DETERMINATION OF SELECTED ORGANOCHLORINE COMPOUNDS IN AIR AND WATER FROM YOUNGSTOWN, OHIO

by

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Youngstown, Ohio

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ABSTRACT

Because organochlorine compounds are toxic, persistent and tend to bioaccumulate in the food chain, assessing their concentrations in the environment is important. Air and water samples from Youngstown, OH, were collected for a week during the summer of 1996 and concentrations of pentachlorophenol (PCP, derivatized to pentachlorophenolacetate, PCPA), pentachloroanisole (PCA) and hexachlorobenzene (HCB) were determined. All three compounds were found in air, but only PCP was found in water. Besides quantitation of the analytes, collection efficiencies of polyurethane foam, XAD-2 resin, glass fiber filters and resin-based extraction cartridges were also examined for each compound. While PCPA recoveries from water and the polyurethane foam were good, recoveries from XAD-2 resin and glass fiber filters were extremely low. PCA and HCB recoveries were low in all sampling media. Incomplete extraction is the most likely reason for the low recoveries. The presence of these compounds suggests atmospheric transport and deposition may be an important source of contaminants to air and water in the Youngstown area.

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF TABLES

Page

LIST OF TABLES (continued)

LIST OF FIGURES

Page

CHAPTER ONE

INTRODUCTION

ORGANOCHLORINE COMPOUNDS

The use of pesticides became popular during the twentieth century due to their ability to increase both the quality and quantity of agricultural products at a reasonable cost.[1] First generation pesticides included inorganics (containing arsenic, lead or mercury) and botanicals, such as pyrethrins derived from chrysanthemums and nicotine sulfate made from tobacco.[2] The inorganics proved to be extremely toxic not only to pests, but also to humans and animals. Botanicals were too limited in their effectiveness, often controlling only one type of pest. Second generation pesticides were introduced after World War II primarily with the advent of dichlorodiphenyltrichloroethane, or DDT. From the end of the 1940's to the late 1960's, DDT was the pesticide of choice for all applications; its low water solubility and volatility combined with its chemical stability allowed it to remain on plants for extended periods of time.[3] This persistence combined with its effectiveness in killing pests made it the "ideal" pesticide; however, the same properties which made it so popular also became its downfall. Being both hydrophobic and resistant to degradation, DDT tended to bioaccumulate within the food chain. Its broad spectrum effectiveness made it toxic to many organisms besides the intended victims. With the downfall of DDT came numerous replacements, all of which had similar properties: persistence, effectiveness and broad spectrum applications. Although the actual structures of these

initial replacements varied greatly, all were organic and contained chlorines: the organochlorine class of pesticides.

Organochlorine compounds (OCs) are non-polar, lipophilic and inert to oxidation and hydrolysis reactions.[4] The slow degradation and low reactivity of OCs made them popular for many applications other than pesticides, including uses as lubricants, plasticizers, fire retardants, solvents and refrigerants.[5] As with DDT, the OCs were later found to bioconcentrate and biomagnify in the food chain. The resulting effects on wildlife have caused the Environmental Protection Agency to designate many organochlorine compounds as priority pollutants and to issue strict guidelines and standards for their use.[1] Various public interest groups have been actively trying to stop all use of OCs and a large number have been banned in the U.S. and Canada since the 1980's.[4] However, some OCs are still used commercially for drinking water purification and sewage treatment, as well as for pesticides and seed dressings. Also, most OCs are still used heavily in Asia, Africa and Central America. Their physical and chemical properties combined with their cost effectiveness make them more popular than newer compounds which tend to be less persistent, more specific, more chemically complicated and ultimately more expensive to use. Some common organochlorine pesticides include DDT, hexachlorocyclohexanes, toxaphene, aldrin, mirex, dieldrin, pentachlorophenol and hexachlorobenzene.

PENTACHLOROPHENOL

Uses

The high demand for lumber has made forests one of the world's most valuable resources. Because of limited supply, any technique which extends the life of the wood is quickly embraced. Various preservation methods developed over the years have extended the service life of lumber 5-15 times.[6] During the nineteenth century, creosote, a by-product of the coking industry, was applied to wood to increase its lifetime. Although creosote is difficult to characterize chemically, it contains approximately 85% polynuclear aromatic compounds, 12% phenols, and 3% heterocyclic nitrogen, oxygen and sulfur compounds.[7] Although creosote was the most highly used industrial wood preservative in the United States in 1975, its use declined during World War I due to the decrease in industrial coke production.[8] Several alternatives were quickly discovered, including a multi-salt mixture consisting chiefly of sodium fluoride and sodium arsenate. This preservative was abandoned in 1923 after it was found to leach out of wood during wet conditions. Subsequently in 1933, another alternative, copper chrome arsenate (CCA), was found to be effective and is one of the most widely used preservatives today.[6]

Pentachlorophenol (PCP, Figure 1) began its use as a wood preservative in 1936.[9] It was considered an excellent choice due to its wide biocidal properties, easy application, relatively cheap production and its effective mode of action.[10] Application to the lumber was made easy by dissolving solid PCP within an organic solvent, such as a petroleum distillate, to form a 5% concentration.[6,8] This solution could then be applied through various means, including immersion, spray, brush and pressure treatment. The

organic salt of PCP, sodium pentachlorophenate (NaPCP), was also used in high quantities. NaPCP is water soluble and is easily applied to wood by immersion or deluge dripping techniques. Like PCP, NaPCP is also quite cost effective.

The use of PCP grew enormously during the 1950's. It was often combined with various other chemicals, including water repellents, colorants, tributylin oxide and γ-hexachlorocyclohexane.[8] Additives, such as zinc 2-ethyl hexanoate, actually enhance the properties of PCP by increasing its protective value while decreasing its volatility and leaching into the environment. Approximately 3500 pressure treatment plants existed worldwide in 1990 which used approximately 110 million liters of organic solvent wood preservative.[6] It was estimated that 40% of the wood treatment plants used PCP as their chief preservative, while the remainder used creosote or arsenic salts.[11] The bulk of the companies using PCP were located in the south, southeast and northwest. The main application of PCP in the wood industry has been for preserving utility poles and railroad ties. Even though questions about PCP's toxicity have led to restricted use in most of the world, 30,000 tons were produced worldwide in 1989.[12,8]

Although PCP's chief application was wood treatment, about 22% of production was for a variety of other uses.[11] PCP was used as an herbicide and pre-harvest desiccant. It was added to building materials such as roof tiles, asbestos shingles, concrete blocks, and wallboard to deter molding. The FDA permitted the use of PCP in the packaging of multiple food products and the textile industry incorporated PCP into rope, twine, canvas, burlap and even leather used for shoes. Many paints and stains contained PCP as a preservative, as well as adhesives containing vegetable protein,

starch or animal protein. Pulp mills used PCP to ward against mildew, termites and rot, and some photography solutions contained PCP as a slime and fungus deterrent.

Pentachlorophenol is a general use pesticide with a wide range of biocidal activity. The U.S. E.P.A. has registered it as a fungicide, insecticide, herbicide, disinfectant, algaecide and an anti-fouling agent. It is known by a variety of names such as chlorophen, penta, Dowicide G, Penta-kil, Permaguard, and Weed-Beads.[12,11] In 1977, PCP was the second most prevalent pesticide used in the United States.[11] PCP was also used in the form of its organic salt, NaPCP. Pure PCP comes in the form of light tan or white needle shaped crystals. Impure PCP is brown or dark gray and is found as flakes, beads or dust.[13] With a pK_a of 4.7, PCP is insoluble in acidic water but greater than 99% ionized at the pH of most natural waters.[12] It is also soluble in most organic solvents. Solid PCP has a very strong, distinct odor at high temperatures, but little smell at normal temperatures.[13] In water, however, PCP can be detected by smell at concentrations as little as 12 parts per million. PCP does not occur naturally in the environment and currently is produced by only one company in the United States, Dow Chemical. PCP is made by the catalytic chlorination of molten phenol.[11] In this process, tri- and tetrachlorophenols are chlorinated to form PCP, although tetrachlorophenols persist in the mixture at 4 to 12%.

Technical grade PCP, which is used in the wood industry, contains a large amount of impurities, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorodiphenyl ethers, polychlorophenozyphenols, chlorinated cyclohexanons, cyclohexadienons, hexachlorobenzene, polychlorinated biphenyls and other chlorophenols.[12] While pure

PCP is quite flammable, the technical grade will not burn. The contaminants in the technical grade are of serious concern as many of the impurities are considered toxic and/or carcinogenic and most are persistent in the environment, posing long-term threats.[14] A higher grade PCP solution was manufactured by Dow Chemical for a short time with significantly reduced contaminant levels. However, this solution was quite expensive to produce and could not compete with other cheaper chemicals on the market.

Human Exposure

Humans are exposed to low levels of PCP via indoor and outdoor air, drinking water, food and soil.[13] The most common ways PCP enters the body is through touching treated wood, inhaling vaporous PCP, or imbibing PCP within drinking water. The amount of PCP inhaled varies with location. It is approximated that the general population breathes 0.063 mg/day, while air at PCP wood treatment plants and lumber mills provides a 150 lb human with 10.5 - 154 mg/day. It is estimated that intake of PCP from drinking water is 0.021 mg/day. The U.S. National Academy of Sciences has set acceptable daily intake levels at 3 μg/kg body weight per day.[12]

PCP has a half life within the human body of approximately 33 hours. The majority leaves the body through excretion; however, small amounts build up in various body compartments with the highest amounts in the liver and kidneys. Humans occupationally exposed to PCP have shown enhanced levels in both blood and urine samples long after exposure. Once in the human body, PCP will uncouple oxidative phosphorylation, a biochemical pathway for energy production.[6] Subsequently, the

metabolic rate is increased and hyperpyrexia ensues. Exposure to high levels leads to nausea, fatigue, profuse sweating, and thirst. More developed symptoms include heart palpitations, increased and deeper breathing, increased heart rate, anxiety, restlessness, and fever. Protracted cases may lead to convulsions, coma and death. PCP has also been listed by the E.P.A. as a B2 probable human carcinogen.[9] Acute exposure to high levels can lead to deleterious effects in the kidneys, skin, liver, blood, lungs, immune system, nervous system and gastrointestinal tract.[13] Chronic exposure to low levels can damage the kidneys, liver, nervous system and blood.

Humans are most likely exposed to technical grade PCP and animal studies have suggested that many of the above symptoms may be caused by the impurities found within the technical mixture.[13] However, pure PCP has been found to be highly toxic in animals.[12] It is an irritant to exposed epithelial tissue, causes chloracne, reduces growth rates and decreases serum-thyroid hormone levels. Studies with rats have shown several symptoms of fetal toxicity: developmental delay of the embryos, smaller litter sizes, lower birth weights, decreased neonatal survival and decreased growth of weanlings. Data from both cow and mice studies show that exposure affected both humoral and cellular immunity.[13] Immunotoxicity has been found in chicken and rats.[12]

Levels in the Environment

PCP has been found in almost every environmental medium (Table 1). Its residues have been found in greater than 7% of the hazardous waste sites on the United States National Priorities List[9]. The majority of PCP enters the environment through improper disposal by industry during production and evaporation from treated wood at

both lumberyards and lumber treatment sites. Wastewater originating from wood preserving industries is relatively low in volume; however, the concentrations of chlorophenols can be quite high.[22] Oils and emulsifiers present in wastewater contribute a "carrier" effect, allowing PCP to exceed its normal solubility in water. The E.P.A. has found PCP concentrations in wastewater exceeding 100 mg/L at several sites. At a former wood treating facility in Dania, FL, ground-water slurry PCP concentrations ranged from 0.012 - 230 mg/L.[18] Wastewater from American Creosote Works at Pensacola, FL, analyzed in a 1993 study contained 16.47 mg/L PCP, even though the plant was closed in 1982.[19] Although Germany prohibited the production, sale, and use of PCP in 1989, landfill seepage water has been found to contain PCP at levels of 110 - 280 μg/L.[23] Concentration of PCP within the air varies. Windsor, Ontario had a concentration of 0.87 ng/m^3 in 1990, while in Hamburg, Germany, PCP was found to be 0.67 ng/m^3.[15] In contrast, air analyzed from a poorly ventilated house made of PCP treated wood had levels up to 160 μg/m^3.[12] Soil from a waste sludge pile, formerly the Brookhaven Wood Preserving Facility in Massachusetts, had concentrations ranging from 15 to 342 μg/g PCP.[24] Soil concentrations at point sources have been found to be as high as 9,000 mg/kg.[25] Oysters from Galveston Bay, Texas, showed PCP levels averaging 5.3 ng/g.[21] Fish from Canada's St. Croix and St. John's estuaries contained levels up to 4.0 ng/g while jellyfish in the Gulf of Mexico averaged 1.0 ng/g.

Fish kills in a freshwater lake occurred after an accidental spill of PCP in fuel oil at a wood-treating plant.[11] Water, sediment and leaf litter contained high levels of PCP and the contaminants remained for up to seventeen months after the spill. While PCP

levels in the water ranged from 0.1 to 1518 μg/L, PCP levels within the fish were 4 to 19,000 ng/g in muscle and 26 to 325,000 ng/g in liver.

