophenol
Phenol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol

PURGEABLES

Acrylonitrile
Chlorobenzene
p-Chlorotoluene
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
1,2-Dichloropropane
1,3-Dichloropropane
1,3-Dichloropropene
Ethylbenzene
Hexachloro-1,3-butadiene
Hexachloroethane
Pentachloroethane
Styrene
Tetrachloroethylene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene
1,2,3-Trichloropropane
1,2,3-Trichloropropene

PHENOLS (continued)

2,3,5,6-Tetrachlorophenol
 2,3,4-Trichlorophenol
 2,3,5-Trichlorophenol
 2,3,6-Trichlorophenol
 2,4,5-Trichlorophenol
 2,4,6-Trichlorophenol
 3,4,5-Trichlorophenol

AROMATIC HYDROCARBONS

Biphenyl
 Hexachlorobenzene
 Mercaptobenzothiazole
 Naphthalene
 Polychlorinated biphenyls
 1,2,3,4-Tetrachlorobenzene
 1,2,3,5-Tetrachlorobenzene
 1,2,4,5-Tetrachlorobenzene

BASES

Benzidine
 3,4-Dichloroaniline
 3,3-Dichlorobenzidine
 p-Nitroaniline

PHTHALATES

Butylbenzylphthalate
 Diethylphthalate
 Dimethylphthalate
 Di-N-Butylphthalate
 Di-N-Octylphthalate
 Dioctylphthalate

NITROBENZENES

1Chloro-2,4-dinitrobenzene
 1Chloro-2,6-dinitrobenzene
 1Chloro-3,4-dinitrobenzene
 1Chloro-2-nitrobenzene
 1Chloro-4-nitrobenzene
 2,4-Dinitrotoluene
 2,6-Dinitrotoluene
 Nitrobenzene
 Pentachloronitrobenzene

TRIARYL PHOSPHATE ESTERS

Cresyldiphenyl Phosphate
 Tricresyl Phosphate
 Trixylylene Phosphate

In this study, interest was given to several chlorinated pesticides and polychlorinated biphenyls. (Table 1),

Two hundred-thirty-seven sewage treatment plants throughout Michigan were sampled by the Michigan Department of Natural Resources (Jacobs & Zabik, 1980). These sludges were sampled from various stages of the treatment process which varied from city to city including raw sludge, primary aerobic digested, secondary aerobic digested, anaerobic digested, Purifax sludge, filtered, lagooned, and drying bed sludge. The Purifax sludge is specially treated via a patented super chlorination process in order to decrease its active biological activity and subsequent odor. The sewage treatment plants sampled have inputs varying

Table 1 - Selected Organochlorine pesticides and PCBs

ORGANOCHLORINE PESTICIDES

Lindane	p,p'-DDD
Aldrin	p,p'-DDE
Dieldrin	p,p'-DDT
Endrin	Methoxychlor

POLYCHLORINATED BIPHENYLS (PCBs)

Aroclor 1254

Aroclor 1260

Figure 1



from totally residential to a large percentage in industrial sources. Community population may also vary from a few hundred to several million individuals, therefore each community usually treats its waste in a fairly unique manner which leads to a great diversity in treatment processes.

My purpose in this study is to determine if:

1. The selected organochlorine components are present in the sewage sludges at a measurable level
2. There is any correlation between concentration level of the pesticides and the PCBs and the size of the population
3. There is any correlation between concentration level of the pesticides and the PCBs and the percentage of waste inputs

I. LITERATURE REVIEW

A. Sludge Analysis

Thanks to the Federation of Sewage, Sewage Works and Industrial Wastes Association, two fairly complete volumes on sewage treatment and utilization were compiled in the late forties. At this early date the Subcommittee of Utilization of Sludge as Fertilizer published a 120 page report on the soil requirements, sludge characteristics, treatment processes and economics of sludge application to agricultural lands (Pearse, 1945). Then in 1950, the Subcommittee on Chlorination of Sewage and Industrial Waste Practices released another report taking an indepth look at several waste chlorination practices and chemical effects of chlorination (Gilcreas, 1950). Even though modern analytical techniques for the day were employed in both reports, the trace analytical capability which we have today had not yet been developed. The only reference in either paper to the potential hazards of organic toxicants in sludges concerned was the treatment of phenolics in effluents by Dow Chemical Company in Midland, Michigan. Actual analyses for organics were limited to the various forms of nitrogen present as nutrients. From this date forward, no analytical methods were published on the analysis of sludge for organic compounds until the late 1970s. As a matter of fact, the literature is quite void of any noteworthy strides in sewage or wastewater analysis prior to the early 1970s. Before 1970, less than 100 different organic compounds had been identified in water let

alone municipal sewage sludges. In the early 1970s, a split developed in the area of wastewater analysis. One group became primarily concerned with chlorination of wastewaters and the other with characterization of organics in wastewaters. The developments of both of these groups helped to pave the way for sludge analysis. Some of the key workers in the effects of chlorination include: Jolley, (1973, 1975); Glaze et al. (1973); and Kopperman (1975). In a search for a better understanding of the effect of chlorination on organic components, new techniques were developed and utilized for trace component determinations.

Various techniques also began to emerge once an effort was exerted toward the characterization of organics in wastewater. Workers in this field included: Katz et al. (1972); Kleopfer and Fairless (1972); the Environmental Protection Agency (1973); Baird et al. (1974); Keith (1974, 1976); Manka (1974); Telliard (1977); Lichtenberg (1978); Jungclaus (1978); Cooper (1978); Mousa and Whitlock (1979); Walton and Eicemen (1978); Haller (1978); Narkis (1978); Lamparski (1978); Carter (1978); Waite (1978); Jenkins et al. (1978); Argamon (1978); and Hall (1978). Although a review of all these works would be too extensive and far reaching for the specifics of this paper, please note how the analysis of organic compounds in wastewaters bloomed about 1978. Much of the work during this time period involved either the analysis of phenols or chlorinated pesticides in municipal and industrial wastewaters.

The largest amount of work completed to date involving sludge

analysis has been concerned with heavy metal contamination (Keith, 1974). Several studies have shown the detrimental effects of high heavy metal concentration to both crops and mammals (Jalinec and Broude, 1978).

The first modern techniques used in a comprehensive characterization of organics in sewage effluents was by Garrison, Pope and Allen of the United States Environmental Protection Agency from 1971 to 1976 (Garrison, et al., 1976). In this work, 80 specific volatile organic compounds were identified in raw and treated domestic wastewaters primarily by G.C./M.S. This indeed was the first step toward the characterization of organics in sludge.

In 1977 two publications discussed the management and effect of sludge used on land. The first was a National Science Foundation risk assessment of land application of municipal sludge (Jones and Fred, 1977). The National Science Foundation concluded that chemical contaminants "suspected" to be present in municipal sludge could have adverse effects on the environment as a result of land application practices. The second publication was from the Bureau of Foods, the Food and Drug Administration (Jelinec and Braude, 1977). In the FDA's study, levels of selected chlorinated pesticides, lead and cadmium were considered with the following recommendations made:

- a. Sludges should not contain more than 20 ppm cadmium, 100 ppm lead or 10 ppm PCBs on the dry basis.
- b. In support of the limits proposed by the W 124/NC118 Committees of Land Grant Colleges, the maximum total which should ever be added to an average soil (cation

exchange capacity of 5-15) is 9 lbs. of cadmium/acre and 900 pounds of lead/acre.

- c. Crops which are customarily eaten raw should not be planted within 3 years after the last sludge application.
- d. Crops such as green beans, beets, etc., which may contaminate other foods in the kitchen before cooking should not be grown on sludge-treated land unless the sludge gives a negative test for pathogens.
- e. Because sewage can be regarded as filth, food physically contaminated with sludge can be considered adulterated even though there is no direct health hazard; hence, sludge should not be applied directly to growing or mature crops where sludge particles may remain in or on the food.
- f. Commercial compost and bagged fertilizer products derived from sludges should be labeled properly to minimize any contamination of crops in human food chain which may result from their use.

Richard Doyle (1978) from the University of Maryland completed a brief study under laboratory conditions on the effect of dairy manure sludge on pesticide degradation. This study was carried out with C-14 labeled pesticides. Doyle concluded that sludge application to soils can alter the rate of pesticide degradation, either accelerating or hindering biological activity depending upon conditions. Since this work was carried out totally in the laboratory instead of the field, more work is necessary before any applications can be made to environmental conditions. In 1979, a review was completed on the value and effects of sludges for agricultural

use when contaminated with toxic elements (Sterritt, 1979).

In 1979, interim methods for measurement of organic priority pollutants in sludges were produced by the U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory in Cincinnati, Ohio (E.P.A., 1979). This was the first serious attempt to extract, cleanup and quantitate a group of organic pollutants from sludge. Many extractions and cleanup techniques were attempted, yet all met serious reproducibility problems, due to the sludge matrix. No data on percent recoveries of organics from sludge was presented in this paper. These methods were the basis for the E.P.A.'s officially proposed guidelines for the analysis of priority pollutants in sludge (E.P.A., 1980). Once again, no recoveries were given; the data base was small and inter-laboratory testing was absent.

The environmental Protection Agency began monitoring 50 publicly owned treatment works for the occurrence of organic priority pollutants in sewage influent, effluent and sludge in 1979. In October of 1979, a pilot study for this program was published which indicated large inconsistencies and extremely poor reproducibility in analysis techniques. Fortunately, since 1979, several other groups have initiated sludge analysis programs, each with their own methods of analysis. Hopefully, results from these undertakings will give us a better idea of the problems we face and the potentials for various sludge analysis techniques.

To date, none of the previously mentioned studies have been completed. However, several have released interim reports on their progress (EPA, 1980; Jacobs & Zabik, 1980). Here are

ongoing studies in sludge analysis for organics:

1. Richard Rediske, Muskegon Wastewater Treatment Plant,
Muskegon County Wastewater Management System, Michigan.
An ongoing monitoring program for 30 organic pollutants in
sewage influents, effluents and sludges. Sponsored by the
Environmental Protection Agency.
2. Dr. Tom Clovengor, University of Missouri. Seventy-four
municipal wastewater treatment facilities in Missouri.
Study of the chemical compositions of municipal sewage
sludges in Missouri. Sponsored by Missouri Department of
Natural Resources.
3. Dr. William Glaze, Southern California. Analysis of
reclaimed wastewater for priority pollutants. Department
of Chemistry, North Texas University, Denton, Texas.
4. Vernon L. Stump, Mid-Missouri Engineers Incorporated..
Evaluation of Purifax Process in field operation. A
comprehensive look at chlorinated organic compounds produced
by a "super chlorination" sludge treatment method. Spon-
sored by Basics in Flow Division of General Signal.
5. Howard Feiler, Burns and Roe Industrial Services Corporation.
Fate of Priority pollutants in publicly owned treatment
works. A comprehensive study of 50 POTWs for priority
pollutants.
6. Linn Duling and Jillann Kobbee, Michigan Department of
Natural Resources. The development of methods for the
identification of potential toxic substances from
various wastewater discharges in the state of Michigan.

Michigan Department of Natural Resources through a Toxic Substances Control Act Cooperative Agreement with the U.S. Environmental Protection Agency.

7. Dan Schelton, Crop and Soil Sciences, Michigan State University. Biodegradation of phthalates, cresols, monochlorophenols, methylbenzoic acids, and chlorobenzoic acids in anaerobic sewage sludge. Sponsored by Office of Toxic Substances, The Environmental Protection Agency.
8. Dr. Matthew Zabik, Pesticide Research Center, Michigan State University. Analysis of 80 organic pollutants in 250 municipal sewage sludges throughout Michigan. Sponsored by the Michigan Department of Natural Resources and the Environmental Protection Agency.
9. Dr. Matthew Zabik, Pesticide Research Center, Michigan State University. Field evaluation of the fate of hazardous organic chemicals present in sewage sludge. Fate of organic priority pollutants in sludges under field application. Sponsored by the Michigan Department of Natural Resources.
10. Jackson Elington and Dr. Edo Pellizzari, United States Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia. "A comprehensive method for the analysis of organics on solids, sediments and sludge". EPA Contract No. 68-03-2994.
11. Dr. Zweidinger, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia. "Analytical procedures for proposed toxics in wastewaters

and sludges." EPA Contract No. 68-03-2845.

Very much in line with the type of work now being completed was a recent publication dealing with sludge stabilization and what effects this biological and chemical inner play has on the resulting organic composition (Hautenstein, 1981). Just as the 1970s were the era of blooming organic analysis in wastewaters, the 1980s are becoming the decade for development of sludge analysis techniques. Analysis techniques are an essential tool. Much work has yet to be done in order to characterize and determine the fate of potential xenobiotics in municipal sludges.

B. Volatiles

The only published work to date dealing with the determination of volatile organics in municipal sewage sludge is the Environmental Protection Agency's proposed methods for sludge analysis of organic priority pollutants released in March of 1980. This method suggests analysis via Bellar and Lichtenberg's "purge and trap" method. Samples are to be diluted when the percent solids is too great for accurate quantitation by this method. Since previous work in sludge analysis of volatile and semi-volatile organics is limited, I will highlight the advances made in the area of water analysis for these components.

The most direct means of determining levels of a volatile organic compound in an aqueous medium is by "direct injection" onto a gas/liquid or high pressure liquid chromatographic column (Sugar, and Conway, 1968; ASTM, 1973). This method is only possible when working with extremely clean samples at high levels with column packing and detectors that are inert to water vapor.

Liquid/liquid solvent extraction using either high or low boiling solvents overcomes many of the problems faced with direct aqueous injection techniques (E.P.A., 1971, Duenbostel, 1973). Some of the problems which may plague the solvent extraction technique include erratic or low extraction efficiencies and in some instances solvent impurities. With the advent of capillary chromatography, solvent interference problems have been greatly reduced due to improved separation and resolution of peaks.

Another widely used method for volatile analysis, especially in an industrial setting such as analysis of flavors, is the direct absorption of organics from water onto charcoal followed by solvent extraction, and concentration (Grob, 1973; Polak, 1974). This method, however, can suffer the same solvent contaminant disadvantages as liquid/liquid extraction. Of course, some compounds are preferentially absorbed into the charcoal, while others are not.

The "head-space" or "head-gas" method of volatile analysis has been used for many years. For this technique a sample is sealed in a partially filled container and the volatiles allowed to partition into the gas phase which is directly injected via a gas tight syringe into a gas liquid chromatography (Dow Chemical, 1972). Recovery in this instance is dependent upon the partition coefficient of each compound, which must be known in order to calculate the concentration in the aqueous phase. This equilibrium can be forced in the favor of the gaseous phase by raising sample temperature, replacing the head-space with inert gas of a lower density, or purging.

In 1974, Bellar and Lichtenberg developed a very useful technique for volatile analysis which later was coined as the "purge and trap" method due to two of the phases in the analysis (Bellar and Lichtenberg, 1974). This technique used the principle of head-space analysis but improved the extraction efficiencies by purging with an inert gas. In this way the partitioning continually proceeds in the direction of the less saturated gaseous phase. A porous glass frit is used to bubble nitrogen through the sample solution. The gas is then passed through a series of absorbants at ambient temperature to trap the organic

constituents. After a sufficient volume of gas has swept through the sample and the specific organic compound(s) of interest has been concentrated on the absorbent, it is then quickly desorbed. The key to the desorption process is removal of the organic components of interest in a single concentrated slug onto a chromatographic column by raising the trapping column temperature at a rapid rate.

