ENANTIOMERIC COMPOSITION OF CHIRAL PESTICIDES IN SOIL AND AIR FROM THE U.S. CORNBELT REGION

by

Andrea D. Leone

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Chemistry

Program

SCHOOL OF GRADUATE STUDIES

YOUNGSTOWN STATE UNIVERSITY

June, 1998

Enantiomeric Composition of Chiral Pesticides in Soil and Air
from the U.S. Cornbelt Region

Andrea D. Leone

I hereby release this dissertation to the public. I understand this dissertation will be housed at the Circulation Desk of the University library and will be available for public access. I also authorize the University or other individuals to make copies of this dissertation as needed for scholarly research.

Signature: Andrea D. Leone 6/7/98
Student Date

Approvals: Dennis J. Falconer 6/7/98
Dissertation Advisor Date

James S. Cotton 6/5/98
Committee Member Date

Timothy L. Wagner 6/6/98
Committee Member Date

[signature] 6/8/98
Dean of Graduate Studies Date

Abstract

Past research has shown that selective enzymatic degradation of enantiomers by microorganisms does occur. This work was done to determine if enantiomeric ratios can be used to distinguish biotic from abiotic sources of pesticide degradation. Concentrations and enantiomeric ratios were determined for several chiral organochlorine pesticides in soils and air from the cornbelt region. Concentrations were determined for eleven compounds (*o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, dieldrin, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, heptachlor, heptachlor epoxide, and α-hexachlorocyclohexane) in 28 agricultural soils and one garden soil. The DDT compounds were found in the most samples and had the highest concentrations of all the compounds analyzed in the soil. Enantiomeric excesses were found for five compounds: *o,p'*-DDT, *trans*-chlordane, *cis*-chlordane, oxychlordane, and heptachlor epoxide, with the largest excesses for heptachlor epoxide. Six air samples were taken directly above agricultural soils, and enantiomeric patterns in air-above-soil samples mimicked the soils both in direction and relative magnitude of degradation. Seven ambient air samples were taken which showed the same general trends of enantiomeric degradation as soil and air-above-soil samples, although not as pronounced. Twenty-three indoor air samples were taken and concentrations determined for all eleven compounds as well as aldrin. Enantiomeric patterns were determined for three compounds, *trans*-chlordane, *cis*-chlordane and α-hexachlorocyclohexane. Most of these values were racemic or very close to racemic. Enantiomeric analysis can be useful for distinguishing sources of pesticides to the atmosphere.

Acknowledgments

Thanks to Atmospheric Environment Service, Environment Canada for funding this research project.

Thanks to all of the farmers and homeowners who were kind enough to let us sample on your property. We greatly appreciate your generosity.

Thanks to Elin Ulrich from Indiana University in Bloomington, Indiana for collecting all of the indoor air samples from Indiana and Illinois (silent "s").

Thanks to Dr. Curtin and Dr. Wagner of the YSU Chemistry Department for reading this thesis and for all of your helpful corrections. (Hope the "recycled" paper wasn't too distracting!)

Thanks to Terry Bidleman for giving me the opportunity to work with you, for being so understanding about the nightmares of thesis writing, and for being the perfect example of a great scientist.

Thanks to Liisa Jantunen and Tom Harner for all of your help, expertise, and patience with me in the lab in Toronto. "Can I ask you a question?" I can't believe you haven't strangled me yet!

Thanks to Liz (Purple) Shultz for lending me soil sample OH13-S, for training me in the ways of environmental research, and for all of the silliness and good times in the lab.

Thanks to Katie Leslie Cripe, for insisting that we both finish this quarter and for being so motivational by progressing at thesis writing so much faster than me! Thank you for making me so excited about chemistry by being such an enthusiastic and interesting high school chemistry teacher. (You got me into this mess!)

Thanks to Amy Cecil for always being there for me, for all of the encouragement (and teasing!), for forever making me laugh, and for being such a good listener and a great friend. By the way...YOU UGLY!!!!

Thanks to Colleen Bodnar for all of your help in the lab and sampling. Thanks for putting up with my frustrations on those cold sampling mornings when the equipment wouldn't quite fit together. Thanks for brightening up the lonely lab after everyone left and for making lab work enjoyable again. You deserve a pizza and some loud music!!!!

Thanks to Katie, Hannah and Jeremy for being so patient and good while Mommy was helping me with my thesis. You're just soo cute!

Thanks to all of the capable vehicles that took me on all of those sampling trips across the cornbelt, lugged the sampling equipment around, and crossed the border for sample analysis in Toronto: the Toyota Rav-4, the Ford Ranger, the Saturn, the two little Geo Metros that could (and boy could they!), both Chevy Spints (even the red one that made it across Indiana but couldn't make it to Ashtabula), the Subaru wagon, the old Dodge van, my sweet little Toyota Tercels (past and present), the Suzuki Samarai, which was second only to the old standby that never let us down and went everywhere, the Millennium Falcon.
Oh yeah-thanks to all of the owners of these vehicles for letting me borrow them!

Thanks to my Mom for all of the bookmarks and the food. They really came in handy!

Thanks to my Dad for creating the beautiful map of the cornbelt used in this thesis (see Figures 8 & 9), for your excellent proofreading abilities, and for all of the restraint you exercised to not ask me how the thesis was coming along. (Sorry I'm such a difficult kid.)

Thanks to Grandma, Mom, Dad, Aunt Jan, Maria, Brendan, Michael, Kevin, Christopher, Shannan, Elena, Jim, Jimmy, Steve, Tom, Jason, Carmen, Gayle, Vince, Joey, Dom, Dan, Gene, Chris, Fran, Dave, Simone, Teresa, Shannon, Shari, Nick, Alayne, and cute little Gina for always being there for me, for putting up with me when I'm ornery, for all of your support, for being willing to do anything for me anytime, and for providing all the necessary distractions that make life memorable and enjoyable. I love you guys!

Thanks to Tony Warminski for letting me use his computer any time I needed it (even when he could have been playing the Crafts!)

Thanks to Jim Powell, my brother-in-law, for the computer help, your enthusiasm, and for putting up with all of the loud yelling that ensued when the computer disagreed with me. Hope I didn't give you too many heart attacks!

Thanks to Robert Grapes for all of the down to earth encouragement, for cheering me up, for putting up with me whenever I was cold, tired, or hungry, for all of the fun times on campus, and for being my vomitous, creepy friend.

Thanks to Mikey Patrick for always being there for me, for inspiring me to "just do it!", for relaying all of Tony's bad jokes, and for being my 6th big brother.

Thanks to Max, Violet, Jane, Kiddo, Charlie, Josie, Paco, Filo, and Manny for all of your unconditional love, for being so dang cute and fun, and for staying with me all those long nights when the rest of the world was asleep. I love you all!

Thanks to Alayne Leone, my friend who just happens to be my sister-in-law, for being so understanding, for letting me steal her husband all the time, for cooking for us, for the

bookmarks, for marking my pages, for proof reading, and for doing all the things that Nick couldn't do because he was helping me.

Thanks to Shannon Tesone for helping me with the poster, for collating papers, for keeping me company while I was writing, for trying to help me find whichever paper or book I misplaced every five minutes, for all of the countless little things I can't think of right now, and for being such a great friend.

Thanks to my big sister, Teresa Leone, for taking care of me and looking out for me for the past 26 years. What would I do without you??!!! Thank you for helping me with the poster, for typing the title and signature page, and for putting so much time and energy into the bumblebee figures. Thank you for packing food for all my trips, for doing my shopping, for doing my laundry, and for running countless errands for me while I was in Toronto or busy writing. Thank you for making me laugh, for listening to me cry, for dealing with all of my frustrations and disappointments, for always trying to make me (and everyone) happy, for taking care of our dogs (and any other animal that happens by), for showing me how to be a good person, and for being my best friend.

I could write another entire thesis dedicated to thanking my little brother, Nick Leone. For the months worth of computer time that you put into my talk for IAGLR, my poster for SETAC, and my thesis in the form of formatting, creating charts, making figures look pretty, page numbering, printing, proof reading, and so on, and so on, and so on, and so on. Thank you, thank you, thank you, thank you, thank you, thank you, thank you, thank you! Thank you a bazillion times over and over again for staying up half the night or all night to finish the job (even when you had to work the next day!), for sacrificing your weekends and evenings for me, for making it your problem, for doing anything I asked, and for being so dang agreeable the whole time you were doing it!!! In short, even though you're a worthless piece of something one of the dogs threw up after eating a dead animal they found out back, you're the reason this thesis looks so "awesome" and I'm finally graduating.

Finally (in more ways than one!), thank you to my wonder-woman of an advisor, Renee Falconer, who is constantly going way above, beyond, over and around the call of advisor duty to help me (and everyone else who needs it). Thank you for being so enthusiastic and encouraging, for putting up with my never ending questions and interruptions (how rude!!!), and for going out of your way all the time to drop this off, pick that up, proof this section, toss that one out, etc., etc. Your patience, intelligence, and motivation are amazing! You are an excellent scientist and teacher and a wonderful person (no fabricating!). I chose wisely!!! (for once!) Through your guidance I gained knowledge and enthusiasm for environmental chemistry and this fascinating project. I also gained a lifelong friend! I just have one more question.....I know.....42!

Table of Contents

List of Figures

Appendix

List of Tables

Appendix

Chapter One
Introduction

Pesticides

Pesticide use can be traced back as early as 1763 when nicotine was used for aphid control (White-Stevens, 1971). Since then, pesticides have been used to eliminate unwanted pests for everything from agriculture to disease control. With the introduction of DDT during World War II, pesticide usage increased dramatically. In the mid 1990's, 365 million kg of pesticides were used for agricultural purposes while 900 million kg were used for non-agricultural purposes, such as forestry and personal home and lawn care (Manahan, 1994).

Pesticides are separated into groups according to the type of organism targeted. The main classifications are herbicides (plant control), insecticides (insect control), and fungicides (fungal control). Within the larger classifications there are smaller groupings, designed for specific organisms, such as bactericides, molluscicides, and algicides. Each of the main classes of pesticides contains a large number of different compounds that range in chemical composition, from organics to metals to organometallics. Presently, herbicides constitute two thirds of agricultural pesticides, replacing many land cultivation methods in weed control (Manahan, 1994). However, with respect to adverse effects on human health, insecticides and fungicides pose the greater threat, due to direct exposure through food consumption.

Organochlorine Pesticides

One of the most common and well known groups of pesticides is the chlorinated hydrocarbons, also known as organochlorines (OCs). These compounds were used primarily as insecticides for agriculture, disease control, and home pest control. OCs were used heavily during the 1960s and 1970s. Ironically, the chemical properties that make them effective pesticides are the same responsible for their eventual cancellations.

Because of their chemical stability, OCs are very slow to degrade in the environment, many with half lives of decades. Due to their low volatility, they do not readily evaporate, but tend to adhere tightly to the soil particles where they were applied. OCs are not easily washed away due to their hydrophobicity and low water solubility. Furthermore, the lipophilic nature of OCs allows them to penetrate into the lipids of their target where their pesticidal properties can act. All of these characteristics make OCs extremely powerful and convenient pesticides. However, they also make them (as well as some of their metabolites) very dangerous to the environment. The OCs' persistence, non-volatility and hydrophobicity all combine to increase their lifetimes in the environment. Their lipophilic nature allows them to bioaccumulate in organisms other than the target species. With each step up the food chain, the concentrations of the pesticide can be enhanced, causing a biomagnification in higher organisms. Their ability to bioaccumulate and biomagnify, as well as their inherent toxicity, has caused many OCs to be limited or banned in the United States and Canada, although they are still used in Asia, Africa, and Central and South America (ECE-LRTAP, 1994). These same properties have led OC pesticides to become some of the most studied environmental contaminants to date.

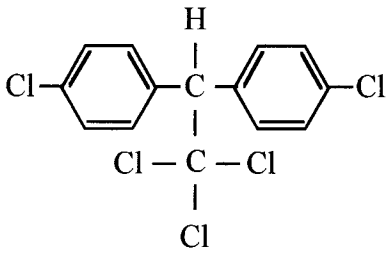
Target species are usually attacked by OCs through their nervous systems. The insecticide penetrates the waxy layer of the insect and binds to the nerve cells in such a way as to force open the molecular channels that allow sodium ions into the nerve, causing continual firing of the nerves and eventual death (Spiro and Stigliani, 1996). Other OCs act as contact and stomach poisons instead of neurotoxins.

DDT

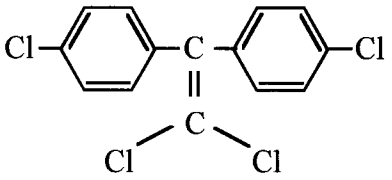
Dichlorodiphenyl trichloroethane, DDT (Figure 1), is the most prominent member of the OC pesticide family. It was first synthesized in 1874 but its insecticidal abilities were not discovered until 1939. The technical mixture is made from chloral hydrate, chlorobenzene, and sulfuric acid. Technical DDT contains 85% *p,p'*-DDT, 15% *o,p'*-DDT, and trace amounts of *o,o'*-DDT. DDE and DDD, breakdown products of DDT, are also found as contaminants in the technical mixture (PHS, 1992).

DDT was introduced during WWII to control diseases spread by insects, such as malaria and typhus. It went on to become an "all-purpose" insecticidal agent for agricultural crops such as cotton and soybean, as well as for vector-transmitted disease control worldwide. In 1962, at its peak, 82 million kg of DDT were produced in the United States alone (PHS, 1992). Ten years later, the US-Environmental Protection Agency (EPA) banned the use of DDT except for public health emergencies (PHS, 1992). The dehydrochlorination of DDT to its metabolites, such as DDE, (which is not insectidally active but is a major contaminant in the environment) occurs in countless microorganisms, insects, fish, birds, and animals (McEwen and Stephenson, 1979).

DDT



DDE



DDD

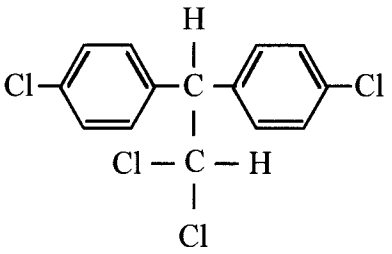


Figure 1. Structures of DDT, DDE, and DDD

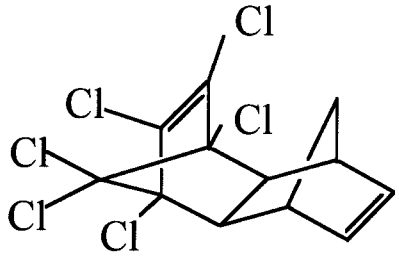
Aldrin/Dieldrin

Hexachlorohexahydrodimethanonaphthalene (aldrin, Figure 2) and hexachloroepoxyoctahydrodimethanonaphthalene (dieldrin, Figure 2) are both members of the OC cyclodiene subgroup. Aldrin was synthesized in 1948 for use as a pesticide. Once introduced into the environment or a living organism, aldrin is quickly transformed into dieldrin. Aldrin is synthesized by the condensation of hexachlorocyclopentadiene with bicyclo[2.2.1]-2,5-heptadiene through a Diels-Alder reaction. Dieldrin is produced upon epoxidation of aldrin by a peracid or hydrogen peroxide. Both compounds were used heavily from the 1950s to the 1970s to combat insects on corn, cotton, and citrus crops. They were also used to protect wood, rubber, and plastic from termite infestation. Aldrin usage peaked in 1966, with 19 million pounds being produced in the United States (PHS, 1992). At the same time, dieldrin use began to plummet dramatically due to its environmental toxicity and the increased incidence of insect resistance. All uses of aldrin and dieldrin were banned in the U.S. in 1987 (PHS, 1992).

Chlordane

Chlordane, another member of the cyclodiene family, was introduced in 1948 as a pesticide for agriculture (corn and citrus), lawns/gardens, residential termite control, and fumigation. Chlordane is synthesized by the chlorination of cyclopentadiene to form hexachlorocyclopentadiene which forms chlordene upon condensation with cyclopentadiene. The chlorination of chlordene at elevated temperature and pressure produces chlordane. The most abundant components in the technical mixture, which contains over 100 components, are *trans*-chlordane (TC), *cis*-chlordane (CC), *trans*-nonachlor (TN) (Figures 3 & 4), β-chlordene, and heptachlor (PHS, 1992). Some of the

Aldrin



Dieldrin

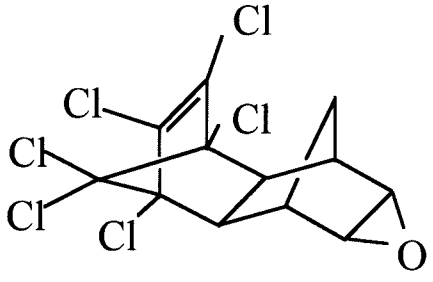


Figure 2. Structures of aldrin and dieldrin

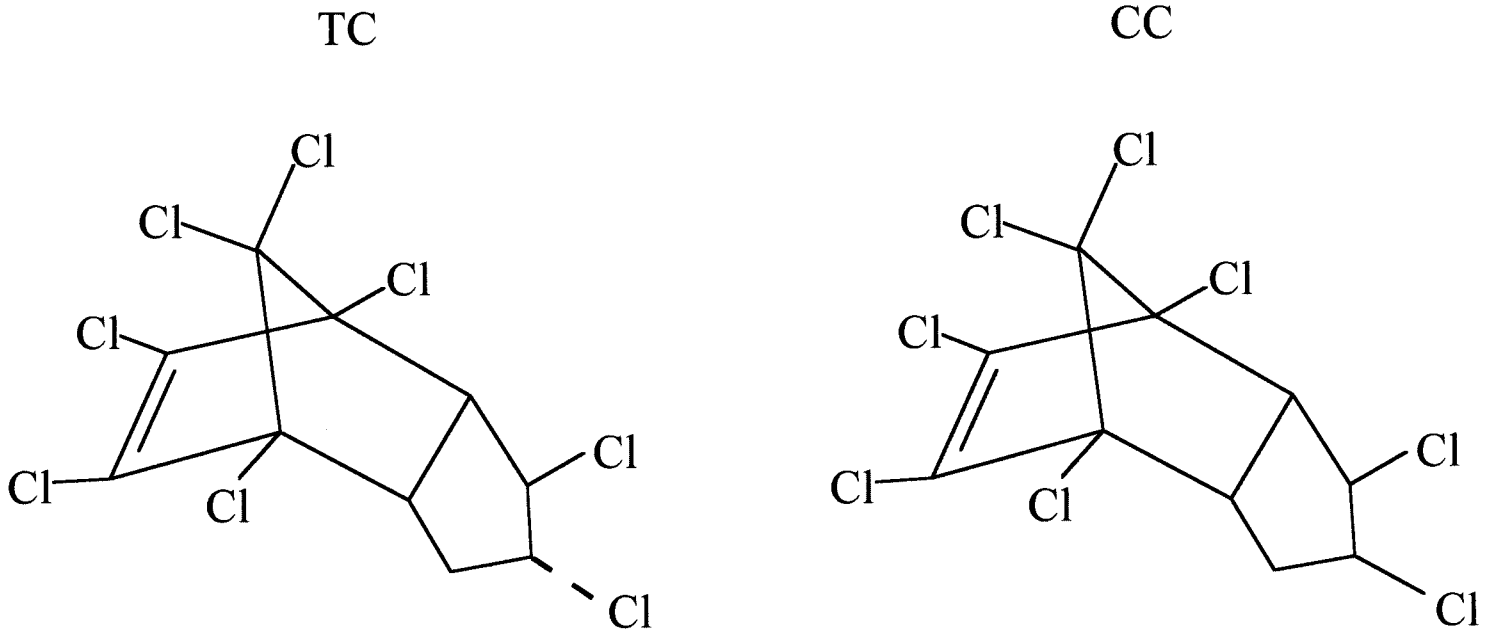


Figure 3. Structures of *trans*- and *cis*- chlordane

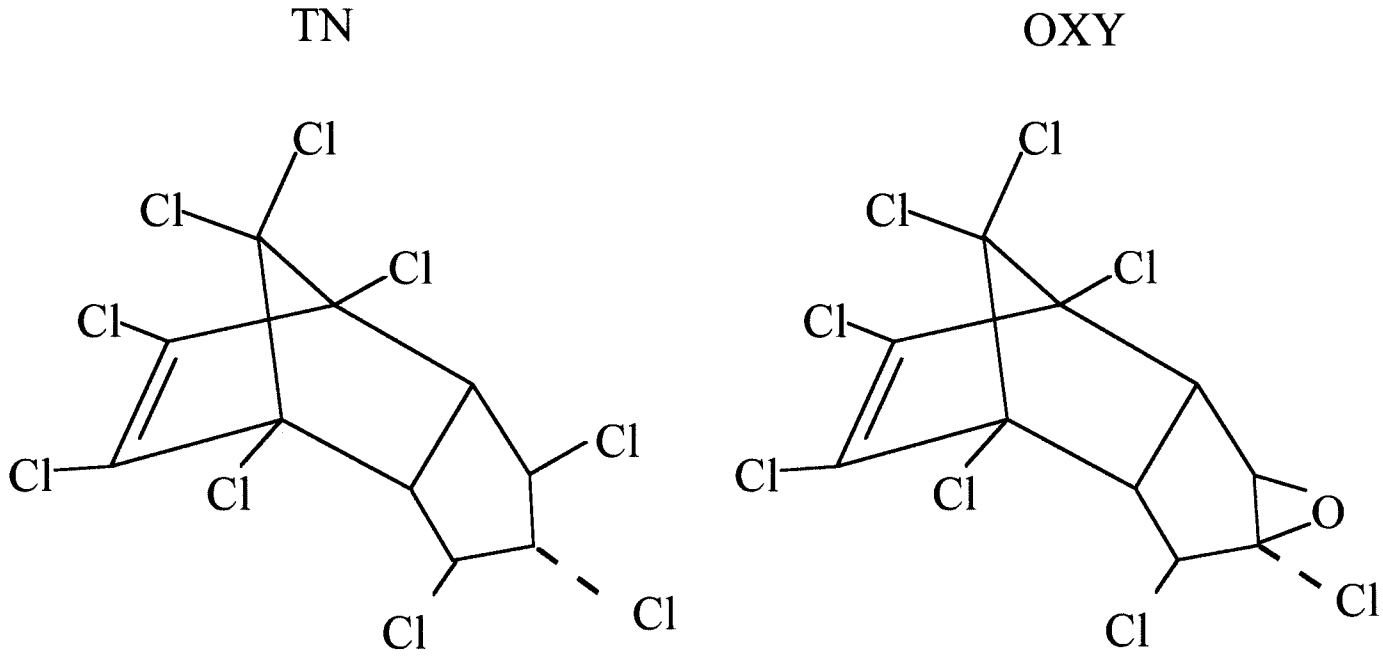


Figure 4. Structures of *trans*-nonachlor and oxychlordane

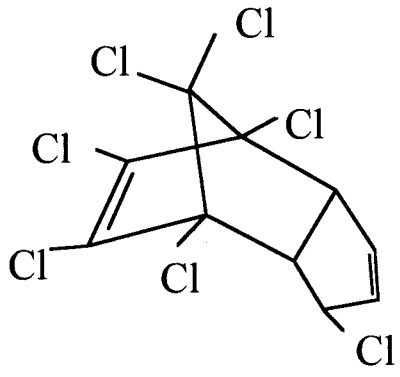
minor components in the mixture include MC4-7, *cis*-nonachlor and compound K, a caged structure (Buser and Müller, 1992a). The two primary breakdown products of technical chlordane are the two epoxides: heptachlor *exo*-epoxide, which is a metabolite of heptachlor (see heptachlor section) and oxychlordane (OXY, Figure 4) which is the epoxide metabolite of CC, TC, and TN (Nomeir and Hajjar, 1987). Both HEPX and OXY are found extensively in environmental and biological samples as contaminants (Buser and Müller, 1992; Buser et al., 1992). Chlordane is now classified as a likely human carcinogen (WHO/IARC,1991).