Lu *et al.* studied ^{14}C-PCP in a laboratory model ecosystem to determine its environmental fate.[11] The major degradation products were tetrachlorohydroquinone and pentachlorophenol acetate, as well as various conjugates produced by reductive dechlorinations. ^{14}C-PCP and its metabolites were found to accumulate in the aquatic food chain organisms in the study. The ecosystem ended up with 51% ^{14}C-PCP in air, 48% in soil and 1% in animals after a 20 day experiment.

Because of the problems associated with PCP, the federal government created guidelines and standards to protect the environment and ensure human safety. The Occupational Safety and Health Administration (OSHA) set a limit for PCP levels in workplace air at 5 ppb and drinking water at 22 μg/L.[13] Any release of PCP to the environment greater than 10 pounds must be reported. The U.S. E.P.A. has set the maximum contaminant level in drinking water at 1 μg/L.[9]

Environmental Fate and Remediation

PCP degrades in the environment by photochemical, microbiological and chemical means.[11] In soil, PCP breaks down by reductive dehalogenation to tetra-, tri- and dichlorophenols. Factors influencing the degradation of PCP include soil type, temperature, and amount of organic matter. Photodegradation in water breaks PCP down into various intermediates, such as tetrachlorocatechol and tetrachlororesorcinol, before degrading these into smaller fragments.[26] Dechlorination occurs more in seawater than distilled water, most likely due to higher concentrations of dissolved

organic matter in the marine environment. This organic matter is hypothesized to act as a hydrogen donor in the PCP photoreduction mechanism.[26]

PCP has been shown to break down during production into the more toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).[27] These contaminants are formed by condensation reactions of PCP and the tetrachlorophenols and, thus, PCDD/Fs are often present in technical grade PCP formulations.[23] Sediment core samples taken from the Baltic Proper, near the east coast of Sweden, show a highly significant increase of PCDD/Fs during the time frame of 1970-1985, largely accredited to PCP usage.[28]

Bioremediation provides one solution to the problem of cleaning up PCP in the environment. A number of microbes have been studied for this purpose. *Desulfomonile tiedjei* DCB-1 is an anaerobe which can reductively dehalogenate PCP in the *meta* position to yield 2,4,6-trichlorophenol.[29] Ultra-high concentrations at point sources, however, make bioremediation impossible. Less than 10% of the technologies used for PCP cleanup at Superfund sites in 1989 used bioremediation. Recently, researchers isolated *Pseudomonas* species strain RA2 from highly contaminated soil.[25] It was found to have one of the highest tolerances to excessive PCP levels, being able to mineralize PCP to CO_2, HCl and H_2O at soil levels as high as 160 mg/L. Another study, using white rot fungus to degrade PCP within soil, gave promising results.[30]

Irradiation with UV has been explored as a possible approach to depleting PCP levels in the environment.[11] PCP absorbs at λ_{max} = 320 nm and is changed into various compounds; however, PCDD/Fs are often formed as byproducts.[23] Combined treatments are now being explored, such as pairing UV irradiation with an oxidizing reagent such as

hydrogen peroxide or ozone to destroy byproducts. Another alternative under consideration is semiconductor photocatalysis where UV light and TiO_2 particle suspensions are used to mineralize PCP.[31]

Research is underway to determine the best method for dealing with the large abundance of lumber treated with PCP. Treated utility poles have been found to contain up to 27,000 μg/g of PCP.[32] Leachate from treated poles in a Palo Alto, CA, study showed PCP concentrations of 1.92 mg/L.[31] Pulping, incinerating and landfill disposal are inadequate options for pole disposal as all three methods pose additional problems, including release of chlorinated organic compounds into the environment, dioxin formation, and leaching of contaminants into ground water.[32] At present, the best solution is extraction of PCP from wood followed by bioremediation treatments.

PENTACHLOROANISOLE

Chlorophenols in the environment are susceptable to oxygen methylation to form chloroanisoles.[33] The anisoles are more lipophilic and thought to be more toxic than the parent phenol, and bioaccumulation within higher organisms can occur. PCP is transformed to pentachloroanisole (PCA) by methylation of the hydroxyl group (Figure 2). Information on the environmental characteristics of PCA is limited; however, it is known that PCA has a low solubility in water and a high partitioning from water to fish.[11]

Very few studies have been done on the toxicology of PCA. Ikeda and Sapienza (1995) administered oral doses of radiolabelled PCA to dogs and pigs and found that the

majority was demethylated to PCP and excreted.[34] Small amounts of PCA (9-27%) remained in the liver, blood, muscle and fat.

PCP is thought to be methylated to PCA by microorganisms within sediment.[33] Studies examining the degradation of ^{14}C-PCP in aerobic soils identify PCA as the principal product (51.5%). Conversely, PCA can be reduced back to PCP with only limited success in aerobic soils (5.6%) but with greater yields in anaerobic soils (42.1%).

Table 2 lists concentrations of PCA in various compartments of the environment. PCA has been found in the air in both the Northern and Southern Hemispheres by Atlas *et al.*[36] Levels averaged 2.1 pg/m^3 in New Zealand and 9.0 pg/m^3 in American Samoa. These levels were similar to those of other high molecular weight halogenated hydrocarbons found in the region. The source of PCA in air is thought to be microbial methylation of PCP followed by volatilization of the anisole from land or water. Because pine needles absorb pesticide residues within atmospheric air, they have been theorized to be both excellent monitors and indicators of air levels. Pesticides partition between the atmospheric vapor state and the lipophilic phase of the waxy covering of vascular plant leaves.[20] PCA was found on the outer waxy coat of pine needles in an isolated Swedish forest at a concentration of 1 ng/g in a 1992 study. PCP levels in 1986 at the same site contained only 0.48 ng/g. Atmospheric transport of PCA was suggested as the source.

Sediment studies of PCP and PCA in the Mississippi River and its tributaries showed no PCP affiliated with the sediment.[37] However, PCA was found at every site with the most abundent level (2.8 ng/g) at the lock-and-dam lake system near St. Louis.

It was theorized that stagnation of water in the dam provided an increased opportunity for degradation to PCA.

Seventeen months after a spill of technical PCP in a freshwater lake, PCA levels ranged from 0.03-1.94 μg/L in water and 0.2 - 80 ng/g in sediment.[11] Since technical grade PCP contains no PCA, degradation of PCP to PCA was asssumed. Uptake from the water into fish led to levels of PCA in fish muscle ranging from 4 to 250 ng/g and in liver from 10 to 1200 ng/g.

PCP was used quite extensively as an herbicide in rice paddies in Japan during the 1960's, but due to its toxicity, was later prohibited. In a 1981 study, oysters from Keihinjima, Tokyo Bay, Japan, contained 20 ng/g PCA and 2 ng/g PCP.[38] Drawing from data of past research and their own findings, Miyazaki *et al.* suggested that PCA is more persistant than PCP.

HEXACHLOROBENZENE

Uses

Hexachlorobenzene (HCB, Figure 3) is a white, crystalline solid that does not occur naturally in the environment.[39,40] HCB has also been called hexachlorobenzol, perchlorobenzene, amatin and Anti-Carie.[40] HCB has a relatively low water solubility at 0.006 mg/L at 25° C and is considered semivolatile with a vapor pressure of 0.0023 Pa.[39]

HCB was first used in 1940 as a seed dressing for wheat, barley, rye and oats with most formulations consisting of an 80% pure solution.[39] It was also used in the production of pyrotechnics and ordnance materials for the military, as well as in the manufacture of synthetic rubber.[40,39] HCB was a common fluxing agent in aluminum

production and has been used as a wood preserving agent.[39] During graphite production, HCB was utilized as a porosity control agent. In Canada, use as a seed dressing ceased in 1972, but in the United States, HCB was used as a pesticide well into the mid-80's.[40] Although all manufacture of HCB has ceased in the states, it is a common by-product in the production of chlorinated solvents. One study conducted in 1984 found 11,500 kg of HCB produced in this manner. HCB is also found as an impurity during the production of pesticides such as PCP, dacthal and atrazine.[39] Approximately 10,000 kg/year of HCB was produced this way until the cessation of usage of these pesticides in the late 1970's. Disposal of remaining stores of HCB is subject to federal regulations including restrictions for land disposal. Incineration at high temperatures is a common method of disposal but often results in the creation of more deleterious by-products.

Human Exposure

Exposure of humans to HCB occurs by consumption, respiration and absorption through the skin.[40] Only small amounts are usually imbibed from drinking water since HCB is only slightly soluble in water and average drinking water contains only trace amounts. Ingestion of HCB can occur from contaminated dairy products, meat, poultry and peanuts. Human ingestion of HCB is estimated to be up to 68 μg/g per year in food. The U.S. E.P.A. has set drinking water limits for HCB at 0.05 ppm for a maximum of 10 days for children and 0.2 ppm for adults. Minimal risk levels are set at 0.17 ppm for 15 weeks or 0.029 ppm for 130 weeks.

Acute effects from short-term exposure to HCB include both hepatotoxic and neurologic symptoms in humans.[39] Six hundred cases of porphyria cutanea tarda were

found in Turkish children between 1955-1959 who ingested bread made from HCB contaminated wheat. The amount of HCB ingested was estimated at 50 to 200 mg/day over a period of months. Children developed dermal lesions and had dysfunctional porphyrin metabolism. Ninety-five percent of the children nursed by mothers with the same condition died within a year of birth with levels of HCB up to five times the amounts found in the mothers.[40] A follow-up study twenty years later showed dermatological, orthopedic, and neurological symptoms in most subjects. Other problems associated with acute exposure include damage to the liver, immune system, kidneys, blood eruptions and abnormal pigmentations of the skin. Chronic exposure to HCB is suspected to cause cancer of the liver and thyroid.

Levels in the Environment

Levels of HCB found in the environment by other researchers are listed in Table 3. A study of HCB levels in Lake Ontario revealed the amount of HCB in the sediment was a million times greater than its concentration in water.[40] Suspended solids within the St. Clair River contained 14,000 ng/g dry weight, while sediment in the Great Lakes has given values of 0.2 to 97 μg/kg.[39,40] Deeper sediment layers within the Great Lakes dating from 1971 to 1976 have even higher values averaging 460 μg/kg. A 1988 study by Rostad *et al.* revealed that suspended-sediment transport of HCB from tributaries into the Mississippi River increased from upstream to downstream.[37] Near Winfield, Missouri, HCB levels contributed by sediment were 0.02 ng/L, while downstream on the Mississippi near St. Francisville, Louisiana, concentrations of HCB in water peaked at 0.20 ng/L. HCB in the water of the Great Lakes and Niagara River show a range of

concentrations from 0.02 to 17.0 ng/L with the highest levels found near a waste disposal dump site.[40] Lake Erie levels averaged 0.078 ng/L in a study conducted from 1978 to 1989.[39] Water in the Mississippi River near Baton Rouge, Louisiana, had higher levels of HCB reaching 2 μg/L, while HCB levels in the St. Clair River near Dow Chemical soared to 87 ng/L in 1985 and then dropped to 75 ng/L in 1986.[40,39] In 1980, HCB in drinking water in Ontario averaged 0.1 ng/L.

Ambient air levels of HCB on average are quite low with one study reporting values of 0.3 to 0.5 ng/m^3 in urban air from various U.S. cities.[40] Columbia, SC, air contained 0.29 ng/m^3 while air from Denver, CO, contained 0.24 ng/m^3 HCB.[46] Rural Ontario air obtained by Hoff *et al.* in 1992 averaged 0.054 ng/m^3 for HCB.[35] Because HCB has an average atmospheric lifetime of approximately 80 days, there is a potential for long range transport. Air sampled from the Bering and Chukchi Seas of the Arctic contained 0.210 ng/m^3 of HCB when measured in the summer of 1988.[49,50]

In 1986, Jensen *et al.* found that HCB was ubiquitous in Scots pine needles collected from southern France to northern Sweden.[20] The average value was 0.13 ng/g with a high of 0.49 ng/g. A follow-up study in 1989 from pines (*P. sylvestris*) in rural areas of West Germany, Denmark, Norway and Sweden revealed HCB concentrations within the waxy coat from 0.05 ng/g to 0.43 ng/g fresh weight, signifying a decrease in HCB concentrations.[51]

Environmental Fate and Remediation

HCB is persistent in the environment with a half life of 30-300 days in water and 3-6 years in soil.[40] Due to its physical and chemical properties, HCB prefers to be bound

to particles. Large amounts of HCB are transported long distances in the troposphere and hundreds of miles in the water.[39] While volatilization of HCB adsorbed onto the suspended particles is the principal route for HCB to enter air, wet deposition of gaseous HCB is the primary mechanism for entering the water. Desorption from resuspended bottom sediment is also a source of input of HCB to water. Within the sediment, HCB undergoes slow biodegradation with a half life of 2.7 to 5.7 years for aerobic sediments and 10 to 23 years for anaerobic.