In 1976, Steichen of the Good Year Tire and Rubber Company developed a head-space analysis technique for acrylonitrile and styrene sensitive down to the 0.5 and 1.0 ppm level respectively (Steichen, 1976). One year later workers at Dow Chemical devised a more sensitive colorimetric method that had been used in the past for acrylonitrile determination in aqueous media (Hall and Stevens, 1978). This technique was based on the formation of a yellow colored acrylonitrile pyridine complex read by a spectrophotometer at 535 nm.

Determination of volatile organic acids in municipal wastewater was performed via steam distillation onto a silicic acid column in 1977 (Narkis and Henfeld-Furie, 1978). Volatiles were recovered from the silicic acid column by elution with n-butanol in chloroform and directly injected into a gas chromatographic column. This was the first attempt at characterizing the short chain organic acid content in sewage.

In 1978 two methods surfaced for analysis of acrylonitrile by G.L.C. that were more sensitive, selective and reproducible than ever before (Marano, et al., 1978; Pasquale, 1978). Both authors used Carbowax 20 M on Chromsorb W 60-80 mesh which allowed better recovery

of acrylonitrile through the column and nitrogen phosphorous specific flame ionization detectors which achieved a 10 ppb level of detection.

The Adolph Coors Company in conjunction with the University of Colorado, developed a modified "purge and trap" method for trace analysis of volatile organics in aqueous mediums (Peterson and Eiceman, 1978). In this method small compact cartridges of porous polymer sorption traps are used to collect the volatiles while sparging the sample with an inert gas. These cartridges were then directly inserted into a gas chromatograph inlet system and heated for desorption. This method is currently used in industrial hygiene for analysis of volatiles in the work place.

In 1978 a team of scientists from the Institute of Chemical Technology in Czechoslovakia looked at the efficiency of the purge and trap method previously described by Bellar and Lichtenberg (Vozhakova, et al., 1978). In this study several variables were considered including the stripping vessel design, volatility and the effectiveness of various polymers in the concentration of organic compounds. A porous glass fritted system was found to give the greatest stripping efficiency and linearity over a wide concentration range in the case of less volatile components. Each volatile compound tested was shown to have unique recovery curves depending on purge time, concentration, temperature and rate of desorption from the porous polymer trap.

Much work was completed on the analysis of halogenated volatile organics in drinking and waste water in 1979. Bellar and Lichtenberg described in detail a semi-automated purge and trap system for volatile analysis in drinking water. In this report purge efficiencies for various compounds were discussed in relation to purge volume and flow rate (Bellar and Lichtenberg, 1979).

✓ Comparisons were also made on levels of halogenated volatiles from various preservation techniques in aqueous matrices containing free chlorine over an 8 day time period (Kopfler, et al., 1976). The results showed a rapid increase in some halogenated compounds over time when unpreserved, a gradual but linear increase when samples were stored at 4°C and only a slight increase in samples preserved with ferrocyanide. Both ferrocyanide and sodium thiosulfate proved effective in reducing continued chlorination when compared to non-preserved samples.

An article published in American Water Works Association discussed in detail a precise analysis technique of trihalomethanes by liquid/liquid extraction with pentane (Trussell, et al., 1979). The results demonstrated that the technique was accurate, sensitive, reproducible, and workable for large numbers of routine samples. In another study a comparison of recoveries of trihalomethanes in drinking water was made between purge and trap and liquid/liquid extraction with Methylcyclohexane. Both methods showed comparable results with compensating advantages to both procedures. Overall, the liquid/liquid extraction technique maintained higher recoveries (Reding, et al., 1979).

Perkin Elmer Corporation described a newly designed head-space analysis mechanism for adaption to gas chromatography (Widomski, 1979). This technique solved the common problem of inadequate temperature control and non-reproducibility of many poorly designed systems.

Purge and trap in conjunction with G.C./M.S. was applied to the E.P.A.'s list of 19 volatile priority pollutants for analysis in various types of waters. The method was tested successfully at the 5-50ug/L level and provided qualitative and semi-qualitative analysis (Pereira and Hughes, 1980). The purge and trap G.C./M.S. priority pollutant scan has become the most popular method of analysis for environmental monitoring. Present E.P.A. recommended methods include purge and trap in conjunction with G.C./M.S. The E.P.A.'s Methods 1624 and 1625 combine a radio isotope labeled dilution with purge and trap G.C./M.S. for volatile and semivolatile organic compounds (E.P.A., 1980, 1980).

James Misure from Monsanto undertook a survey of six techniques for low-level multi-component volatile organic techniques in water (Misure, 1980). Included in the general overview were: static head-space analysis, purge and trap, solid sorbents, liquid/liquid extraction, steam distillation, and semipermeable membranes. Increased demand for purge and trap analysis techniques have resulted from governmental recommendations. Researchers from the Tekmar Company recently presented two papers taking an extensive look at the optimization of purge and trap parameters and design considerations for automatic sampling (Westendorf, 1981; Westendorf et al., 1981).

C. Phenols

Until 1980 no analysis of phenols from sludge had been reported. However, several important developments in the area of phenol analysis have been published. The past developments which have potential importance in sludge analysis include: sorption resins, derivitization techniques, organic acid G.L.C. columns, high pressure liquid chromatography coupled with ultraviolet, fluorescence and electrochemical detection, preservation of phenols and gas chromatography mass spectrometry.

A dimethylbenzene polystyrene copolymer resin produced by the Rohm and Haas Company was shown to be effective in the sorption of substituted phenols (Paleos, 1969). Both the XAD-2 and XAD-7 resins were tested for adsorption from water of phenol, m-chlorophenol, o-nitrophenol, p-nitrophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol at concentrations up to 2.4 mol/liter. A more extensive study of the separation of nitrophenols on Amberlite XAD-2 resin was completed in 1972 (Grieser, 1972). Application of the XAD resin to chromatographic techniques for determination of phenols in water originated at Iowa State University (Chriswell, 1975). Later the XAD-2 resin was shown to be effective in separating a large group of chloro-, nitro-, and alkyl phenols via elution with buffers adjusted to various pHs. Sorption of phenol, o-cresol, m-cresol and 2,6-xyleneol from water on a macroporous polymer and subsequent thermal desorption onto a G.L.C. column was demonstrated in 1979 by a group of Czechoslovakian scientists (Voznakova and Pope, 1979). XAD resins have been used for concentrating organics from

wastewaters before and after treatment (Jolly, 1973; Glaze, 1981). Recovery efficiencies from XAD polymers are good for some compounds and poor for others. The reason for poor recoveries may be either poor absorption (polar organics, such as natural organics after oxidation with ozone or chlorine, low molecular weight acids and alcohols) or poor desorption (some long chain aliphatics and polynuclear aromatics).

Throughout the years many procedures have been used for the derivitization and analysis of phenolic compounds by gas chromatography (Seiber et al., 1972). Markedly improved resolution of derivatized methyl phenols was provided with the introduction to open tubular columns and eventually capillary columns (Hvivnak, 1971). In 1979 an extensive reference of phenolic trimethylsilyl derivatives was compiled according to their retention time on methyl and phenyl silicone G.L.C. columns (Mattsson and Peterson, 1977). This study attempted to draw a relationship between structure and retention of various phenolic derivatives. Two groups showed the use of derivatization in order to magnify sensitivity of certain phenols on a electron-capture detector (Lamparski and Nestrik, 1978; McCallum and Armstrong, 1973). Heptafluorobutyrylimidazole, pentafluorobenzoate and dimethyldichlorosilane were used as derivatizing agents for this extremely sensitive technique able to detect phenols in the part per billion range. The effectiveness of these two techniques was proven when both capillary chromatography and derivatization were combined in the analysis of a complex environmental matrix of coaltar waste (Buryan et al., 1978).

In an attempt to improve separation of phenolics by gas liquid chromatography without derivatization, several "organic acid" columns were developed (Supelco, 1978). A special high pressure liquid chromatographic column has also been introduced for better resolution of more complex organic acid mixtures Bio-Rad, 1980).

High performance liquid chromatography is well suited for the analysis of phenolic components. A comparison between several normal-phase and reverse-phase systems demonstrated the specificity of each column. For example, alkyl phenols were shown to have superior separation on a reverse phase C-18 column (Schabron, 1978). Good separation of E.P.A. priority pollutant phenols has also been demonstrated with a newly developed micropak 5u C-18 column (Realin, 1981). Various detection systems have been coupled with H.P.L.C. in the past. Trace level detection of phenols including the priority pollutants has been shown to be achievable by direct ultraviolet detection (Bhatia, 1973; Realini, 1979). Fluorescence has been applied to phenol and alkylphenols demonstrating superior relative detectability over ultraviolet detection systems (Ogan and Katz, 1979 & 1981). A highly sensitive technique down to 0.4 ppb has been reported by using fluorescence spectroscopy and detecting Cerium III after phenols react with Cerium IV (Wolkoff and Lavose, 1974).

Since 1952 the use of electrochemistry to monitor liquid chromatographic column effluent has been realized. The advent of amperometric detectors especially designed for liquid chromatography in lieu of colorimetric detectors has revolutionized this area (Kissinger, 1974, 1977, 1978). Electrochemical analysis is the most sensitive and selective method of detection for most easily oxidizable

or reducible components. Amperometric detection has been shown to be 100 to 1,000 times more sensitive than ultraviolet detection for various aromatic phenols and amines (Sternson and DeWitte, 1977). Application of amperometric electrochemical detection to the analysis of phenols in environmental samples has been widespread. Several recent papers have dealt extensively with the exact parameters for the determination of various phenolics in water and wastewater (Armentrout, et al., 1979; King, 1980; Mayer, 1981; Shroup, 1981; McCrory, 1981).

Quantitation and characterization of phenols from complex environmental samples via gas chromatography mass spectrometry has been reported by several authors (Schmidt, 1974 et al., Shackelford and Webb, 1979).

An indepth study on preservation techniques for phenolic compounds in wastewaters by an Environmental Protection Agency team indicated the necessity of chemical preservation as well as storage at 4 C immediately upon sample collection (Carter and Huston, 1978). An exhaustive report on the environmental effects of and accepted detection methods for all of the chlorophenol isomers was conducted by a group from the University of Wisconsin (Kozak, et al., 1979). Kozak's report may very well be considered "out of date" in respect to the analytical techniques suggested due to the great stride in analysis over the past few years.

D. Aromatic Hydrocarbons

Polychlorinated hydrocarbons have been the object of much attention in recent years due to their inertness in the environment. Of particular interest are the chlorinated pesticides and PCBs. Following heavy usage as agricultural pesticides and in industry respectively, these groups of chemicals had been widely distributed throughout the environment (Brown et al., 1970-72; Veith, 1971; Ahmed, 1976; Edwards, 1971; Peakall, 1970). They found their way to sewage plant systems via domestic and industrial wastes. Sharing similar physical and chemical properties, they were found to interfere with each other's analysis (Jensen, 1966; Reynolds, 1969; Risebrough et al., 1971). Therefore, the proper determination of each group had relied greatly on adequate methodology to separate them before gas-liquid chromatography analysis is performed.

The first attempt was to destroy or alter the pesticides through a nitration treatment in order to determine the PCBs, or to convert PCBs in decachlorobiphenyl whose EC signal was compared to a known amount of Aroclor 1254 converted to decachlorophenyl. Neither method had proven effective and was quickly abandoned. The nitration treatment affected the less polychlorinated biphenyls, but not all pesticides (Reynolds, 1969; Risebrough, 1969). Furthermore, the nitrated compounds had longer retention times and interfered with subsequent injection. The conversion method required an additional analytical step.

The second group of analytical techniques was aimed to allow the

special separation of many chlorinated hydrocarbon pesticides from PCBs. Authors involved in finding a device for the separation included Reynolds (1969, 1970), Armour and Burke (1970), Koeman et al. (1969), Mulhern (1968), and EPA (1971, 1979, 1980, 1982). Reynolds reported on an activated florisil column technique which separated heptachlor, aldrin, DDE, and PCB with the first elution (60 ml n-hexane) from lindane; heptachlor epoxide, DDD, and DDT with the second elution (40 ml 50% ethyl ether in hexane). Armour and Burke developed a method utilizing a silicic acid-celite column which elute aldrin and PCBs with the first fraction (250 ml petroleum ether), and lindane, heptachlor, dieldrin, endrin, p,p' - DDE, o,p' - DDT, p,p' - DDT, and p,p' - DDD with the second fraction (200 ml acetonitrile-hexane-methylene chloride 1:19:80). Koeman et al., used an activated florisil column, eluted the apolar compounds including DDE and PCB with hexane, and then dieldrin and endrin with 10% diethyl ether in hexane (Peakall and Lincer, 1970). Mulhern reported on a method which utilized silica gel-coated thin layer plates and a hexane/ethyl ether solvent system (Ibid).

The EPA also has followed the same trend in developing better methodology for the analysis and water and wastewater. The first report to be published was in 1971 and gathered the "current best available procedure for the analysis of water and wastewater". Other EPA reports appeared in 1979, 1980 and 1982 devoted specifically to chlorinated hydrocarbons and PCBs and aimed, among other goals, to provide a reliable means of separating the chlorinated compounds from the sample

matrix, isolating them from interferences and separating and detecting the individual compounds. Also, extensive data were presented on extraction efficiencies of single component pesticides and multicomponent formulations, comparison of florisil and gel permeation chromatography procedures.

The problem with most of these methods was that they were not totally reproducible, or if they were, there did not exist a clearcut separation between the compounds to separate. An interesting paper was published by McIntyre et al. (1980) who evaluated individual steps in the analytical procedure for the determination of PCBs and organochlorine pesticides in sewage sludge. The influence of solids concentrations upon extraction efficiency were also statistically analyzed. Another problem resides in the quantitation of PCBs. As a matter of fact, there does not exist a single uniform method to quantify PCBs chromatograms, although some attempts were made by Chan and Sampson (1975) and by Webb and McCall (1973).

E. Phthalates

The potential of phthalate ester plasticizers leaching into various contents stored in plastic containers is real (Jaeger and Rubin, 1970, 1972). Phthalates may also enter the environment through production of wastes both during the industrial process

and due to the disposal of plastics. Several authors have assessed the environmental safety of phthalate ester exposure (Gledhill et al., 1980; Lawrence and Tuell, 1980).

F. Aryl Phosphates

Aryl phosphates are routinely used as flame retardant plasticizers and in hydraulic fluids, both of which offer an avenue to environmental exposure. One publication has been released which discusses an analytical technique for analysis of triaryl phosphate esters in fish (Lombardo and Egvy, 1979). Several reports have been published concerning the environmental impact of aryl phosphate esters (E.P.A., 1978; Howard and Deo, 1979).

G. Aromatic Amines

Benzidine and 3,3-dichlorobenzidine are used in dyes and pigments; both have received much attention due to their potential carcinogenicity to humans (E.P.A., 1978, 1979). 3,3-dichlorobenzidine has also been shown to photodegrade to benzidine (Banerjee et al., 1978). A gas liquid chromatographic detection technique has been described for benzidine and other aromatic amines in the aquatic environment (Jenkins, et al., 1978). Aromatic amines which can be easily oxidized are well suited for high pressure liquid chromatography and electrochemical detection. Several publications have addressed

the question of aromatic amine determinations by liquid chromatographic electrochemical detection (Rice and Kissinger, 1979; Riggin and Howard, 1979; Shoup, 1980).