Chlordane was banned for above ground pesticide control in 1983 (PHS, 1992). For the next five years chlordane was used only as a structural termiticide, until 1988, when all uses were canceled in the United States (PHS, 1992).

Heptachlor/Heptachlor Epoxide

Heptachlor (HEPT, Figure 5) was introduced in 1953 as a soil and seed insecticide for such crops as corn and sorghum as well as for home termite control. HEPT is also a contaminant in and a metabolite of chlordane (PHS, 1992). Technical heptachlor is 72% heptachlor and 28% numerous contaminants including the chlordane compounds (PHS, 1992). HEPT was used as a seed dressing on corn and grains, as an insecticide to target such pests as maggots and termites in cultivated and uncultivated soils, and as a termiticide for non-agricultural purposes. HEPT is more insecticidally active than chlordane and more toxic to mammals (McEwen and Stephenson, 1979). Heptachlor's phase out began in 1974 due to its possible carcinogenicity, persistence in the environment, and bioaccumulation in food chains. It was canceled for agriculture and

HEPT



HEPX

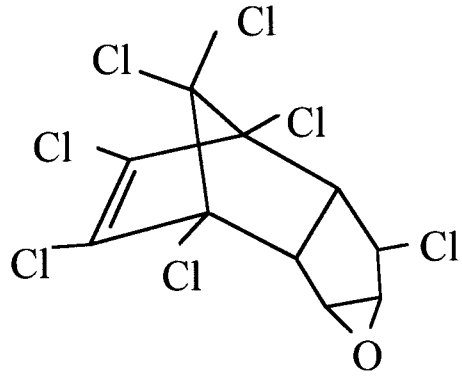


Figure 5. Structures of heptachlor and heptachlor epoxide

home pest control use in 1988 (PHS, 1992). Remaining stocks are still used for the elimination of fire ants in power transformers.

Heptachlor epoxide (HEPX, Figure 5) is produced by the breakdown of heptachlor, either through photodecomposition or through enzymatic breakdown in living organisms. HEPT is readily converted into HEPX by bacteria in soil, water, and plants where it breaks down at a much slower rate than HEPT. HEPT is also converted into HEPX in animals where it tends to bioaccumulate in fatty tissue.

Hexachlorocyclohexane

Hexachlorocyclohexane (HCH, Figure 6), also known (albeit incorrectly from a chemical perspective), as benzene hexachloride (BHC), was first synthesized in 1825. Like DDT, its insecticidal properties were not discovered until years later in 1940. HCH is produced through the chlorination of benzene in the presence of ultraviolet light. Five isomers, named after the first five letters of the Greek alphabet, *alpha* (α), *beta* (β), *gamma* (γ), *delta* (δ), and *epsilon* (ε) constitute technical HCH (PHS, 1992). These five isomers are represented in the technical mixture in the following percentages: α-70%, β-6%, γ-13%, δ-6%, and ε in trace amounts (Cremlyn, 1979). This crude mixture, administered as a dust, was used to combat soil pests such as flea beetles and mushroom flies. The crude mixture of technical HCH was banned in the U.S. in 1978 (*Fed. Regist.*, 1978).

Gamma-HCH, also known as lindane, is the only insecticidally active isomer and the least persistent in the environment (Ware, 1983). For these reasons, lindane was manufactured alone as a pesticide (99% pure) and was used as a spray for pests such as ticks and mosquitoes, and as a smoke to keep grain storage facilities pest free (Cremlyn,

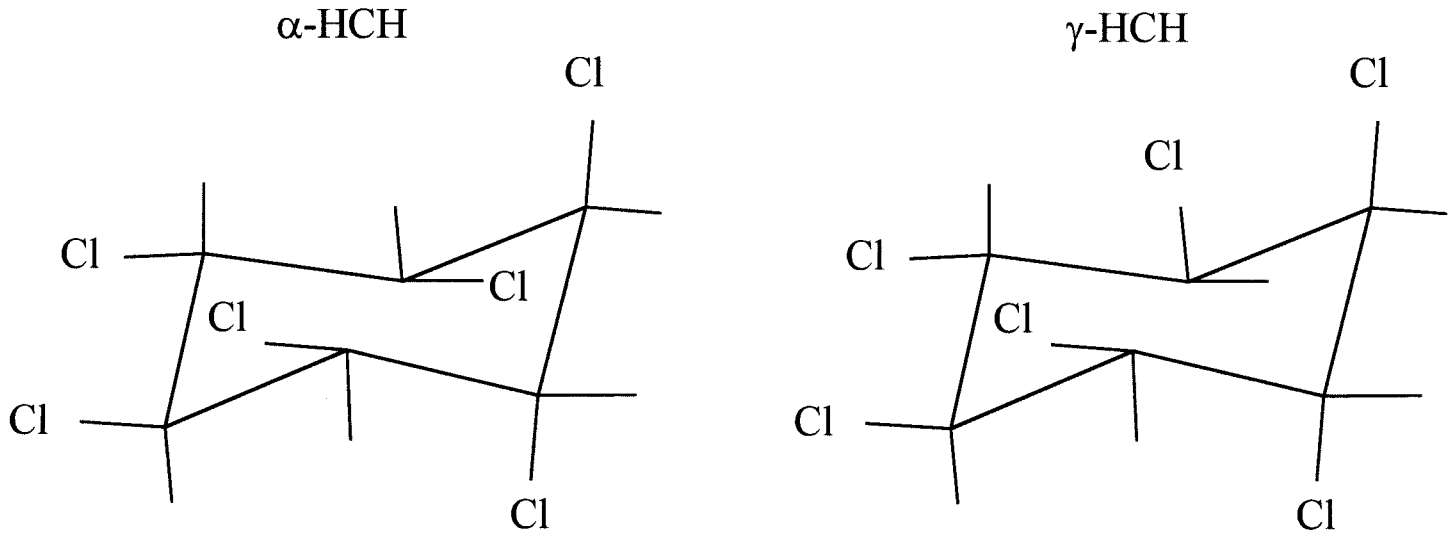


Figure 6. α and γ hexachlorocyclohexane

1979). Because γ-HCH has a high volatility, it was also sold in the form of a pellet that could be attached to a light bulb, or in a small cup that could be plugged into an outlet, and heated to vaporize the lindane and fumigate the home (Frear, 1955). This use was discontinued when γ-HCH was found to be a human health hazard and insect resistance to the pesticide rendered it less effective. γ-HCH is still used in the U.S. and Canada, primarily as a seed treatment for corn.

Enantiomers

Many pesticide mixtures contain several isomers of a given component. Isomers are compounds that share the same molecular formula but not the same structure. For any group of atoms, there are as many possible isomers as there are correct ways to join the atoms together.

Stereoisomers are isomers in which atoms are connected in the same order but with different three-dimensional orientations in space. Stereoisomers that are non-superimposable, mirror images of one another are called enantiomers. Enantiomers share the same physical and chemical properties. They differ only in their rotation of plane polarized light and in reactions with biological organisms. Another group of stereoisomers which are not mirror images of each other are called diastereomers, or geometric isomers. Diastereomers have different chemical and physical properties and are often designated as *cis-* and *trans-* isomers.

Objects which are non-superimposable, mirror images are often said to be chiral. The word chiral is derived from the Greek word for hand. Right and left hands are non-superimposable, mirror images and can be used to understand the "handedness" of

molecules. Achiral, or non-chiral objects, such as nails, balls, and spoons, are superimposable mirror images.

In order to differentiate between enantiomers, a chiral probe is needed. Gloves can be thought of as chiral probes in the case of hands: they will only fit one hand. Plane polarized light was the first chiral probe used to distinguish enantiomers. Optically active substances are capable of rotating the plane of polarized light. The enantiomer which rotates plane polarized light counterclockwise is designated as the (-) enantiomer, and the enantiomer which rotates plane polarized light clockwise is designated as the (+) enantiomer. Enantiomers can also be represented by the Greek words levorotatory (l) and dextrorotatory (d), which mean left-rotating and right-rotating, respectively. Another representation of the two enantiomers uses the Latin words sinister (S) and rectus (R), which mean left and right, respectively. Determining the exact stereochemical formula of an enantiomer requires X-ray crystallography. Enantiomers are often called optical isomers due to their optical activity.

Biological reactions can also be chiral probes. Since biological reactions are catalyzed by enzymes that contain active sites which are usually chiral, enzymes are capable of distinguishing between two enantiomers. In fact, many enzymes will only fit or bind with one enantiomer, making enzymes enantioselective.

In mixtures of chiral molecules where the enantiomers exist in equal amounts or in a 1:1 ratio, the mixture is said to be a racemate or racemic. The enantiomeric ratio (ER) is the ratio of the (+) enantiomer to the (-) enantiomer and is 1.00 for a racemic mixture. For processes or reactions that are not enantioselective (non-biological processes such as hydrolysis and photolysis) the racemic nature of the mixture is preserved. For processes

or reactions that are enantioselective (such as biological processes) one enantiomer will be formed or reacted with preferentially.

Many OC pesticides contain chiral components, including *o,p'*-DDT, *trans*- and *cis*- chlordane, α-HCH, and heptachlor. Heptachlor epoxide and oxychlordane are chiral metabolites or breakdown products of these pesticides. Figure 7 shows the two enantiomers of α-HCH with a dotted line representing a mirror to show that the two forms are mirror images of one another. When manufactured, the technical formulation of chiral pesticides is a racemic mixture where the enantiomers exist in a one to one ratio. Non-biological or abiotic processes (including chemical processes such as oxidation and hydrolysis, distribution processes such as adsorption, absorption, and desorption, transport processes such as photolysis) will degrade the pesticide enantiomers in a one to one ratio (Buser and Müller, 1992). Biological processes which are enzymatically controlled, on the other hand, can preferentially degrade or deplete one enantiomer. When this occurs, the ER will be different than 1.00.

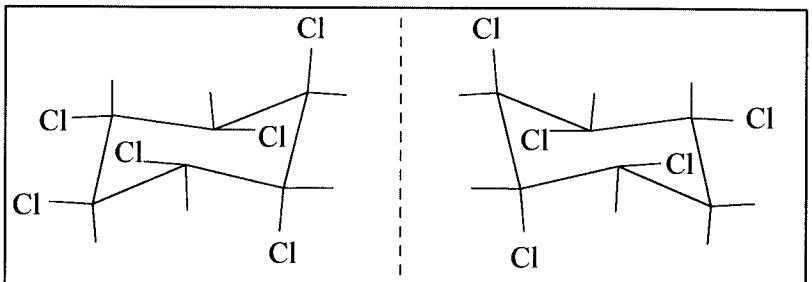


Figure 7. (+) and (-) enantiomers of α-HCH

Chiral Phase Analysis

Many chiral organic compounds are utilized by humans for purposes such as pharmaceuticals, flavors, and pesticides. As in the case of HCH, one isomer in a mixture is frequently more active, while the others may be toxic, have harmful side effects, or at the very least, may dilute the effective isomer so that it takes a larger amount of product

to obtain the desired effect. For example, a chiral treatment for Parkinson's disease known as "dopa" has a (+) and (-) enantiomeric form. The effective enantiomer is the (-) enantiomer (L-dopa) while the (+) enantiomer is not as effective, and is also more toxic. (Umland, 1993). For cases like this and countless others, the necessity for manufacturers to understand the stereochemistry of components of a mixture is essential. E.J. Ariëns (1989) summed up the importance of this type of work: "Neglect of stereochemistry in the study of drugs, crop protectants, pesticides and so on, has resulted in massive and wasteful generation of pseudo-scientific nonsense." For reasons such as these the development of chiral phase separation methods has been absolutely crucial and long overdue.

Relatively recent development of chiral phase gas chromatography columns capable of resolving enantiomers has made the analyses of pesticide enantiomers possible. Cyclodextrins (CDs) and their substituted derivatives have been used for decades as the mobile phase in thin layer chromatography (TLC), high performance liquid chromatography (HPLC), and gel permeation chromatography (GPC), and as stationary phases in packed column GC, HPLC, and GPC. In 1987, Juvancz et al. successfully coated GC capillary columns with derivatized CDs and discovered that the chiral structure of cyclodextrins allows them to act as chiral recognition sites and to separate enantiomers. Most chiral work to date has been done by either capillary GC or HPLC, as can be seen in a review by Vetter and Schurig (1997). The reviewers discuss chiral stationary phases (CSPs) made from cyclodextrin derivatives for the purpose of separating chiral OCs by GC. Garrison et al. (1996) have also reported using capillary electrophoresis to separate the enantiomers of the chiral herbicide dichlorprop.

It is unclear exactly how cyclodextrins are able to separate chiral molecules. Berthod et al. (1992) hypothesized that the solute is retained by the cyclodextrin through inclusion within the cavity and interaction with the actual cyclodextrin ring and any substituent groups attached to the ring.

Chiral Pesticides in the Environment

Even though most OC pesticides have been banned in the U.S. and Canada for at least ten years, residues have been found in soil, air, water, sediment, and living organisms in all parts of the world. Even remote areas, such as the Arctic and Antarctic, thought to be pristine locations untouched by the pollution that plagues the warmer climates, seem to be sinks for air-borne pesticides. Tanabe et al. (1983) reported residue values as high as 240 pg/m^3 for the sum of DDTs in Antarctic air. Hargrave et al. (1992) studied OCs in an arctic marine food web and found residues increasing from tens of ng/g lipid in plankton to hundreds of ng/g lipid in amphipods to thousands of ng/g lipid in mammals.

Falconer et al. (1995) showed the first confirmation of the occurrence of biological degradation of pesticides in the arctic environment by obtaining ER values considerably different from 1.00 (0.74-0.92) for α-HCH in snow and water samples.

A number of studies were carried out which looked at residues in soils and air from different regions. Falconer et al. (1997) reported concentration and ER values for OC pesticides in agricultural soils from the Fraser Valley of British Columbia for silt loam and muck soils. The silt loam soils were generally four orders of magnitude lower in concentration than the muck soils for most of the OCs with DDT levels high in both soil types. They found enantiomeric excesses for α-HCH, HEPT, HEPX, OXY, and *o,p'*-

DDT. ERs were determined in air by Finizio et al. (1998) at one of the farms studied by Falconer et al. They found ER signatures which closely matched those found in the soil for air at heights of 5-140 cm above the ground.

Indoor air samples were collected from homes in Columbia, South Carolina and analyzed for ERs of TC and CC (Wiberg et al., 1997). They reported values very close to racemic for both compounds (1.00 for TC and 1.02 for CC). They also determined ERs for ambient air in Columbia, SC and Muscle Shoals, Alabama and again found values very close to racemic for both TC and CC.

Chapter Two

Statement of Purpose

Because OC pesticides and their metabolites are highly persistent, residues remain in many soils, especially those of high organic content. Volatilization of OC pesticides may be a significant source of contaminants to the atmosphere. Once in the atmosphere, these compounds may be transported and later deposited in the Great Lakes. Pesticides are lost from soils by physical processes, chemical breakdown and microbial attack. The latter is the only known mechanism that can result in enantioselective degradation. All of the chiral pesticides in this study are manufactured as racemic mixtures of the two enantiomers. If no metabolism occurs, the enantiomeric ratios (ERs) of the pesticide residues should be 1.00. This would be expected for new releases from countries still using these chemicals and for volatilization from house foundations where little microbial breakdown can occur. Enantioselective breakdown in soils (ERs $\neq$ 1.00), however, signifies biological degradation and may be used as a source signature to track releases of chiral pesticides to the atmosphere.

Past research has shown that selective enzymatic degradation of enantiomers by microorganisms does occur. This work was done to determine concentrations and enantiomeric ratios of several chiral organochlorine pesticides in soils and air from the cornbelt region. Soil samples were collected from the cornbelt region for the purpose of obtaining a broader spectrum of soil data (since there is very little published to date on OCs in soil) and to obtain enantiomeric ratio data for soils for use in modeling soil volatilization. Air-above-soil samples were taken to determine whether or not enantiomeric signatures of OCs were altered upon volatilization from the soil into the

atmosphere. Indoor air samples were taken across the cornbelt region in order to increase the available information on OC pesticide concentrations in homes as well as to determine if enantioselective degradation is occurring in home air. Ambient air samples were taken in rural, non-agricultural locations to obtain background signals and for comparison with ambient air from the Great Lakes region.

Enantiomeric data will be combined with concentration data and used to try to differentiate between agricultural and termiticide sources of OC pesticides to the atmosphere.

Chapter Three

Materials

Pesticide grade solvents including acetone, hexanes, isooctane, dichloromethane, and petroleum ether were purchased from Fisher Scientific (Pittsburgh, PA) or Omnisolv (EM Science, Cherry Hill, NJ). Concentrated sulfuric acid was purchased from BDH Inc. (Toronto, Ontario). Analytical standards were purchased from Accustandard (New Haven, CT), Supelco (Bellefonte, PA) and Ultra Scientific (North Kingstown, RI). Single enantiomer standards of chiral pesticides used to determine elution orders on chiral columns were purchased from AXACT Standards (Commack, NY). Compressed, dry grade nitrogen, used for sample concentration, was purchased from Praxair (Danbury, CT) and cleaned with a Tenax-GC resin trap. Ultra-high purity grade helium, hydrogen, methane, and nitrogen used in chromatographic instruments were purchased from Air Products Canada, Ltd. (Brampton, ON). Anhydrous, granular, sodium sulfate (Fisher Scientific) and neutral alumina (Al_2O_3, 70-230 mesh, Sigma, St. Louis, MO) were baked overnight (18-24 hours) in a muffle furnace at 450 °C. Silicic acid (SA, 100-mesh, Mallinckrodt Chemical Works, Chesterfield, MO) was baked overnight at 250 °C. All solid chemicals were stored in clean glass jars with Teflon-lined lids.

Single thickness, 3.5 x 11.8 cm cellulose thimbles used for soil extraction were purchased from Whatman (Fairfield, NJ). Thimbles were cleaned overnight by soxhlet extraction with dichloromethane (DCM) and wrapped in clean aluminum foil for storage. Glass wool was baked overnight at 450 °C and stored in a clean glass jar. Boiling chips were cleaned overnight by soxhlet extraction with petroleum ether (PE) in a cellulose extraction thimble, dried at 250 °C, and stored in a clean glass jar with a Teflon-lined lid. Type A/E glass

fiber filters (GFFs, 20.3 x 25.4 cm) used for air sampling were purchased from Gelman Sciences (Ann Arbor, MI). Filters were baked overnight at 450 °C, wrapped in clean aluminum foil, and stored in sealed plastic bags. Polyurethane foam plugs (PUF) were purchased from Graseby Andersen (Cleves, OH). PUF used for high volume samples were 8 cm length x 8.5 cm diameter and low volume sample PUF were 3.5 cm length x 5 cm diameter. PUF were cleaned overnight by soxhlet extraction with acetone followed by overnight soxhlet extraction with PE. The PUF were dried overnight in a dry seal vacuum dessicator with low heat and stored in clean glass jars with Teflon-lined lids.