HCB tends to bioaccumulate and higher concentrations are found at higher trophic levels.[39] Plankton have been found to contain an average of 1.6 ng/g HCB, while salmonids average 38 ng/g wet weight. Bioaccumulation introduces a problem for birds and mammals that feed on lower trophic organisms, especially in remote regions such as the Arctic where food sources are limited.[47] Biomagnification factors (BMFs) determine the rate in which a pesticide will accumulate in various organisms. From water to fish, the BMF for HCB is 9.6×10^6 and from fish to bird, 7.5. Ingestion of animal fat is one of the largest sources of persistent environmental contaminants for humans. Data from a study in Bayreuth, Bavaria, Germany, found the following levels: air, 460 pg/m^3; soil, 360 pg/g dry weight; corn, 430 pg/g fresh weight; cows' milk, 9,000 pg/g and human milk, 230,000 pg/g of fat.[52]

One promising remediation technique for HCB is extraction from soil with supercritical carbon dioxide ($SCCO_2$).[53] $SCCO_2$ is desirable because it is nontoxic, nonflammable, nonhazardous, inexpensive, and causes no contamination upon disposal. So far, much promising research has been conducted in this area with the result of pilot plants being constructed for mass removal of HCB.

SAMPLING METHODS

Due to their physical properties, for example vapor pressure, organochlorine compounds can exist in air in the gaseous phase or bound to particles. The high volume air sampler containing filters for particulate collection and an adsorbent trap for vapor collection is the most common sampling technique for these compounds.

Polyurethane foam (PUF) plugs came into favor for air sampling in the 1970's due to favorable airflow characteristics and simplicity of use in the field.[46] PUF plugs have a low specific surface area (0.007 - 0.035 m^2/g) and efficiently capture organic compounds with vapor pressures less than 0.1 Pa (semivolatile organic compounds, SOCs).[54] The more volatile compounds, including HCB and chlorophenols, are not retained well on PUF at air temperatures above 1 ^{o}C.

The use of a second PUF plug has beed used to check for breakthrough and collection efficiency. Migration of a pesticide through the PUF is dependent upon the temperature and volume of air passing through the sampler.[46] The amount of breakthrough from the front PUF to the back PUF increases with temperature and air volumes. The optimal situation is to trap all of the analytes on the front PUF, thereby allowing the back PUF to be used as a blank during analysis.

Due to problems with breakthrough of the more volatile compounds, researchers began using adsorbent resins such as XAD and Tenax for increased collection efficiencies. Because XAD-2 has a greater surface area (300-360 m^2/g) and a smaller pore size (8.5 nm dia.) than other collection media, it is more suitable for trapping compounds with relatively high votilities.[54,55] XAD-2 not only has a high capacity for

retaining contaminants, it also remains inert to the captured compounds and does not give spurious contaminant responses upon extraction and analysis.

Standard techniques allow for collection of compounds in low air volumes by passing air through XAD packed within glass tubes.[49] Analytes are then thermally desorbed from the XAD directly into the injection port of a gas chromatograph. However, most pesticide studies in ambient air require higher air volumes due to low analyte concentration.

To increase collection efficiencies of semivolatile compounds at ambient temperatures, several methods have been tried. In the early 1980's, Lewis and Jackson showed that compounds with vapor pressures up to 40 Pa could be efficiently collected at ambient temperatures by sandwiching XAD-2 between two PUFs in a sampling train.[49] Higher flow rates compared to the thermal desorption method could be used so that standard high volume air sampling equipment could be employed. Patton *et al.* demonstrated that using Tenax-GC with the PUFs resulted in collection efficiencies of up to 96% for several chlorophenols.[56] Zaranski *et al.* collected nonpolar organic compounds, including HCB, at ambient temperatures using 15 g of XAD-2 between two PUFs in a high volume air sampler.[54] Likewise, Billings and Bidleman found improved collection efficiencies using the PUF/XAD sandwich for HCB collections with recoveries 2-3 times higher than on PUF alone.[46] Air volumes for this study ranged from 35 to 385 m^3 and collection efficiencies for all compounds averaged 93%. Less volatile compounds in the gaseous phase are typically trapped within the front PUF, while more volatile compounds, such as HCB and chlorophenols, are primarily captured within the adsorbent.

Organic solvents are used to extract the compounds from the PUF and XAD. Most researchers extract the entire sandwich cartridge, both the PUFs and granular adsorbent, at the same time.[54,56,49] In a study using PUF/Tenax traps, McConnell averaged 88 ± 47% collection efficiency for PCP and 86 ± 20 for HCB, while Zaranski *et al.* found HCB recoveries with PUF/Tenax ranging between 88 and 100% and with PUF/XAD from 86-92%.[49,54] Tan *et al.* extracted PCP from XAD-2 alone with dichloromethane (DCM) and a small amount of hydrochloric acid (HCl) and obtained an average recovery of 90 ± 6%.[57]

A variety of methods have been employed for collection of PCP in water and soil. For quick analysis of PCP concentrations, magnetic particle-based enzyme immunoassay can be used.[9] A specific PCP antiserum covalently coupled to a magnetic particle solid phase allows quantification of PCP in water at levels greater than 100 ng/L and in soil greater than 100 mg/L. The method is precise, quick and inexpensive for analyzing large volumes at higher concentrations. Another method to detect both PCP and its carrier oil within sediments, soils and wood requires the use of a fourier transform-infrared in combination with a gas chromatograph.[10] Accurate detection of low level concentrations (<5 μg/L) and efficient utilization of small sample sizes (1 g) are two benefits of this method. For detection of very low levels in water, PCP can be detected by passing moderate volumes of water through adsorbent resins or extraction cartridges containing these resins followed by extraction of the compound using organic solvents.

CHAPTER TWO

STATEMENT OF PURPOSE

The slow degradation and low reactivity of organochlorine compounds have made them popular for many applications including uses as pesticides, lubricants, plasticizers, fire retardants, solvents and refrigerants. Their persistence, toxicity and tendency to bioaccumulate, however, make them a threat to both humans and the environment. A large number of OCs have been banned in the U.S. since the 1980's; nevertheless, many are still used heavily in Asia, Africa and Central America. Their effects on wildlife have caused the U.S. E.P.A. to designate many OCs as priority pollutants, ensuring the continued monitoring of their levels in the environment and biota. Standard methods for sampling and analysis of OCs in air and water generally work well. However, collection efficiencies vary for some of the more volatile compounds.

This work examines the efficiency of collection of three organochlorine compounds, pentachlorophenol, its breakdown product, pentachloroanisol, and hexachlorobenzene, in air and water using a filter/sorbent trap for air collection and extraction cartridges for water. Tentative concentrations of these compounds in air and water from Youngstown, Ohio, are also determined.

CHAPTER THREE

MATERIALS

All solvents were pesticide grade (Fisher Scientific Company, Pittsburgh, PA). Other materials included 80-200 mesh alumina, anhydrous granular sodium sulfate, anhydrous sodium carbonate, and acetic anhydride (Fisher Scientific Company, Fair Lawn, NJ). Analytical standards were purchased from Ultra Scientific (North Kingstown, RI). Pentachlorophenol acetate (PCPA) was obtained from Atmospheric Environmental Services, (Downsview, Ontario, Canada) and ^{13}C-pentachlorophenol (^{13}C-PCP) from Cambridge Isotope Laboratories (Andover, MA). Nitrogen for concentrating samples was dry grade; helium and methane for chromatographic instruments were ultra pure carrier grade.

Amberlite XAD-2 resin (Sigma Chemical Company, St. Louis, MO), with a surface area of 330 m^2/g and a pore diameter of 90 Å, was used for collection of vapor phase compounds along with 2.5 in. dia. x 1.75 in. ht. polyurethane foam (PUF) plugs (Graseby Anderson, Cleves, OH). Glass fiber filters (GFFs), type A/E, were purchased from Gelman Sciences (Ann Arbor, MI). Isolute Env+ Sorbent water cartridges were purchased from International Sorbent Technology Ltd. (Mid Glamorgan, U.K). Water filters were type GD 1UM (Whatman International Ltd., Maidstone, Eng). Pure cellulose extraction thimbles for extraction of XAD-2 were purchased from Whatman (Fairfield, NJ).

CHAPTER FOUR

EXPERIMENTAL

SAMPLE COLLECTION AND EXTRACTION

Air

XAD-2 resin was prepared for sample collection by soxhlet extraction for 24 hours with 50/50 ethyl ether/petroleum ether (EE/PE), dried in a desiccator for 24 hours, resoxhleted with 50/50 EE/PE (24 hours), dried, and stored in clean glass jars with Teflon-lined lids. PUFs were cleaned by soxhlet extraction with 50/50 EE/PE for 24 hours and dried in a desiccator before storing in clean jars with Teflon-lined lids. GFFs were baked at 400°C for 24 hours, placed in clean aluminum foil and sealed in plastic bags. The Isolute Env+ cartridges were cleaned with 15 mL of 50/50 EE/PE prepped with 15 mL of deionized water (lowered to pH 2 with HCl) and dried with nitrogen.

Air samples were obtained between August 21 - 28, 1996, from the top of Stambaugh Stadium, Youngstown State University, Youngstown, Ohio. The 24 hour samples were collected using a GPS-1 air sampler (Graseby Anderson) at an average flow rate of 4.43 m^3/hour. Weather conditions during the sampling period are given on Table 4. Particulate bound compounds of interest were collected on 102 mm glass fiber filters. Vapor phase compounds were collected on a trap consisting of 15 grams XAD-2 sandwiched between two PUF plugs. The front PUF was spiked with 10 ng of ^{13}C-pentachlorophenol to check collection efficiencies. After sampling, the vapor phase trap was sealed in a clean glass jar and transported to the lab for immediate extraction. Front and back filters were separated, placed in clean aluminum foil, sealed in plastic bags and

stored at 4 ^{o}C until extracted. PUFs were extracted by soxhleting with 50/50 EE/PE for 24 hours. XAD-2 resin was placed into clean extraction thimbles, topped with clean glass wool and soxhlet extracted with 50/50 EE/PE for 24 hours. GFFs were extracted by cutting into strips and soxhleting with dichloromethane (DCM) for 24 hours.

After extraction, sample volumes for all collection media were reduced to approximately 10 mL and transferred into hexane by rotary evaporation. The resulting volume was further concentrated using a gentle stream of nitrogen and transferred into 5 mL isooctane.

Water

Water samples were collected each day at approximately the same time from Lake Glacier, a broadening of the Mahoning River, located in Mill Creek Park, Youngstown, Ohio (approximately 2 miles from the air collection site). Water sampling conditions are given in Table 5. Samples (4 L) were collected about 1 ft. below the surface of the water with clean glass jars and stored at 1.7 ^{o}C. Prior to workup, samples were adjusted to pH 2 by adding 5 mL hydrochloric acid. Recoveries were checked by spiking 10 ng of ^{13}C-PCP into each water sample. Samples were extracted by placing water into clean 20 L metal canisters and using nitrogen to push water through a GFF (particulate fraction) and an ENV+ cartridge (dissolved fraction). Cartridges were dried with nitrogen and extracted with 15 mL 50/50 EE/PE and extracts concentrated into 5 mL of isooctane.

SEPARATION AND DERIVATIZATION

Sample components were separated and the PCP derivatized into pentachlorophenol acetate (PCPA) by the following procedure (Figure 4). To separate the non-polar components, pentachloroanisol (PCA) and hexachlorobenzene (HCB) from the polar component, PCP; approximately 5 mL of 0.5 M anhydrous sodium carbonate was added to each sample, vortexed for one minute, and the organic layer drawn off and saved. Two 1 mL aliquots of isooctane were added to the water fraction, vortexed for one minute, and the organic layer combined with the previous portion. This fraction (containing PCA and HCB) was concentrated with nitrogen to 1 mL of isooctane and passed through a cleanup column consisting of 2 g alumina topped with 1 g sodium sulfate. The compounds of interest were eluted with 20 mL 10% DCM/PE. The eluent was concentrated and transferred into isooctane with nitrogen to a final volume of 4 mL for PUFs and XAD-2 and 1 mL for GFFs.

PCP was derivatized to PCPA by adding 1 mL of isooctane and 200 μL of acetic anhydride to the aqueous fraction, mixing for one minute and saving the organic layer. Two 1 mL aliquots of isooctane were added to the aqueous portion, mixed and the organic layer combined with the previous portion. This second organic fraction (containing the PCPA derivatized from PCP) was concentrated using nitrogen into 4 mL isooctane for PUF and XAD-2 and 1 mL for GFFs. As an internal standard for GC analysis, 226 ng of d_6-α-hexachlorocyclohexane (α-HCH-d_6) was added to the PUF and XAD-2 samples and 56.5 ng α-HCH-d_6 to the GFFs.

ANALYSIS

Samples were analyzed with a Hewlett-Packard 5890 Gas Chromatograph-5970 Mass Spectrometer (GC-MS) using the negative chemical ionization (NCI) mode. A DB-5 capillary column (30 m length, 0.250 mm i.d., 0.25 μm film thickness) was used. The injector temperature and detector temperatures were 250 °C. The GC oven temperature program was 90 °C (1 minute hold time), 15 °/min to 140 °C, 5 °/min to 200 ° C(2 min hold), and 20 °/min to 250 °C(2 min hold). Samples (2 μL) were injected using split/splitless injection (split opened after 1 min). The MS source temperature was 150 °C and quadripole temperature was 100 °C. Helium was used as the carrier gas at a flow rate of 1.4 mL/minute and a linear velocity of 44.4 cm/second. Selected ion monitoring mode was used. The ions monitored for each compound are listed in Table 6. Samples were quantified against four standards spanning a 1000-fold concentration range (0.0001-0.1 ng/μL) using d_6-α-hexachlorocyclohexane as an internal standard. Chromatographic data were collected and processed using a Hewlett-Packard Chemstation. Examples of calibration plots are shown in Figures 6-9.