II . ANALYTICAL METHODS

A. Materials

1. Glassware preparation

All glassware (separatory funnels, flasks, teflon seals, and chromatographic columns) were thoroughly washed with detergent in hot water as soon as possible, rinsed several times with tap water, then distilled water and finally with acetone. The glassware was then heated overnight at 450 C. Teflons were dried in an oven at less than 100 C to prevent degradation of the silicone layers.

Glassware which had contained PCBs extracts was treated differently. Being thermally stable, PCBs were not eliminated by heating in the furnace alone. Also, the glassware which had previously contained PCBs was first rinsed several times with acetone and "pesticide-quality" hexane before heating in the furnace.

2. Sample collection

Sewage sludge samples were collected from 203 municipal wastewater treatment plants and 10 industrial and non-municipal facilities statewide (Figure 1) by the Michigan Department of Natural Resources, Water Quality Division, over a six-month period (from June 1980 to December, 1980). Two types of samples were collected at each site: one for volatile and semi-volatile organics, and another for non-volatile organics and inorganics. The volatiles and semi-volatiles were collected in 200 ml widemouth screw cap bottles with zero head-space and sealed with teflon-lined caps. The non-volatiles were

collected in 2-liter wide-mouth, amber screw cap jars with aluminum foil lined caps. Every sample was properly labelled (number, date and time) with an indelible ink and kept at 4 C. In our work we were interested only in the non-volatile samples.

For data handling, manipulation and storage, a program was written for a Digital PDP-11 computer. This program had the following purposes:

1. To store information on:
 - a. all sample sites
 - b. all cities, counties or townships
 - c. the population served by each treatment facility
 - d. the percent industrial input into each treatment system
 - e. all municipal sewage plant treatment parameters
 - f. all solids parameters
 - g. all organic compound levels
2. To perform various mathematical and statistical functions on the data.
3. To list specific information requested from all sites in a variety of formats.

3. Reagents

- Solvents: Hexane (H), Acetonitrile (ACN), Dichloromethane (DCM)-all of pesticide quality.

- Solvent mixtures:

1. Mixture A: 50% DCM-0.35% ACN - 49.65% H
2. Mixture B: 80% DCM - 1% ACN - 19% H
3. Mixture C: 10% DCM in hexane

- Chemicals

1. Sodium hydroxide NaOH - 0.1N and 6 N
2. Sulfuric acid H_2SO_4 - 0.1 N
3. Sodium sulfate - Na_2SO_4 (ACS) granular, anhydrous
4. Florisil - PR grade, 60-100 mesh, activated in oven at $135^{\circ}C$ for 48 hr. After cooling in dessicator at room temperature, the activated florisil was stored in dark in glass containers with foil-lined screw cap. Enough florisil from the same batch has been submitted to the same treatment to be used during the entire work.
5. Silica gel 60, particle size 0.063-0.200mm (70-230 mesh ASTM), activated at $130^{\circ}C$ for 48 hr., cooled in a dessicator at room temperature and kept in glass containers with foil-lined screw cap.

B. Methods

1. Extraction of organochlorine pesticides and PCBs

The chlorinated pesticides and PCBs may be classified as neutral compounds. Their extraction is not straight forward. In most cases, they are co-extracted with base compounds. Neutrals are ultimately obtained by separating bases, usually by liquid-liquid.

a. Solid samples

Solid samples were completely dried at 50 C and then soxhlet extracted with 200 ml DCM for 24 hours. Usually, 50 g samples were weighed for the extraction. The extract then passed through a

series of liquid-liquid extraction to ultimately yield the neutral fraction which contained the pesticides and PCBs. The extraction procedure was as follows:

- the soxhlet extract was transferred quantitatively to 250 ml centrifuge bottle, 100 ml 0.1N NaOH was added and shaken for 1 minute, and then centrifuged at 2500 rpm for 10 minutes. The aqueous layer was kept aside and the sample was extracted two more times as before using 100 ml 0.1N NaOH.
- The aqueous fractions were combined for acid components extraction.
- The solvent fraction was the base/neutral fraction. It was extracted three times with 100 ml 0.1N H_2SO_4 . The aqueous fractions were kept for base compounds extraction.
- The remaining solvent fraction contained the pesticides and the PCBs (neutrals).

b. Liquid samples

Liquid samples were extracted as follows:

- a determined volume of sample (usually 250 ml) was quantitatively transferred to a 500 ml separatory funnel and made basic (tested with pH paper) with 6N NaOH and then extracted three times with 50, 25 and 25 ml DCM. The aqueous fractions contained the acid compounds, the solvent fraction was the base/neutral fraction.
- Bases and neutrals were separated through acid/base partitioning with 0.1 N H_2SO_4 . Bases were extracted three times with 100 ml

0.1 N H_2SO_4 . The DCM fraction contained the neutrals, i.e. PCBs and organochlorine pesticides which were kept for the next step.

Figure 2 summarizes the overall scheme of the extraction procedure.

2. Cleanup procedure and early separation of polar pesticides

All environmental samples required one or more cleanup steps before analysis. This was especially true for sewage sludges containing up to 100% organic materials. They may be constituted by fatty acids; fats, proteins, phthalates, triglycerides, asphalts, detergents, and petroleum fuels. An appreciable amount (10-15%) of these organic materials was co-extracted with the compounds of interest. It was therefore necessary to remove those organic substances through cleanup procedure.

Several cleanup methods have been used, alone or in combination; they include: separation based on the size of the components with gel permeation chromatography (GPC), separation by polarity using alumina, florisil or silica gel columns and acid-base partitioning. The GPC method has been frequently used for the removal of fats and fatty acids (Stalling, L., Tindle, R.C., and John, J.L., 1972; Meuser, J.M. and Cooke, W. M., 1981; Hopper, M.L., 1981). Silica gel, florisil and alumina chromatographic columns are even more popular (Mills, F.A., 1959 and 1970; Wessel, J.R., 1969; Pesticide Analytical Manual, Vol. 1, 1971; Mills, P.A. et al., 1972; Ambrus, A. et al., 1981; Longbottom, J.E., 1982). In this

Figure 2. Scheme of the Extraction Procedure

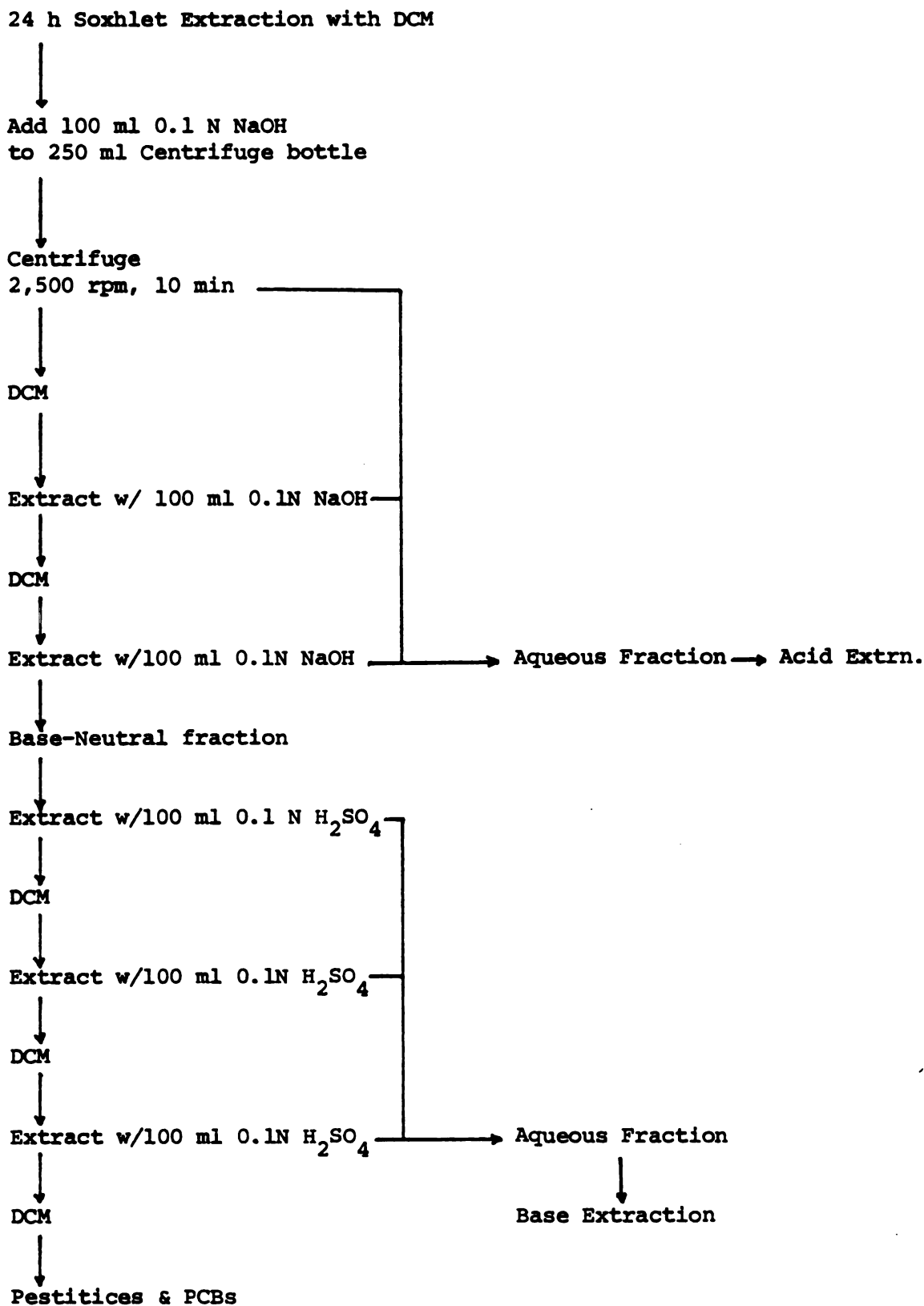


TABLE 2. Recovery of pesticides and PCBs studied

Compound	Average percent recovery %
Lindane	79.2
Aldrin	-
Dioldrin	73.1
Endrin	85
Methoxychlor	91
DDD	83.1
DDE	79.6
DDT	82.5
PCB-1254	82.2
PCB-1260	81.3

study acid/base partitioning followed by a florisil column separation were the cleanup steps. The acid/base partitioning was carried out throughout the extraction procedure.

a. Florisil chromatographic column preparation and cleanup procedure

The chromatographic column separation by florisil was performed using glass columns with 10 mm internal diameter and 51 cm long. The columns were dry-packed with 10 gms of fully activated florisil over 20 cm. This was done by taping gently the chromatographic tube. These conditions facilitated greater resolution of polar from non-polar pesticides from mixtures of pesticides of PCBs. Each column was topped with 2 cm anhydrous Na_2SO_4 , and pretreated with 50 ml hexane.

Two solvent systems were used for the elution. The procedure was as follows:

a) The extract was transferred to the column, letting it pass through; then the container was rinsed two times with 5 ml hexane and rinse washes were transferred to column; finally, the column walls were rinsed. The column was not allowed to dry during this procedure until the cleanup was completed.

b) The nonpolar pesticides (Lindane, Aldrin, DDE, DDD and DDT) and the PCBs were eluted with 150 ml eluant C, consisting of 10% DCM in hexane (Fraction S).

c) The polar pesticides (endrin, dieldrin, methoxychlor) were eluted with 250 ml eluant A (50% DCM - 0.35% ACN - 49.65% H). The fraction collected was named fraction A. This fraction was concentrated and put into 0.1 ml vial for injection on GC-EC column.

This procedure was adapted from Mills, P.A. et al., procedure (1972) which was an alternative to the old method using mixtures of ethyl ether-petroleum ether in the florisil column chromatographic cleanup for pesticide residue analysis.

b. Note on the variability in the activity of florisil

Florisil is a polar adsorbent reported to have a large surface area, which is the basis for its adsorptive properties. It has been shown that the adsorptive capacity of florisil varies from lot to lot, due to varying sodium sulfate content (Mills, Paul A., 1968). Several methods had been attempted to compensate or adjust for the variability of adsorbancy of different batches of florisil. Among them, lauric acid method is largely used. In our experiment, we did not feel it necessary to go through that step. Rather, the chromatographic column was standardized using a mixture of pesticides and PCBs. Great care has been taken to keep florisil activity constant by avoiding long exposure of the treated florisil to humidity.

3. Separation of the pesticides from PCBs by silica gel 60

For the quantitative determination of the DDT group of pesticides and PCBs, it was necessary to separate one group from the other as it is now well established that they interfere with determination of the other. Several column chromatographic separation

procedures, more or less successful, have been published. The procedure we used was based on that of Armour and Burke (1970), which was refined by Griffin, D.A. et al. (1980), and by Nowicki, H.G. (1981). It was as follows:

a) The chromatographic column was dry-packed with 10 g of fully activated silica gel 60 over 22 cm, and topped with 2 cm Na_2SO_4 anhydrous.

b) The column was prewashed with 30 ml hexane. An approximate column flow of 1 cm/min was maintained. The column was not allowed to go dry from this point.

c) The cleaned up extract containing PCBs and pesticides in 3 ml solvent or less was transferred quantitatively to the column, and eluted in this order:

- first, aldrin and PCBs with 65 ml hexane (Fraction C)
- then, lindane, DDE, DDD and DDT with 250 ml eluant B (Fraction B). Both fraction B and C were concentrated to 0.05 ml for injection.

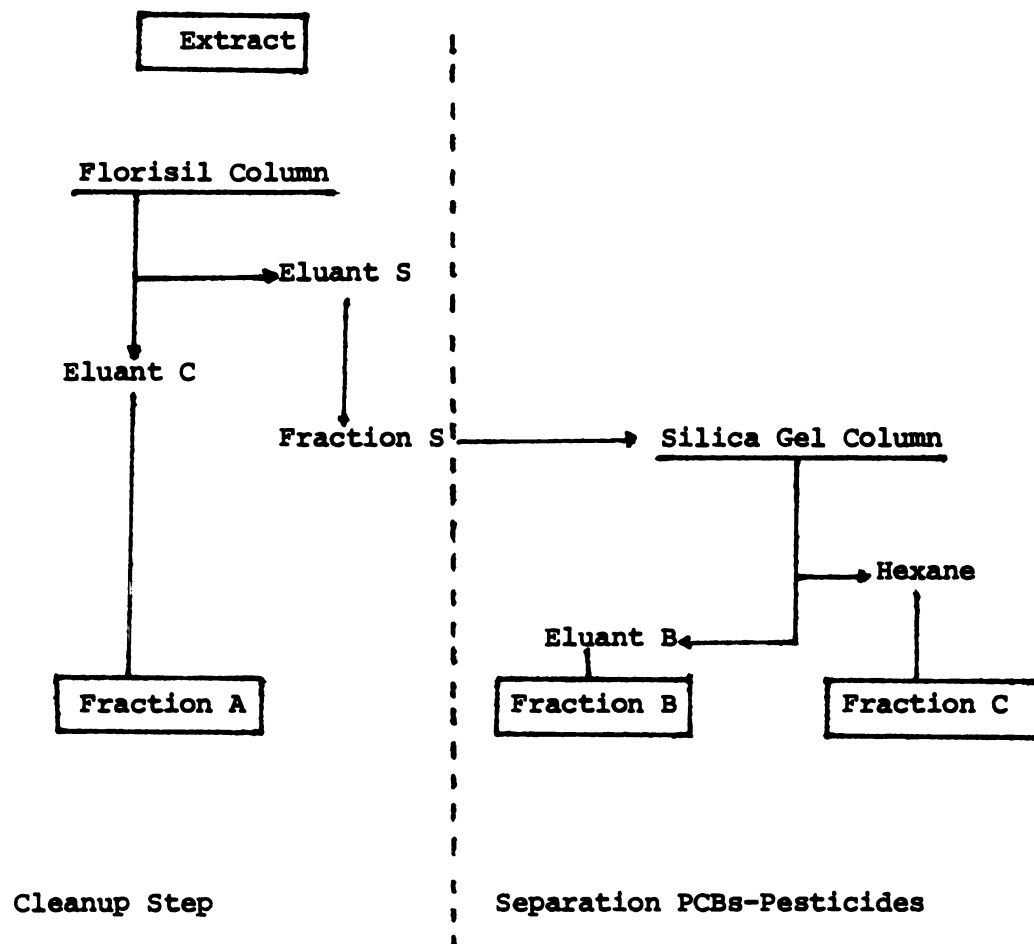
Figure 3 summarized the cleanup and separation procedures and Table 3 the composition of the different fractions collected.