The high volume air sampler consisted of a stainless steel sampling head attached to a Rotron DR-313 brushless pump (Rotron Corporation Woodstock, NY). The PUF and filter were protected from rain by a stainless steel cover on the sampling head. The low volume air sampler consisted of a Teflon sampling head (Cole-Parmer, Vernon Hills, IL) followed by a mass flow meter (Sierra TrakII, Sierra Instruments, Inc., Monterey, CA) attached to a Gast DOA P104-AA single-stage vacuum pump (Gast Corporation, Bridgman, MI).

Chapter Four

Experimental

Sample Collection

Soil

Twenty-nine soil samples were collected during the Spring/Fall of 1996 from farms in Pennsylvania, Ohio, Indiana and Illinois (see Figure 8). Seventeen samples were from government or university experimental farms, and the remaining twelve, (including one garden soil) from private farms. Samples were collected using pre-cleaned garden tools. Eight cores were taken from a depth of ~15 cm and pooled for a representative sample (total sample weight 1-2 kg). Samples were placed into pre-cleaned aluminum foil, sealed in plastic bags, and stored at 4 °C until further workup.

Air

Three types of air samples were collected during Fall of 1996, Spring/Fall of 1997, and Winter/Spring of 1998 in PA, OH, IN and IL. Six above-soil air samples were collected for 4-8 hours approximately 15 cm above the soil using a high volume sampler. Air was passed through a glass fiber filter (to remove particulate matter) and target compounds collected on a single 8 x 8.5 cm PUF plug (flow rate = 500 L/min). Above-soil samples were collected in fields previously analyzed in this study and found to contain high levels of OC pesticides. Seven ambient air samples were collected for 20-48 hours (flow rate = 500 L/min) in PA and OH using the high volume sampler as described above. Ambient air samples were collected ~80 cm above the ground in rural, non-agricultural locations. Twenty-three indoor air samples were collected using a low volume sampler,

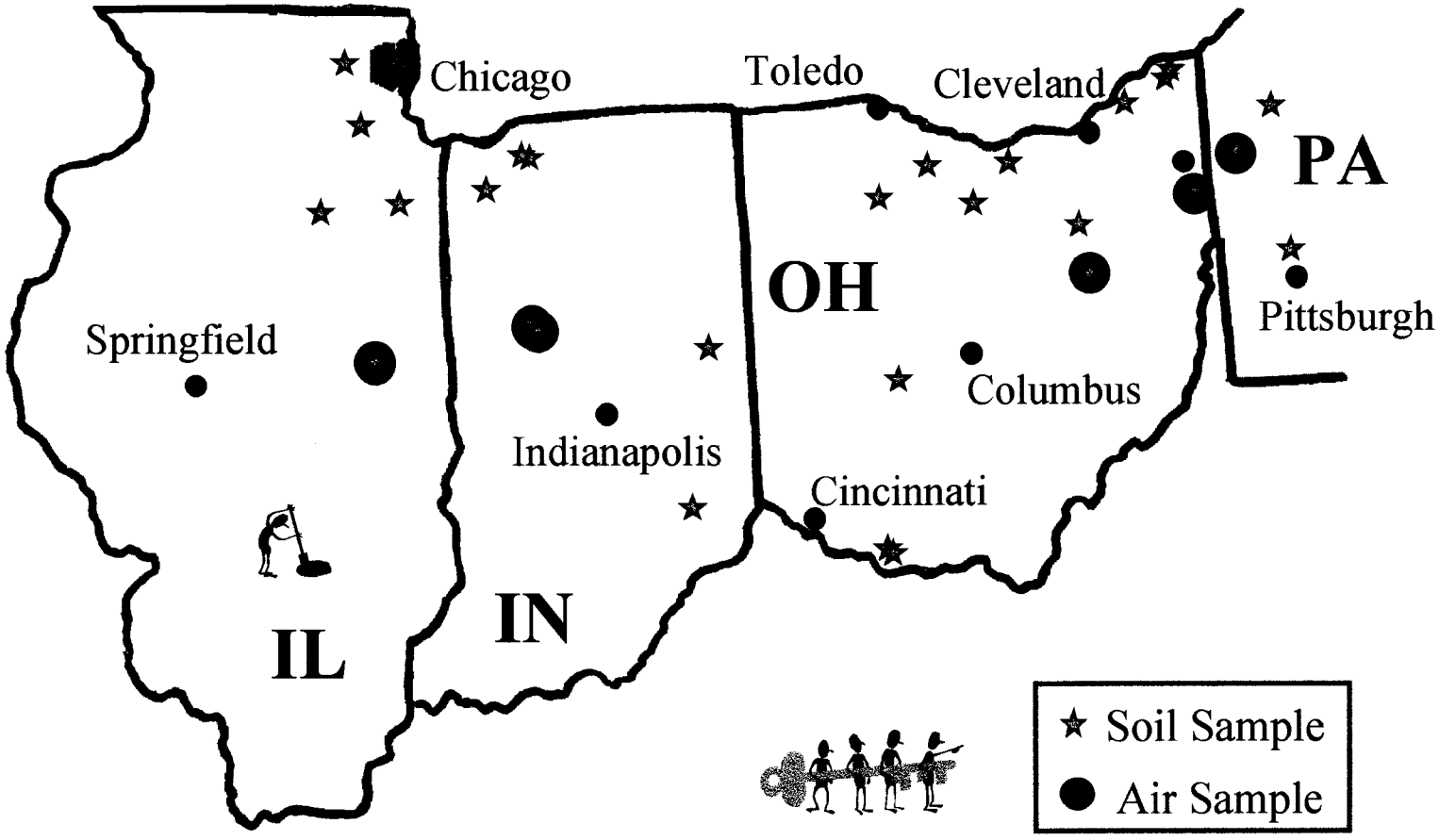


Figure 8. Soil and Air Above Soil Sampling Map

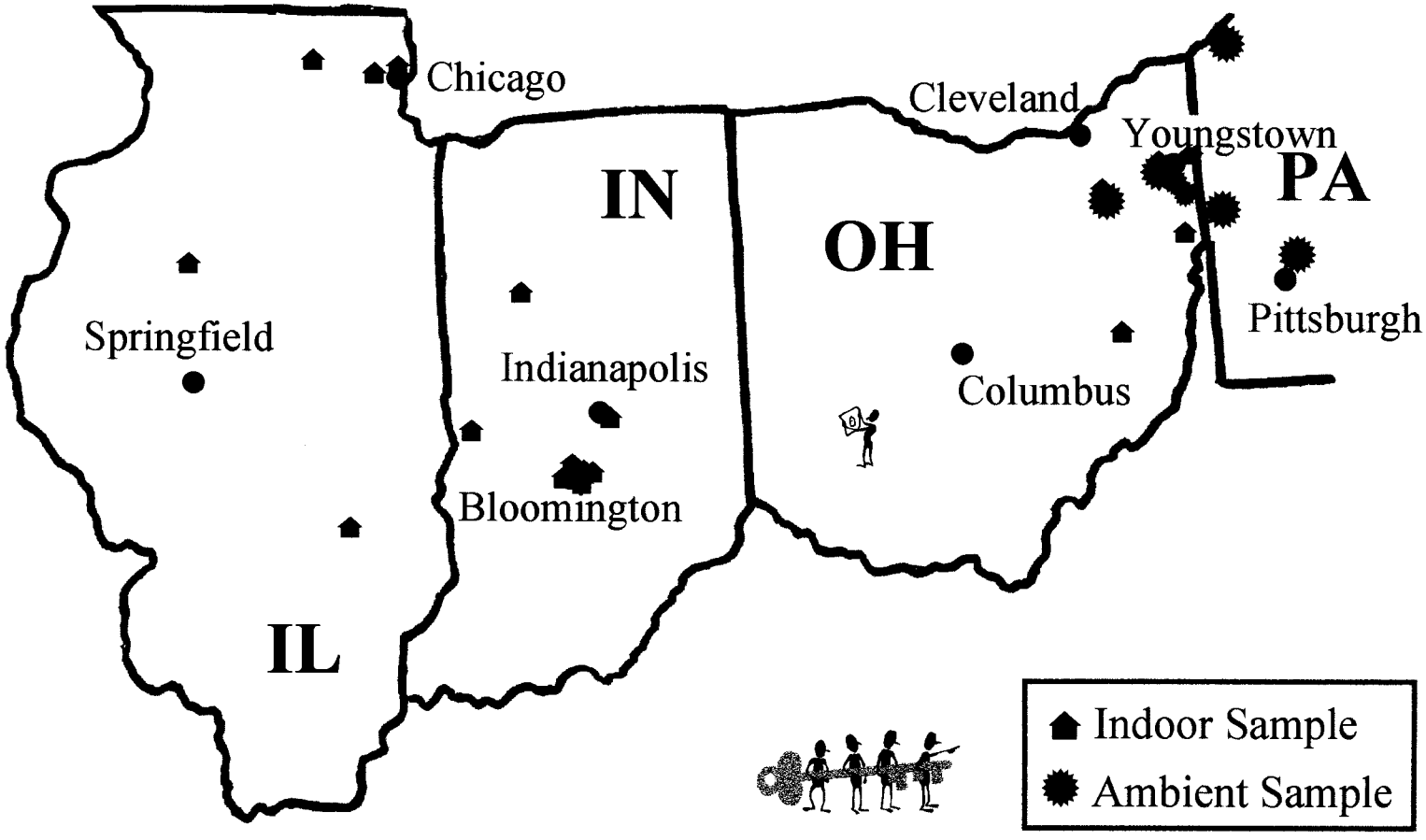


Figure 9. Ambient and Indoor Air Sampling Map

using 3.5 x 5 cm PUF plugs. Samples were collected for periods of 6-8 hours in the basement or first floor level of homes in the four states. Immediately following sampling, PUF were placed individually into pre-cleaned glass jars with Teflon lined lids, and stored at 4 °C until further workup. Figures 8 and 9 show locations for all samples collected.

Extraction and Cleanup

Soil

Each sample was thawed and mixed to ensure homogeneity of the sample. Sodium sulfate was mixed with approximately 15-20 g of wet soil to remove water. The dried soil was spiked with 452 ng PCB-103 (for a field recovery spike), transferred to a pre-cleaned cellulose thimble, and Soxhlet extracted overnight (18-24 hours) with DCM. Extracts were reduced by rotary evaporation, transferred into hexanes and concentrated to 1-2 mL with a gentle stream of nitrogen. A portion of wet soil from each sample was weighed, dried at ~50 °C and re-weighed to obtain % water (Table A-1). All soil values are reported in ng/g soil on a dry weight basis.

Soil extracts were cleaned using an alumina column composed of (bottom to top) a glass wool plug followed by 2 g Al_2O_3 and ~1 cm Na_2SO_4. The alumina column was cleaned before sample application with 5 mL 5% DCM in PE. The sample was added to the column and eluted with 20 mL 5% DCM in PE. The eluent was concentrated and solvent exchanged into isooctane with a gentle stream of nitrogen.

Immediately before analysis, 194 ng Mirex, an OC pesticide internal standard, was added to samples. A portion (10%) of each sample was removed and analyzed for HEPX and Dieldrin. The remainder of the sample was cleaned by shaking with ~0.5 mL 18 M H_2SO_4, and adjusted to ~2 mL for analysis.

Air

Sample PUF plugs were Soxhlet extracted with PE for 18-24 hours. Extracts were reduced and solvent exchanged into hexanes by rotary evaporation, concentrated to ~1 mL with nitrogen, and fractionated on a silicic acid (SA) cleanup column. The column was composed of three layers packed in a 1 cm i.d. column with a glass frit bottom. The three layers consisted of (bottom to top) 3 g silicic acid (3% H_2O added), 2 g alumina (6% H_2O added), and ~2 cm sodium sulfate. The column was pre-cleaned with 25 mL DCM followed by 25 mL PE. The sample was added and eluted in two fractions. The first fraction (F1) was eluted with 30 mL PE and contained HEPT, aldrin and a portion of the TN, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT. The second fraction (F2) was eluted with 30 mL DCM and contained HCH, HEPX, TC, CC, Dieldrin, and the remainder of the TN, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT. Both fractions were concentrated to ~2 mL and transferred into isooctane with a gentle stream of nitrogen.

Analysis

Quantitative analysis of samples was carried out with a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector (GC-ECD) using a DB-5 column (60 m, 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). Samples were injected splitless (split opened after 1.0 min) at an initial temperature of 90 °C. After a 1-min hold, the oven was ramped at 10 °C min^{-1} to 160 °C, 2 °C min^{-1} to 240 °C, 20 °C min^{-1} to 270 °C, and held for 10 min. Injector and detector temperatures were 250 °C and 300 °C, respectively. The carrier gas was hydrogen at 60 cm s^{-1}. Samples were quantified versus 4-8 standards that spanned an 80-100 fold concentration range for soil samples and a 1000 fold concentration range for air

samples. Examples of calibration curves are shown in the Appendix (Figures A-1 to A-23). Chromatographic data was collected and processed using HP Chemstation software.

Determination of enantiomeric composition was done with a Hewlett-Packard 5890 GC-5989B MS Engine mass spectrometer (GC-MS) operated in the negative ion mode (NIMS). Separations were carried out using either a Betadex-120 column (20% permethylated β-cyclodextrin in SPB-35, 30 m, 0.25 mm i.d., 0.25 μm film thickness; Supelco Corp.) or a BSCD column (20% *tert*-butyldimethylsilylated β-cyclodextrin in OV-1701, 30 m, 0.25 mm i.d., 0.25 μm film thickness; BGB Analytik AG, Lettenstrasse 97, CH8134 Adliswil, Switzerland, column designation BGB-172). Samples (2 μL) were injected splitless (split opened after 1.0 min) at an oven temperature of 90 °C. After a 1-min hold, the following oven programs were used for the two columns: Betadex, 15 °C min^{-1} to 140 °C, 1 °C min^{-1} to 190 °C, hold 10 min, 20 °C min^{-1} to 230 °C, hold 10 min; BSCD, 15 °C min^{-1} to 140 °C, 2 °C min^{-1} to 210 °C, hold 10 min, 20 °C min^{-1} to 240 °C, hold 15 min. Carrier gas was helium at 50 cm s^{-1}; injector and transfer line temperatures were 250 °C. The ion source and quadrupole temperatures were 150 °C and 100 °C, respectively. Methane pressure was 1.0 Torr. The instrument was operated in the selected ion monitoring mode using the ions and columns listed in Table 1. Elution orders for the compounds (Table 1) were confirmed for HEPX, OXY, TC, CC and α-HCH enantiomers in this work with standards of the single-enantiomer pesticides. The elution order for *o,p'*-DDT was determined from previously published work using the same column type. Endosulfan I was not quantified in this work but was monitored by GC-MS due to its interference with the (-)CC enantiomer on the Betadex column. If large amounts of endosulfan I were present, a three fraction silicic acid procedure was used for

clean-up (Hargrave et al., 1988). Small amounts were corrected for by using the 410/404 or 412/404 ion ratios.

Table 1. Elution Orders for Chiral OC Pesticides on Selected Columns

Compound	Ions Monitored (*m/z*)	Column	Elution Order
o,p'-DDT	246, 248	BSCD	(-) (+) [abc]
α-HCH	255, 257	BSCD	(-) (+) [abc]
		Betadex	(+) (-) [cd]
HEPX	386, 388 or 316, 318	BSCD	(+) (-) [cd]
OXY	420, 422	BSCD	(+) (-) [cd]
TC, CC	410, 412	Betadex	(+) (-) [cd]
TN	444, 446	Betadex	NA
Endosulfan	404	Betadex	NA

[a]Buser and Müller, 1995a
[b]Buser and Müller, 1995b
[c]Müller and Buser, 1994
[d]Falconer et al., 1995

Chapter Five

Results and Discussion

Quality Control

Quantitative Data

Soil

Because of the wide range of concentrations for pesticide residues in the soils, a decision was made to quantitatively determine residues that were above a certain limit. This "limit of quantification" (LOQ) was defined for this study by multiplying the final extract volume (2.0 mL) by the concentration of the lowest calibration standard and dividing by the dry weight of an average soil sample. These LOQ values were 0.04 - 0.06 ng/g for HCHs, chlordanes, HEPT and HEPX, 0.1 ng/g for dieldrin and 0.5 ng/g for the DDT compounds.

Five soil blanks were processed by placing ~15 g of sodium sulfate into a Soxhlet thimble, extracting, and analyzing using the same procedure as for samples. The concentrations of OCs in blank extracts at 1.0 mL volume were all lower than the LOQ; therefore, no blank corrections were made. Five spike recovery experiments were done with soil where residues were close to or below the detection limit. Approximately 15 g of soil was spiked with the components of interest, extracted, and analyzed as for samples. After correcting for the native amounts in the soil, recoveries ranged from 78-127% (Table A-2). For environmental samples, recoveries within ± 30% are typically considered acceptable; thus, no recovery corrections were made. One original soil sample which contained moderate levels of OC pesticides was extracted a second time immediately following the first extraction to determine completeness of extraction. Only one compound (dieldrin) was found in the second extraction at a value of 3.8% of the amount found in the first extraction. As this amount was

less than the experimental error, no corrections were made. Due to analytical problems, recoveries of the field spike, PCB-103, were not quantified.

Air

Air blanks were processed by extracting and analyzing clean PUF plugs using the same procedure as for samples. Four blanks were done for each size PUF and a limit of detection (LOD) determined. The LOD equals the mean blank value ± 3 times the standard deviation of the mean. Samples above the LOD were blank corrected by subtracting the mean blank (Table A-3) from the nanogram value for each compound. Most of the target compounds were not detected in the blanks for either size PUF and thus were not blank corrected. Large PUF plugs had mean LOD values of 0.95 ng for TC, 0.71 ng for dieldrin, and 26.6 ng for *p,p'*-DDT. Small PUF plugs had mean LOD values of 0.46 ng for TC, 0.63 ng for TN, and 41.5 ng for *p,p'*-DDT. A very large, unexplainable interference with the *p,p'*-DDT peak resulted in very few *p,p'*-DDT concentration values being above LOD.

Five spike recovery experiments were done for each size PUF. Clean PUF plugs were spiked with the components of interest, extracted, and analyzed following the same procedure as for samples. Recoveries ranged from 75-132% for all compounds analyzed for both PUF sizes, with the exception of the HCHs (Table A-4). HCH recoveries were consistently below 50%; therefore, HCH concentration data from air samples is not reported. Concentration data for the remaining eleven compounds required no recovery corrections.

Enantiomeric Data

The enantiomeric ratio (ER) is defined as the area ratio of the (+)/(-) peak eluting from the cyclodextrin column. Single enantiomer standards were used when available to determine elution order of the enantiomers. For several compounds previously published elution orders

using the same column type were used (Table 1). Replicate injections of analytical standards reflected racemic compositions with a standard deviation of $\pm$ 0.03 or less for all compounds, demonstrating that chiral-phase GC-MS is capable of highly precise enantioselective analysis. As a quality control protocol, the following limits for acceptable ER values were set: (a) agreement of ER values at each of the two monitored ions within $\pm$ 0.05; (b) agreement of area ratios of the two monitored ions for samples and standards within ± 5 %. Aigner et al. (1998) previously showed that soil matrix does not alter enantiomeric ratios, so no corrections for matrix effects were made.

OC Pesticide Concentrations in Soils

Concentration data for all soils is given in Tables 2 & 3. A frequency distribution for all compounds is shown in Figure 10. Tables A-5 & A-6 give the nanograms of OCs used for calculating soil concentrations. Information on soil type, pH and organic matter content was available for only a limited number of soils. For this reason, no attempts were made to correlate these properties to concentration data. Total organic carbon (%TOC) was determined for twenty-three soils (Table A-7). Twenty-one soils had values between 0.74 and 3.2 while the remaining two, IN2 and OH4, had values of 7.6 and 33.7 %TOC, respectively. No correlation was found between ER and %TOC for any of the soils. Soil samples are designated by the sample name followed by -S (for soil).