CHAPTER FIVE

RESULTS AND DISCUSSION

QUALITY CONTROL

Blanks

Clean PUFs, GFFs and XAD-2 were used as procedural blanks for air samples. Distilled water (4 L) was used for water blanks. Blanks for all media were extracted and analyzed as for samples. The instrument limit of detection, ILOD, was determined by the lowest calibration standard as 0.00001 ng/μL. Blank values above ILOD were averaged and are given in Table 7 as mean ± standard deviation (sd). A sample was rejected for a specific compound if the level was lower than the mean blank plus three standard deviations. Samples with acceptable levels were blank corrected by subtracting the average blank value from the sample.

Spike Recovery Experiments

Derivative Recoveries

The analysis of PCP by GC requires a derivatization step to convert PCP to the corresponding acetate, PCPA. The efficiency of this derivatization was checked by derivatizing three different quantities of ^{13}C-PCP in 3 mL isooctane. Since there is no ^{13}C-PCPA standard commercially available, the recovery was determined against a PCPA standard. The results ranged from 56.0 - 73.2% yield with an average of 65.4 ± 8.71% (Table 8). Other researchers have found similar derivatization recoveries using the same procedure.[56,58] The ^{13}C-PCPA produced in this experiment was used as a

standard for further recovery experiments after accounting for derivatization losses and calculating the concentration. The average derivatization yield from this experiment (65.4 %) was used to correct for derivatization losses of PCP in samples and spike recovery experiments.

Collection Efficiency Experiments

To monitor collection efficiency, 10.0 ng of ^{13}C-PCP was spiked below the surface of the front PUF immediately prior to air sampling to mimic the frontal movement of the unlabeled compounds through the trap. The average recovery of ^{13}C-PCPA for the two samples analyzed was determined (after correction for derivatization) to be 79.9 ± 19.9% (Table 9). This recovery was for PUF alone, however, and it is expected that at least some portion of the ^{13}C-PCP would breakthrough the PUF and be retained by the XAD.[56] Unfortunately, analysis of the XAD-2 and remaining PUFs for the ^{13}C-labeled product was not done due to equipment failure. McConnell found the average collection efficiency recovery for ^{13}C-PCPA on a PUF/Tenax/PUF trap (analyzed as one unit) to be 101 ± 35 % .[17]

As a collection efficiency check for water, 10.0 ng ^{13}C-PCP was added to all water samples immediately before collection and extraction on the ENV+ cartridges. After derivatization adjustments were applied to the ^{13}C-PCPA yields, the average recovery in water samples was 89.9 ± 68.4% (Table 9). McConnell, in a similar experiment, averaged 86 ± 48% recovery of ^{13}C-PCP using column extraction with XAD-4 resin and 70 mL diethyl ether as the eluent.[17] Spike recoveries of ^{13}C-PCPA in water samples were lower than recoveries from distilled water (89.9% vs. 118%). A

possible explanation for this difference is the adsorption of some ^{13}C-PCP onto particles and humic material within the water. Prior research has shown that higher chlorinated chlorophenols have significant association with particulate matter in environmental samples.[59]

Analytical Method Recoveries

To determine losses due to the analytical method, clean PUF, GFF, XAD-2 and distilled water were spiked with known amounts of the target compounds (Table 10). Spikes were extracted and analyzed as for samples. The levels of PCA and HCB were blank corrected and the recoveries calculated, while PCPA and ^{13}C-PCPA values were both blank and derivatization corrected before calculating recoveries. Average percent recoveries for all compounds in all media are given in Table 11. Spike recoveries for each medium are given in Tables 12-15.

HCB & PCA

HCB recoveries were low in all media with the highest recovery for PUF (48.4 ± 7.92%) and the lowest for water (29.9 ± 4.19%) . PCA recoveries were also lower than expected: 52.7 ± 8.71% for PUF, 46.4 ± 6.56% for XAD, 40.7 ± 5.86% for GFF and 37.2 ± 5.69% for water. Reasons for the low recoveries of these two compounds are not known. In a study testing the collection efficiency of a PUF/Tenax trap using 15% EE/PE for extraction, HCB had an average recovery of 89 ± 16%.[49] Another study gave HCB recoveries from PUF alone of 68 ± 3% after extraction for 8 hours with PE.[45] In a

study where a florisil trap was used for collection and 30% DCM/hexane used for extraction, HCB spike recoveries averaged 102 ± 4.3%.[60]

Areas of possible problems within the analytical procedure for HCB and PCA include: volatilization losses during sample concentration, losses during separation/derivatization, losses during sample clean-up, and errors in GC analysis. Since spike recoveries were done with clean media, analytes measured against both external and internal standards and compounds analyzed in selected ion monitoring mode with two separate ions; problems with GC analysis are unlikely. Sample clean-up for PCA and HCB consisted of passing samples through 2 g alumina and 1 g sodium sulfate to remove water and other interferences. Compounds of interest were eluted with 20 mL 10% DCM/PE. Similar procedures (usually also including several grams of silicic acid) have been used in the past with no significant loss of OCs during the clean-up step.[61,62] The possibility that the separation of HCB and PCA from PCP caused loss of the analytes was not directly checked. However, a subsequent experiment adding hydrochloric acid when extracting XAD-2, showed marked improvements in yields of HCB and PCA. The experiment is discussed in more detail in the next section; however, it suggests that the extraction of HCB and PCA from XAD-2 could be a major source of problems, while the separation/derivatization step (which was done the same way in both cases) is probably not an important factor. Volatilization losses during sample concentration are possible due to higher volatilities of the analytes compared to other OCs. However, the recoveries of PCPA and ^{13}C-PCPA (which have similar vapor pressures) in PUF and water were within acceptable ranges, suggesting that volatilization losses are unlikely.

PCPA

PCPA and ^{13}C-PCPA recoveries varied in the different media. In both water and PUF, the compounds showed good recovery yields. PCPA recoveries averaged 123 ± 53.0% in PUF and 118 ± 10.2% in water, while ^{13}C-PCPA averaged 106 ± 16.8% for PUF and 88.2 ± 7.13% for water. ^{13}C-PCPA recoveries from analytical spikes vs. collection efficiency spikes in water agreed well on average (88.7% vs. 89.9%). However, the collection efficiency spikes had an extremely large standard deviation (± 68.4%). McConnell found comparable recoveries with high standard deviations in a similar study, although the PCP in that study was collected using column extraction with XAD-4 and elution with 70 mL diethyl ether.[17] For the McConnell work, analytical recoveries averaged 81 ± 40% and collection efficiencies averaged 86 ± 48%. In both studies (McConnell and this study) the water was acidified to pH 2 before extraction to convert PCP to its protonated form to increase collection efficiencies.

Average recoveries of ^{13}C-PCPA from analytical spikes compared to two collection efficiency spikes in air are not as close: analytical, 106 ± 16.8%; collection efficiency, 79.9 ± 19.9%. However, in the collection efficiency experiments, the recovery is from PUF alone, and it is expected that some portion of the PCP would end up on the XAD which was not analyzed. In the McConnell study using the PUF/Tenax trap, analytical recoveries were 88 ± 47% for PCPA and 101 ± 36% for ^{13}C-PCPA with a collection efficiency for ^{13}C-PCPA of 101 ± 35%.[17]

PCPA recoveries on XAD and GFFs were extremely low. PCPA was recovered from only one XAD spike at 40.4% recovery; all others were below detection limits (0% recovery). On GFFs, PCPA was found in only two of the four spikes for an average

recovery of 14.9%. ^{13}C-PCPA recoveries in the same experiment were 11.5 ± 14.3% for XAD and 17.1 ± 9.15% for GFFs. Comparison of individual recovery values for PCPA and ^{13}C-PCPA showed consistency in the recovery of the two compounds. Poor recovery yields of PCP from XAD has been found previously. Tan and Liem found 0% recovery of PCP from spiked XAD-2 using both DCM and toluene as extraction solvents.[57] They did, however, find that the addition of HCl to the extraction solvent (DCM) boosted recovery yields to 95 ± 4%. To determine if addition of acid to our extraction procedure would improve recoveries, varied concentrations of HCl were added to XAD-2 resin spiked with PCP, PCA and HCB (Table 16). The spikes were soxhleted 24 hours with 50/50 EE/PE and extracts were separated, derivatized and analyzed as previously described. In this study, addition of HCl did not significantly boost PCP recoveries (Table 17). The average recovery for PCPA was 24.1 ± 17.6%, with a maximum yield found with 5 M HCl added (40.5%). The low yields of PCP in this experiment could be due to inadequate mixing of HCl with the nonpolar solvent. It is interesting to note, however, that the addition of HCl enhanced recoveries of both HCB and PCA from XAD. The average yield for HCB in this experiment was 70.3 ± 7.69% and for PCA, 75.6 ± 9.03%, compared to 44.3 ± 6.37% for HCB and 46.4 ± 6.56% for PCA with no acid added. This suggests that the extraction step could be a major factor in the loss of analytes.

CONCENTRATIONS IN AIR AND WATER

Sampling Site

Beginning in Salem, OH, the Mahoning River stretches 108 miles before it joins the Shenango River near New Castle, PA, to form the Beaver River, a tributary of the Ohio River (Figure 5). The river drains an area of 1133 square miles and during the majority of this century, has been the site of concentrated industrial activity. At the peak of activity, eight major steel mills were releasing over 600 million gallons of wastewater into the river every day containing large amounts of oil, grease, and iron. Coke plant wastes and used pickling acids were often jettisoned into the river as well, and at several points in the river's history, no aquatic life existed due to high water temperatures (over 100 ^{o}F). Untreated sewage from both residential and commercial areas also found its way into the river. By 1970, most sewage was being treated at municipal plants; however, it was not until the closing of the last steel mill in 1983 that the river received relief from the heavy onslaught of pollution. Conditions have improved; an Ohio E.P.A. study in 1996 showed that both the numbers and types of fish have increased in the Mahoning River Basin between 1980 and 1994. Existing fish do, however, show higher than normal occurrences of tumors, lesions, fin erosions and deformities. The Ohio E.P.A. has declared that the ecology within the main stem of the river and many sections of its tributaries is threatened due to the high concentrations of polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals trapped in the sediments. The river still continues to receive runoff containing a variety of pollutants from "Brownfields" (abandoned industrial property), suburban drainage and nonpoint source pollution.

Data Treatment

All air and water samples for HCB and PCA were blank and recovery corrected by the following equation:

(ng sample - ng average blank)/average fractional spike recovery (1)

Since recoveries for PCPA in PUFs and water cartridges were acceptable (above 80%), these PCPA values were only corrected for blanks and derivatization recovery (65.4%). PCPA in XAD and GFFs were corrected by Equation 1. As the air is drawn through the sampler, compounds in the particulate phase are caught on the front filter. The majority of compounds within the gaseous phase are caught on the adsorbent trap which can consist of polyurethane foam plugs, adsorbent resins (such as XAD-2 or Tenax) or a combination of the two. Small amounts of analyte existing within the gaseous phase may be caught on the filters.[63] To correct for this, a back filter can be added. The measure of analyte on particulates (C_p) is calculated with Equation 2:

$$C_p = FF\text{-}BF \qquad (2)$$

where FF is the ng found on the front filter after blank correction and BF is the back filter value after blank correction. The measure of gases in the vapor phase (C_g) includes the ng found on the polyurethane foam plugs (PUF) plus the amount in ng adhered to the filters and is calculated by the following equation:

$$C_g = PUF + 2BF \qquad (3)$$

Air and water values were divided by the respective daily volume (Table 18) and the resulting concentrations of PCPA, PCA and HCB within each type of media listed in Tables 19-25. Since recoveries for these compounds were so low, concentrations should be considered tentative.

PCP in Air

The average air value for PCP, measured as PCPA, was 0.962 ± 0.672 ng/m^3 with a range from 0.219 - 2.02 ng/m^3. The majority of the PCP (64.0%) was found on the front PUF, averaging 109 ± 48.4 ng. Only one XAD fraction was above detection limits (36.0 ng for sample 2). This is unusual as XAD normally collects PCP more efficiently than PUF. However, the extremely low recovery of PCP from XAD is most likely to blame for the lack of detection. Particle-bound PCP averaged 25.2 ± 6.63 ng. A chromatogram of PCP from PUF is shown in Figure 10. The average PCP level in Youngstown is similar to that found by Bruckman in the urban setting of Windsor, Ontario (0.87 ng/m^3) but higher than values reported by McConnell *et al.* in a pristine marsh located 0.5 miles from a Kraft pulp mill (0.067 ng/m^3) and Georgetown, SC (0.320 ng/m^3), located within a mile from both steel and pulp mills.[49,17] PCP concentrations at Green Bay, WI, were also low (0.160 ng/m^3 in the winter and 0.130 ng/m^3 in the summer) even though the sampling site was in an industrialized area. There is no known point source of PCP to the greater Youngstown region, although the area

has a history of heavy industrialization. Atmospheric transport of volatilitized PCP from treated wood, such as utility poles, is the most likely source of PCP.