The Armour and Burke method utilized a silicic-celite-545 (4 to 1 ratio) column for the separation which required air pressure to deliver an elution rate of 5ml/min. This was inconvenient in our case because we did not have the available material to devise a system applicable to several columns at the same time. Further, it has been

TABLE 3. Composition of the different fractions collected

	Absorbent	Solvent System	Fraction	Eluate Content
Clean up	Florisil	50% DCM-0.35% ACN- 49.65%H	A	Endrin, Dieldrin, Methoxychlor
	Florisil	10% DCM	2	Lindane, Aldrin, DDD, DDE, DDT, PCBs
Separation	Silica gel 60	Hexane	B	Aldrin, PCBs
	Silica gel 60	1% ACN-19% H-80% DCM	C	Lindane, DDD, DDE, DDT

Figure 3. Cleanup and Separation Procedures of PCBs and Pesticides



reported (Masumoto, H.T., 1972; Huckins, J.N., et al., 1976) that silicic acid-celite mixture is not always homogeneous, causing the elution pattern to vary from column to column. Another problem of the separation resided in the coelution of aldrin with PCBs and the lack of clear cut separation between p,p'-DDE and PCBs. Improvement of the method has been attempted using an internal standard such as azulene, acting as a visual aid to monitor column chromatographic fractionation (Nowicki, G., 1981), or eliminating celite in the procedure and adding azulene as monitor (Griffin, D.A. et al., 1980). While Armour and Burke and Nowicki methods utilized 3% water deactivated silicic-celite, Griffin used fully activated silicic acid and reported the best separation with less than 8% p,p'-DDE in the PCBs fraction. Our own separation using fully activated silica gel 60 has provided acceptable fractionation, except that aldrin eluted in the PCBs fraction as in the case of Armour and Burke method. This did not pose a serious problem since aldrin was eluted before or at the same time as the very first eluting peaks of the less chlorinated PCBs. In addition, aldrin was more sensitive than the PCBs to the GC-EC detector at the same concentration. The problem arose, however, during the course of analysis when we realized that a huge interference masked the first eluting peaks, including aldrin. Aldrin could thus not be quantitated.

The silicic acid-celite 545 chromatographic column of Armour and Burke, and similar methods developed by other researchers (Berg, O.W., et al., 1972; Wells, D.E. et al., 1977) for the quantitative separation of DDT and analogs from PCBs, suffered many variations, as reported in the literature. Although some attempts were made to improve the method, none had given to date a complete separation of the two classes of compounds. This denoted the difficulty of reproducing this separation.

4. Quantitation

a. Organochlorine pesticides

A standard curve was constructed for each pesticide from different concentrations of standard solutions. A 2 ul-volume of standard solution was injected into a gas liquid chromatograph equipped with Ni⁶³ electron capture detector at the following parameters:

- detector: 300 C
- column: 6 ft x 1/8 in. i.d., packed with 11% ov-17+QF1 on 80-100 gas chrom. Q, 190 C
- nitrogen flow: 30 ml/min
- Chart speed: 0.2 inch/min
- Attenuation 10x8
- E C voltage: 30V

The concentration for each compound was determined by the computer from its standard and the following equation:

$$\text{ug./l} = \frac{(A) (V_t)}{(V_i) (V_s)}$$

where: A = amount of material injected (in nanograms)

V_i = volume of extract injection in ul (here 2ul)

V_t = volume of total extract (ul)

V_s = volume of liquid sludge (ml) or weight of solid sludge (gm)

b. PCBs

No unified way exists to quantitate PCBs in environmental samples.

It is generally recognized that the prime area of uncertainty in PCBs methodology lies in the interpretation of the gas chromatogram (Burke, J.A., 1972; Sawyer, L.D., 1973) although some laboratories (Chau, A.S.Y. and Sampson, R.C.J., 1975; Webb, R.G. and McCall, A.C., 1973) attempted to present a uniform approach. But generally, quantitation was based on

the direct comparison of an unknown electron capture chromatogram with those of PCBs standards. Our method of quantitation was based on the following observations:

1. The gas chromatogram profiles of the sludge samples closely approximated those obtained from a mixture of PCBs-1254 and 1260.

2. The PCBs-1260 standard peak with retention time $RT=174mm$ (peak 13) did not get any contribution from PCB-1254 in the mixture, while peak 9 of PCB-1260 and peak 11 of PCB-1254 showed up at the same retention time $RT=95mm$

Therefore:

1. The peak 13 of PCB-1260 was used to quantitate PCB-1260 in sludge samples.

2. The peak 11 of PCB-1254 in the mixture (PCBs 1260 and 1254) was used to quantitate PCB-1254 in the sample, the contribution of PCB-1260 peak being deducted.

Standard curves of peak 13 and peak 9 of PCB-1260 and peak 11 of PCB-1254 were constructed and used to quantitate levels of the compounds in the samples. The gas chromatograph employed was a Tractor 560 equipped with a ^{63}Ni EC detector. Chromatograph conditions were as follows:

Column - 6 ft x 1/8 in i.d. glass coil packed with 3% SE-30 on

Chromosorb W-HP

Temperature - oven 200 C

Carrier - N_2 at 50 psi with flow maintained at 30 ml/min at column

temperature 200 C

Injection - 2 ul, on column

Attenuation - 8×10

Figure 4 Gas chromatogram of PCB 1254 standard

Chromatographic conditions:

Column: 3% silicone SE-30% on 80/100 Chrom. W-HP

Oven - 190 C

Detector - 63NiEC, 300 C

Carrier - N₂, 30 ml/min.

Chart speed - 0.2 inch/min.

Attenuation - 8 x 10

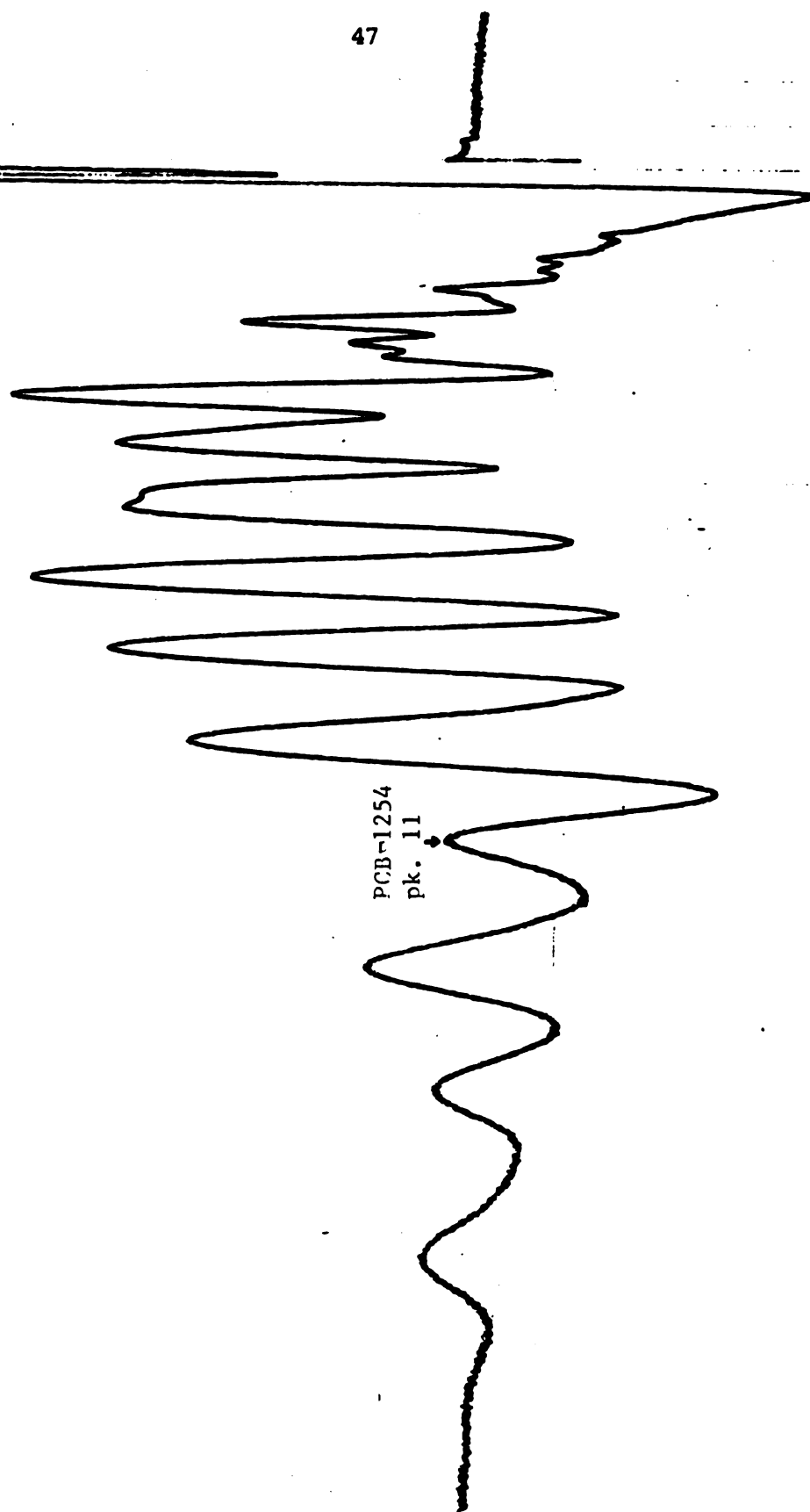


Figure 5 Gas chromatogram of PCB 1260 standard

Gas chromatographic conditions:

Column - 3% silicone SE-30 on 80/100 Chrom. W-HP

Oven - 190 C

Detector - ^{63}Ni EC, 300 C

Carrier - N_2 , 30 ml/min.

Chart speed - 0.2 inch/min.

Attenuation - 8 x 10

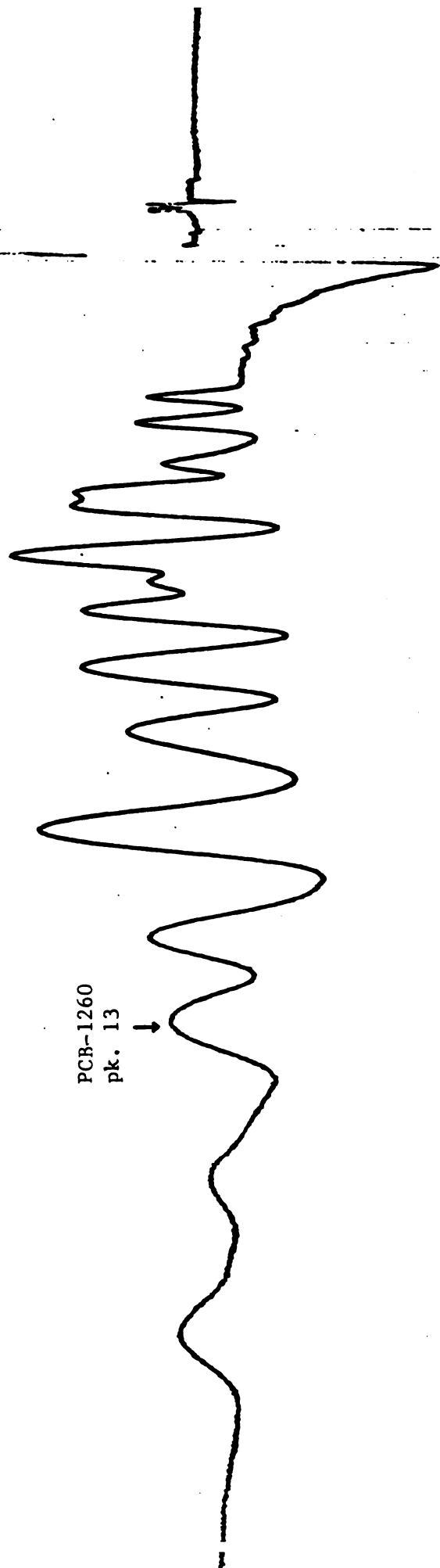


Figure 6 Gas chromatogram of the mixture PCB 1254 and PCB 1260 standard

Chromatographic conditions

Column - 3% silicone SE-30 on 80/100 Chrom. W-HP

Oven - 190 C

Detector - 63 N1 EC, 300 C

Carrier - N₂, 30 ml/min.

Chart speed - 0.2 inch/min.