DDT

Levels for ∑DDT (*p,p'*-DDT + *p,p'*-DDD + *p,p'*-DDE + *o,p'*-DDT) in this study ranged from below LOQ to11846 ng/g with a geometric mean (GM) of 9.63 ng/g (Table 2) and at least one of the four DDT components was found in twenty-two of the

Table 2. Concentrations of DDT Components in Soil (ng/g)

Sample	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	*o,p'*-DDT	ΣDDTs	DDT/DDE Ratios
Pennsylvania						
PA1-S	ND*	1.27	ND	ND	1.27	ND
PA2-S	1.07	ND	ND	ND	1.07	ND
PA3-S	ND	ND	ND	ND	ND	ND
PA4-S	ND	1.15	ND	ND	1.15	ND
Ohio						
OH1-S	236	138	3.20	15.4	392	0.58
OH2-S	ND	ND	ND	ND	ND	ND
OH3-S	ND	ND	ND	ND	ND	ND
OH4-S	1601	7635	461	2147	11846	4.77
OH5-S	ND	0.62	ND	ND	0.62	ND
OH6-S	7.64	8.03	ND	2.46	18.1	1.05
OH7-S	0.71	1.10	ND	1.02	2.84	1.56
OH8-S	1.23	2.10	ND	ND	3.33	1.71
OH9-S	ND	0.59	ND	0.52	1.11	ND
OH10-S	11.4	5.59	ND	0.58	17.6	0.49
OH11-S	ND	ND	ND	ND	ND	ND
OH12-S	1.88	2.67	ND	0.72	5.27	1.42
OH13-S	77.0	90.0	23.0	15.0	205	1.17
Indiana						
IN1-S	ND	1.28	0.88	ND	2.16	ND
IN2-S	ND	1.54	ND	0.92	2.46	ND
IN3-S	ND	1.01	1.95	ND	2.96	ND
IN4-S	ND	ND	ND	ND	ND	ND
IN5-S	ND	ND	ND	ND	ND	ND
IN6-S	48.2	106	14.8	45.3	214	2.20
IN7-S	ND	2.08	ND	0.67	2.75	ND
Illinois						
IL1-S	ND	1.05	ND	ND	1.05	ND
IL2-S	2.39	4.85	ND	0.67	7.91	2.03
IL3-S	9.61	11.6	ND	1.83	23.0	1.21
IL4-S	ND	0.51	ND	0.81	1.32	ND
IL5-S	23.4	14.0	ND	2.05	39.5	0.60
Minimum	0.71	0.51	0.88	0.52		
Maximum	1601	7635	461	2147		
Geometric Mean	3.75	4.67	1.20	1.79	9.63	

*ND = Not determined; below detection

Table 3. Concentrations of Pesticides in Soil (ng/g)

Sample	TC	CC	TN	HEPT	HEPX+OXY	DIELDRIN	α-HCH	TC/CC Ratios
Pennsylvania								
PA1-S	0.05	0.13	0.25	ND	ND	ND	0.06	0.40
PA2-S	10.1	20.5	22.8	0.33	1.27	3.47	0.53	0.50
PA3-S	ND*	ND	ND	ND	ND	ND	0.42	ND
PA4-S	0.61	0.23	0.15	ND	0.07	ND	0.15	2.67
Ohio								
OH1-S	ND	ND	ND	0.38	ND	ND	0.31	ND
OH2-S	6.08	6.36	5.39	ND	1.59	ND	0.07	0.96
OH3-S	ND	ND	ND	ND	ND	ND	ND	ND
OH4-S	564	188	94.9	56.2	121	4246	ND	3.00
OH5-S	4.36	1.94	2.15	0.35	15.2	70.9	0.14	2.25
OH6-S	ND	0.07	0.07	0.13	ND	0.66	0.05	ND
OH7-S	1.50	0.32	0.16	0.39	0.95	0.47	0.32	4.75
OH8-S	0.07	0.22	0.14	ND	0.29	ND	ND	0.33
OH9-S	0.74	0.15	0.07	0.15	0.37	ND	ND	5.00
OH10-S	ND	0.44	ND	0.15	ND	ND	0.44	ND
OH11-S	ND	ND	ND	ND	ND	ND	0.06	ND
OH12-S	0.58	1.23	1.23	ND	0.94	23.6	0.07	0.47
OH13-S	13.0	23.0	33.0	ND	11.0	20.0	ND	0.57
Indiana								
IN1-S	0.05	0.14	0.14	ND	ND	28.4	0.20	0.40
IN2-S	3.08	0.92	0.69	1.00	6.84	1.15	0.15	3.33
IN3-S	0.81	0.13	0.40	ND	0.13	ND	0.07	6.00
IN4-S	0.41	ND	2.43	0.41	0.61	14.0	0.27	ND
IN5-S	1.37	0.82	2.47	0.27	11.3	51.2	0.27	1.67
IN6-S	165	199	98.1	2.39	29.7	ND	1.23	0.83
IN7-S	14.0	5.17	4.83	1.21	39.8	68.9	0.07	2.70
Illinois								
IL1-S	0.14	0.14	0.28	ND	0.98	13.2	ND	1.00
IL2-S	0.06	0.07	0.22	0.15	0.45	11.5	ND	0.80
IL3-S	4.43	1.91	1.91	0.38	12.4	12.3	0.08	2.32
IL4-S	0.07	0.15	0.07	ND	0.29	ND	0.15	0.50
IL5-S	1.63	0.92	2.90	0.43	10.1	1.98	0.14	1.77
Minimum	0.05	0.07	0.07	0.13	0.07	0.47	0.05	0.33
Maximum	564	199	98.1	56.2	121	4246	1.23	6.00
Geometric Mean	0.49	0.43	0.51	0.11	0.58	1.05	0.09	0.09

*ND = Not determined; below detection

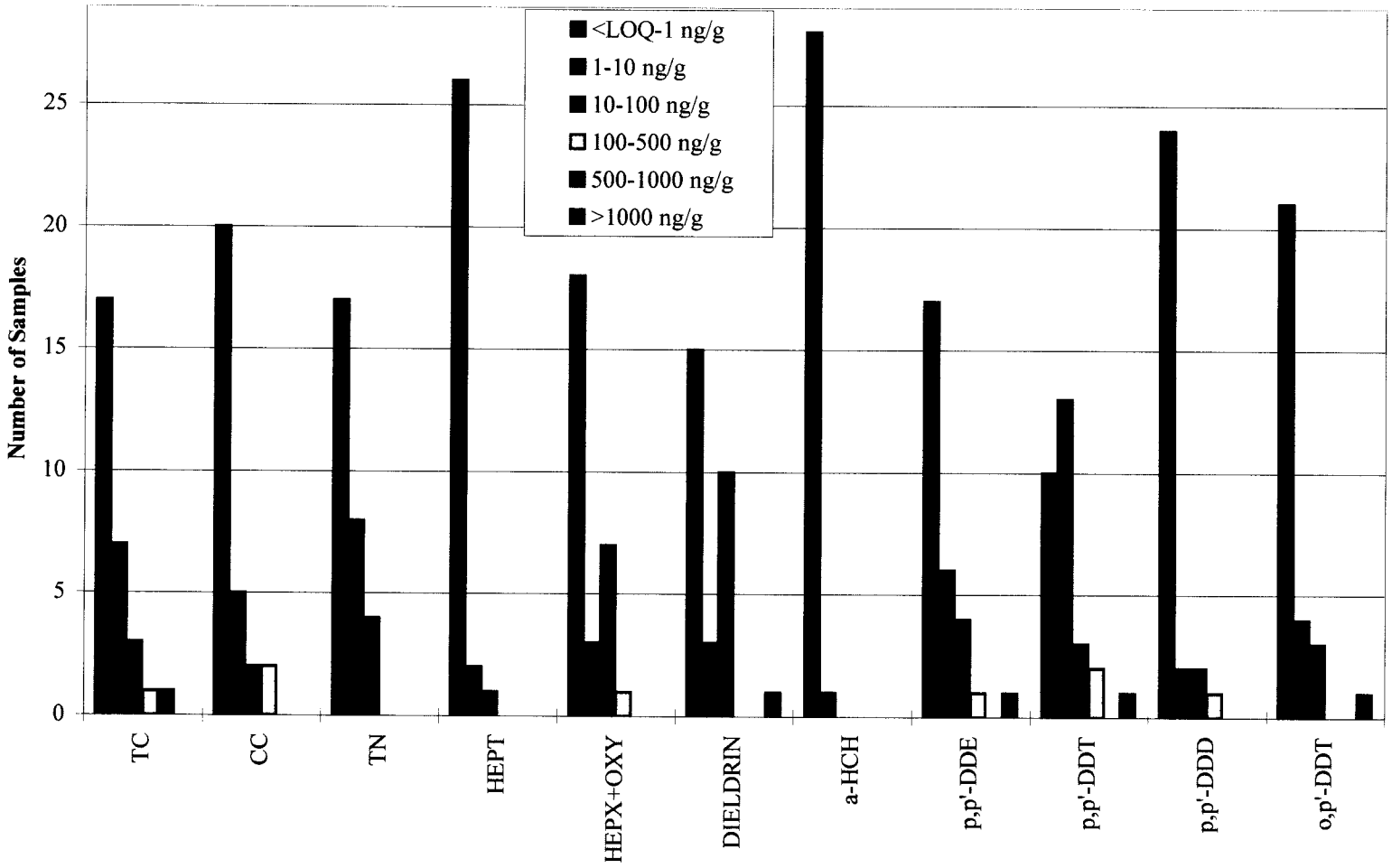


Figure 10: Frequency distribution for 11 OC compounds (out of 29 soil samples)

twenty-eight agricultural soils sampled. *o,p'*-DDD was below detection in all samples. The garden soil had a ∑DDT value of 1.07 ng/g (PA2-S). Of the twenty-three soils above LOQ, three had levels above 200 ng/g while the remaining samples were all below 40 ng/g. The ∑DDT concentration in the most contaminated soil (OH4-S = 11846 ng/g) was 30 times higher than the nearest sample and at least a factor of 1000 higher than most of the samples. OH4-S is a muck soil (33.7 %TOC) in which the major crops are celery, leeks and radishes. It has been previously reported that OC pesticides persist much longer in soils with high organic matter content than soils with low organic matter content (Edwards, 1973, Szeto and Price, 1991). Forest soils in Maine which had been exposed to aerial application of DDT from 1958-67 were sampled in 1993 for DDT levels (Dimond and Owen, 1996). ∑DDT in these soils ranged from 270-1898 ng/g in sprayed areas and from 0-11 ng/g in unsprayed locations. By comparison to earlier studies in the same location, the authors suggested a 'half time' for disappearance of DDT residues of 20-30 years (Dimond and Owen, 1996). Szeto and Price (1991) found ∑DDT levels in agricultural soils from British Columbia, Canada ranging from 194-763 ng/g in silt loam soils and 2984-7162 ng/g in muck soils. They reported a 70% reduction of DDT in the muck soils over a nineteen year period along with the virtual disappearance in loamy sand soils (Szeto and Price, 1991). DDT breaks down to DDE and DDD in soil and, generally, with time the parent/metabolite ratio decreases (Dimond and Owen, 1996); however there is a large variability with soil type (Hitch and Day, 1992). Ratios of *p,p'-DDT*/p,p'-DDE in the present study were quite variable, ranging from 0.5 to 4.8 (Table 2). Of the twelve soils which contained both components, three soils had ratios below 1.0, while the remaining nine had ratios above 1.0. The OH4-S soil, which contained the highest

concentrations of DDTs, also had the highest DDT/DDE ratio, not surprising as this was a muck soil.

Chlordane

Levels of chlordanes in samples above the LOQ ranged from 0.05-564 ng/g for TC and 0.07-199 ng/g for CC (Table 3). TC was found in twenty-three of the agricultural soils while CC was found in twenty-four of the twenty-nine soils. The majority of the soils were below 14 ng/g for TC and 23 ng/g for CC, except for two soils which had extremely high values for both compounds. One of the two outliers was the muck soil mentioned earlier (OH4-S, TC = 564 ng/g, CC = 188 ng/g). The other soil (IN6-S, TC = 165 ng/g, CC = 199 ng/g) was formerly the site of a house which had been treated for termites using chlordane. The house was torn down approximately 25 years ago and the site has since been farmed for corn, soybean and wheat. The PA2-S garden soil had a concentration of 10.2 ng/g for TC and 20.5 ng/g for CC, values which are higher than most of the agricultural soils, but not surprising as one of the major applications of chlordane before 1973 was for home and garden usage (PHS., 1992). The ratio of TC/CC in soils ranged from 0.33 - 6.0 (Table 3), while the ratio in technical chlordane is 1.8 (Sovocool et al., 1977). Szeto and Price (1991) reported the mean concentration for CC as 48 ng/g dry weight in silt loam, 174 ng/g in muck soils, and for TC as 63 ng/g in silt loam, 508 ng/g in muck soils from British Columbia.

Trans-nonachlor, (TN), another component of technical chlordane, had concentrations for samples above LOQ in 24 of 29 samples ranging from 0.07-98.1 ng/g (Table 3). Again, the two soils which were outliers for TC and CC had much higher concentrations of TN than the majority of soils. The garden soil had concentrations of TN

higher than most of the agricultural soils (22.8 ng/g for PA2-S), similar to the trend for TC and CC. In British Columbia, Szeto and Price (1991) found an average concentration of 59 ng/g in silt loam soils and 148 ng/g in muck soils.

Heptachlor and Heptachlor epoxide

HEPT was found in only sixteen of the samples with levels ranging from 0.13-2.39 ng/g for all of the soils except OH4-S which contained 56.2 ng/g (Table 3). HEPT was 0.33 ng/g in the PA2-S garden soil. In the British Columbia study, HEPT was found to be non-detectable in silt loam soils and ranged from 37-278 ng/g in muck soils (Szeto and Price, 1991).

Residues of HEPX and OXY were quantified as HEPX+OXY because the two compounds co-eluted on the DB-5 column. Twenty-one samples were above LOQ for HEPX+OXY, ranging in concentration from 0.07-121 ng/g (Table 3). The OH4-S soil again showed the highest value, with the other soil concentrations below 40 ng/g. The level in the garden soil fell within the range of the majority of agricultural soils with a value of 1.27 ng/g. In British Columbia soils, HEPX averaged 16 ng/g in silt loam soils and 174 ng/g in muck soils (Szeto and Price, 1991). One of the soils analyzed in the present study (OH5-S) was an experimental farm used in the 1960's and 70's for studies on volatilization of some OC pesticides from soils. For one study, the soil was treated with a single application of HEPT in May 1969 immediately before maize planting (Freeman et al., 1975). The average values found in this soil four years after application were HEPT - 50 ng/g and HEPX - 200 ng/g (Freeman et al., 1975). Our analysis of the same soils 23 years later showed a HEPT concentration of 0.35 ng/g and a HEPX+OXY concentration of 15.2 ng/g.

Dieldrin

In this study, levels of dieldrin in samples above the LOQ (16 out of 29) ranged from 0.47-4246 ng/g (Table 3). This range of concentrations was again dominated by the OH4-S soil with all other soil concentrations below 71 ng/g. The garden soil was similar to most agricultural soils in concentration at 3.47 ng/g. Szeto and Price (1991) reported an average concentration of dieldrin in muck soils as 692 ng/g, but they were not able to detect this compound in silt loams. At the OH5-S site, dieldrin was also studied after application in 1969 (Freeman et al., 1975). The concentration of dieldrin found in the soil in 1973 was reported as 800 ng/g (Freeman et al., 1975) while in the present study (23 years later) we found 70.9 ng/g. Loss of dieldrin at the OH5-S site was followed for seven years after the 1969 application (Freeman et al., 1975). We constructed a first-order plot of mean soil residues (C_s, μg/g, Table V in Freeman et al., 1975) vs. time (t, years) and, after removing two outlying points at 0.34 and 1.31 years, obtained log C_s = -0.0574t + 0.525 with r^2 = 0.90. Projecting this disappearance relationship to 1996, thirty-one years after application, gives an estimated C_s = 0.056 μg/g, which agrees excellently with 0.0709 μg/g found in the present study.

α-Hexachlorocyclohexane

α-HCH was found in twenty-two samples but at very low levels (0.05-1.23 ng/g, Table 3). IN6-S had the highest concentration while α-HCH in the OH4-S soil (the high end outlier for almost all other compounds) was below detection. Most soils were below 0.05 ng/g for lindane (γ-HCH), another component of technical HCH. Szeto and Price (1991) reported α-HCH as non-detectable in the British Columbia silt loam soils, and an average of 56 ng/g in muck soils.

Enantiomeric Composition of OC Pesticides in Soils

All of the chiral pesticides in this study are manufactured as racemic mixtures of the two enantiomers. If no metabolism occurs, the ERs of the pesticide residues should be 1.00. ERs were determined for those samples from which good peak integrations could be obtained (as defined in the Quality Control section). ER values for the soils are given in Table 4 and shown in Figure 11 and sample chromatograms are shown in Figures 12. Standard deviations for the soil ERs (Table 4) ranged from 0.00 - 0.07, with an average value of 0.02.

o,p'-DDT

Enantioselective degradation of *o,p'*-DDT occurred in seven of nine soils. Selective degradation was observed for the (+) enantiomer in three soils with ERs ranging from 0.82-0.86, while four soils showed selective degradation of the (-) enantiomer (ER = 1.07-1.19). A sample chromatogram showing the change in the more abundant enantiomer for *o,p'*-DDT in different soils is shown in Figure 12. Residues in the remaining two soils were close to racemic (ER = 0.98 & 1.04). The garden soil (PA2-S) had a concentration of *o,p'*-DDT high enough to determine an ER (ER = 0.99). In a previous study of soils from British Columbia, Canada, Falconer et al. (1997) found depletion of (+)-*o,p'*-DDT (ER = 0.8) in one silt loam soil out of the six agricultural soils analyzed. Two other silt loam soils and three muck soils contained racemic *o,p'*-DDT. No apparent relationship between *o,p'*-DDT concentrations and enantiomeric ratios was found for soils.

Chlordane

The (+) enantiomer of TC was preferentially degraded in all soils with ERs ranging from 0.57-0.93. The (-) enantiomer of CC was degraded in most soils (ER = 1.08-1.40),

Table 4. ERs* ± Standard Deviation for Chiral Pesticides in Soils

Sample	TC	CC	HEPX	OXY	*o,p'*-DDT
Standards	*0.99 ± 0.01*	*0.98 ± 0.02*	*1.00 ± 0.01*	*0.98 ± 0.03*	*1.01 ± 0.01*
Pennsylvania					
PA1-S	0.63 ± 0.00	1.27 ± 0.00	NA[§]	NA	NA
PA2-S	0.60 ± 0.01	1.23 ± 0.04	ND[#]	1.73 ± 0.02	ND
Ohio					
OH1-S	NA	NA	ND	ND	0.83 ± 0.01
OH2-S	0.81 ± 0.01	1.04 ± 0.02	1.75 ± 0.00	0.96 ± 0.04	ND
OH4-S	0.90 ± 0.00	1.01 ± 0.01	1.17 ± 0.05	1.14 ± 0.03	0.98 ± 0.02
OH5-S	0.66 ± 0.00	1.31 ± 0.06	3.57 ± 0.00	0.98 ± 0.01	ND
OH8-S	0.75 ± 0.00	1.32 ± 0.01	NA	ND	0.82 ± 0.03
OH10-S	NA	NA	NA	NA	1.04 ± 0.01
OH12-S	0.70 ± 0.03	1.08 ± 0.01	2.20 ± 0.06	0.80 ± 0.03	1.19 ± 0.04
OH13 -S	0.79 ± 0.01	1.10 ± 0.01	1.60 ± 0.01	0.89 ± 0.01	0.82 ± 0.01
Indiana					
IN1-S	0.74 ± 0.00	1.20 ± 0.02	NA	NA	NA
IN2-S	0.93 ± 0.01	1.04 ± 0.01	1.78 ± 0.03	1.08 ± 0.03	1.07 ± 0.02
IN5-S	0.57 ± 0.01	1.28 ± 0.02	4.26 ± 0.07	0.80 ± 0.01	ND
IN6-S	0.85 ± 0.01	0.99 ± 0.02	ND	1.34 ± 0.02	ND
IN7-S	0.74 ± 0.00	NA	NA	NA	NA
Illinois					
IL1-S	0.55 ± 0.00	1.35 ± 0.01	NA	NA	NA
IL2-S	0.62 ± 0.01	1.20 ± 0.00	NA	NA	NA
IL3-S	0.74 ± 0.00	1.13 ± 0.01	2.36 ± 0.04	0.89 ± 0.02	1.14 ± 0.03
IL4-S	0.59 ± 0.01	1.25 ± 0.02	NA	NA	NA
IL5-S	0.66 ± 0.01	1.40 ± 0.02	3.36 ± 0.02	0.67 ± 0.03	1.08 ± 0.02

*Enantiomeric Ratio is designated as (+) enantiomer / (-) enantiomer

[§]NA = Not analyzed

[#]ND = Not determined; below detection

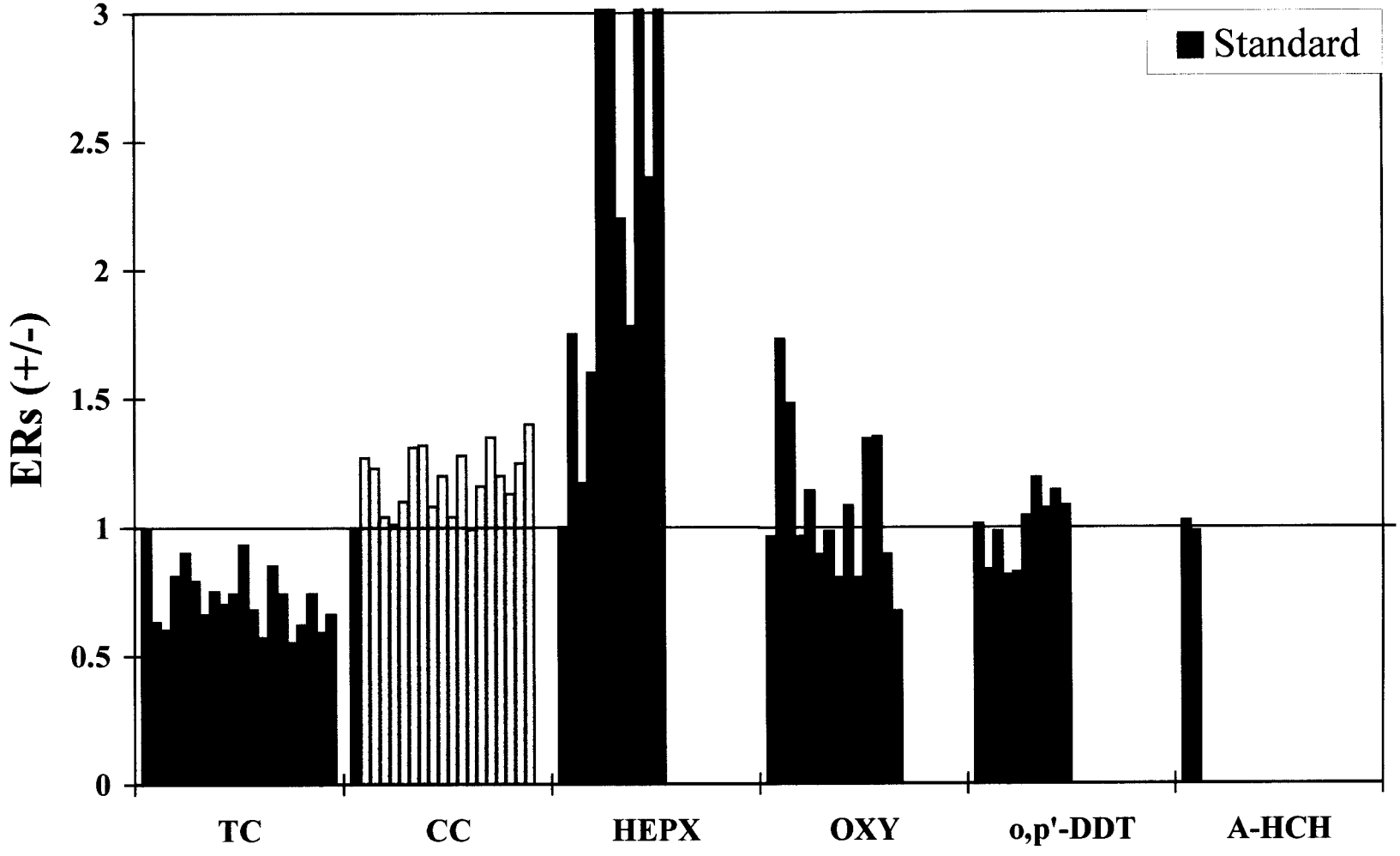


Figure 11. ERs for Soil Samples (Four HEPX ERs were > 3. See Table 4.)