PCA in Air

Air levels for PCA averaged 1.77 ± 0.487 ng/m^3 and ranged from 1.23 ng/m^3 to 2.62 ng/m^3. The bulk of the PCA (84.5%) was captured on the XAD (163 ± 69.2 ng) with the PUF contributing 29.2 ± 9.74 ng and the GFFs 0.738 ± 0.618 ng. A chromatogram of PCA from XAD-2 is shown on Figure 11. Hoff found air levels of PCA in rural Ontario of 0.028 ng/m^3 while Atlas found only 9.0 pg/m^3 in the air at the remote 90-Mile Beach, New Zealand.[35,36] PCA concentrations in America Samoa were even lower (2.1 pg/m^3). The high levels of PCA in Youngstown air are not totally unexpected when the relatively high levels of PCP are considered but all concentrations should be considered tentative. PCP was not analyzed in either the Ontario or the New Zealand studies.

HCB in Air

Of the three analytes, HCB had the lowest air concentration with an average of 0.556 ± 0.156 ng/m^3 and a range from 0.338 to 0.765 ng/m^3. As with the PCA, the majority of HCB (87.1%) was found on the XAD, most likely due to breakthrough from PUF at such high ambient temperatures (averaging 32.4^o C, Table 4). A chromatogram of HCB in XAD-2 is shown in Figure 11. Although the target ion for HCB is 284, PCA also contains a small amount of this same ion which shows up at a different retention time. Hoff *et al.* found a range of HCB from 0.00004 to 0.640 ng/m^3 in rural Egbert,

Ontario, and levels in Denver, CO, averaged 0.24 ng/m^3.[35] Other urban HCB values at various sites were 0.076 ng/m^3 in Portland, OR, 0.15 ng/m^3 in Windsor, ON, and 0.160 ng/m^3 in Green Bay, WI.[41,16,17] Higher values were found in the air above Lake Baikal in the Russian Republic, (0.138 - 0.250 mg/m^3).[17] Although this lake is surrounded by mountains, three large industrialized cities are within 50 miles and the lake is thought to be fed pollutants from the Selenga River. The Dover Chemical Company, located approximately 70 miles west of Youngstown, was noted as a major producer of HCB in past years and volatilization of residues from the site may possibly be contributing to the current levels.

PCP, PCA and HCB in Water

Of all three compounds, only PCP had levels in water above the ILOD. This could be due in part to the good recovery of PCP from water cartridges (118%) compared to HCB (29.9%) and PCA (37.2 %). The PCP level in Lake Glacier averaged 14.1 ± 6.71 ng/L with a range from 4.18 to 23.7 ng/L (Table 25). Other studies have found PCP ranging from 4.6 pg/L in a pristine marsh and 9.2 pg/L at Winyah Bay, SC[17] to 16.47 mg/L in groundwater at American Chemical Works in Pensacola, FL.[19] At a former wood treatment site in Dania, FL, ground water levels ranged from 0.012 - 170 mg/L.[18] Seventeen months after a PCP spill in Hattiesburg, MI, water levels of PCP were 0.28 ng/L.[11] The most probable sources of PCP to the Mahoning River are leaching of treated lumber and atmospheric transport. Although water filters were not analyzed in this study, association with particles has been found to be an important factor for these compounds.[59] McConnell suggested from studies of chlorophenols in water as a

function of distance from a point source, that removal by sedimentation is significant.[17] Sediment mediated conversion of PCP to PCA and subsequent revolatilization may explain higher levels of PCA in the air.

CHAPTER SIX

CONCLUSIONS

OCs are persistent, toxic compounds which pose a threat to the environment. Their analysis in various compartments of the environment is important in determining their fate and effects. Initially, the goal of this research was to determine concentrations of organochlorine compounds in air and water using established methods. With this purpose in mind, air and water samples from the Youngstown, Ohio, area were collected over seven days in August, 1996.

Although methods for collection and extraction of PCP, PCA and HCB in air and water were adapted from published procedures, collection efficiencies in this study were lower than expected. Standard air sampling methods require the use of PUF/Tenax or PUF/XAD traps to collect the more volatile OCs followed by solvent extraction of the entire trap. Collection efficiency values reported in previous studies of PCP varied greatly (high standard deviation), possibly compromising the concentration calculations. In the present study, PUF and XAD were extracted separately for both recovery experiments and samples and although PUFs gave satisfactory recoveries for PCPA (the derivatized form of PCP), recovery from XAD was drastically low. This may explain the great variability found in previous research where traps were extracted as a whole. Recent research by Tan and Liem suggested use of HCl for improving collection of PCP from XAD.[57] However, in the present study, addition of acid to the XAD extraction procedure increased recoveries of PCPA only slightly, although PCA and HCB recoveries improved by almost a factor of two. Protonation of the hydroxyl group would

explain why addition of acid might improve recoveries of PCP from the adsorbent resin; however, acid should not affect the extraction of HCB and PCA. Inadequate mixing of the HCl with the extraction solvent (EE/PE) used in this experiment may explain the lack of increased recoveries of PCP from XAD.

Recoveries of PCPA from water (which was acidified before extraction) were good, but recoveries of PCPA from GFFs and HCB and PCA in all sampling media were low. More studies are needed to determine the exact reasons for such low recoveries as well as to lessen the great variability in collection efficiencies (high standard deviation). Some areas which need to be studied further include: losses during sample concentration, derivatization and separation effects on sample recoveries, effects of different solvents on extraction recoveries, losses during clean-up and effect of acid on extraction recoveries. Preliminary results from this study suggest incomplete extraction as the most probable cause of loss; unfortunately, the reasons for this are not known.

Levels of PCP, PCA and HCB were determined for the first time in air and water in Youngstown, OH. The presence of these compounds, which have no point source in the region, suggests atmospheric transport and deposition as an important source of contaminants to air and water in the Youngstown area; however, concentrations reported in this study should be considered tentative due to the low recoveries found during quality control experiments. It is expected during summer months that the majority of the more volatile OC compounds would be caught by XAD rather than PUF. However, due to low recoveries, only PCA was found to be primarily on XAD. Nondetection of HCB and PCA in water may be due to low recoveries and/or low concentrations in the dissolved fraction. Improved sampling and extraction methods need to be developed

and more samples need to be taken, possibly during different times of the year, to accurately determine levels of these pollutants in the Youngstown area.

Table 1. PCP Concentrations from Selected Studies

MEDIUM	CONCENTRATION	LOCATION	REFERENCE
air	0.67 ng/m^3	Hamburg, GE	15
air	0.87 ng/m^3	Windsor, ONT	16
air	0.38 ng/m^3	Walpole Is., ONT	16
air/winter	0.160 ng/m^3	Green Bay, WI	17
air/summer	0.130 ng/m^3	Green Bay, WI	17
air/winter	0.320 ng/m^3	Georgetown, SC	17
air/summer	0.270 ng/m^3	Georgetown, SC	17
air	0.067 ng/m^3	North Inlet, SC	17
air	0.075 ng/m^3	Winyah Bay, SC	17
air/first month	30 μg/m^3	House made of PCP-treated wood	12
air/ poor ventilation	160 μg/m^3	House made of PCP-treated wood	12
air/one to several years	1 - 25 μg/m^3	House made of PCP-treated wood	12
water	4.6 pg/L	North Inlet, SC	17
water	9.2 pg/L	Winyah Bay, SC	17
ground water	0.012-170 mg/L	Dania, FL	18
ground water	16.47 mg/L	Pensacola, FL	19
sediment	3.3 ng/g	Hattiesburg, MI	11
surface wax of pine needles	1 ng/g	Sweden	20
fish muscle	7.0 ng/g	Hattiesburg, MI	11
oysters	5.3 ng/g	Galveston Bay, TX	21

Table 2. PCA Concentrations from Selected Studies

MEDIUM	CONCENTRATION	LOCATION	REFERENCE
air	0.028 ng/m^3	Egbert, ONT	35
air	2.1 ± 0.8 pg/m^3	American Samoa	36
air	9.0 ± 3.9 pg/m^3	90-Mile Beach, NZ	36
water	6 - 600 ng/L	Dania, FL	18
water	0.095 ng/L	Mississippi River, Winfield, MO	37
water	< 0.01 ng/L	Hattiesburg, MI	11
suspended sediment	2.8 ng/g	Windfield, MO	37
sediment	0.1 ng/g	Hattiesburg, MI	11
fish muscle	1 ng/g	Hattiesburg, MI	11

Table 3. HCB Concentrations from Selected Studies

MEDIUM	CONCENTRATION	LOCATION	REFERENCE
air	0.076 ng/m^3	Portland, OR	41
air	0.15 ng/m^3	Windsor, ONT	16
air	0.16 ng/m^3	Walpole Is., ONT	16
air	0.071 ng/m^3	Southern Ontario	42
air	0.15 ng/m^3	Alert, NWT	43
air	0.11 ng/m^3	Pacific Ocean	44
air	0.054 ng/m^3	Egbert, ONT	35
air	0.160 ng/m^3	Greenbay, WI	17
air	0.120 ng/m^3	Georgetown, SC	17
air	0.138 - 0.250 ng/m^3	Lake Baikal, Russian Republic	17
air	0.076 ng/m^3	Glendora, CA	17
air	0.153 ng/m^3	N. Ellesmere Is., Canada	17
air	0.098 ng/m^3	North Inlet, SC	17
air	0.137 ng/m^3	Winyah Bay, SC	17
air	0.119 - 0.233 ng/m^3	Ice Island, Canadian Arctic	45
air	0.29 ng/m^3	Columbia, SC	46
air	0.24 ng/m^3	Denver, CO	46
air	0.18 ng/m^3	New Bedford Landfill, MA	46
water	17 - 22 pg/L	Ice Island	45
water	< 30 pg/L	Norwegian Sea	47
water	0.20 ng/L	St. Francisville, LA	37
ice	40 - 50 pg/L	Norwegian Sea	47
pine needles	0.02 - 1.9 ng/g	South Is., NZ	48
oysters	0.63 ng/g	Galveston Bay, TX	21

Table 4. Air Sampling Conditions

DATE	PRESSURE (in. Hg)	HUMIDITY (%)	WIND DIRECTION	TEMPERATURE (^{o}C)
8-21-96	28.94	63-100	CALM, N-NW	34.0
8-22-96	28.90	57-100	CALM, S-SW	25.5
8-23-96	28.87	59-100	CALM, N-NW	27.0
8-24-96	28.92	44-98	CALM, NE-W-NW	28.0
8-25-96	28.84	43-100	CALM, S-SW	29.2
8-26-96	29.40	43-100	CALM	28.0
8-27-96	30.04	46-100	CALM, N-NE	27.5
8-28-96	30.11	55-100	CALM	27.6

Table 5. Water Sampling Conditions

DAY	TEMPERATURE (^{o}C)	pH
8-22-96	28.0	8.65
8-23-96	26.0	7.50
8-24-96	26.0	7.89
8-25-96	26.0	7.52
8-26-96	29.0	7.52
8-27-96	28.0	7.61
8-28-96	27.2	9.20
AVERAGE ± S.D.	27.2 ± 1.21	7.98 ± 0.675

Table 6. Selected Ions Monitored for Target Analytes

Compound	Target Ion	Qualifying Ion
α-HCH-d_6	261	-
^{13}C-PCPA	318	320
PCPA	308	306
PCA	280	282
HCB	284	282

Table 7. Average Blank Values (ng) for Target Analytes in All Sampling Media

MEDIUM	^{13}C-PCPA	PCPA	PCA	HCB
PUF	0.104 ± 0 (2)*	1.48 ± 2.03 (7)	0.595 ± 0.958 (7)	0.249 ± 0.435 (7)
XAD	0 (2)	1.39 ± 2.40 (3)	0.442 ± 0.674 (4)	0 (4)
GFF	0 (2)	0.347 ± 0.603 (3)	0 (4)	0 (4)
WATER	ND**	2.60 ± 1.95 (4)	0.465 ± 0.930 (4)	5.33 ± 2.03 (4)

* Average ± S.D. (N)
** ND = Not Determined

Table 8. % Recoveries of ^{13}C-PCPA from Derivatization Experiments

TRIAL	SPIKE AMOUNT (ng)	% YIELD
1	600	56.0
2	900	73.2
3	1200	67.0
AVERAGE ± S.D.	-	65.4 ± 8.71

Table 9. Recoveries of ^{13}C-PCPA (%) from Collection Efficiency Experiments in Water and PUF

DAY	WATER	PUF
8-22-96	78.1	65.9
8-23-96	ND*	NA**
8-24-96	ND	NA
8-25-96	90.9	NA
8-26-96	204	NA
8-27-96	48.9	NA
8-28-96	27.6	94.0
AVERAGE ± S.D. (N)	89.9 ± 68.4 (7)	79.9 ± 19.9 (2)