Attenuation - 8 x 10

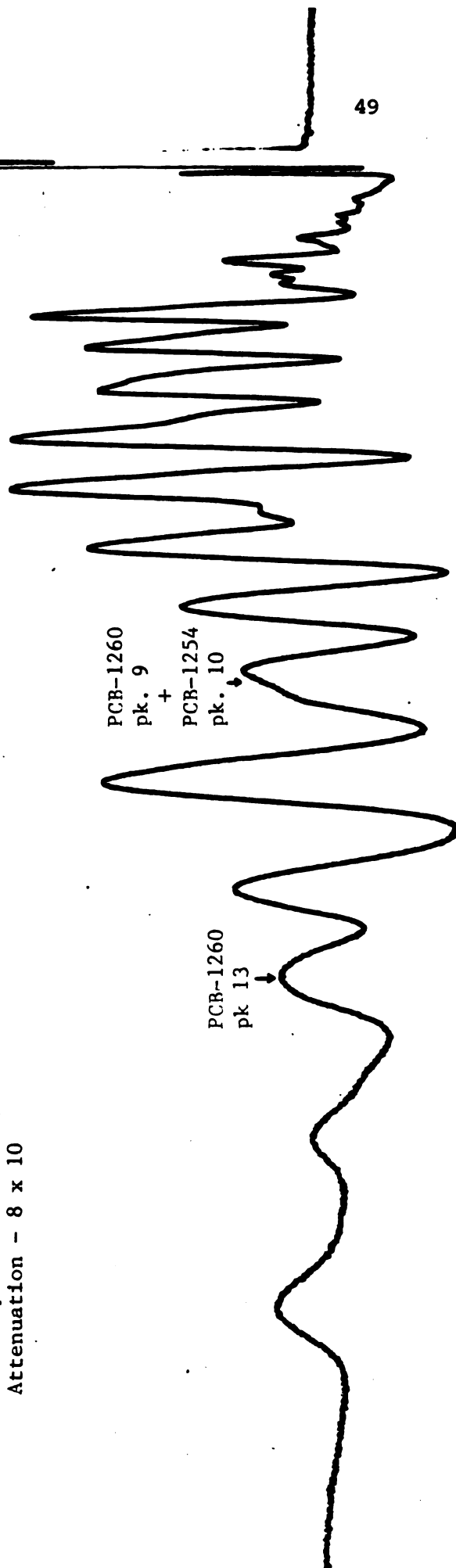
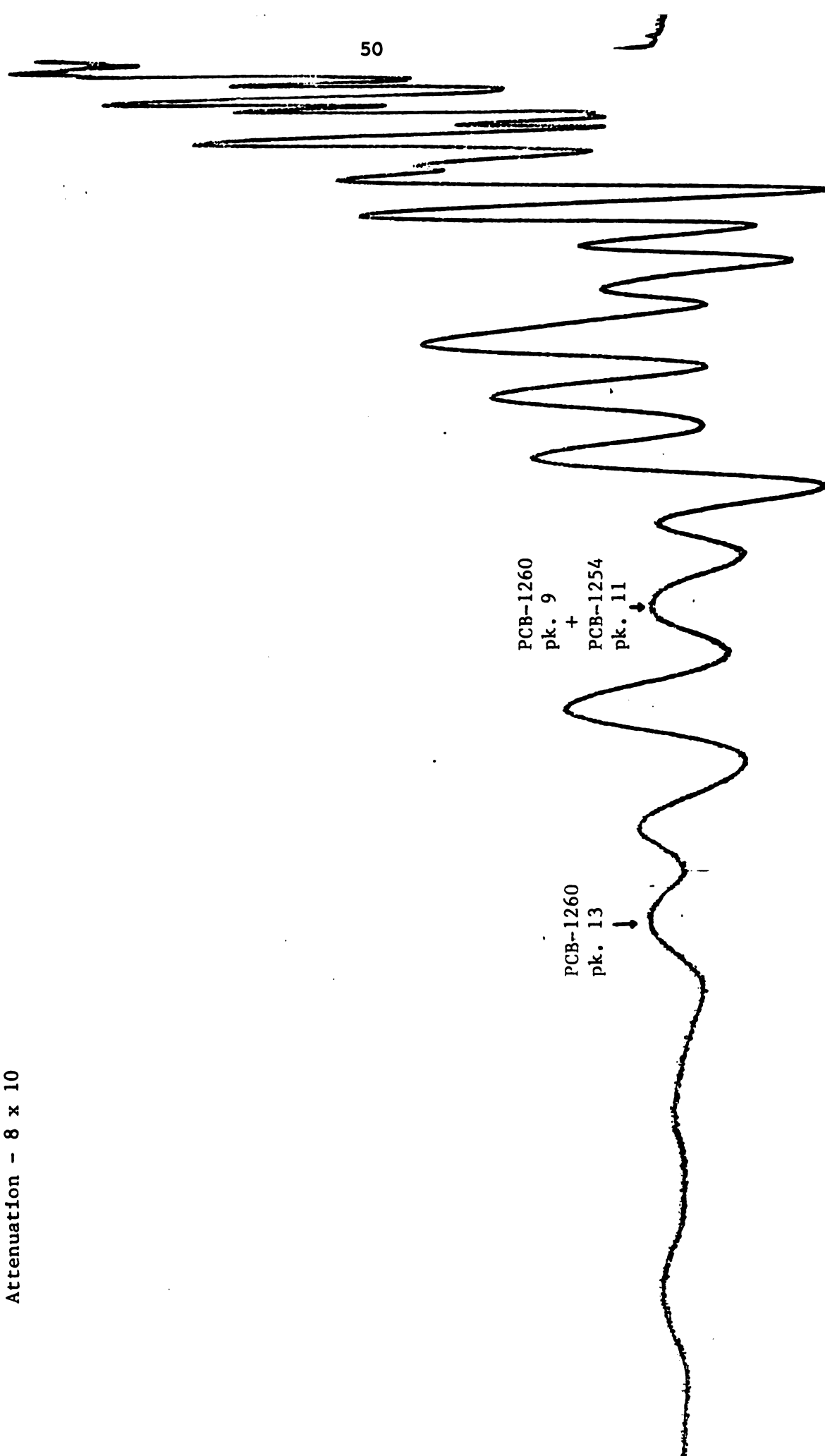


Figure 7 Gas chromatogram of a sample analyzed
Chromatograph conditions
Column - 3% silicone SE-30% on 80/100 Chrom. W-HP
Oven - 190 C
Detector - 63 N1 EC, 300 C
Carrier - N₂, 30 ml/min
Chart speed - 0.2 inch/min
Attenuation - 8 x 10



III RESULTS AND DISCUSSION

A. Results

Residue concentrations of PCBs present in sludge varied from traces to 1.9 ppm. Pesticides concentrations were lower. DDT showed th highest concentration among the pesticides at 17.50 ppb (Tables 5 and 6). Endrin and methoxychlor were not detected. A clean separation was not obtained for aldrin. A summary of the results is given in table 4.

The concentrations found were scattered, especially for PCB-1254 ranging from nearly 2 ppm down to 1.13 ppb, and for PCB-1260 from 433 ppb to 0.51 ppb, DDT from 17.5 ppb to 0.08 ppb, and DDD from 12.4 ppb to 0.02 ppb. This wide dispersion of the results may represent the variable nature and composition of sewage effluents.

Among the pesticides, DDT was found in the highest concentrations with levels as high as 17.5 ppb and an average level of 1.75 ppb. DDD was next highest with an average level of 0.58 ppb and with the highest concentration being greater than 12 ppb. The higher concentrations of DDD were recorded on the sites where DDT levels were high. DDE and lindane were present apparently in similar concentrations with 0.24 ppb and 0.26 ppb respectively.

Higher concentrations of PCBs than the pesticides were present. PCB-1254 was determined to have the highest level (1.9 ppm) in the sludges analyzed with an average above 0.6 ppm.

B. Comparison of the results with those available in the literature

An analytical survey of several municipal sewage sludges of American cities by Fur, et al. (1976) showed PCB concentrations

Table 4 - Summary of data for the 103 sites analyzed

Compound	Average amount found	High value	Low value	Median value	Standard deviation
		----- (ug/kg dry wt. (ppb)) -----			
Dieldrin	0.78	2.28	0.13	0.64	0.58
DDD	0.68	12.40	0.02	0.16	1.80
DDE	0.24	0.65	0.02	0.22	0.16
DDT	1.75	17.50	0.08	1.03	2.62
Lindane	0.26	2.94	0.04	0.12	0.51
PCB-1254	61.0	1960	1.13	6,20	309
PCB-1260	20.7	433	0.51	5,10	61

Table 5 Pesticides concentrations (ng/kg dry wt.) in sewage sludges analyzed

	ALDRIN(N)	DIELDRIN(N)	ENDRIN(N)	DDEP(N)	DDE(N)	DOT(N)	LINDANE(F)	METHOXYCHLOR(F)
1	0.0	0.0	0.0	0.0	0.0	51.5	0.0	0.0
5	0.0	0.0	0.0	16.5	5.0	42.0	0.0	0.0
16	0.0	64.4	0.0	0.0	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	22.1	0.0	0.0	0.0	5.0	0.0
21	0.0	25.3	0.0	3.7	0.0	44.9	0.0	0.0
22	0.0	0.0	0.0	3.7	0.0	28.9	0.0	0.0
23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	2.3	0.0	0.0	3.1	0.0
25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
26	0.0	32.1	0.0	0.0	0.0	0.0	0.0	0.0
27	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0.0	0.0	0.0	0.0	0.0	20.0	0.0	0.0
32	0.0	0.0	0.0	0.0	0.0	40.1	0.0	0.0
34	0.0	24.9	0.0	3.7	0.0	23.6	0.0	0.0
35	0.0	0.0	0.0	3.7	0.0	28.5	0.0	0.0
36	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0
39	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
40	0.0	0.0	0.0	6.7	5.5	53.4	0.0	0.0
52	0.0	0.0	0.0	6.7	17.4	37.2	12.9	0.0
54	0.0	0.0	0.0	5.2	0.0	40.1	4.0	0.0
55	0.0	0.0	0.0	118.0	21.4	314.2	22.4	0.0
56	0.0	0.0	0.0	2.1	0.0	10.3	0.0	0.0
57	0.0	0.0	0.0	2.6	0.0	22.4	5.9	0.0
59	0.0	0.0	0.0	0.0	0.0	14.2	28.4	0.0
60	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
61	0.0	24.3	0.0	0.0	0.0	0.0	0.0	0.0
62	0.0	0.0	0.0	6.7	0.0	58.1	13.7	0.0
68	0.0	0.0	0.0	2.6	0.0	20.7	0.0	0.0
73	0.0	0.0	0.0	6.6	13.7	15.2	3.6	0.0
77	0.0	846.4	0.0	0.0	0.0	0.0	0.0	0.0
81	0.0	0.0	0.0	5.9	0.0	23.1	0.0	0.0
84	0.0	0.0	0.0	44.2	17.3	0.0	0.0	0.0
85	0.0	0.0	0.0	16.7	5.3	0.0	0.0	0.0
87	0.0	0.0	0.0	0.0	3.0	281.0	2.5	0.0
88	0.0	0.0	0.0	3.9	0.0	48.7	6.7	0.0
90	0.0	0.0	0.0	8.1	5.2	57.7	5.7	0.0
93	0.0	98.1	0.0	10.7	6.7	256.1	12.5	0.0
94	0.0	0.0	0.0	2.3	0.0	23.9	0.0	0.0
95	0.0	0.0	0.0	3.7	0.0	11.6	0.0	0.0
98	0.0	0.0	0.0	30.1	0.0	115.5	4.5	0.0
99	0.0	0.0	0.0	6.4	0.0	20.7	0.0	0.0
101	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
104	0.0	40.5	0.0	25.2	19.1	179.7	0.0	0.0
108	0.0	40.5	0.0	3.3	0.0	79.0	0.0	0.0
114	0.0	0.0	0.0	23.1	19.7	102.5	3.5	0.0
116	0.0	0.0	0.0	55.4	29.4	61.2	0.0	0.0
117	0.0	0.0	0.0	30.7	2.4	34.3	3.0	0.0
118	0.0	0.0	0.0	56.7	25.6	92.1	0.0	0.0
120	0.0	0.0	0.0	0.0	4.4	0.0	0.0	0.0

Table 5 continued

121	0.0	0.0	0.0	0.0	13.5	0.0	0.0	0.0	0.0	0.0	32.4	0.0
123	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
125	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17.1	0.0
126	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
129	0.0	105.8	0.0	0.0	8.2	0.0	0.0	0.0	0.0	0.0	54.8	0.0
130	0.0	74.6	0.0	0.0	62.1	0.0	0.0	0.0	17.9	0.0	420.5	18.0
138	0.0	0.0	0.0	0.0	4.3	0.0	0.0	0.0	0.0	0.0	10.3	3.4
141	0.0	20.6	0.0	0.0	12.4	0.0	0.0	0.0	7.4	0.0	40.1	0.0
143	0.0	24.6	0.0	0.0	20.5	0.0	0.0	0.0	23.9	0.0	73.1	7.9
144	0.0	0.0	0.0	0.0	41.6	0.0	0.0	0.0	14.8	0.0	71.2	2.2
145	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
146	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.2	0.0
148	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0
150	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0	0.0	34.3	0.0
152	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
153	0.0	0.0	0.0	0.0	2.4	0.0	0.0	0.0	0.0	0.0	11.3	3.2
154	0.0	0.0	0.0	0.0	10.2	0.0	0.0	0.0	0.0	0.0	87.2	0.0
155	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
156	0.0	22.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
157	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
159	0.0	0.0	0.0	0.0	6.9	0.0	0.0	0.0	3.0	0.0	14.2	0.0
160	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
161	0.0	0.0	0.0	0.0	3.5	0.0	0.0	0.0	0.0	0.0	7.9	6.8
162	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
163	0.0	0.0	0.0	0.0	17.6	0.0	0.0	0.0	2.2	0.0	77.7	0.0
164	0.0	1.0	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	10.6	0.0
165	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
169	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	143.4	0.0
170	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	73.7	0.0
171	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
173	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	2.4
175	0.0	0.0	0.0	0.0	160.9	0.0	0.0	0.0	3.6	0.0	0.0	0.0
176	0.0	21.7	0.0	0.0	3.2	0.0	0.0	0.0	2.2	0.0	15.6	0.0
177	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	0.0	34.3	5.1
178	0.0	34.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
179	0.0	0.0	0.0	0.0	11.7	0.0	0.0	0.0	20.2	0.0	14.8	0.0
180	0.0	0.0	0.0	0.0	12.6	0.0	0.0	0.0	12.0	0.0	122.4	0.0
181	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
183	0.0	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0	6.0
186	0.0	0.0	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
187	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.6
190	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	176.7	0.0
191	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0	0.0	0.0	79.5	0.0
193	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
194	0.0	39.3	0.0	0.0	13.4	0.0	0.0	5.1	0.0	0.0	0.0	0.0
195	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8
199	0.0	0.0	0.0	0.0	37.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
200	0.0	0.0	0.0	0.0	5.4	0.0	0.0	0.0	0.0	0.0	31.4	4.0
201	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
202	0.0	0.0	0.0	0.0	2.4	0.0	0.0	0.0	0.0	0.0	0.4	3.9
203	0.0	0.0	0.0	0.0	12.6	0.0	0.0	0.0	0.0	0.0	30.4	0.0
204	0.0	0.0	0.0	0.0	4.1	0.0	0.0	0.0	0.0	0.0	12.0	0.0
205	0.0	12.1	0.0	0.0	33.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
207	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
210	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

5000.1108 0 100 1151)

Table 6 PCBs concentrations (ng/kg dry wt.) in sewage sludges analyzed

	PCB 1254(N)	PCB 1260(N)	FBB(N)
1	2695.7	1991.5	0.0
5	1200.0	1904.2	0.0
16	0.0	6297.6	0.0
19	4000.0	0.0	0.0
20	10804.6	0.0	0.0
21	10269.9	0.0	0.0
22	2981.4	2702.9	0.0
23	9016.0	1203.2	0.0
24	1249.1	4228.9	0.0
25	2500.0	1671.2	0.0
26	41969.4	0.0	0.0
27	0.0	0.0	0.0
30	6292.9	0.0	0.0
32	0.0	505.5	0.0
34	0.0	1286.5	0.0
35	0.0	708.1	0.0
36	0.0	0.0	0.0
39	0.0	1466.8	0.0
40	0.0	11812.0	0.0
52	4056.4	5097.9	0.0
54	0.0	1972.8	0.0
55	0.0	13701.7	0.0
56	0.0	0.0	0.0
57	0.0	3374.8	0.0
59	20424.9	0.0	0.0
60	0.0	0.0	0.0
61	0.0	0.0	0.0
62	3330.6	0.0	0.0
68	0.0	0.0	0.0
73	0.0	6035.4	0.0
77	0.0	0.0	0.0
81	67464.6	0.0	0.0
84	0.0	0.0	0.0
85	14050.0	0.0	0.0
87	13141.5	29742.3	0.0
88	12473.3	0.0	0.0
90	0.0	32618.8	0.0
93	3662.8	10997.7	0.0
94	0.0	36140.5	0.0
95	0.0	6858.3	0.0
98	10335.0	23190.0	0.0
99	0.0	0.0	0.0
101	6350.0	11208.3	0.0
104	1.196349E 7	148939.0	0.0
108	0.0	72380.3	0.0
114	0.0	52980.0	0.0
116	0.0	18779.5	0.0
117	0.0	4049.6	0.0
118	0.0	4178.8	0.0