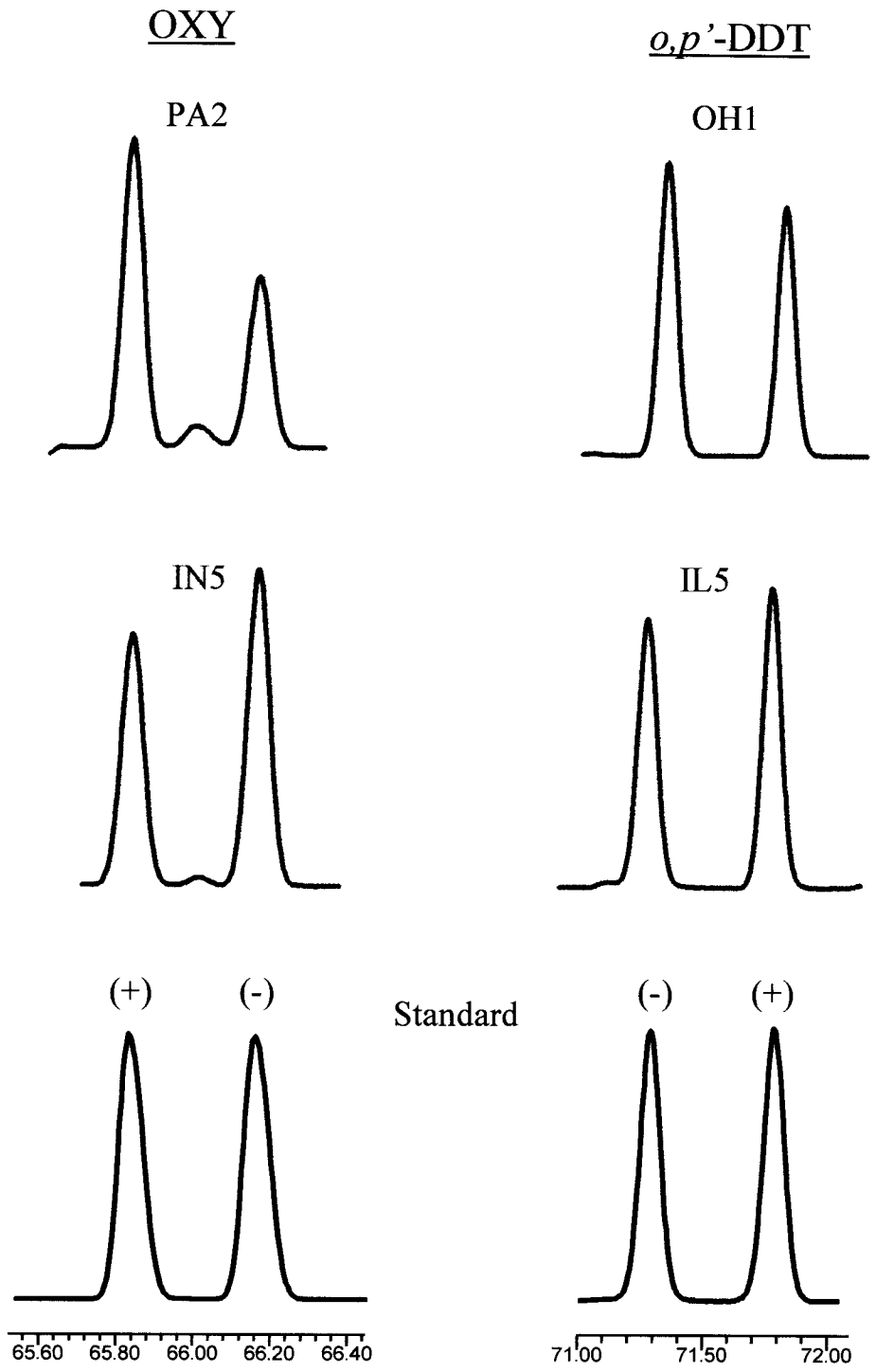


Figure 12. Chromatograms of OXY and *o,p'*-DDT in standards and soils showing variation in degradation pattern.

except for three soils in which CC was close to racemic (ER = 1.01-1.04). A third pair of chlordane enantiomers was separated on the Betadex column and was tentatively identified as MC-5 from the published elution profiles of technical chlordane on a 20-m column containing 10% permethylated β-cyclodextrin in PS086 (Buser and Müller, 1995). In the present study, the first-eluting enantiomer of this compound was depleted in many of the soils. The garden soil also showed preferential loss of (+)TC and (-)CC. Falconer et al. (1997) found that both TC and CC were racemic in all six samples (both silt loam and muck soils) from British Columbia. No correlation to concentration was found in either study.

Heptachlor epoxide

Levels of HEPT were too low for accurate enantioselective analysis in any of the soils in this study. HEPX was found in nine of the soils and showed an enantiomeric excess of the (+) enantiomer in all (Table 4). It is unclear, however, whether non-racemic HEPX arises from selective degradation of HEPX, selective formation from HEPT, or a combination of both. Of the five chiral compounds, HEPX showed the largest differences with ERs ranging from 1.17-4.26. The OH4-S soil, which had much higher concentrations of HEPX than the other soils, had the lowest ER (1.17); however, no other trends with concentration were discernible. The PA2-S garden soil was below detection. Falconer et al. (1997) found HEPX in four British Columbia soils (3 muck and 1 silt loam), all showing an excess of the (+) enantiomer.

Oxychlordane

OXY is the principal metabolite of CC, TC, and the nonachlors (Buser and Müller, 1992). The more abundant enantiomer [(+)OXY vs. (-)OXY] varied in different soils

(Figure 12). Out of eleven soils, five showed an excess of (-)OXY, four showed an excess of (+)OXY and two were close to racemic (Table 4). As with HEPX, it is not known if enantiomeric differences of OXY are due to preferential degradation, selective formation or both. The garden soil showed an ER greater than 1.00. Falconer et al. (1997) found an excess of the (-) enantiomer of OXY in two British Columbia soils (one silt loam, one muck) where OXY was detectable. The ERs for OXY in soil may depend on the relative amounts of (+) and (-) TC and CC that are biologically metabolized since the (+) and (-) enantiomers of the chlordanes are expected to degrade to the corresponding OXY enantiomers (Müller and Buser, 1994). OXY was not determined quantitatively due to co-elution with HEPX on the DB-5 column.

α-Hexachlorocyclohexane

α-HCH was too low for enantioselective analysis in all but one sample, a muck soil (OH4-S) which showed an ER of 0.98. Falconer et al. (1997) found α-HCH in three silt loam soils from British Columbia to be close to racemic, while three muck soils showed degradation of the (-) enantiomer (ER = 1.21-1.36). Müller et al. (1992) examined α-HCH in one soil near a former HCH factory and found a slight depletion of the (-) enantiomer (ER = 1.099).

OC Pesticide Concentrations in Air

Above-Soil Air Samples

Concentrations in above-soil air samples are not reported, as exact air volumes could not be determined due to equipment malfunctions. Above-soil air samples are designated by the sample name followed by -AS (for above-soil).

Indoor Air Samples

Concentration data for indoor air samples are given in Tables 5 and 6. A frequency distribution for the eleven compounds analyzed is shown in Figure 13. Table A-8 gives air volumes for indoor air samples and Table A-9 gives nanograms of OCs in indoor air. Indoor air samples are designated by the sample name followed by -IA (for indoor air).

DDT

Twenty of twenty-three samples had detectable levels of the DDT compounds (Table 5). The ΣDDT (*p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'-DDT*) ranged from 0.02 ng/m^3 to12.9 ng/m^3 with a geometric mean (GM) of 0.30 ng/m^3. Due to blank problems, only two samples had detectable levels of *p,p'*-DDT (IN2-I and IN8-IA). For this reason, DDT/DDE ratios were not calculated. Of the twenty samples above LOD, only three had levels above 1 ng/m^3 while the remaining seventeen were below 1 ng/m^3. The ΣDDT concentration in the most contaminated sample (IN8-IA=12.9ng/m^3) was two times higher than the nearest sample (IN2-IA=6.10 ng/m^3) and at least 12 times higher than the remainder of the samples. The two highest level samples were both taken in the basement level of the homes. Past studies have shown that concentrations of pesticides used as termiticides in house foundations tend to be higher in the lower levels of the house (Anderson and Hites, 1989).

Chlordane

TC and CC were found in twenty out of twenty-three indoor air samples (Table 6). Levels of chlordanes in samples above the LOD ranged from 0.02 ng/m^3 to 87.0 ng/m^3 for TC and from 0.02 ng/m^3 to 37.2 ng/m^3 for CC. The GMs were 0.89 and 0.42 ng/m^3 for

Table 5. Concentrations of DDT Components in Indoor Air (ng/m^3)

Sample	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	*o,p'*-DDT	Σ DDTs
Pennsylania					
PA1-IA	0.17	ND	0.02	0.20	0.39
PA2-IA	0.16	ND	ND	0.11	0.27
PA3-IA	0.28	ND	0.08	0.49	0.84
Ohio					
OH1-IA	0.17	ND	0.03	0.06	0.26
OH2 -IA	0.15	ND	ND	0.13	0.28
OH3-IA	0.05	ND	ND	0.03	0.08
OH4-IA	0.49	ND	0.13	0.58	1.20
OH5-IA	0.07	ND	ND	ND	0.07
OH6-IA	0.02	ND	0.06	ND	0.08
OH7-IA	ND*	ND	ND	ND	ND
Indiana					
IN1-IA	ND	ND	ND	ND	ND
IN2-IA	1.32	0.34	0.81	3.64	6.10
IN3-IA	0.16	ND	0.30	0.33	0.79
IN4-IA	0.03	ND	ND	ND	0.03
IN5-IA	0.20	ND	0.34	0.28	0.81
IN6-IA	0.02	ND	ND	ND	0.02
IN7-IA	0.18	ND	0.39	0.15	0.72
IN8-IA	4.15	2.50	0.48	5.74	12.9
Illinois					
IL1-IA	ND	ND	ND	ND	ND
IL2-IA	0.04	ND	ND	ND	0.04
IL3-IA	0.09	ND	0.03	0.09	0.21
IL4-IA	0.20	ND	ND	0.07	0.27
IL5-IA	0.20	ND	ND	0.11	0.31
Minimum	**0.02**	**0.34**	**0.02**	**0.03**	**0.02**
Maximum	**4.15**	**2.50**	**0.81**	**5.74**	**12.9**
Geometric Mean	**0.14**	**0.92**	**0.13**	**0.23**	**0.30**

*ND = Not determined; below detection

Table 6. Concentrations of OC Pesticides in Indoor Air (ng/m^3)

Sample	TC	CC	TN	HEPT	HEPX+OXY	Aldrin	Dieldrin	TC/CC Ratios
Pennsylania								
PA1-IA	0.17	0.09	0.04	0.23	ND	ND	0.26	1.86
PA2-IA	ND*	ND	ND	0.20	ND	ND	0.07	ND
PA3-IA	0.10	0.09	0.06	0.14	ND	ND	0.13	1.09
Ohio								
OH1-IA	2.63	0.94	0.73	5.50	ND	ND	0.78	2.80
OH2 -IA	2.08	0.76	0.48	2.15	ND	ND	0.07	2.75
OH3-IA	0.34	0.16	0.11	0.25	ND	ND	0.13	2.10
OH4-IA	0.21	0.09	0.06	0.37	ND	ND	0.24	2.20
OH5-IA	1.25	0.42	0.26	2.51	ND	ND	0.15	3.01
OH6-IA	ND	ND	ND	0.08	ND	ND	ND	ND
OH7-IA	0.03	0.03	0.01	0.13	ND	ND	ND	1.01
Indiana								
IN1-IA	1.92	0.54	0.82	7.89	ND	ND	0.07	3.58
IN2-IA	87.0	37.2	12.6	78.6	4.36	ND	0.54	2.34
IN3-IA	6.96	2.52	2.35	8.61	0.41	ND	0.68	2.76
IN4-IA	0.38	0.31	0.30	0.81	ND	ND	0.07	1.26
IN5-IA	6.36	1.79	1.71	1.07	ND	ND	0.12	3.54
IN6-IA	0.44	0.19	0.13	0.59	ND	ND	0.08	2.32
IN7-IA	31.0	11.4	7.65	45.8	1.71	5.75	0.09	2.71
IN8-IA	14.6	5.26	3.58	8.51	1.45	42.8	17.7	2.77
Illinois								
IL1-IA	ND	ND	ND	ND	ND	ND	ND	ND
IL2-IA	0.02	0.02	ND	0.05	ND	ND	0.44	0.65
IL3-IA	3.19	0.57	0.40	11.8	0.57	ND	0.22	5.57
IL4-IA	0.11	0.07	0.03	0.23	ND	ND	0.18	1.63
IL5-IA	0.15	0.08	0.07	0.54	ND	ND	0.18	1.90
Minimum	**0.02**	**0.02**	**0.01**	**0.05**	**0.41**	**5.75**	**0.07**	
Maximum	**87.0**	**37.2**	**12.6**	**78.6**	**4.36**	**42.8**	**17.7**	
Geometric Mean	**0.89**	**0.42**	**0.33**	**1.13**	**1.20**	**15.7**	**0.22**	

*ND = Not determined; below detection

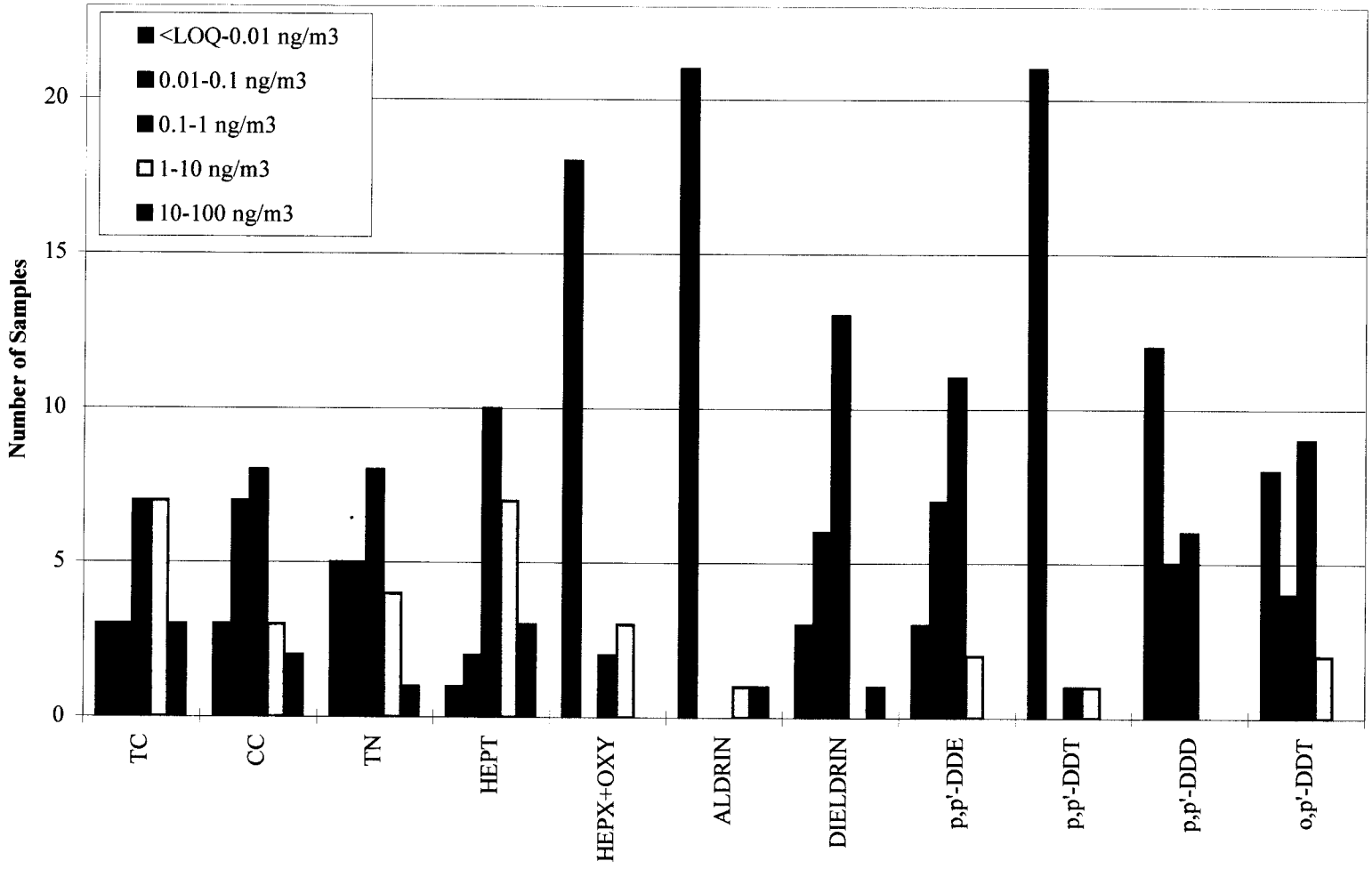


Figure 13: Frequency distribution for 11 OC compounds (out of 23 indoor air samples)

TC and CC, respectively. The majority of the samples were below 14 ng/m^3 for TC and 11 ng/m^3 for CC with the exception of two samples (IN2-IA, TC = 87.0 ng/m^3, CC = 37.2 ng/m^3 and IN7-IA, TC = 31.0 ng/m^3, CC = 11.4 ng/m^3). IN2-IA residues of TC and CC were three times higher than those of the nearest sample and thirty to forty times higher than most of the other samples. This sample was collected from the basement level of a home; however, the sample with the next highest concentration (which was 10-20 times higher than the majority of samples) was taken on the first floor. The ratio of TC/CC in indoor air for the present study ranged from 0.65 to 5.57 (Table 6). Anderson and Hites (1989) found levels of chlordanes in indoor air from four different homes (basement level), also in Bloomington, IN, with levels ranging from 2.2-200 ng/m^3 for TC and 1.7-200 ng/m^3 for CC. In their study, the high level sample was collected from a home that was treated for termites through injection into the foundation just one year before samples were taken. The basement contained a sump pump which created an open area on the basement floor and the walls of this home contained many cracks, both of which would enable volatilization of the pesticides out of the foundation into the home air. TC/CC ratios for the Anderson and Hites (1985) study ranged from 1.0-4.0.

TN was found in nineteen of the twenty-three samples, most of which were below 3 ng/m^3 (Table 6). TN levels for indoor air samples above LOD ranged from 0.01 ng/m^3 to 12.58 ng/m^3 with a GM of 0.33 ng/m^3. The IN2-IA sample, again, had the highest level, which was two times higher than the nearest sample and at least twelve times higher than the majority of the samples. In the Anderson and Hites study (1989) basement level residues of TN ranged from 2.3-160 ng/m^3 and first floor levels ranged from 0.6-19 ng/m^3. Again, in this study the highest level sample was the recently treated home. Wallace et al.

(1996) found TN concentration levels of 0.3 ng/m^3 and 0.2 ng/m^3 for the basement and first floor of a home, respectively. Air from homes in Columbia, SC and rural Alabama were analyzed for ∑TC, CC and TN and averaged 10.1 ng/m^3 (n=3) for Columbia and 34.2 ng/m^3 (n=5), for Alabama (Bidleman et al., 1998).