* ND = Not Detected
** NA = Not Analyzed

Table 10. Spike Amounts (ng) for Analytical Recovery Experiments

ANALYTE	PUF, XAD & WATER	GFF
^{13}C-PCPA	40.0	10
PCPA	40.0	10
PCA	39.3	9.82
HCB	128	32

Table 11. Average % Recoveries for Analytical Spike Experiment

COMPOUND	PUF	XAD	GFF	WATER
^{13}C-PCPA	106 ± 16.8 (4)*	11.5 ± 14.3 (4)	17.1 ± 9.15 (4)	88.2 ± 7.13 (3)
PCPA	123 ± 53.0 (4)	40.4 (1)	14.9 ± 18.0 (4)	118 ± 10.2 (4)
PCA	52.7 ± 8.71 (3)	46.4 ± 6.56 (4)	40.7 ± 5.86 (3)	37.2 ± 5.69 (4)
HCB	48.4 ± 7.92 (3)	44.3 ± 6.37 (4)	36.9 ± 4.93 (3)	29.9 ± 4.19 (4)

* Average ± S.D. (N)

Table 12. % Recovery from GFF for Analytical Spike Experiment

SAMPLE	^{13}C-PCPA	PCPA	PCA	HCB
1	6.73	ND**	NA+	NA
2	28.4	36.2	46.3	42.1
3	13.8	ND	41.1	36.3
4	19.4	23.3	34.6	32.3
AVERAGE	17.1 ± 9.15 (4)*	14.9 ± 18.0 (4)	40.7 ± 5.86 (3)	36.9 ± 4.93 (3)

* Average ± S.D. (N)
** ND = Not Detected
+ NA = Not Analyzed

Table 13. % Recovery from PUF for Analytical Spike Experiment

SAMPLE	^{13}C-PCPA	PCPA	PCA	HCB
1	97.8	52.7	NA**	NA
2	128	177	57.2	54.6
3	110	146	58.3	51.2
4	89.2	117	42.7	39.5
AVERAGE	106 ± 16.8 (4)*	123 ± 53.0 (4)	52.7 ± 8.71 (3)	48.4 ± 7.92 (3)

*Average ± S.D. (N)
** NA = Not Analyzed

Table 14. % Recovery from XAD for Analytical Spike Experiment

SAMPLE	^{13}C-PCPA	PCPA	PCA	HCB
1	32.3	40.4	NA[+]	NA
2	2.31	ND	42.9	40.9
3	ND[*]	ND	47.6	44.6
4	9.56	ND	55.1	53.1
5	1.96	ND	40.1	38.6
AVERAGE	11.5 ± 14.3 (4)[**]	40.4 (1)	46.4 ± 6.56 (4)	44.3 ± 6.37 (4)

[*] ND = Not Detected
[**] Average ± S.D. (N)
[+] NA = Not Analyzed

Table 15. % Recovery from Water for Analytical Spike Experiment

SAMPLE	^{13}C-PCPA	PCPA	PCA	HCB
1	89.7	120	36.1	30.2
2	88.0	114	30.1	24.4
3	79.0	106	38.6	30.3
4	96.3	134	43.8	34.6
AVERAGE	88.2 ± 7.13 (4)*	118 ± 10.2 (4)	37.2 ± 5.69 (4)	29.9 ± 4.19 (4)

* Average ± S.D. (N)

Table 16. Amounts of Target Analytes Spiked for HCl Experiment

HCl (M)	PCP (ng)	PCA (ng)	HCB (ng)
0	400.00	392.77	438.00
0.5	400.00	392.77	438.00
1	400.00	392.77	438.00
2	400.00	392.77	438.00
5	400.00	392.77	438.00

Table 17. % Recovery of Target Analytes from HCl Experiment

SAMPLE	PCPA	PCA	HCB
NO HCl	ND*	81.4	68.0
0.5 M HCl	5.58	71.5	73.0
1 M HCl	ND	63.6	79.6
2 M HCl	26.2	74.3	72.0
5 M HCl	40.5	87.0	58.7
AVERAGE ± S.D.	24.1 ± 17.6	75.6 ± 9.03	70.3 ± 7.69

* ND = Not Detected

Table 18. Sample Volumes for Air and Water

DAY	AIR (m^3)	WATER (L)
1	108	3.64
2	110	3.43
3	91.8	3.59
4	93.4	4.08
5	132	3.89
6	96.3	4.16
7	120	1.89
AVERAGE ± S.D.	107 ± 14.9	3.52 ± 0.768

Table 19. Air Concentrations (ng/m^3)

DAY	PCPA	PCA	HCB
1	0.717	2.62	0.632
2	1.34	1.59	0.765
3	0.219	1.23	0.510
4	0.270	1.65	0.419
5	0.680	2.20	0.719
6	2.02	1.75	0.508
7	1.49	1.35	0.338
AVERAGE ± S.D.	0.962 ± 0.672	1.77 ± 0.487	0.556 ± 0.156

Table 20. Levels (ng) of Analytes on GFF

SAMPLE	PCPA	PCA	HCB
1	NA**	0.0243	ND
2	26.0	ND+	ND
3	20.1	ND	ND
4	25.2	1.10	ND
5	29.0	ND	ND
6	35.0	ND	ND
7	16.1	1.09	ND
AVERAGE*	25.2 ± 6.63 (6)	0.738 ± 0.618 (3)	-

* Average ± S.D. (N)
** NA = Not Analyzed
+ ND = Not Detected

Table 21. Levels (ng) of Analytes on PUF

SAMPLE	PCPA	PCA	HCB
1	77.4	25.4	3.68
2	85.9	32.1	12.5
3	ND**	16.8	6.90
4	ND	37.9	8.92
5	60.7	24.0	3.76
6	160	45.0	11.9
7	163	22.9	ND
AVERAGE*	109 ± 48.4 (5)	29.2 ± 9.74 (7)	7.94 ± 3.85 (6)

* Average ± S.D. (N)
** ND = Not Detected

Table 22. Levels (ng) of Analytes on XAD

SAMPLE	PCPA	PCA	HCB
1	ND**	257	64.6
2	36.0	143	71.7
3	ND	95.8	39.9
4	ND	115	30.2
5	ND	266	91.1
6	ND	124	37.0
7	ND	140	40.5
AVERAGE*	36.0 (1)	163 ± 69.2 (7)	53.6 ± 22.5 (7)

* Average ± S.D. (N)
** ND = Not Detected

Table 23. % of Analytes on Sampling Media

MEDIA	PCPA	PCA	HCB
PUF	64.0	15.1	12.9
XAD	21.2	84.5	87.1
GFF	14.8	0.4	0

Table 24. Water Concentrations (ng/L)

SAMPLE	PCPA	PCA	HCB
1	11.6	ND**	ND
2	21.1	ND	ND
3	23.7	ND	ND
4	14.3	ND	ND
5	14.4	ND	ND
6	4.18	ND	ND
7	9.21	ND	ND
AVERAGE*	14.1 (7)	0 (7)	0 (7)

* Average (N)
** ND = Not Detected

Table 25. Levels (ng) of Analytes in Water

SAMPLE	PCPA	PCA	HCB
1	42.1	ND**	ND
2	72.3	ND	ND
3	85.2	ND	ND
4	58.4	ND	ND
5	56.1	ND	ND
6	17.4	ND	ND
7	17.4	ND	ND
AVERAGE*	49.8 ± 25.9 (7)	-	-