Table 6 continued

121	0.0	432917.0	0.0
123	0.0	1726.5	0.0
125	4502.2	0.0	0.0
126	0.0	10.8	0.0
129	0.0	17981.5	0.0
130	0.0	36332.1	0.0
138	0.0	3237.5	0.0
141	0.0	1946.3	0.0
143	1650.4	2907.1	0.0
144	0.0	9285.4	0.0
145	0.0	22859.3	0.0
146	0.0	8390.9	0.0
148	23764.7	0.0	0.0
150	0.0	6669.5	0.0
152	11776.5	0.0	0.0
153	1393.9	0.0	0.0
154	4443.3	0.0	0.0
155	0.0	0.0	0.0
156	0.0	0.0	0.0
157	0.0	611.8	0.0
159	1208.9	0.0	0.0
160	0.0	0.0	0.0
161	1133.3	0.0	0.0
162	0.0	0.0	0.0
163	0.0	3161.6	0.0
164	0.0	6821.9	0.0
165	0.0	0.0	0.0
169	2276.7	0.0	0.0
170	0.0	0.0	0.0
171	0.0	0.0	0.0
173	0.0	0.0	0.0
175	0.0	6815.4	0.0
176	3342.2	0.0	0.0
177	0.0	720.0	0.0
178	6114.0	0.0	0.0
179	0.0	3112.0	0.0
180	11884.8	24032.7	0.0
181	0.0	20277.9	0.0
183	0.0	4092.7	0.0
186	81830.0	7250.0	0.0
187	9315.4	0.0	0.0
190	0.0	2133.7	0.0
191	3497.1	0.0	0.0
193	0.0	0.0	0.0
194	0.0	0.0	0.0
195	0.0	6092.3	0.0
199	1313.5	1094.2	0.0
200	0.0	3537.5	0.0
201	0.0	0.0	0.0
202	29043.3	0.0	0.0
203	26775.0	0.0	0.0
204	0.0	0.0	0.0
205	0.0	3516.7	0.0
209	0.0	5910.0	0.0
210	0.0	0.0	0.0
SUBTOTAL (O FOR LIST)7			

ranging from about 23 ppm (Denver) to 0.01 ppm (San Francisco). Erikson and Pellizzari (1979), using GC/MS/computer detected individual isomer, with total PCBs of about 11 ppm. In 1974, Dube, et al. reported concentrations of 0.05 - 2.8 ppb PCBs in sewage effluents collected at numerous Wisconsin cities. The concentrations in those studies were all expressed on a wet weight basis. They would be even higher if they were reported on a dry weight basis, as in this study. Consequently, the concentrations of PCBs found in sludges in this study were equal to or relatively lower than those reported in the literature.

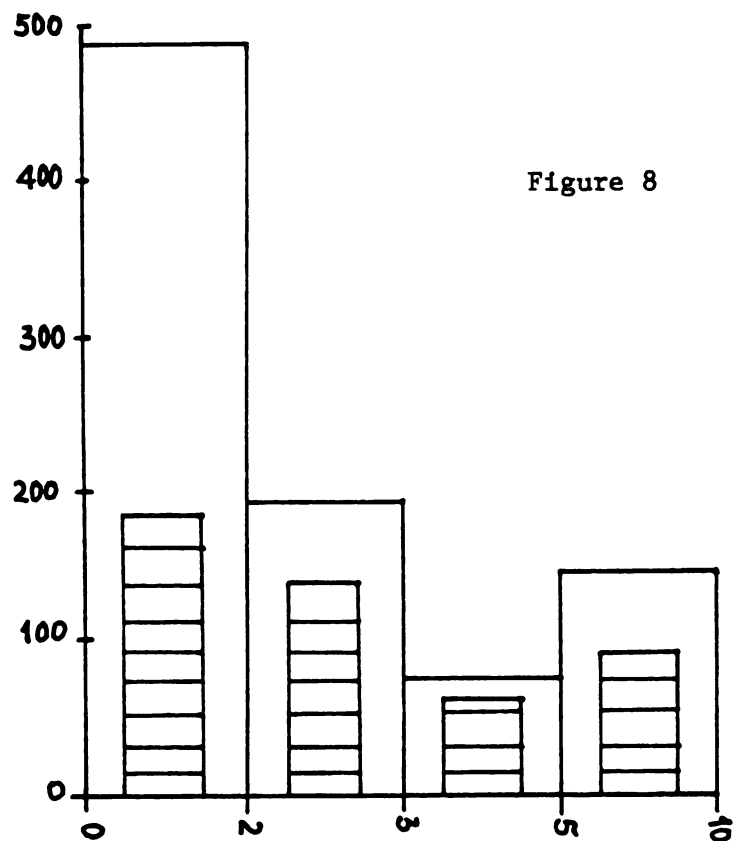
Likewise, DDT analogs and other pesticides reported in this study were equal or lower than those published in the literature (Harper and Gotte, 1977; Frank, et al., 1977).

C. Parameters tested

An attempt has been made to find if any trend exists between the level concentration detected and the number of population and the percentage of industrial input (Figures 8-25). The percent industrial input is defined as the ratio of the total industrial input over the flow of the treatment facility.

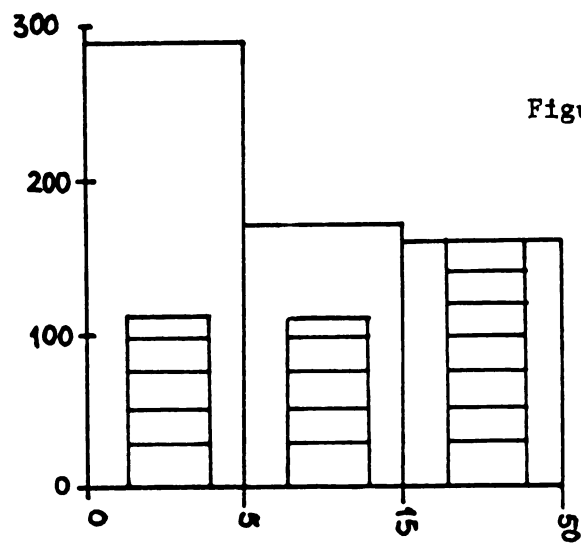
For most of the chemicals studies, there seems to exist a decreasing trend in the concentration as the population increases (Figures 8, 9, 11-15). This is in accordance with previous similar comparisons with total phenols analyzed in sewage (Phillips, 1981). However, this trend was not observed when different groupings of population were made (Figures 18 and 19). A study by Harper, et al. (1977) showed a linear regression between total BHC concentration in a river water and urban population density.

Lindane mean and median concentration
ng/kg dry wt.



Population in thousands

Lindane mean and median concentration
ng/kg dry wt.



Population in thousands

Figure 10

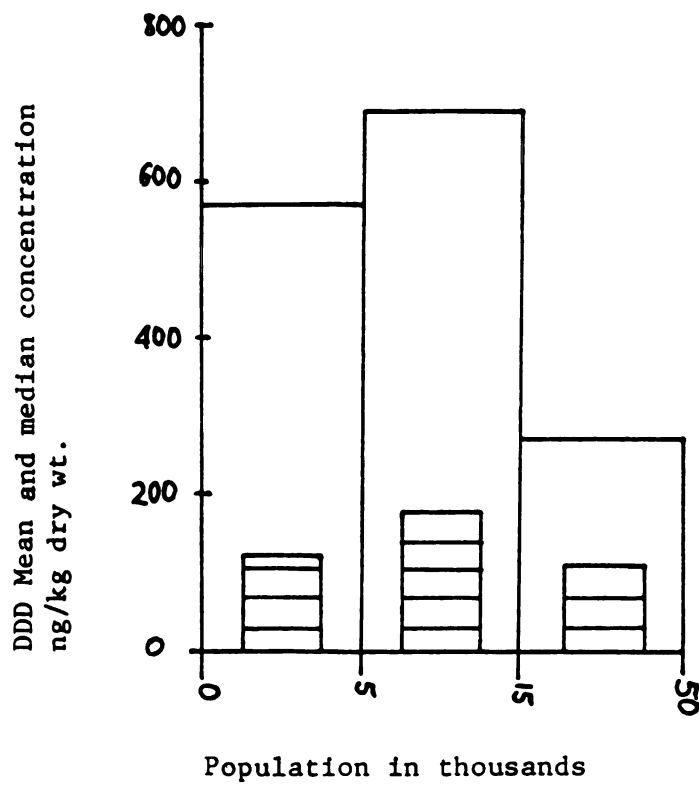
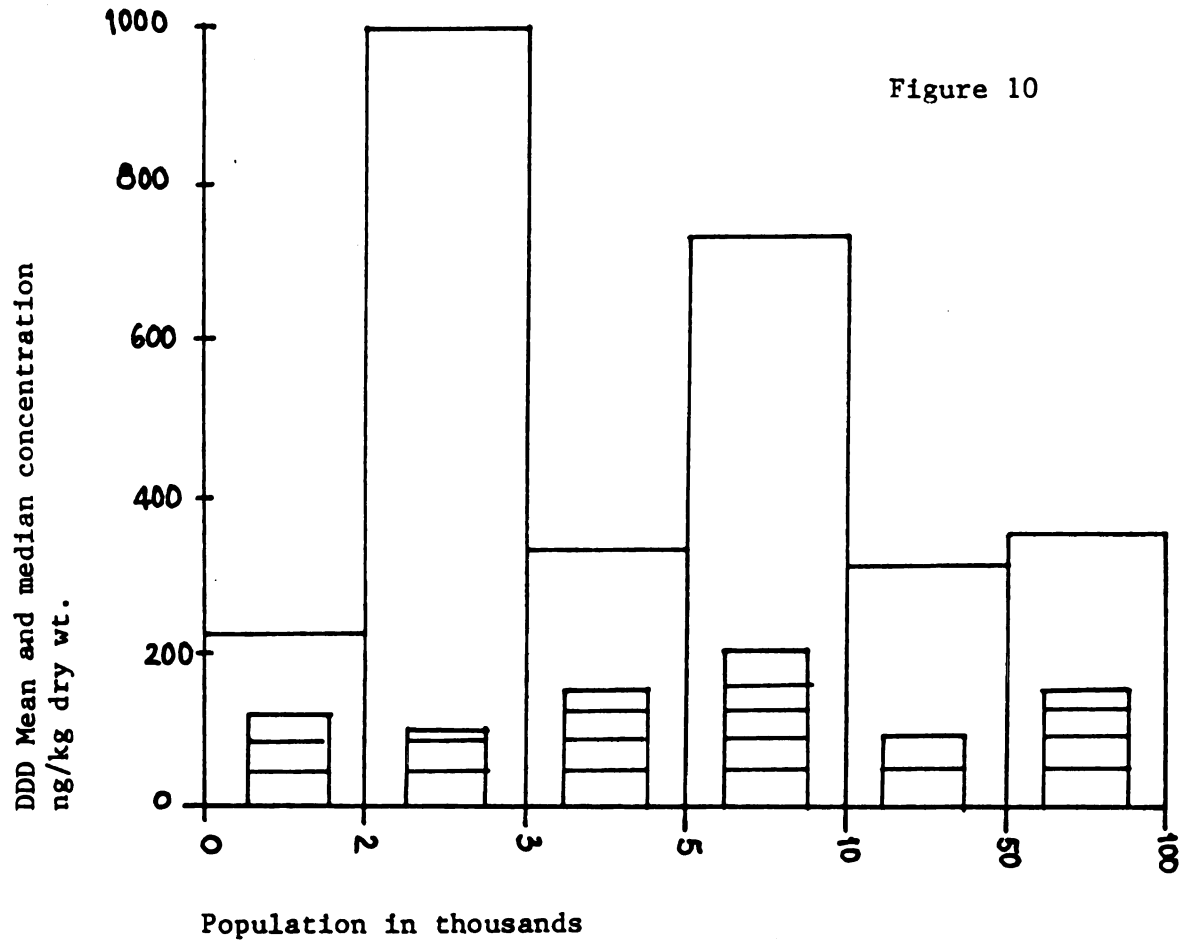