Heptachlor and Heptachlor epoxide

HEPT was found in all but one of the twenty-three samples (Table 6). Residue levels for samples above LOD ranged from 0.05 ng/m^3 to 78.6 ng/m^3 with a GM of 1.13 ng/m^3. With the exception of two high residue samples (IN2-IA and IN7-IA), the majority of the samples were less than 11 ng/m^3. The IN2-IA sample again had the highest levels, which were two times higher than the nearest sample and at least forty times higher than the majority of the samples. HEPT levels found by Anderson and Hites (1989) ranged from 4.0 ng/m^3 to 110 ng/m^3 for the basement level of four homes and from 2.6 ng/m^3 to 66 ng/m^3 for the first floor. Wallace et al. (1996) found HEPT levels of 3.3 ng/m^3 and 0.5 ng/m^3 for the basement and first floor levels, respectively.

As in the quantification of soil residues, HEPX and OXY were quantified together because the two compounds coelute on the DB-5 column. Only five of twenty-three samples contained levels of HEPX + OXY above the LOD (Table 6). The concentrations ranged from 0.41 ng/m^3 to 4.36 ng/m^3 with a GM of 1.20 ng/m^3. Neither HEPX or OXY was reported in any of the other indoor air studies.

Aldrin and Dieldrin

Aldrin was only detected in two of the twenty-three samples (Table 6) at levels of 5.75ng/m^3 (IN7-IA) and 42.8 ng/m^3 (IN8-IA). Interestingly, IN2-IA, which had the highest residue levels for all the chlordane compounds, had non-detectable levels of aldrin.

The sample with the highest concentration of aldrin (IN8-IA) was taken in the basement level of the home. Anderson and Hites (1989) found aldrin levels ranging from 10-5000 ng/m^3. In their study, the highest concentration sample was from a home built in 1985 that was treated for termites by spraying aldrin into the spaces in the basement block walls upon construction of the house. The sample was taken two years after application of the termiticide.

Dieldrin residues above LOD were found in twenty of twenty-three samples (Table 6). Concentrations ranged from 0.07 ng/m^3 to 17.7 ng/m^3 with a GM of 0.22 ng/m^3. The high level sample (IN8-IA) was twenty-eight times higher than the nearest sample and at least thirty-four times higher than the rest of the samples. The high levels of dieldrin in this sample are not surprising considering the high concentrations of aldrin also found in this sample (aldrin degrades into dieldrin in the environment). In the Anderson and Hites (1989) study dieldrin levels ranged from 0.4-28 ng/m^3.

Ambient Air Samples

Concentrations were determined for four out of the seven ambient air samples taken and are shown in Table 7. Sample concentrations for the remaining three ambient air samples are not reported as exact air volumes could not be determined due to equipment malfunction. On average, concentrations in ambient air were at least two orders of magnitude lower than most indoor air concentrations for all compounds detected. Ambient air samples are designated by the sample name followed by -AA (for ambient air). Table A-10 gives air volumes for ambient air samples and Table A-11 gives nanograms of OCs used to calculate ambient air concentrations.

Table 7. Concentrations (ng/m^3) of Organochlorine Pesticides in Ambient Air

Sample	HEPT	HEPX+OXY	TC	CC	TN	Dieldrin	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	ΣDDT	ΣChlordanes	TC/CC Ratios
PA2-AA	0.005	0.052	0.003	0.007	0.003	0.027	0.003	ND*	ND	ND	0.003	0.013	0.436
PA3-AA	0.006	0.004	0.008	0.008	0.007	ND	0.005	0.001	0.004	ND	0.010	0.023	0.985
OH3-AA	0.022	0.007	0.016	0.012	0.008	0.007	0.033	0.001	0.004	ND	0.038	0.035	1.330
OH4-AA	0.008	0.008	0.014	0.019	0.010	0.011	0.015	0.002	0.003	ND	0.020	0.042	0.750
Minimum	**0.005**	**0.004**	**0.003**	**0.007**	**0.003**	**0.007**	**0.003**	**0.001**	**0.003**		**0.003**	**0.013**	
Maximum	**0.022**	**0.052**	**0.016**	**0.019**	**0.010**	**0.027**	**0.033**	**0.002**	**0.004**		**0.038**	**0.042**	
Geometric Mean	**0.009**	**0.010**	**0.008**	**0.010**	**0.006**	**0.013**	**0.009**	**0.001**	**0.004**		**0.012**	**0.026**	

*ND = Not determined; below detection

DDT

Levels for ΣDDT ranged from 0.003ng/m^3 to 0.038 ng/m^3 with a GM of 0.012 ng/m^3 for the four ambient air samples quantified (Table 7). In all four samples *p,p'-DDT* was non-detectable. All samples contained *p,p'*-DDE with a range of 0.003-0.033 ng/m^3 and a GM of 0.009 ng/m^3. Three samples contained *p,p'*-DDD and *o,p'*-DDT and had GMs of 0.001 ng/m^3 and 0.004 ng/m^3, respectively.

Chlordane

TC, CC, and TN were found in all four samples with GMs of 0.008 ng/m^3 and 0.010 ng/m^3, respectively (Table 7). The ranges were as follows: TC- 0.003 ng/m^3 to 0.016 ng/m^3; CC- 0.007ng/m^3 to 0.019 ng/m^3; and TN- 0.003 ng/m^3 to 0.010 ng/m^3. The mean ΣChlordanes (TC + CC + TN) for this study was 0.019 ng/m^3 with a range of 0.013 to 0.042 ng/m^3. TC/CC ratios ranged from 0.435 to 1.330. Concentrations of chlordanes in this study were similar to annual means for ∑chlordanes at Sturgeon Point on Lake Erie (0.034 ng/m^3; Sweet et al., 1996). Another study found higher ambient air level values with means of 0.295 ng/m^3 and 0.109 ng/m^3 for rural Alabama and Columbia, SC (Bidleman et al., 1998). Wallace et al. (1996) measured ambient air in Bloomington, IN and found a range of chlordane concentrations from less than 0.05 to 0.1 ng/m^3.

Heptachlor and Heptachlor epoxide

HEPT was found in all four samples ranging from 0.005 ng/m^3 to 0.022 ng/m^3 with a GM of 0.009 ng/m^3 (Table 7). HEPX + OXY was also found in all four ambient air samples ranging from 0.004 ng/m^3 to 0.052 ng/m^3 with a GM of 0.010 ng/m^3.

Dieldrin

Dieldrin was detected in all but one sample ranging from 0.007 ng/m^3 to 0.027 ng/m^3 with a GM of 0.013 ng/m^3 (Table 7). Wallace et al. (1996) found dieldrin levels for one ambient air sample in Bloomington to be 0.3 ng/m^3.

Enantiomeric Composition of OC Pesticides in Air

Air-Above-Soil

ERs for air-above-soil samples are reported in Table 8. Air samples were taken above five agricultural fields and one garden soil (PA2-S). Figure 14 shows a comparison of ERs for matching soil and air samples.

o,p'-DDT

o,p'-DDT, the only chiral component of DDT was found in both soil and air-above-soil at three sites (Table 8). OH13-S had an ER of 0.81, which signifies preferential degradation of the (-) enantiomer of *o,p'*-DDT. The OH13-AS had an ER of 0.84, which not only resembles the soil ER in direction of degradation but also in magnitude of degradation (97% agreement). The remaining two matching pairs had values at or near racemic for both soil and air. Finizio et al. (1997) sampled soil and corresponding air-above-soil at agricultural sites in the Fraser Valley of British Columbia. They found a nearly racemic *o,p'*-DDT ER value (1.03) in the soil and a very similar ER (1.02 at 5 cm) in the air above the soil. This group also sampled air at different elevations above the soil from 5-140 cm, and the ER values at each level were in agreement by at least 97%.

Chlordane

TC and CC were found in all six sample sets for soil and air-above-soil (Table 8). Figure 15 shows chromatograms of chlordane in a standard, soil and air-above-soil. The

Table 8. Soil and Air Above Soil ER Comparison

	TC		CC		HEPX		OXY		*o,p'*-DDT	
	Soil	Air	Soil	Air	Soil	Air	Soil	Air	Soil	Air
Pennsylvania										
PA2	0.60	0.59	1.19	1.24	ND*	ND	1.73	1.55	ND	ND
Ohio										
OH5	0.66	0.89	1.31	1.07	3.57	3.28	0.98	1.18	ND	ND
OH13	0.79	0.70	1.10	1.16	1.60	1.66	0.89	1.01	0.81	0.84
Indiana										
IN5	0.57	0.81	1.28	1.06	4.26	2.11	0.80	0.87	ND	ND
IN6	0.85	0.72	0.99	1.03	ND	ND	1.34	1.14	ND	ND
Illinois										
IL5	0.66	0.72	1.40	1.11	3.66	2.69	0.67	0.74	1.08	0.98

*ND = Not determined

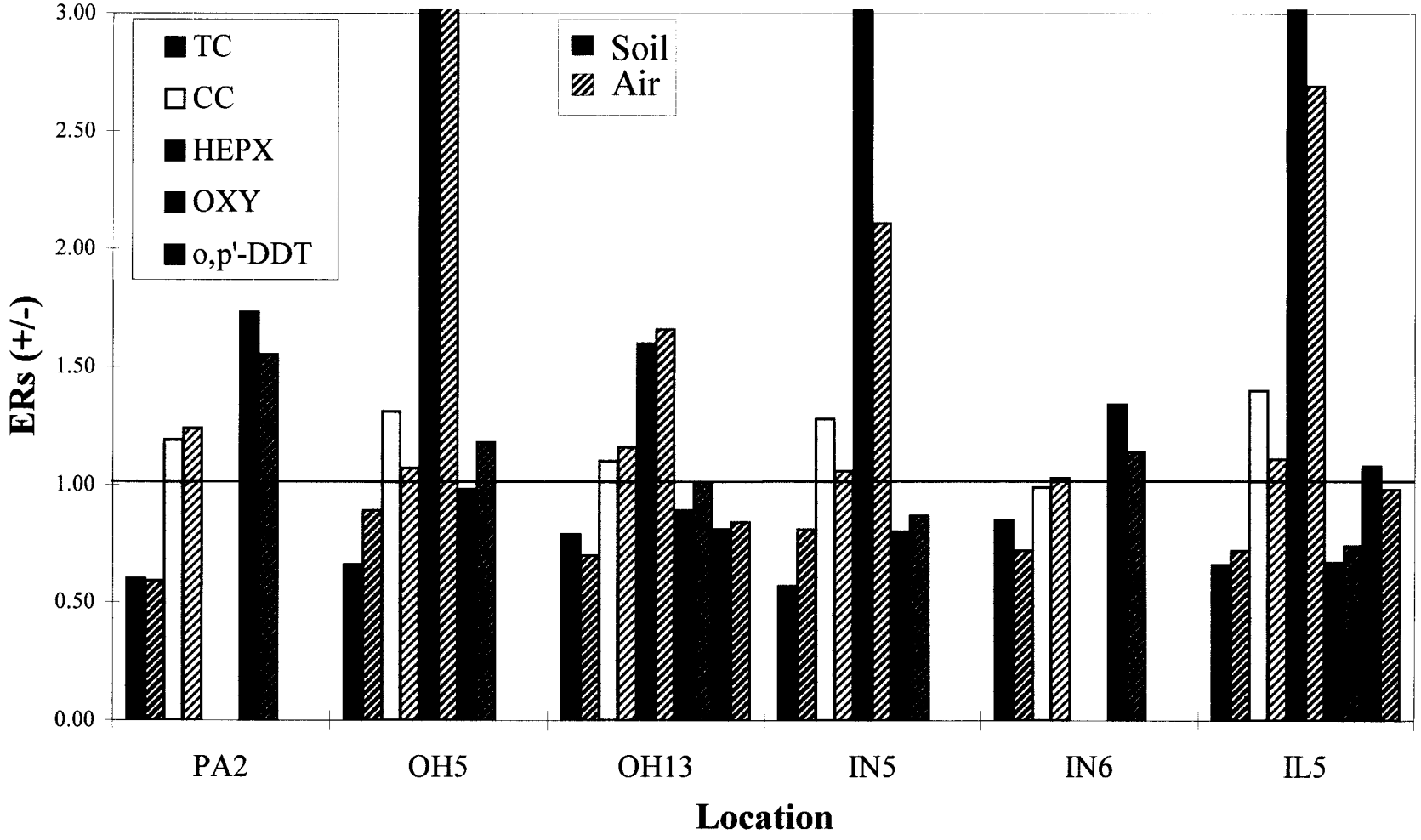


Figure 14. Comparison of soil/air-above-soil ERs by location.

garden soil and air (PA2-S and PA2-AS) showed the greatest amount of degradation for TC with values of 0.61 and 0.59, respectively. Again the "copying" of the soil ER signature into the air can be seen with 98% agreement between these two values. OH5-S, IN5-S, IN6-S and IL5-S all showed more degradation in the soil than was seen in corresponding air samples for TC, probably due to mixing with bulk air. For CC, in all samples, the soil shows more degradation than the air.

Oxychlordane

OXY ERs were determined for all six matched samples (Table 8). Like *o,p'*-DDT, some samples showed selective breakdown of the (-) enantiomer while others showed selective breakdown of the (+) enantiomer (see Figure 12). However, in all samples, air ERs mimicked soil ERs in direction of degradation and general magnitude of degradation (see Figure 16). The garden site (PA2-S) had OXY ER values of 1.66 for soil and 1.55 for air-above-soil (89% agreement). The IL5 site had ER values as low as 0.67 for soil and 0.74 for air-above-soil (93% agreement). Interestingly, the two Indiana sites, which were side by side fields, had opposite degradation patterns, where one degraded (+) OXY selectively and the other degraded (-) OXY selectively. One of these sites was the site of a former house which had been treated for chlordane for termite control.

Heptachlor epoxide

HEPX ERs were obtained for the five agricultural sites (Table 8, see Figure 14). Figure 17 shows chromatograms of HEPX in a standard, soil, and air above soil for IL5. HEPX ER values were considerably greater than 1.00 for both soil and air samples, and again showed a mimicking of direction and magnitude of degradation from soil to air.

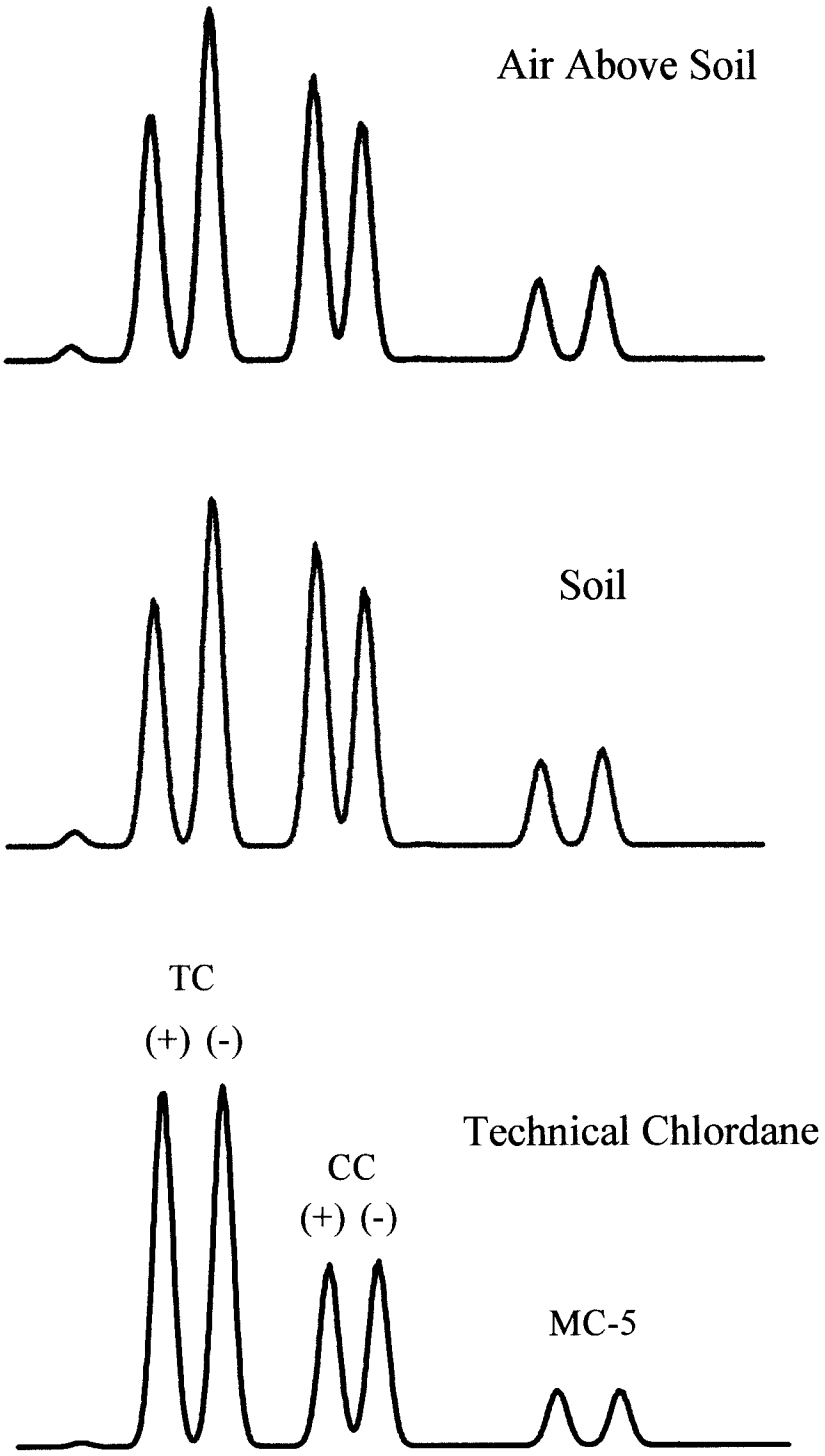


Figure 15. Chromatograms of chlorodanes in a standard, soil, and air above soil. (OH13)

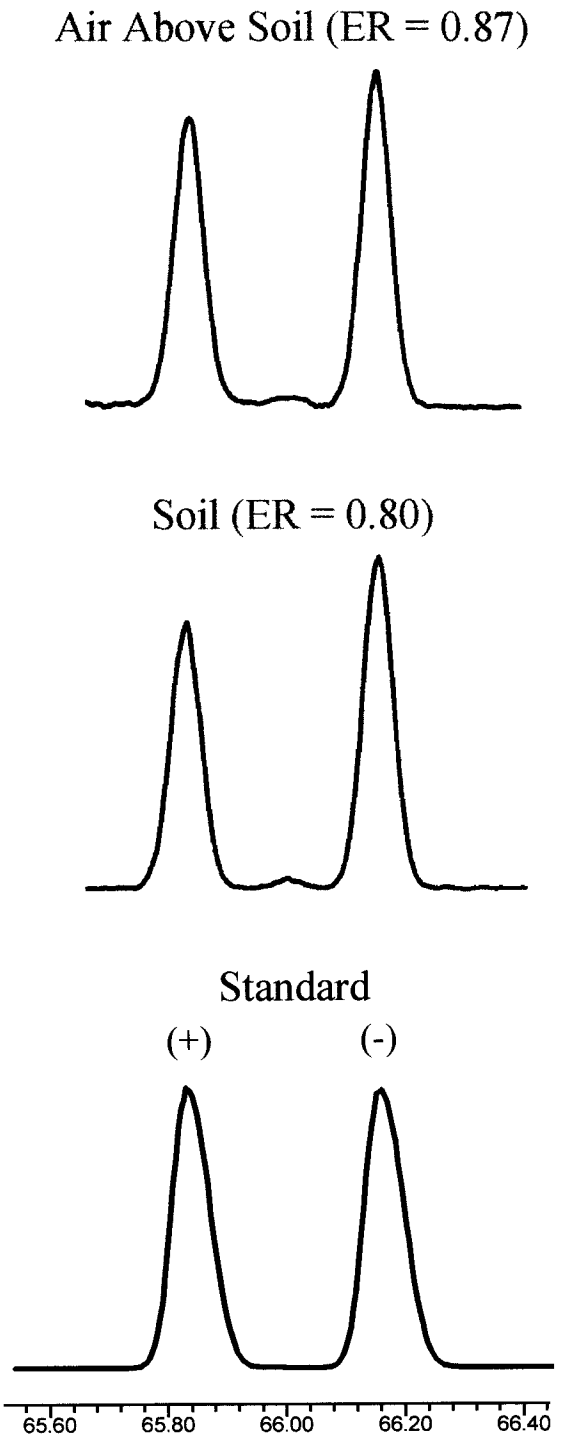


Figure 16. Chromatograms of OXY in a standard, soil, and air above soil (IN5).

Finizio et al. (1997) had a soil ER value of 1.39 and an air ER value of 1.37 (98% agreement) at 5 cm above the soil.

Indoor Air

Indoor air ER values were determined for TC, CC, and MC-5, another chiral chlordane component (Table 9). Figure 18 shows a chromatogram of chlordane in a typical indoor air sample. Twenty out of twenty-three samples taken had residues high enough to be analyzed for enantiomeric data. The standard deviation reported for samples is for the two different ions monitored for each compound, while the standard deviation of the standards are for replicate injections.