* Average ± S.D. (N)
** ND = Not Detected

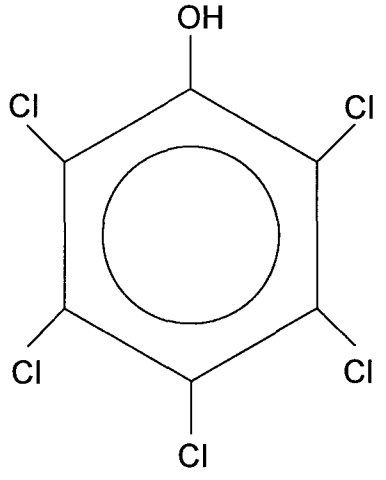

Figure 1. Pentachlorophenol

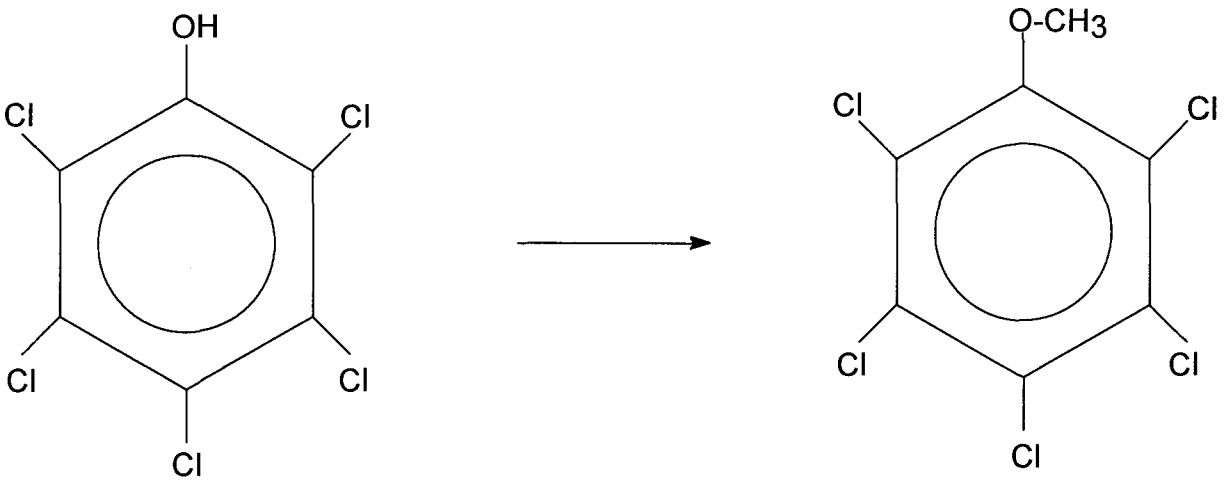

Figure 2. Microbial Degradation of PCP to PCA

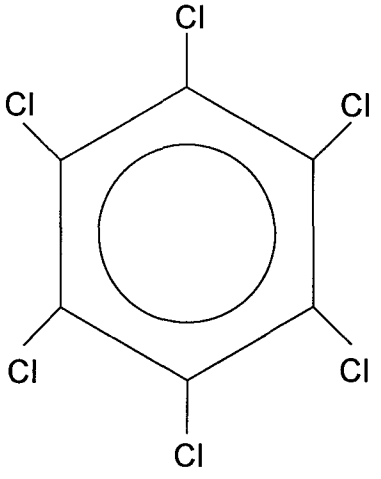

Figure 3. Hexachlorobenzene

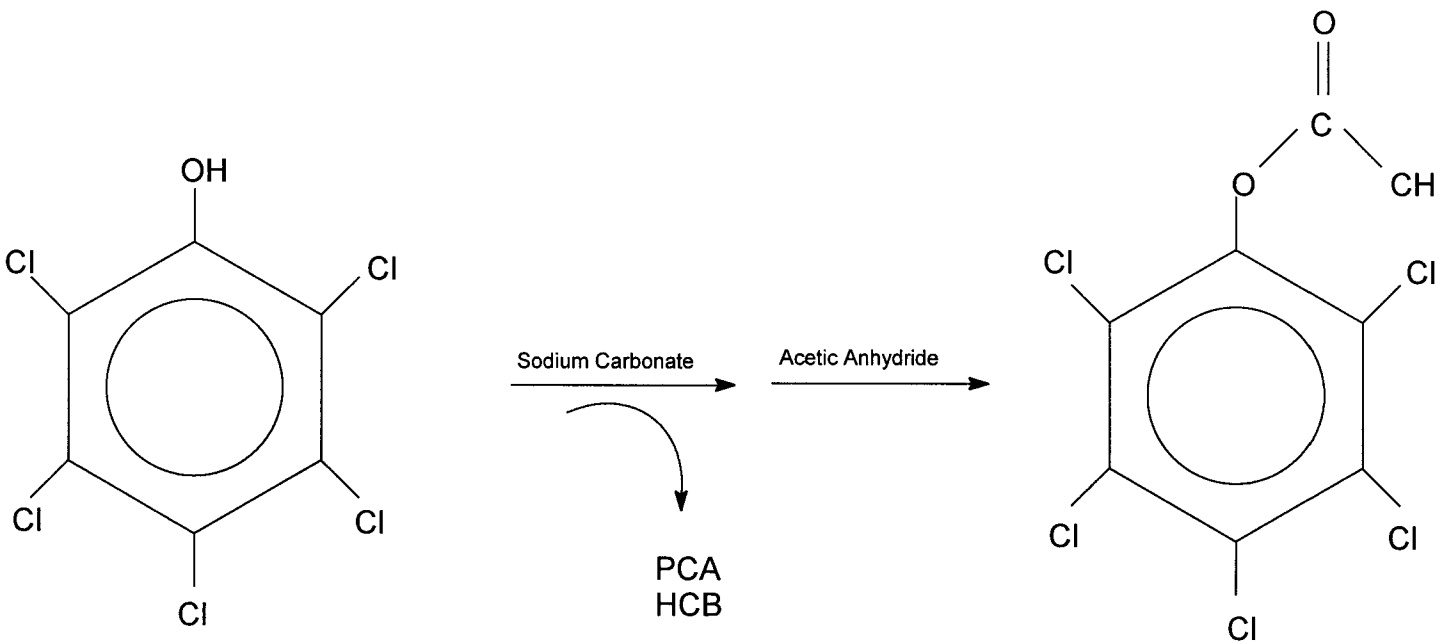

Figure 4. Conversion of PCP to PCPA

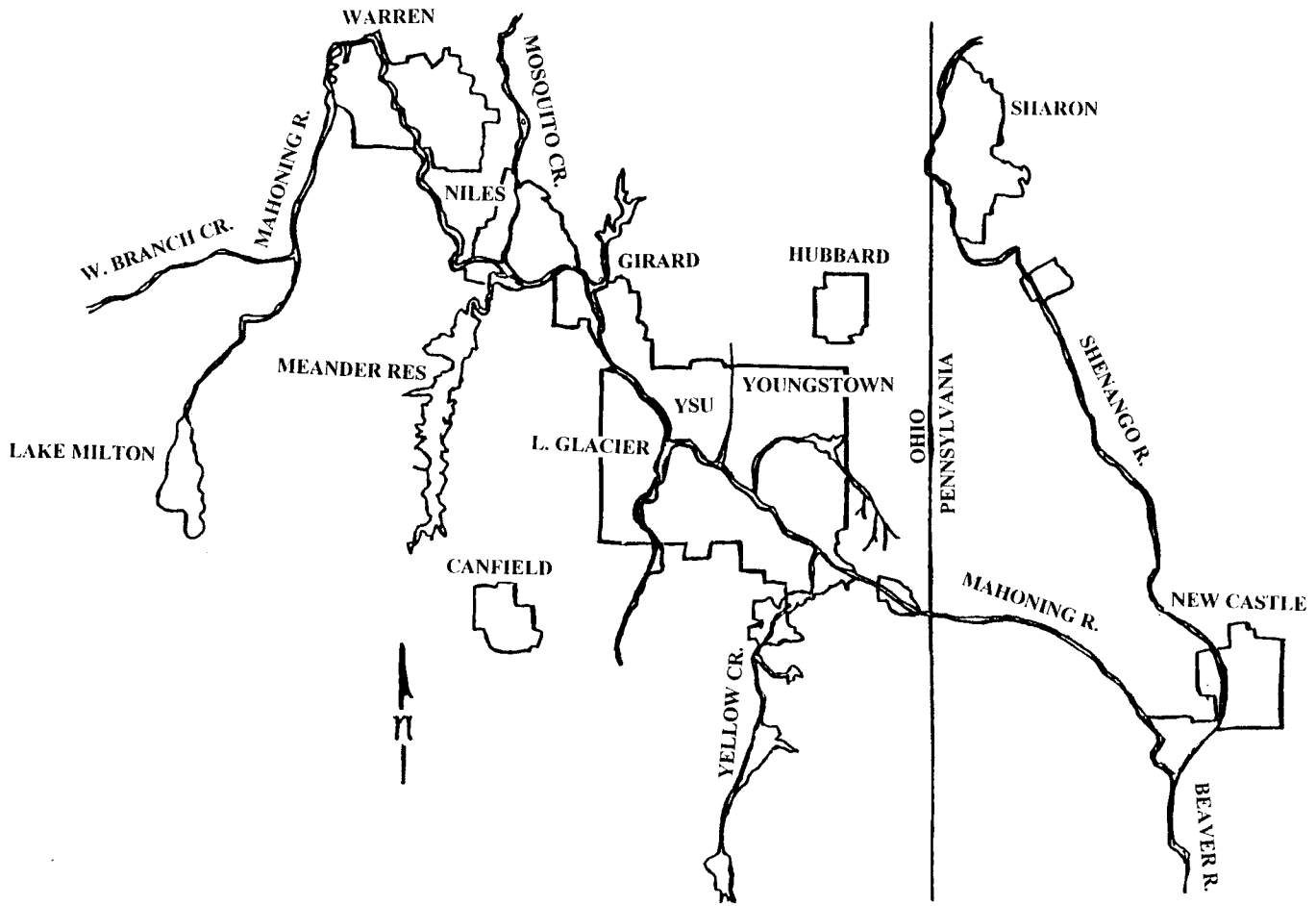

Figure 5. Map of Mahoning River Basin

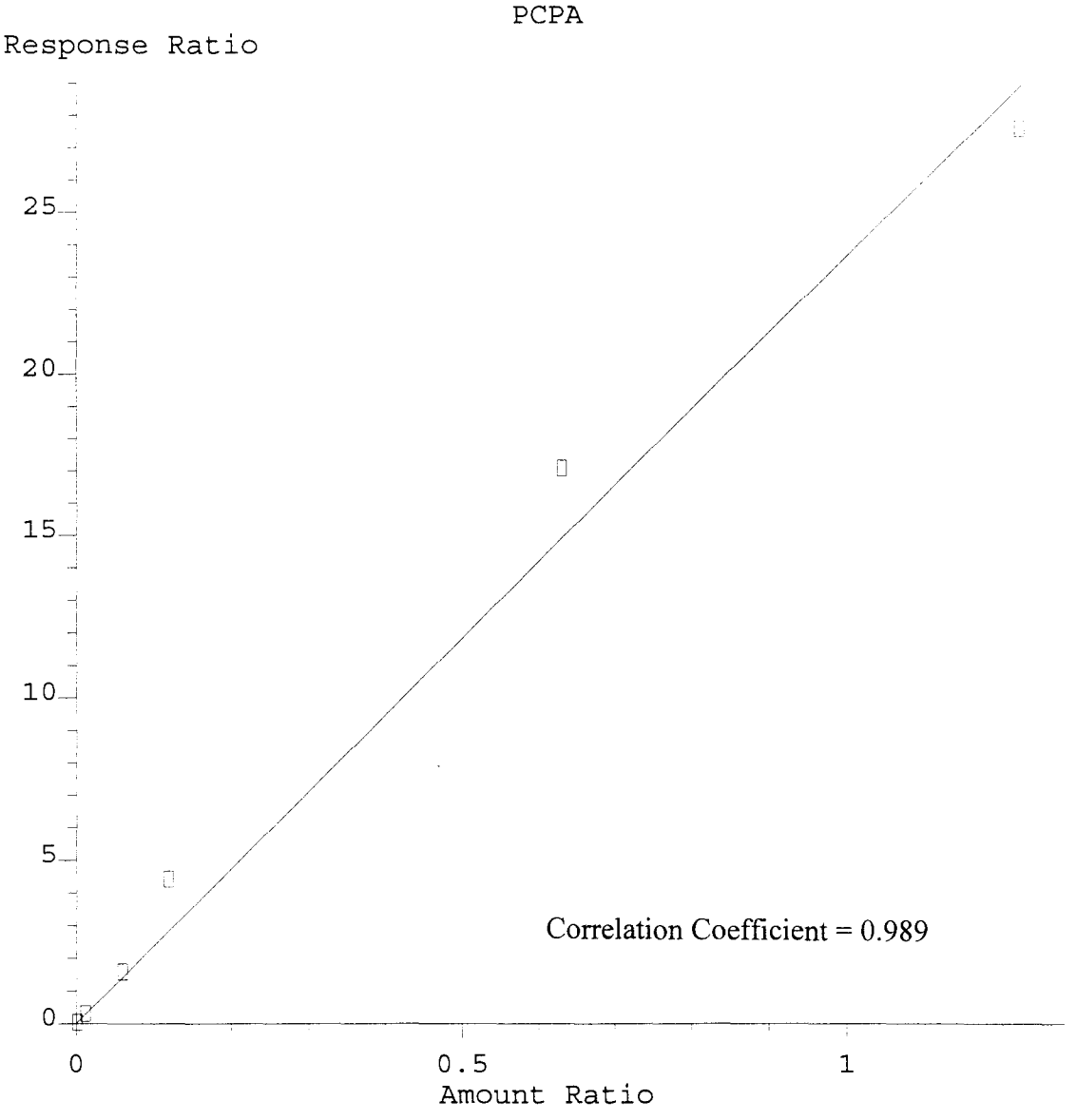