Figure 12

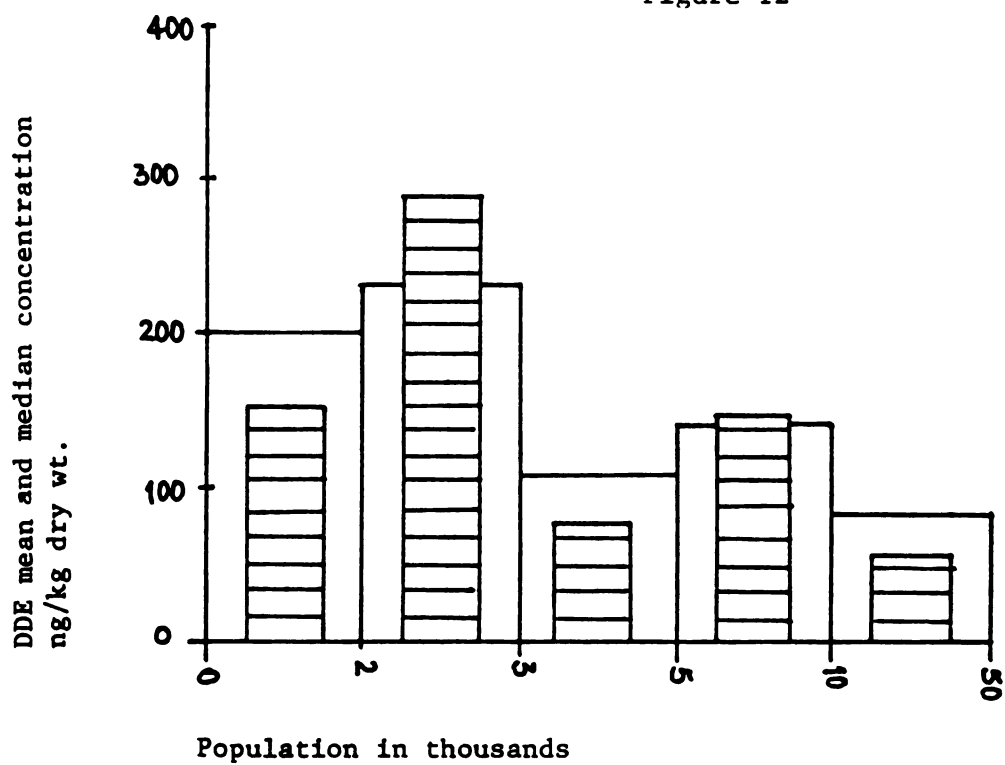


Figure 13

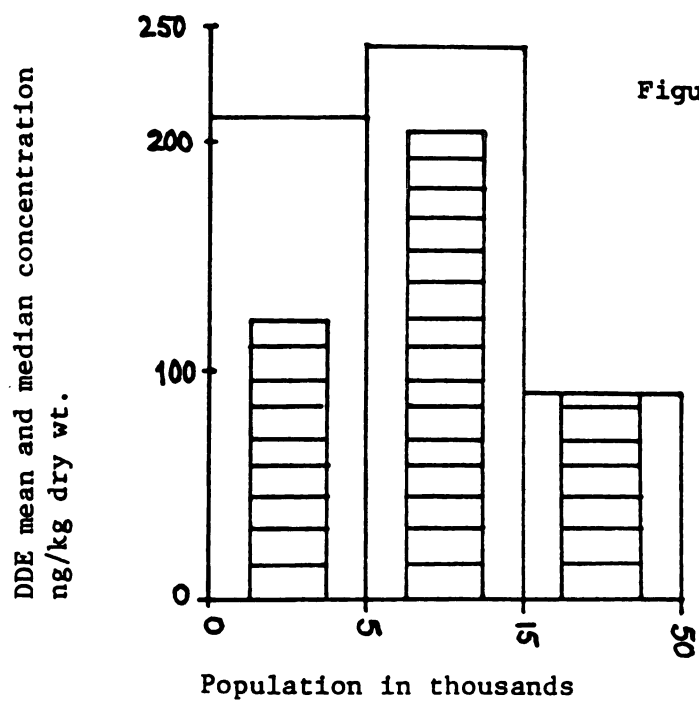


Figure 14

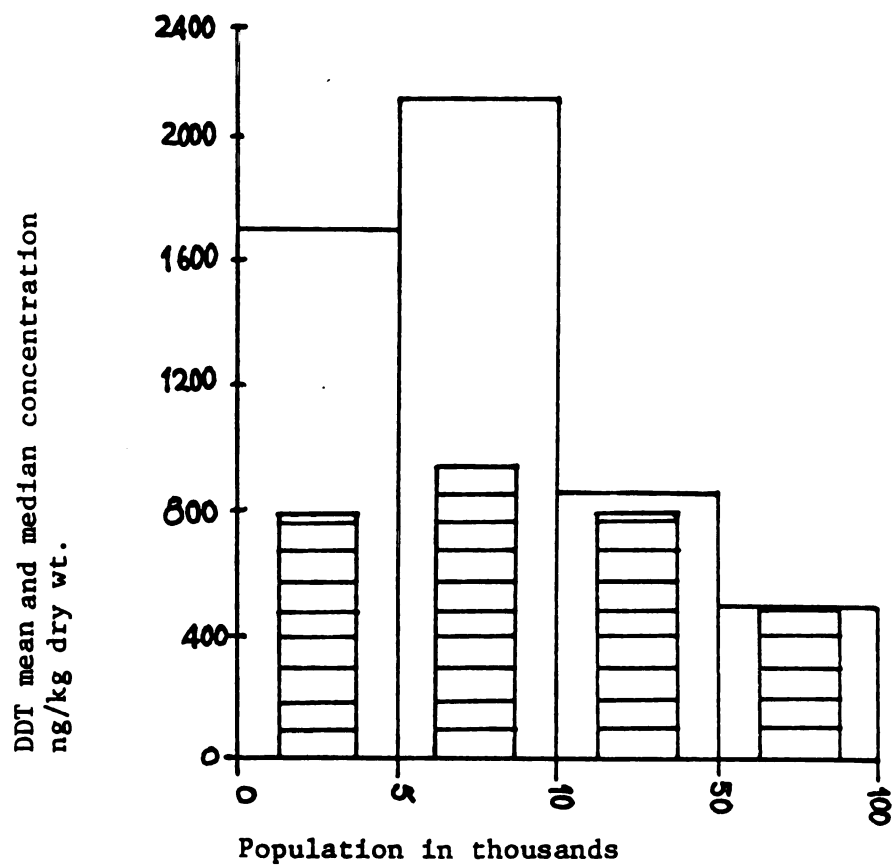
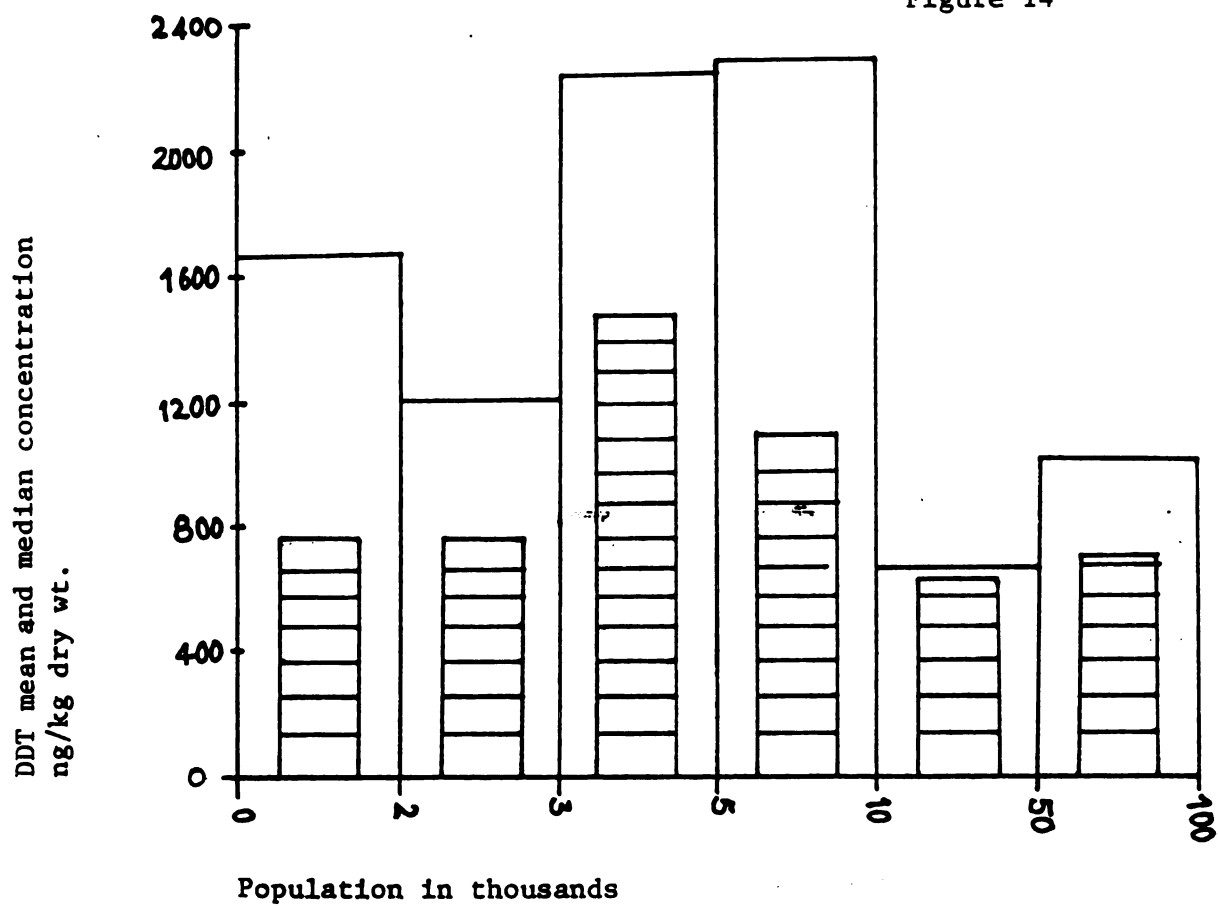