Indoor air ERs for all three components of chlordane were racemic with at least 96% agreement between standards and samples (98% agreement for the majority of samples). The mean ER values ± standard deviation were 0.99 ± 0.01 for TC (n=20), 0.99 ± 0.01 for CC (n=19). For samples with detectable levels of residues for enantiomeric analysis, no correlation was found between concentration and ER values. Wiberg et al. (1997) found values of 0.98 ± 0.01 for TC (n=8), and 1.00 ± 0.01 for CC (n=8) in indoor air of homes in Columbia, South Carolina.

Ambient Air

All seven of the ambient air samples were analyzed for enantiomeric data and ER values for these samples are given in Table 10. Figures 18 and 19 show sample chromatograms of chlordanes in indoor air and ambient air and α-HCH in ambient air.

Chlordane

The mean ER values ± standard deviation (Table 10) were 0.94 ± 0.02 for TC (n=7), and 1.04 ± 0.02 for CC (n=6). TC ER values ranged from 0.90-0.96 and CC ER

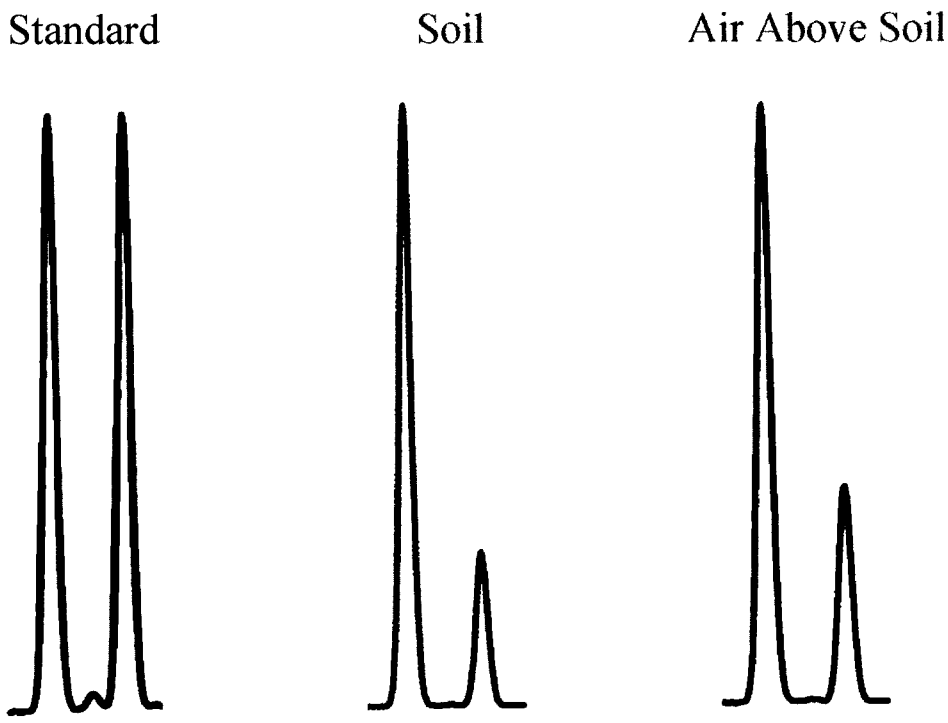


Figure 17. Chromatograms of HEPX in standard, soil, and air above soil (IL5).

Table 9. ERs ± Standard Deviation for Chlordanes in Indoor Air

Sample *Standard*	TC *1.00 ± 0.02*	CC *0.99 ± 0.01*	MC-5 *0.90 ± 0.01*
Pennsylvania			
PA1-IA	1.00 ± 0.01	ND*	ND
PA3-IA	0.99 ± 0.01	0.97 ± 0.01	ND
Ohio			
OH1-IA	1.00 ± 0.00	0.99 ± 0.00	ND
OH2-IA	0.98 ± 0.00	0.99 ± 0.00	0.99 ± 0.01
OH3-IA	1.01 ± 0.01	1.01 ± 0.01	1.01 ± 0.00
OH4-IA	1.00 ± 0.01	0.98 ± 0.04	ND
OH5-IA	0.99 ± 0.00	0.99 ± 0.01	1.03 ± 0.01
OH7-IA	0.99 ± 0.01	1.01 ± 0.01	ND
Indiana			
IN1-IA	1.00 ± 0.00	1.00 ± 0.01	ND
IN2-IA	0.97 ± 0.00	0.97 ± 0.01	1.01 ± 0.00
IN3-IA	0.99 ± 0.01	0.97 ± 0.00	1.01 ± 0.02
IN4-IA	1.00 ± 0.00	0.98 ± 0.02	ND
IN5-IA	1.01 ± 0.01	1.00 ± 0.01	1.00 ± 0.04
IN6-IA	1.00 ± 0.01	0.99 ± 0.00	1.01 ± 0.01
IN7-IA	0.99 ± 0.01	0.99 ± 0.01	1.00 ± 0.01
IN8-IA	0.99 ± 0.01	1.00 ± 0.01	1.00 ± 0.01
Illinois			
IL2-IA	0.97 ± 0.00	0.99 ± 0.01	ND
IL3-IA	1.00 ± 0.01	0.98 ± 0.01	ND
IL4-IA	0.99 ± 0.01	0.99 ± 0.01	0.96 ± 0.00
IL5-IA	0.99 ± 0.00	1.01 ± 0.01	1.03 ± 0.00
Mean:	**0.99 ± 0.01** **n=20**	**0.99 ± 0.01** **n=19**	**1.00 ± 0.02** **n=11**

values ranged from 1.00-1.07. Compared to indoor air from this study, ambient air samples show evidence of biological degradation similar to, although not as pronounced, as soil and air-above-soil samples (see Figure 18). Wiberg et al. (1997) reported ER values of 0.98 ± 0.03 (n=20) for TC, and 1.01 ± 0.04 (n=20) for CC in ambient air from Muscle Shoals, Alabama. They also reported ER values of 1.00 ± 0.01 (n=7) for TC, and 1.02 ± 0.01 (n=7) for CC in ambient air from Columbia, South Carolina. The ER values for ambient air in rural areas in the south (Wiberg et al., 1997) were more racemic than those found in rural areas in the cornbelt (this study). Wiberg et al. (1997) suggested evaporation from soils is only a minor source of chlordane to ambient air in Alabama and South Carolina compared to urban sources and long-range transport. These same authors also reported ERs from air over Lake Ontario as 0.91 ± 0.03 (TC) and 1.03 ± 0.03 (CC), and over Lake Superior as 0.87 ± 0.03 (TC) and 1.09 ± 0.03. Ulrich and Hites (1998) reported an average ER for air over Lakes Erie, Michigan, Ontario, and Superior as 0.88 ± 0.02 for TC and 1.05 ± 0.02 for CC. According to these studies, Great Lakes air shows degradation of chlordane similar to rural ambient air in the cornbelt region. These ERs fall between the ER values in air-above-soil (non-racemic) and home air (racemic), suggesting soils may be an important source of chlordane to ambient air in the Great Lakes region. A number of ambient and indoor air samples were taken at the same locations and the difference in enantiomeric signals are more noticeable by comparing these samples. In particular, a very noticeable difference can be seen in OH2-AA and OH3-IA, with ERs of 0.90 & 1.07 for ambient air and 1.01 & 1.01 for indoor air. OH1-AA and OH2-IA also shows this trend with ERs of 0.94 & 1.06 for ambient air and 0.98 & 0.99 for indoor air.

Table 10. Ambient Air ERs ± Standard Deviation

Sample	TC	CC	MC-5	α-HCH
Standard	***1.01 ± 0.01***	***0.99 ± 002***	***0.99 ± 0.01***	***1.01 ± 0.01***
PA1-AA	0.96 ± 0.02	1.00 ± 0.03	ND*	0.98 ± 0.01
PA2-AA	0.95 ± 0.01	1.02 ± 0.01	0.92 ± 0.04	1.03 ± 0.04
PA3-AA	0.95 ± 0.01	ND	0.95 ± 0.01	1.02 ± 0.01
OH1-AA	0.94 ± 0.01	1.06 ± 0.01	0.94 ± 0.04	0.94 ± 0.01
OH2-AA	0.90 ± 0.01	1.07 ± 0.01	0.91 ± 0.01	0.97 ± 0.01
OH3-AA	0.95 ± 0.01	1.01 ± 0.00	0.96 ± 0.01	1.00 ± 0.01
OH4-AA	0.92 ± 0.01	1.06 ± 0.01	0.94 ± 0.01	1.02 ± 0.00
Mean:	**0.94 ± 0.02**	**1.04 ± 0.03**	**0.94 ± 0.02**	**1.00 ± 0.03**

*ND = Not Determined; Below the Limit of Detection

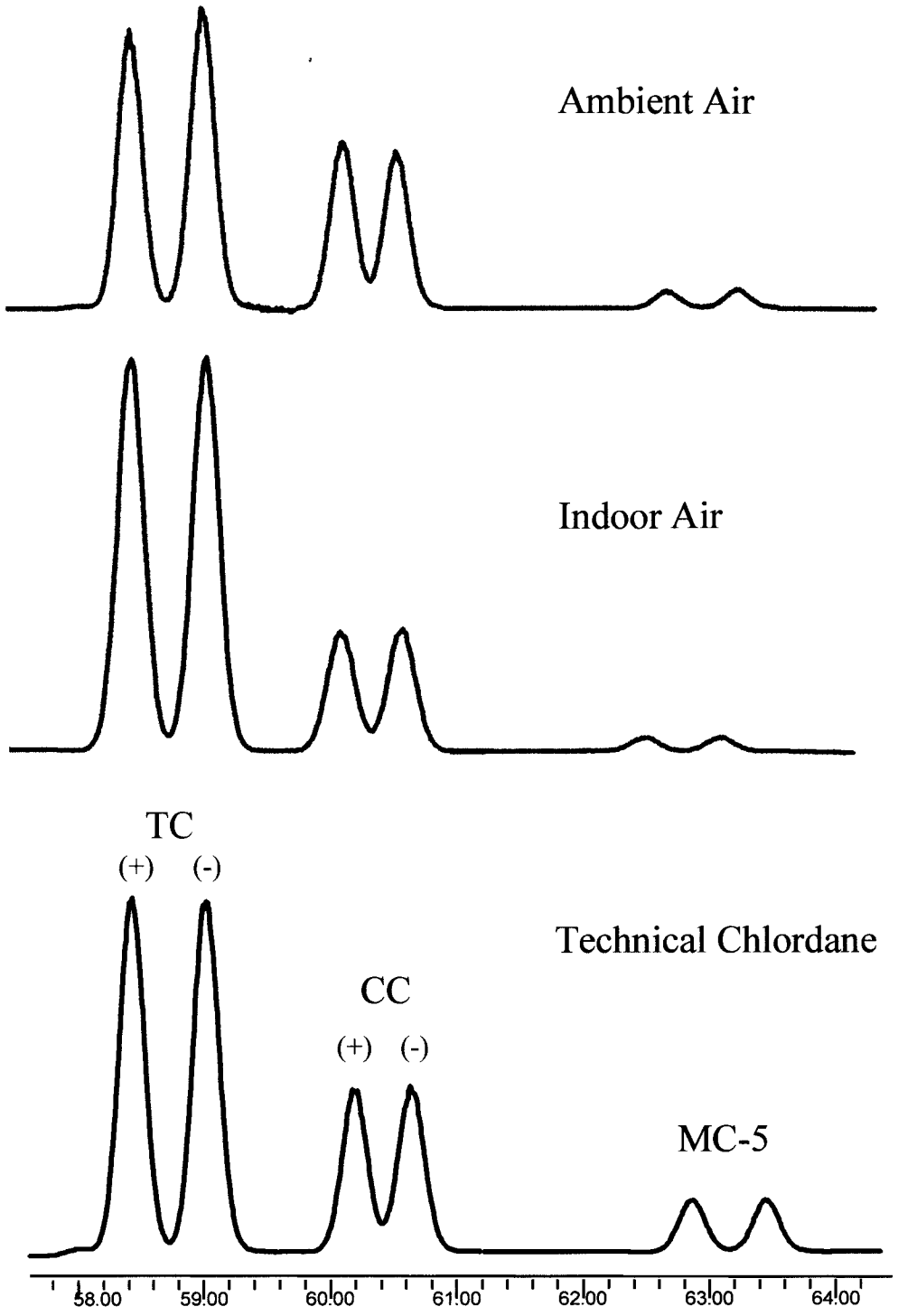


Figure 18. Chromatograms of chlordane in a standard, indoor air (IN1-IA), and ambient air (OH4-AA).

α-HCH

The mean ER ± standard deviation for α-HCH in all ambient air samples was 1.00 ± 0.03 (Table 10). Figure 19 shows chromatograms of α-HCH in a standard and a typical ambient air sample. Ambient air ERs are very close to racemic. Müller et al. (1992) found similar results in Norway where ERs for α-HCH in ambient air were also found to be racemic. Falconer et al. (1995) also found racemic ERs for α-HCH in air over Resolute Bay even though water samples from the small arctic lake showed selective degradation. Finizio et al. (1997) looked at α-HCH enantiomers in air samples above an agricultural soil in the Fraser Valley, British Columbia. Soil ERs showed substantial degradation of the (-) enantiomer (1.35) and the air samples taken above the soil showed a similar depletion of (-) α-HCH. α-HCH was below detection in the present study for all but one soil (where it was racemic) and all air above soils. Ridal et al. (1997) found seasonal variations of α-HCH in air taken over Lake Ontario with near racemic values for spring and fall and values as low as 0.91 for mid-summer. The authors suggest that air above the lake contains a mixture of selectively degraded α-HCH coming from volatilization out of the lake and racemic α-HCH coming from transport from locations where HCH may still be used. When temperatures are elevated, there is more volatilization out of the water and the air shows a stronger signature for an enantioselectively degraded source. During lower temperature seasons, when deposition of OCs into surface water is occurring, air ER signatures are dominated by bulk air coming from other parts of the world. Jantunen and Bidleman (1996) found similar results

in air samples taken over Arctic and sub-Arctic waters with ERs deviating from 1.00 during periods of high temperature.

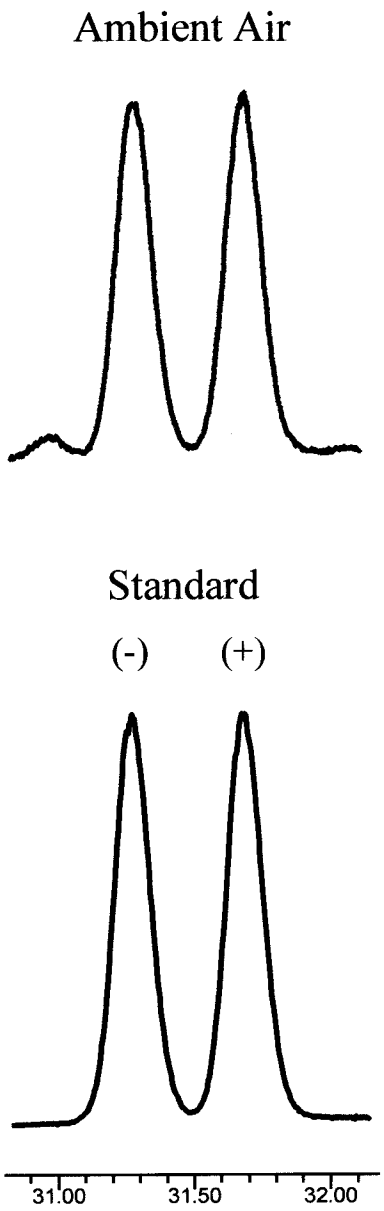


Figure 19. Chromatograms of α-HCH in a standard and ambient air (PA3-AA).

Chapter Six
Conclusions

Concentrations were determined for twelve compounds (*o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *cis*-chlordane, *trans*-chlordane, heptachlor, heptachlor epoxide, aldrin, dieldrin, α-hexachlorocyclohexane, and *trans*-nonachlor) in 29 soil samples, twenty-three indoor air samples, and four ambient air samples. The DDT compounds were found in the largest number of samples (22 out of 29) and had the highest concentrations of all the compounds analyzed in the soil. OC concentrations in air were considerably less than those in soils, and levels in ambient air were, on average, 100 times less than in indoor air. For air, chlordane was found in the largest number of samples (22 out of 23) and had the highest concentrations of all the compounds analyzed.

Enantiomeric analysis of soil and air samples gave enantiomeric excesses for five compounds: *o,p'*-DDT, *cis*-chlordane, *trans*-chlordane, oxychlordane, and heptachlor epoxide, with the largest excesses for heptachlor epoxide. For most compounds, soils showed ERs different from 1.00, implying that biological degradation is occurring in soil. The preservation of ER profiles upon volatilization out of the soil was seen in six air samples taken directly above agricultural soils. Indoor air samples showed values very close to racemic, suggesting that biological, enzyme-driven sources are not breaking down OC pesticides used for termite control in homes. As can be seen in Figure 20, the ambient air samples show an ER somewhere in between those of agricultural soils and indoor air. This suggests that OC pesticides seen in bulk air may be coming from a combination of sources, including volatilization of old soil residues and volatilization out of house foundations previously treated for termites.

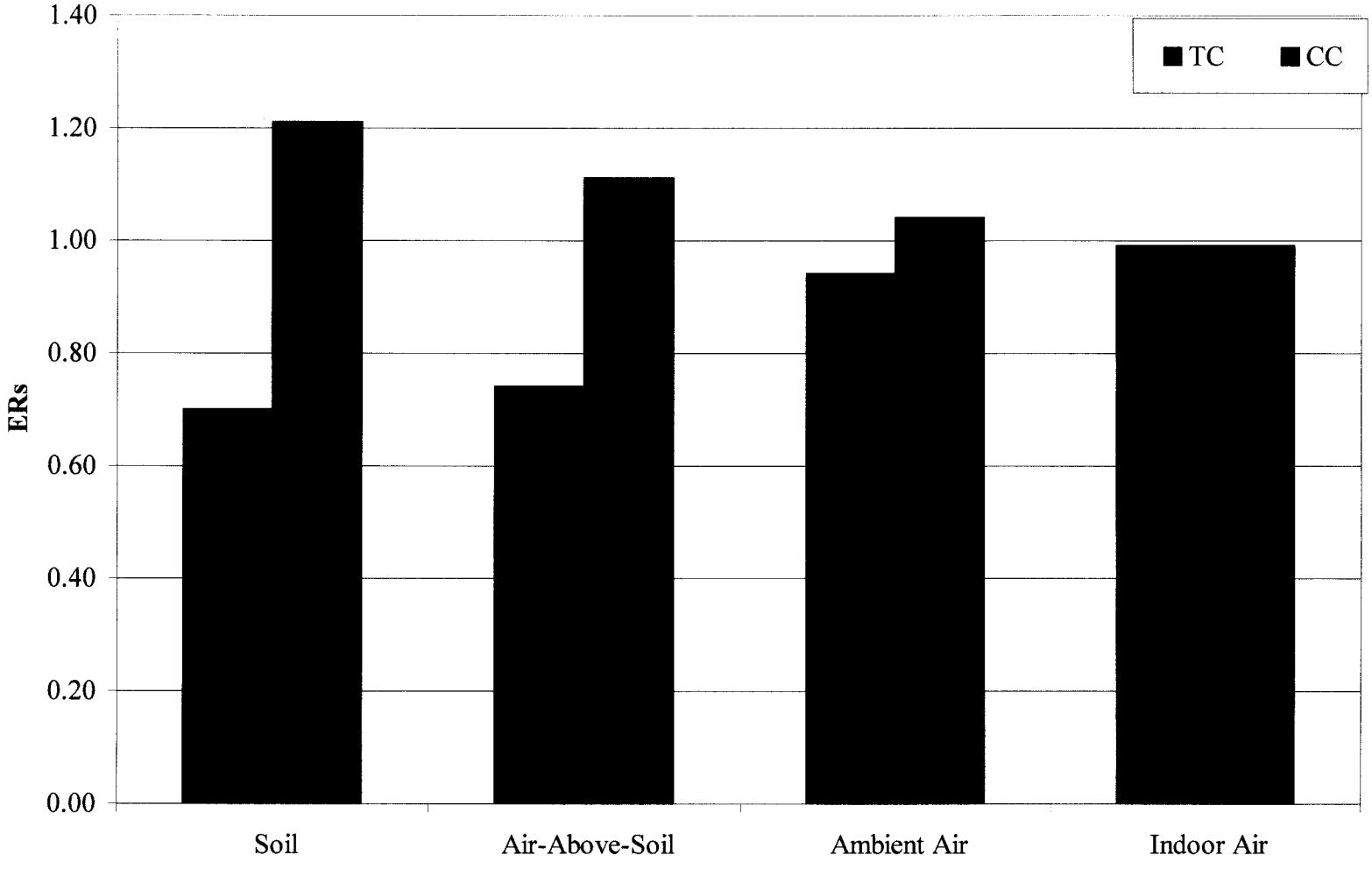


Figure 20. Comparison of ERs for TC and CC in different samples.

Furthermore, countries still using OC pesticides may be contributing significantly to global contamination. This is supported by a study done by Iwata et al. (1993) where considerably higher levels of HCHs were found in northern hemisphere air and water samples (taken from locations that border India and eastern Asia, countries that continue to use HCH heavily) than in southern hemisphere samples. Racemic ERs may signify a source that has not been degraded enantioselectively due to limited exposure to biological activity over time, as in the case of some termiticides. Racemic ERs in the atmosphere may also signify a new source that volatilized before it had time to degrade significantly. Since there is little biological activity in air, freshly applied sources that travel through the air, with very little interaction with soil, sediment, or water, would have the same ER signature as when they were applied. On the other hand, residues volatilizing out of soils contaminated decades ago are likely to show signs of microbial degradation, such as non-racemic ERs. For these reasons, enantiomeric ratios of chiral OC pesticides may be useful as a tool for determining sources to the atmosphere.