Figure 6. PCPA Calibration Plot

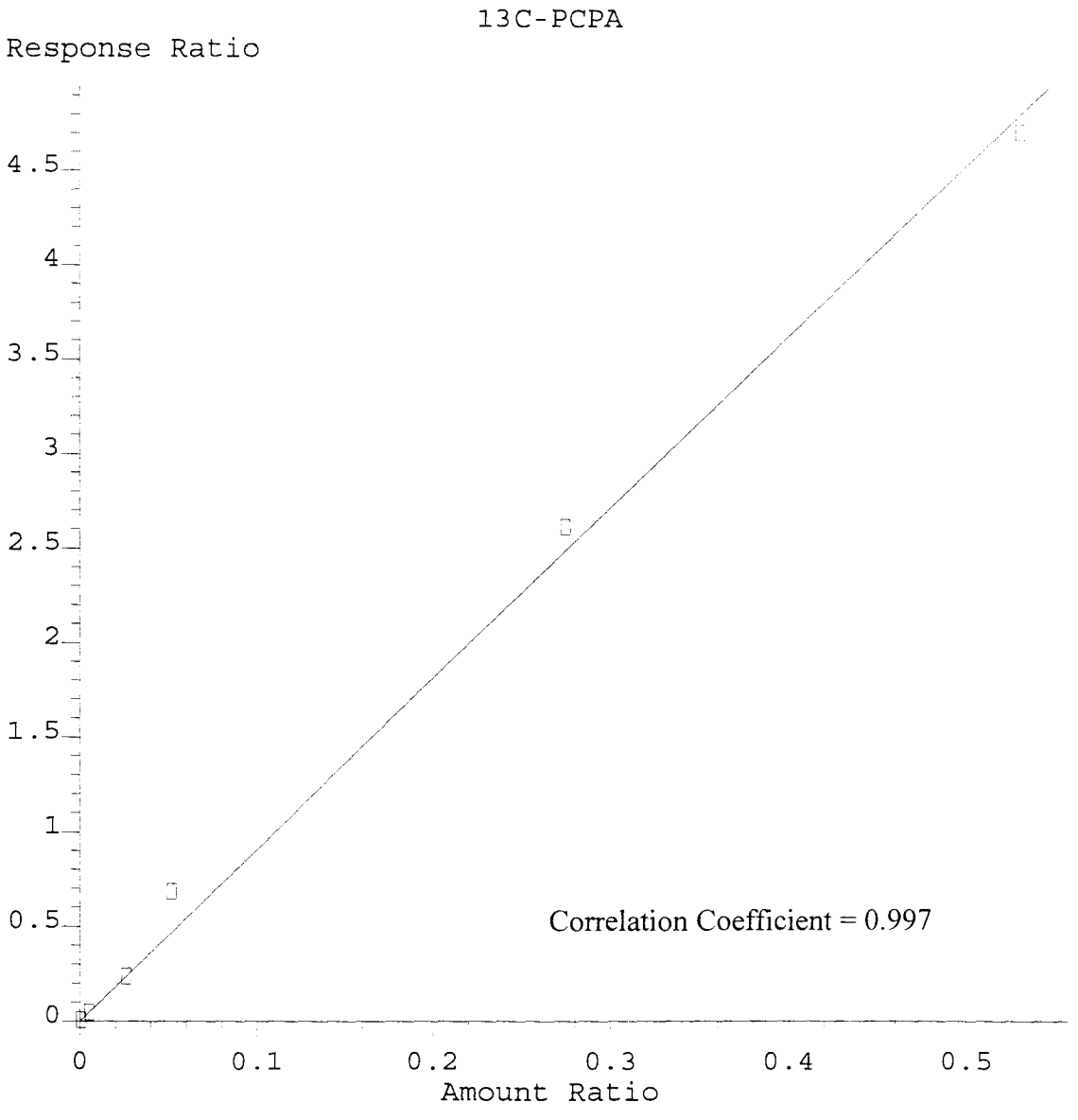

Figure 7. ^{13}C-PCPA Calibration Plot

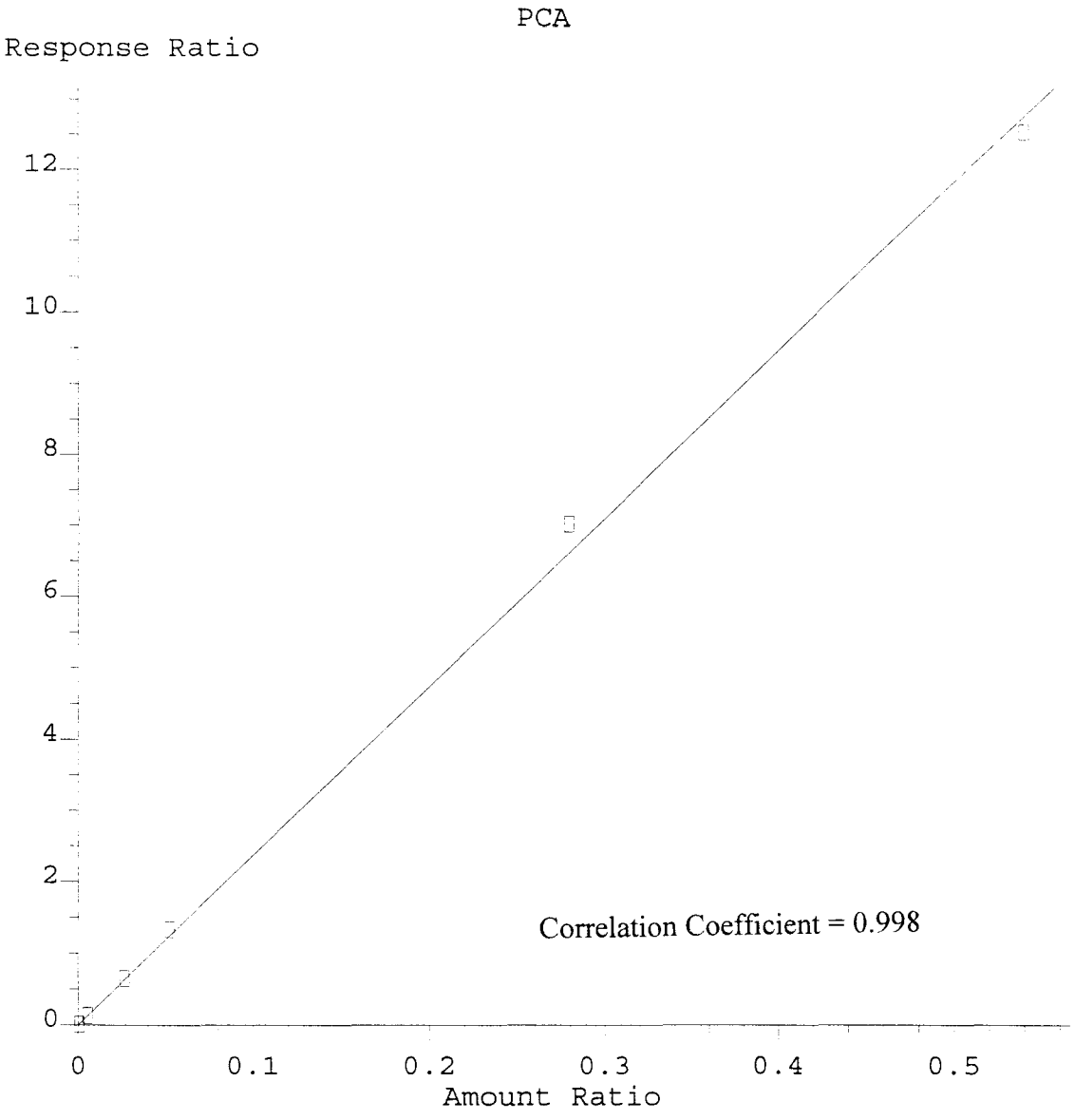

Figure 8. PCA Calibration Plot

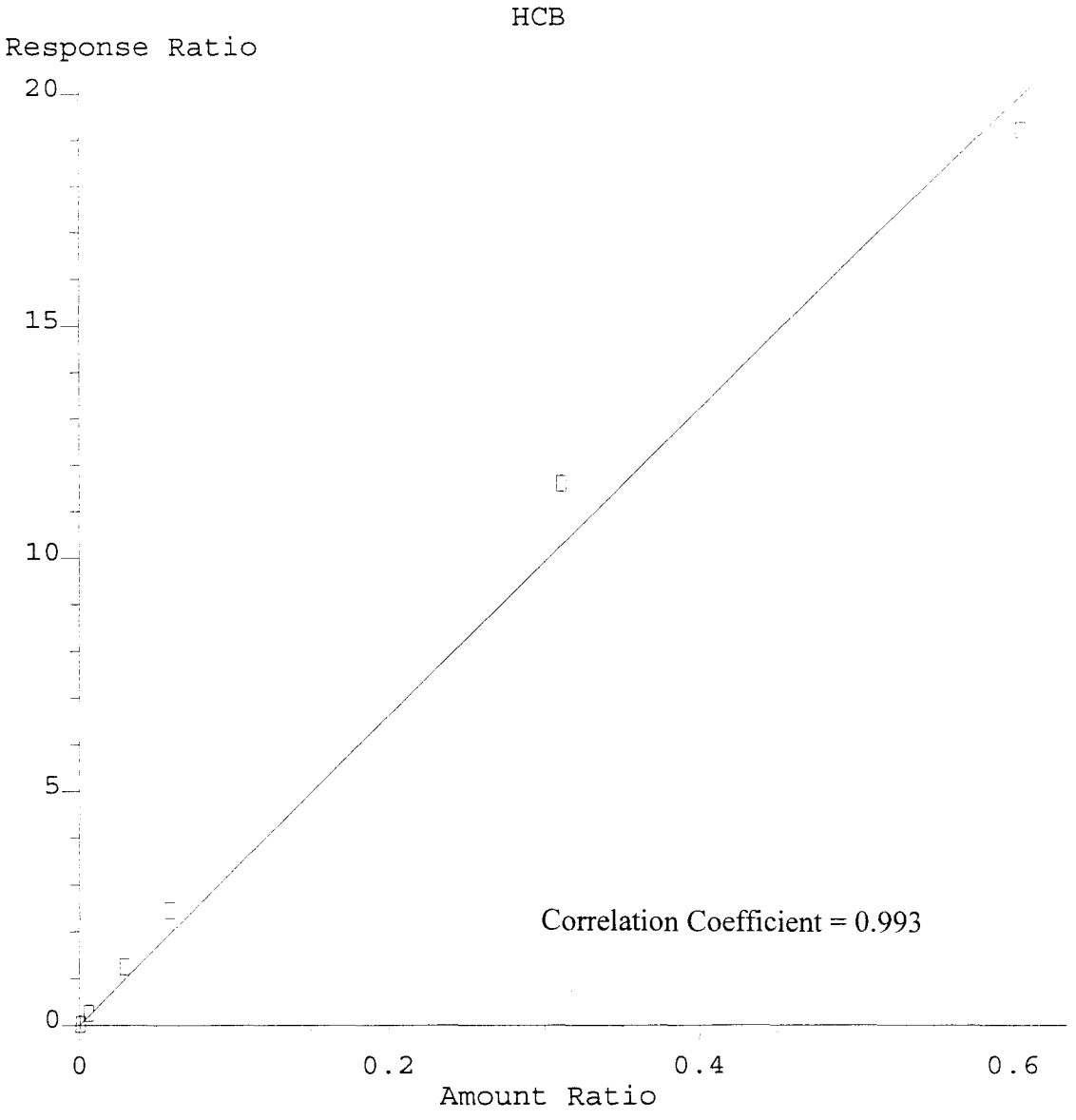

Figure 9. HCB Calibration Plot

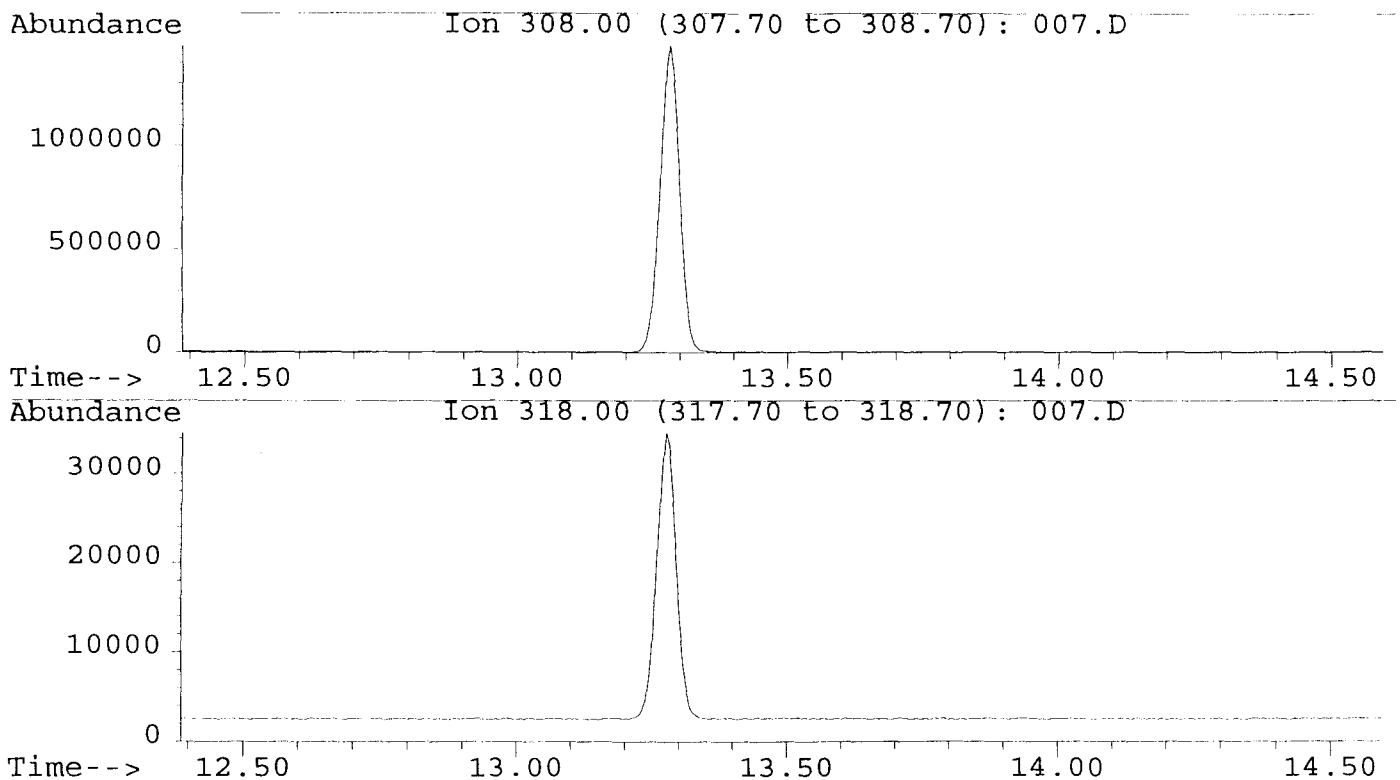

Figure 10. Chromatogram of PCPA in PUF

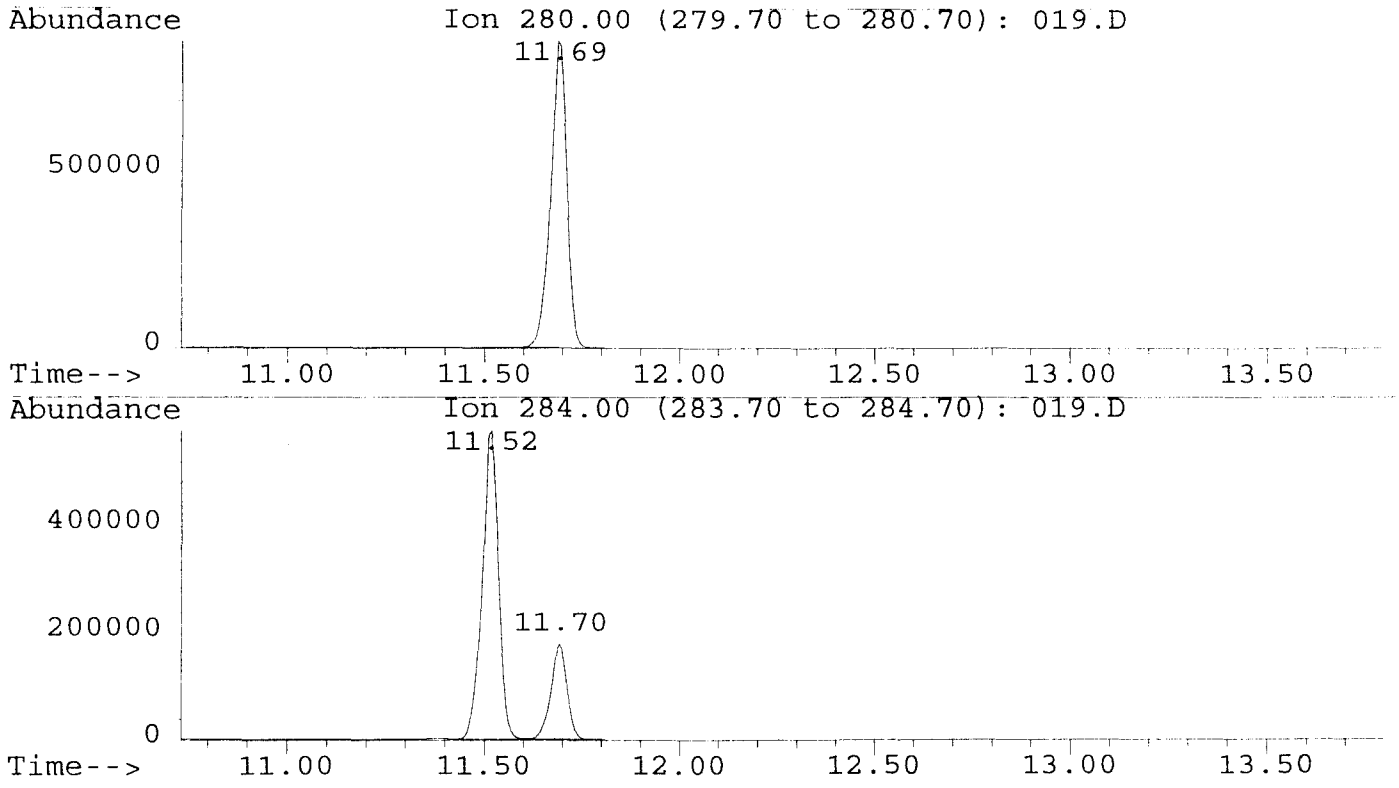

Figure 11. Chromatogram of PCA (280) and HCB (284) in XAD-2

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