Figure 15

Figure 16

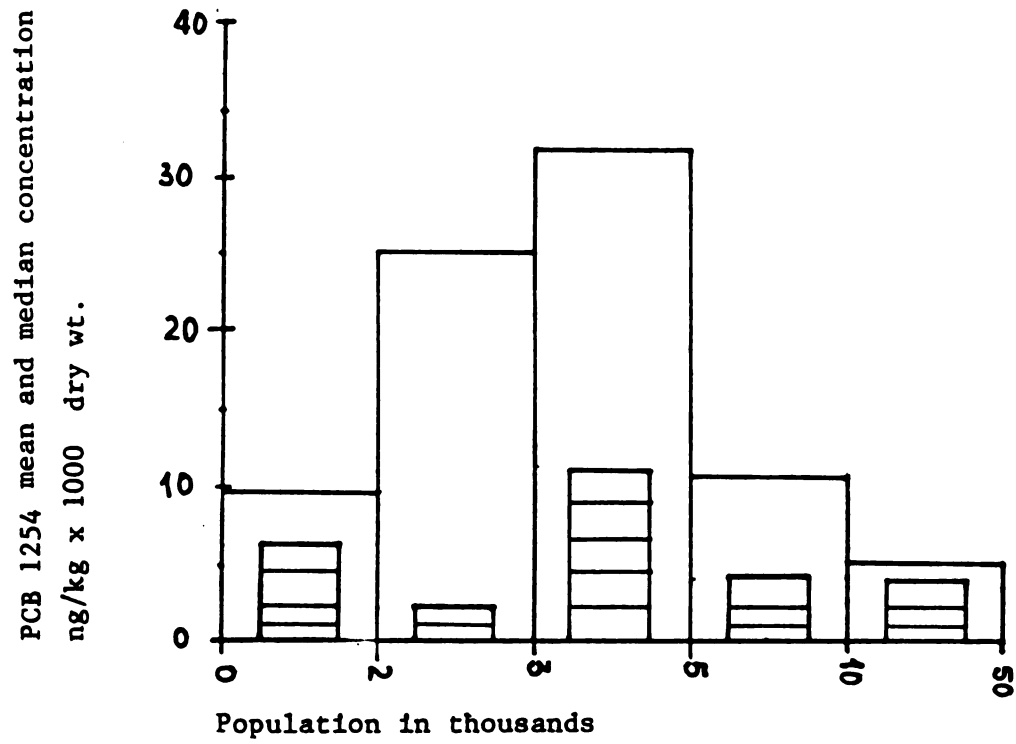


Figure 17

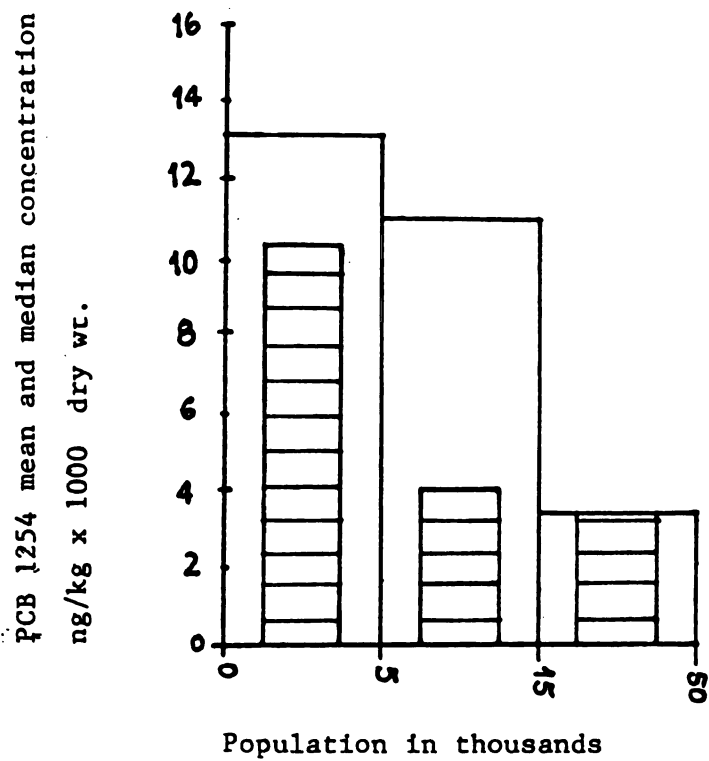


Figure 18

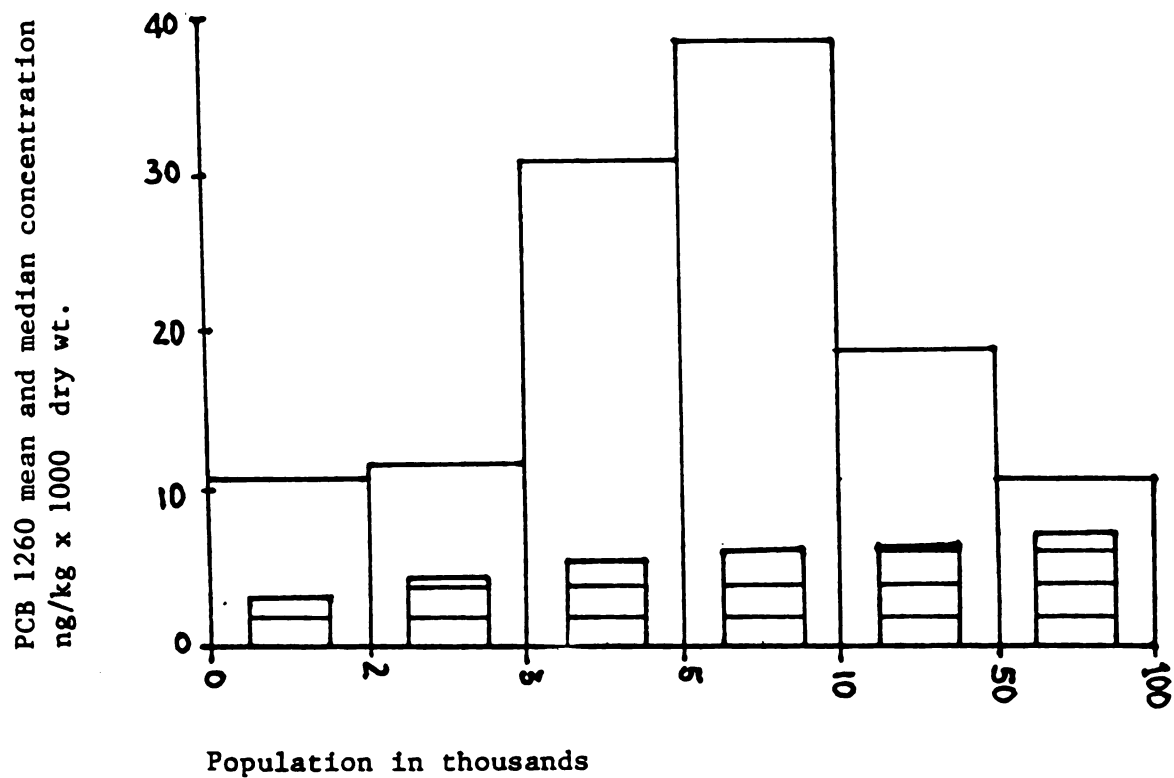


Figure 19



Figure 20

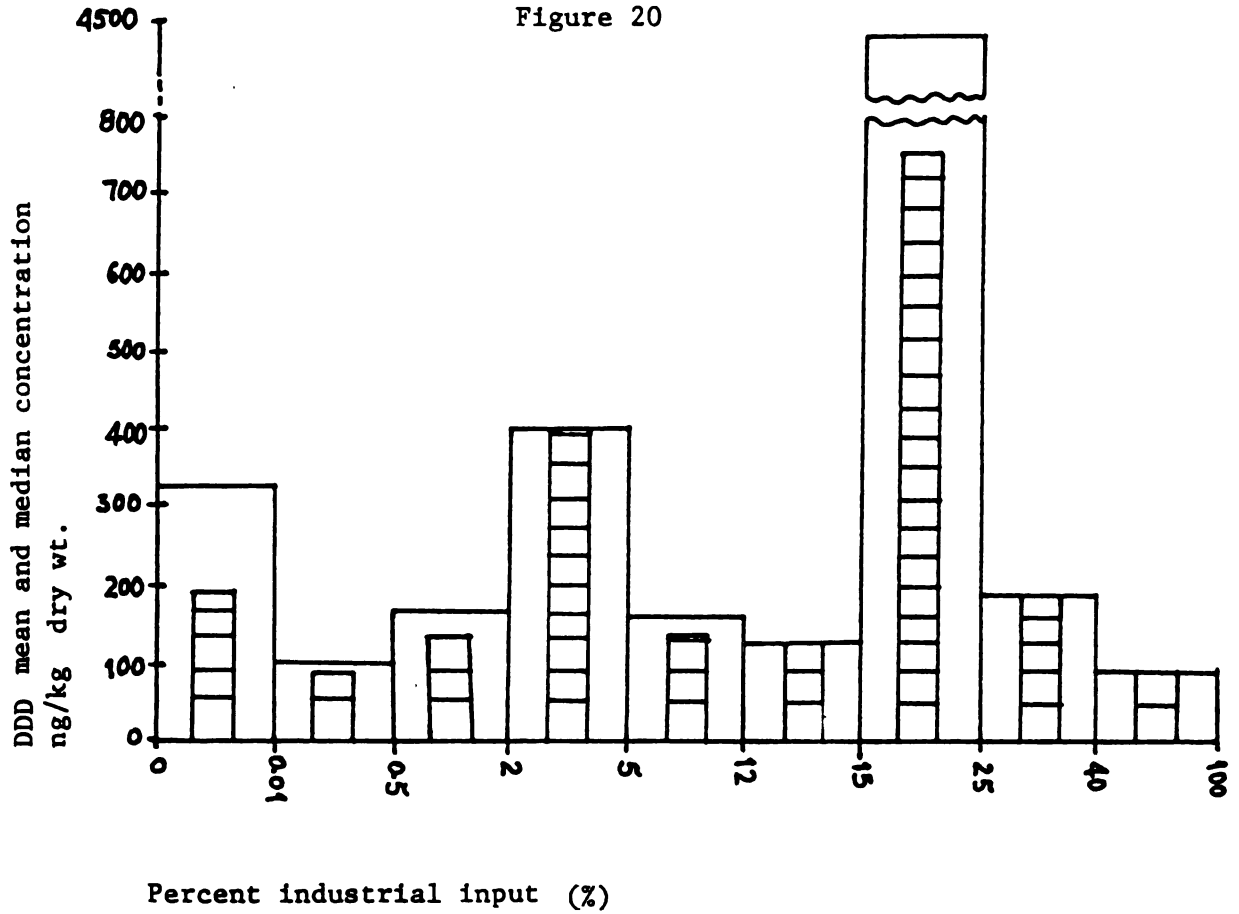


Figure 21

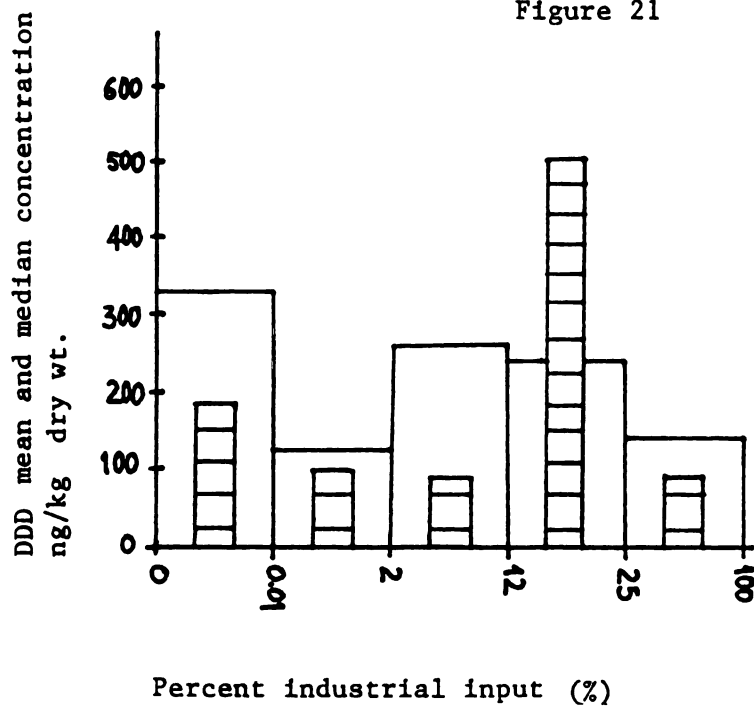


Figure 22

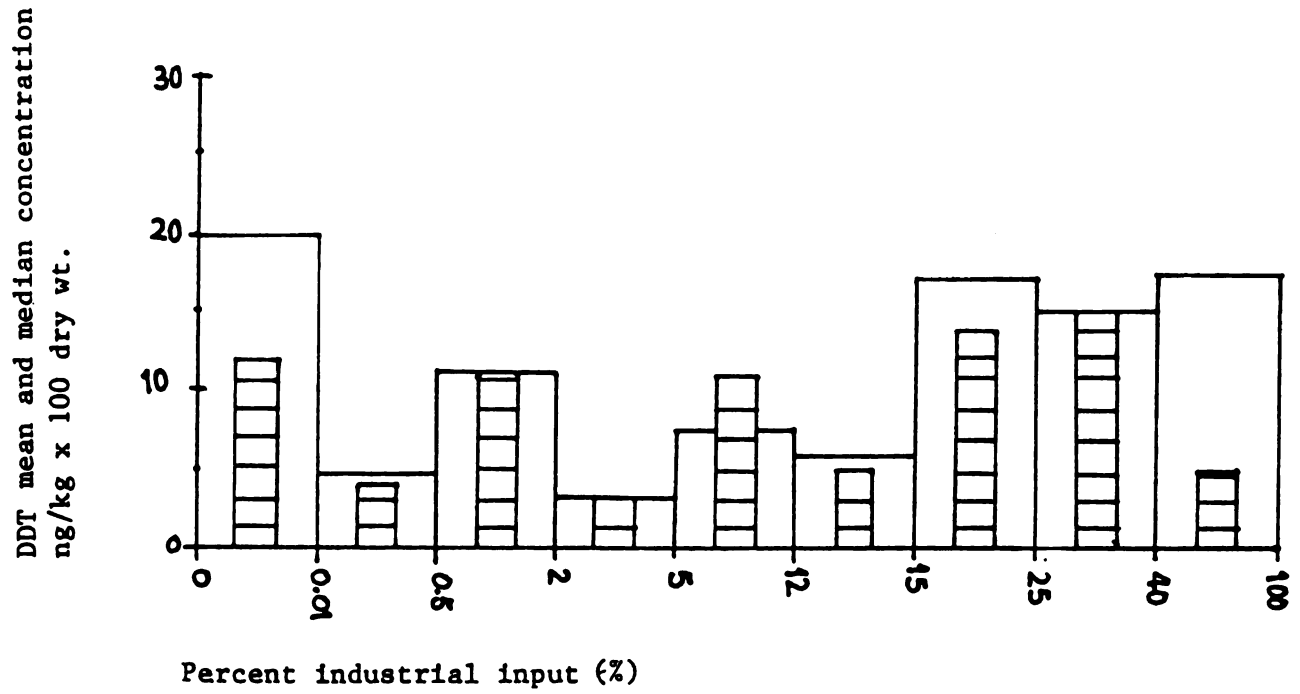


Figure 23

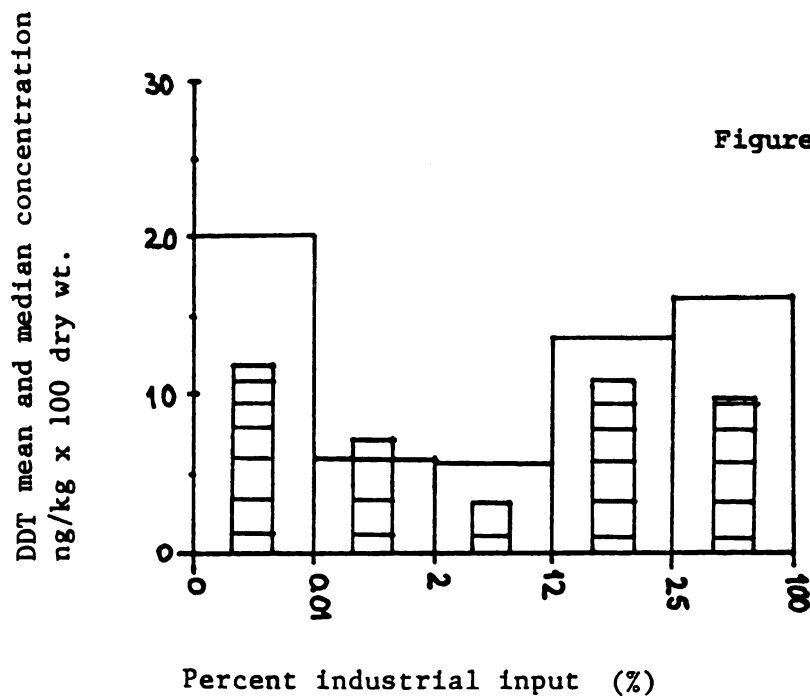


Figure 24

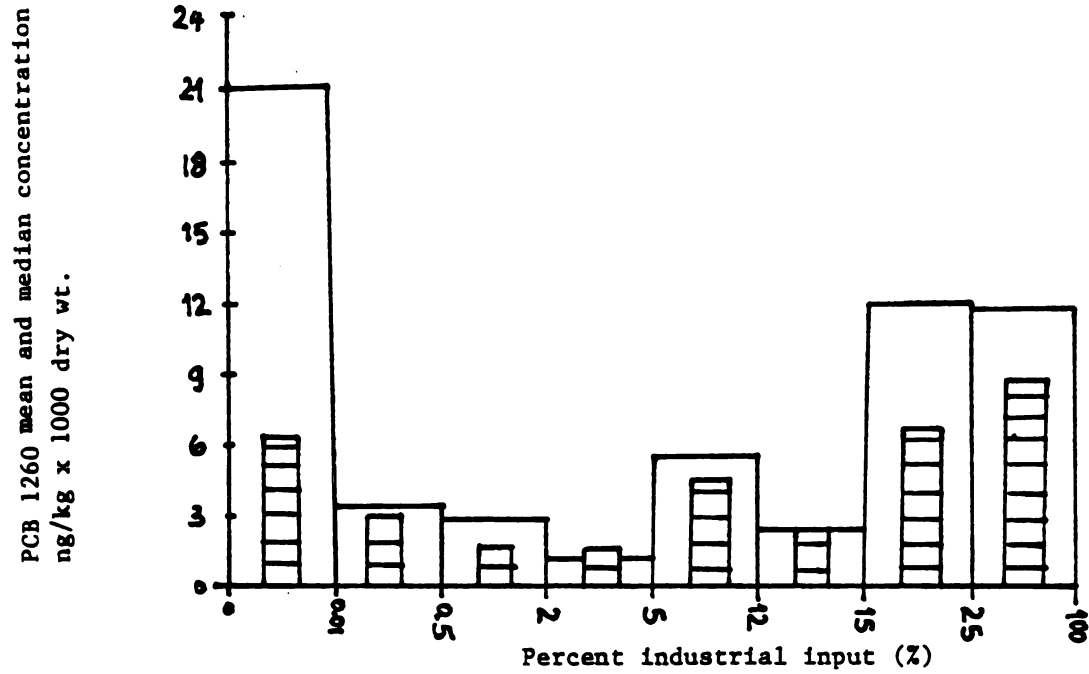
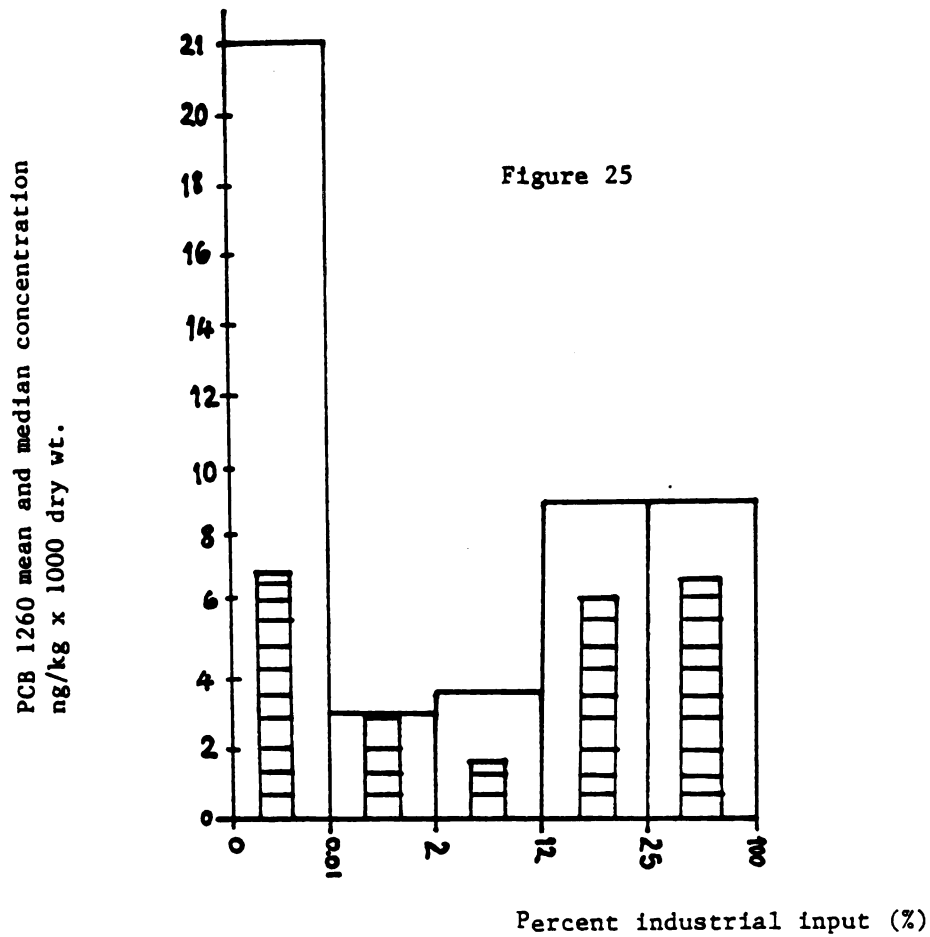


Figure 25



In the case of level concentration vs. percent industry, no trend was observed (Figures 20-25).

IV. CONCLUSION

Thus far, studies concerning organic environmental pollutants in sewage effluents and sludges have been limited. No doubt, interest will increase in an era where energy conservation and safe disposal of hazardous wastes are primary concerns.

Many problems in sewage analysis remain. The areas which require the greatest amount of work at this time include:

1. Uniform and representative sampling
2. sample preservation and stabilization
3. Improved cleanup and separation techniques for solvent extractable materials
4. Development of a quality control program to evaluate analysis techniques.

Most of the compounds analyzed were detected at the ppb level or below. This low concentration level may be in part due to the very nature of the samples and the possible biological decomposition of the components studied. According to the Michigan Department of Natural Resources, sludge management division, no written law regulates the concentration of chlorinated pesticides in sludges to be applied to farmland. Each case is treated individually. However, sewage sludges containing below 50 ppm could be applied to crop land. Thus, the sewage sludges analyzed for the selected PCBs and organochlorine pesticides could be used in the sludge management program. It should be noted that the uses of the chemicals considered in this study were severely restricted more than a decade ago. Therefore, a slow decrease was expected (due to their nature) of their concentrations in environmental samples. Naturally, sludge management program is a coherent program which takes into account other toxic organic chemicals and heavy metals as well.

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