In order to more completely understand the importance of old soil residues as a source to the atmosphere, one could look at gradients above soil, as in the study by Finizio et al. (1997). If ER signatures in the air can be traced back to the soil, source apportionment studies might allow for quantifying the relative impact of different sources. More soil and air data spanning a larger area is necessary to make conclusive statements to develop global trends, and to apply models designed to determine fate and transport of contaminants in the environment. Also, a dire need exists to determine which, if any, microbes are responsible for enantiomeric degradation in environmental media and the

mechanisms they employ. These types of studies could lead to bioremediation technologies for clean-up of contaminated areas.

References

Aigner, E.; Leone, A.; Falconer, R. *Environ. Sci. Technol.* **1998**, *32*, 1162-1168.

Anderson, D.; Hites, R. *Environ. Sci. Technol.* **1988**, *22*, 717-720.

Anderson, D.; Hites, R. *Atmos. Environ.* **1989**, *23*, 2063-2066.

Armstrong, D.W.; Reid, G.L.; Hilton, M.L.; Chang, C.D. *Environmental Pollution.* **1993**, *79*, 51-58.

Ariëns, E.J. *Chiral Separations by HPLC.* **1989**, 31-68.

Berthod, A.; Li, W.; Armstrong, D. *Anal. Chem.* **1992**, *64*, 873-879.

Bidleman, T.; Jantunen, L.; Wiberg, K.; Harner, T.; Brice, K.; Su, K.; Falconer, R.; Leone, A.; Aigner, E.; Parkhurst, W. *Environ. Sci. Technol.* **1998**.

Buser, H.-R.; Müller, M.D. *Anal. Chem.* **1992**, *64*, 3168-3175.

Buser, H.-R.; Müller, M.D.; Rappe, C. *Environ. Sci. Technol.* **1992**, *26*, 1533-1540.

Buser, H.-R.; Müller, M.D. *Anal. Chem.* **1995a**, *67*, 2691-2698.

Buser, H.-R.; Müller, M.D. *Environ. Sci. Technol.* **1995b**, *29*, 664-672.

Connell, D. Basic Concepts of Environmental Chemistry; Lewis: Boca Raton, FL, **1997**, Chapter 8.

Cremlyn, R. Pesticides: Preparation and Mode of Action; John Wiley & Sons: New York, **1978**, Chapter 5.

Dimond, H.; Owen, R.B. *Environ. Pollut.* **1996**, *92*, 227-230.

ECE-LRTAP, **1994**. State of Knowledge Report of the U.N. ECE Task Force on Persistent Organic Pollutants. U.S. Government Printing Office: Washington, D.C., draft.

Edwards, C.A. **1973**. Persistent Pesticides in The Environment; CRC Press: Cleveland, OH, pp. 6-21.

Falconer, R.L.; Bidleman, T.F.; Gregor, D.J. *The Science of the Total Environment.* **1995**, *160/161*, 65-74.

Falconer, R.L.; Bidleman, T.F.; Gregor, D.J.; Semkin, R.; Teixeira, C. *Environ. Sci. Technol.* **1995**, *29*, 1297-1302.

Falconer, R.L.; Bidleman, T.F.; Szeto, S.Y. *J. Agric. Food Chem.* **1997**, *45*, 1946-1951.

Fed. Regist. **1978**, *43*, 12372-31433.

Finizio, A.; Bidleman, T.F.; Szeto, S.Y. *Chemosphere*. **1997**, *36*, 345-355.

Frear, D.E.H. Chemistry of the Pesticides; D. van Nostrand: New York, **1955**, Chapter 4.

Freeman, H.P.; Taylor, A.W.; Edwards, W.M. *J. Agric. Food Chem.* **1975**, *23*, 1101-1105.

Garrison, W.; Schmitt, P.; Martens, D.; Kettrup, A. *Environ. Sci. Technol.* **1996**, *30*, 2449-2455.

Hargrave, B.; Vass, W.; Erickson, P.; Fowler, B. *Tellus*. **1988**, *40B*, 480-493.

Hargrave, B.T.; Harding, G.C.; Vass, W.P.; Erickson, P.E.; Fowler, B.R.; Scott, V. *Arch. Environ. Contam. Toxicol.* **1992**, 22, 41-54.

Hitch, R.K.; Day, H.R. *Bull. Environ. Contam. Toxicol.* **1992**, *48*, 259-264.

Jantunen, L.M.; Bidleman, T.F. *J. Geophys. Res.* **1996**, *101*, 28837-28846.

Juvancz, Z.; Alexander, G.; Szejtli, J. *J. High Resolut. Chromatogr.* **1987**, *10*, 105-107.

Manahan, S.E. Environmental Chemistry; Lewis: Boca Raton, **1994**, p 201.

McEwen, F.; Stephenson, G. *The Use of Significance of Pesticides in the Environment*; John Wiley & Sons: **1979**, Chapters 3 & 4.

Müller, M.D. ; Buser, H.-R. *Anal. Chem.* **1994**, *66*, 2155-2162.

Müller, M.D.; Schlabach, M.; Oehme, M. *Environ. Sci. Technol.* **1992**, *26*, 566-569.

Nomeir, A.; Hajjar, N. *Rev. Environ. Contam. Toxicol.* **1987**, *100*, 1-22.

PHS, **1992**. Toxicological Profile for 4,4'-DDT, 4,4'-DDE, 4,4'-DDD; U.S Department of Health & Human Services. Public Health Service. U.S. Government Printing Office: Washington, D.C., Draft for public comment.

PHS, **1992**. Toxicological Profile for Aldrin, Dieldrin; U.S. Department of Health & Human Services. Public Health Service. U.S. Government Printing Office: Washington, D.C.; TP-92/01.

PHS, **1992**. Toxicological Profile for Chlordane; U.S. Department of Health & Human Services. Public Health Service. U.S. Government Printing Office: Washington, D.C., Draft for public comment.

PHS, **1992**. Toxicological Profile for Heptachlor, Heptachlor Epoxide; U.S. Department of Health & Human Services. Public Health Service. U.S. Government Printing Office: Washington, D.C.; TP-92/11.

Ridal, J.J.; Bidleman, T.F.; Kerman, B.R.; Fox, M.E.; Strachan, W.M. *Environ. Sci. Technol.* **1997**, *31*, 1940-1945.

Sovocool, G.W.; Lewis, R.G.; Harless, R.L.; Wilson, N.K.; Zehr, R.D. *Anal. Chem.* **1977**, *49*, 734-740.

Spiro, T.G.; Stigliani, W.M. Chemistry of the Environment; Prentice-Hall: Upper Saddle River, N.J., **1996**, pp 274-283.

Sweet, C.; Harlin, K.; Gatz, D.; Bauer, S. *Great Lakes Integrated Atmospheric Deposition Network Data Report 1993-1994*, Illinois State Water Survey, Champaign, IL. March, **1996**.

Szeto, S.Y.; Price, P.M. *J. Agric. Food Chem.* **1991**, *39*, 1679-1684.

Tanabe, S.; Hidaka, H.; Tatsukawa, R.; *Chemosphere*. **1983**, 12, 277-288.

Ulrich, E.; Hites, R. *Environ. Sci. Technol.* **1998**, in press.

Umland, J. General Chemistry; West Publishing: St. Paul, M.N., **1993**, Chapter 22.

Vetter, W.; Schurig, V. *Journal of Chromatography A.* **1997**, 143-175.

Wallace, J.; Brzuzy, L.; Simonich, S.; Visscher, S.; Hites, R. *Environ. Sci. Technol.* **1996**, *30*, 2715-2718.

Ware, G. Pesticides: Theory and Application; W.H. Freeman: New York, **1983**, Chapter 4.

White-Stevens, R., Ed. Pesticides in the Environment, Volume 1; Marcel Dekker: New York, **1971**, Chapter 1.

WHO/IARC. *Occupational Exposures in Insecticide Application, and some Pesticides*; IARC Monographs on the Evaluation of Carcinogenic Risks to Humans 53; World Health Organization, International Agency for Research on Cancer; Lyon, France, **1991**; p. 115-177.

Wiberg, K.; Jantunen, L.; Harner, T.; Wideman, J.; Bidleman, T.; Brice, K.; Su, K.; Falconer, R.; Leone, A.; Parkhurst, W.; Alegria, H. *Organohalogen Compds.* **1997**, *33*, 209-213.

Appendix

Table A-1. Percent Water in Soil Samples

Sample	*Wt. Beaker, g*	*Wt. Wet Soil, g*	*Wt. Dry Soil + Beaker, g*	*Wt. Dry Soil, g*	*% Sample*	*% H_2O*
Pennsylvania						
PA1-S	83.2646	18.5636	99.0515	15.7869	*85.0%*	*15.0%*
PA2-S	85.5971	19.8078	100.5762	14.9791	*75.6%*	*24.4%*
PA3-S	83.4730	19.5062	97.7602	14.2872	*73.2%*	*26.8%*
PA4-S	82.7323	17.0847	95.8265	13.0942	*76.6%*	*23.4%*
Ohio						
OH1-S	85.5176	17.1157	98.6273	13.1097	*76.6%*	*23.4%*
OH2-S	81.6012	17.2364	96.0718	14.4706	*84.0%*	*16.0%*
OH3-S	83.2267	17.6654	98.3619	15.1352	*85.7%*	*14.3%*
OH4-S	82.2450	16.3897	90.7174	8.47240	*51.7%*	*48.3%*
OH5-S	84.1771	17.3592	98.6199	14.4428	*83.2%*	*16.8%*
OH6-S	88.4238	17.0846	103.4834	15.0596	*88.1%*	*11.9%*
OH7-S	85.3114	17.1117	98.0096	12.6982	*74.2%*	*25.8%*
OH8-S	82.1735	17.4491	95.9995	13.8260	*79.2%*	*20.8%*
OH9-S	82.6096	16.8753	96.1325	13.5229	*80.1%*	*19.9%*
OH10-S	87.0623	17.0549	100.8419	13.7796	*80.8%*	*19.2%*
OH11-S	87.3081	17.6473	101.4747	14.1666	*80.3%*	*19.7%*
OH12-S	84.0560	17.3777	97.9173	13.8613	*79.8%*	*20.2%*
Indiana						
IN1-S	82.7494	17.5851	97.5634	14.8140	*84.2%*	*15.8%*
IN2-S	83.3042	17.2624	97.8884	14.5842	*84.5%*	*15.5%*
IN3-S	82.6509	16.4731	96.4397	13.7888	*83.7%*	*16.3%*
IN4-S	75.5214	17.3589	88.5288	13.0074	*74.9%*	*25.1%*
IN5-S	84.6843	18.1982	99.5494	14.8651	*81.7%*	*18.3%*
IN6-S	83.3657	16.6348	98.1758	14.8101	*89.0%*	*11.0%*
IN7-S	81.6741	17.7349	96.5662	14.8921	*84.0%*	*16.0%*
Illinois						
IL1-S	83.2527	17.7874	97.6015	14.3488	*80.7%*	*19.3%*
IL2-S	82.1703	17.0730	95.5628	13.3925	*78.4%*	*21.6%*
IL3-S	87.3232	16.8876	100.4278	13.1046	*77.6%*	*22.4%*
IL4-S	75.4796	17.2369	89.0985	13.6189	*79.0%*	*21.0%*
IL5-S	82.7114	17.5679	96.8265	14.1151	*80.3%*	*19.7%*
Ohio	**(Duplicates)**					
OH1-S	85.3463	17.2592	98.5909	13.2446	*76.7%*	*23.3%*
OH2-S	84.2334	18.6548	99.8640	15.6306	*83.8%*	*16.2%*
OH4-S	88.4764	18.6564	98.4480	9.9716	*53.4%*	*46.6%*
OH5-S	82.1873	17.2023	96.5171	14.3298	*83.3%*	*16.7%*
OH8-S	86.4919	17.0568	99.9631	13.4712	*79.0%*	*21.0%*
OH12-S	81.6878	18.9516	96.8389	15.1511	*79.9%*	*20.1%*

Table A-2. Spike Recoveries (%) of OC Pesticides in Soil

Spike #	α-HCH	γ-HCH	HEPT	HEPX+OXY	Dieldrin	TC	CC	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT
1	87.7	93.4	91.1	99.0	102.3	112.7	111.5	124.5	114.0	105.7
2	85.9	90.2	93.0	94.7	106.4	110.3	108.9	120.1	113.9	110.2
3	84.8	88.5	89.9	96.5	104.7	107.9	107.2	120.1	110.3	104.5
4	78.2	83.0	84.0	98.1	106.4	107.9	107.6	119.7	111.0	101.3
5	83.2	86.7	89.3	93.6	112.1	113.5	113.3	127.4	119.5	110.9
Average	**84.0**	**88.4**	**89.5**	**96.4**	**106.4**	**110.5**	**109.7**	**122.4**	**113.7**	**106.5**

Table A-3. Nanograms of OC Pesticides in PUF Blanks and LOD Values

(Limit of Detection (LOD)=Mean Blank(ng)+3 x Standard Deviation of the Means)

Ambient (Large PUF)

	HEPT	HEPX	TC	CC	TN	Dieldrin	*p,p'*-DDE	*p,p'*-DDD	o,*p'*-DDT	*p,p'*-DDT
Blank 1	ND	ND	0	ND	ND	0	ND	ND	ND	9.60
Blank 2	ND	ND	0.05	ND	ND	0.41	ND	ND	ND	17.7
Blank 3	ND	ND	0	ND	ND	0	ND	ND	ND	7.99
Blank 4	ND	ND	0	ND	ND	0	ND	ND	ND	15.6
Mean			**0.01**			**0.10**				**12.7**
Std. Dev.			**0.03**			**0.20**				**4.65**
LOD			**0.10**			**0.71**				**26.6**

Indoor (Small PUF)

Blank 1	ND	ND	0	ND	0	ND	ND	ND	ND	18.1
Blank 2	ND	ND	0	ND	0	ND	ND	ND	ND	28.9
Blank 3	ND	ND	0.26	ND	0	ND	ND	ND	ND	23.7
Blank 4	ND	ND	0	ND	0.36	ND	ND	ND	ND	30.0
Mean			**0.07**		**0.09**					**25.2**
Std. Dev.			**0.13**		**0.18**					**5.46**
LOD			**0.46**		**0.63**					**41.6**

Table A-4. Spike Recoveries of OC Pesticides in Small and Large PUF (%)

Small PUF (Indoor Air)

Spike #	α-HCH	γ-HCH	HEPT	HEPX	TC	CC	Dieldrin	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT
1	13.7	35.1	68.8	104.2	92.2	99.2	99.6	118.5	78.2	88.8
2	3.57	19.9	72.8	121.1	106.9	114.8	114.4	140.9	81.6	95.2
3	22.3	45.0	88.6	119.6	103.8	111.8	113.0	137.1	90.6	102.5
4	29.4	49.5	69.5	115.4	101.9	110.5	111.4	128.5	91.8	98.8
5	3.71	9.85	76.5	107.8	97.6	105.7	106.2	132.8	75.1	96.3
Average	**14.5**	**31.9**	**75.2**	**113.6**	**100.5**	**108.4**	**108.9**	**131.6**	**83.5**	**96.3**

Large PUF (Ambient Air)

Spike #	α-HCH	γ-HCH	HEPT	HEPX	TC	CC	Dieldrin	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT
1	42.6	47.0	71.8	103.4	94.0	101.9	101.5	115.6	85.7	112.6
2	21.7	38.6	78.8	114.6	103.6	111.4	111.8	126.9	89.8	104.6
3	14.7	34.3	75.1	115.4	104.5	112.3	112.7	131.8	89.9	105.2
4	19.1	34.7	74.6	107.0	97.6	104.9	105.5	122.8	86.2	99.9
5	42.9	53.1	78.8	113.0	102.7	111.1	112.1	134.0	97.9	112.9
Average	**28.2**	**41.5**	**75.8**	**110.7**	**100.5**	**108.3**	**108.7**	**126.3**	**89.9**	**107.0**

Table A-5. Nanograms (ng) of DDT Components in Soil

Sample	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	*o,p'*-DDT
Pennsylvania				
PA1-S	ND	20	ND	ND
PA2-S	16	1	ND	ND
PA3-S	ND	ND	ND	ND
PA4-S	2	15	ND	ND
Ohio				
OH1-S	3094	1806	42	202
OH2-S	ND	ND	ND	ND
OH3-S	ND	ND	ND	ND
OH4-S	13567	64689	3910	18194
OH5-S	ND	9	ND	ND
OH6-S	115	121	ND	37
OH7-S	9	14	ND	13
OH8-S	17	29	ND	4
OH9-S	4	8	4	7
OH10-S	157	77	ND	8
OH11-S	ND	6	ND	ND
OH12-S	26	37	ND	10
OH13-S				
Indiana				
IN1-S	5	19	13	ND
IN2-S	ND	20	ND	12
IN3-S	3	15	29	7
IN4-S	ND	ND	ND	ND
IN5-S	ND	ND	ND	ND
IN6-S	664	1460	204	625
IN7-S	ND	31	ND	10
Illinois				
IL1-S	ND	15	ND	ND
IL2-S	32	65	ND	9
IL3-S	126	152	ND	24
IL4-S	1	7	ND	11
IL5-S	330	198.0	ND	29
Minimum	1	1	4	4
Maximum	13567	64689	3910	18194
Geometric Mean	43	45	61	28

*ND = Not determined; below detection

Table A-6. Nanograms (ng) of OC Pesticides in Soil

Sample	TC	CC	TN	HEPT	HEPX+OXY	Dieldrin	α-HCH
Pennsylvania							
PA1-S	0.8	2	4	ND	ND	ND	1
PA2-S	152	307	342	5	19	52	8
PA3-S	ND	ND	ND	ND	ND	ND	6
PA4-S	8	3	2	ND	1	1	2
Ohio							
OH1-S	ND	ND	ND	5	ND	ND	4
OH2-S	88	92	78	0	23	ND	1
OH3-S	ND	0	ND	ND	ND	ND	ND
OH4-S	4778	1594	804	476	1021	35971	ND
OH5-S	63	28	31	5	220	1024	2
OH6-S	ND	1	1	2	ND	10	0.8
OH7-S	19	4	2	5	12	6	4
OH8-S	1	3	2	0.2	4	ND	ND
OH9-S	10	2	1	2	5	1	ND
OH10-S	ND	6	ND	2	ND	ND	6
OH11-S	ND	ND	ND	ND	ND	ND	0.9
OH12-S	8	17	17	ND	13	327	1
OH13-S							
Indiana							
IN1-S	0.8	2	2	0.02	ND	420	3
IN2-S	40	12	9	13	89	15	2
IN3-S	12	2	6	ND	2	ND	1
IN4-S	6	ND	36	6	9	207	4
IN5-S	20	12	36	4	165	747	4
IN6-S	2280	2750	1352	33	410	ND	17
IN7-S	208	77	72	18	592	1026	1
Illinois							
IL1-S	2	2	4	ND	14	189	0.4
IL2-S	0.8	1	3	2	6	154	0.2
IL3-S	58	25	25	5	163	161	1
IL4-S	1	2	1	ND	4	1	2
IL5-S	23	13	41	6	142	28	2
Minimum	0.80	0.02	1.00	0.02	0.90	1.00	0.20
Maximum	4778	2750	1352	476	1021	35971	17
Geometric Mean	17	9	13	3	29	74	2

*ND = Not determined; below detection

Table A-7. Percent Total Organic Carbon in Soils

Sample	% TOC	Duplicates
PA1-S	1.67	
PA2-S	2.24	
OH1-S	2.20	
OH2-S	2.06	
OH4-S	33.74	
OH5-S	1.40	
OH6-S	0.74	
OH7-S	2.40	
OH8-S	1.49	
0H10-S	1.28	
OH12-S	3.17	2.26
OH13-S	1.58	
OH17-S	2.54	
IN1-S	1.25	
IN2-S	7.60	
IN5-S	1.50	
IN6-S	2.13	
IN7-S	1.96	
IL1-S	2.01	
IL2-S	2.75	
IL3-S	3.02	
IL4-S	2.32	
IL5-S	1.94	1.90

Table A-8. Indoor Air Volumes

Sample	Time (min)	Average Flow (L/min)	Liters Air	m^3 Air
PA1-IA	480	28.8	13800	13.80
PA2-IA	420	30.8	12936	12.94
PA3-IA	663	31.1	20619	20.62
OH1-IA	491	29.3	14362	14.36
OH2-IA	485	30.4	14744	14.74
OH3-IA	484	27.9	13479	13.48
OH4-IA	480	27.7	13296	13.30
OH5-IA	449	30.3	13582	13.58
OH6-IA	536	30.5	16348	16.35
OH7-IA	475	30.1	14298	14.30
IN1-IA	496	28.8	14260	14.26
IN2-IA	585	30.3	17726	17.73
IN3-IA	473	30.4	14379	14.38
IN4-IA	588	30.4	17875	17.88
IN5-IA	339	31.3	10611	10.61
IN6-IA	500	29.6	14800	14.80
IN7-IA	518	30.2	15644	15.64
IN8-IA	490	29.5	14431	14.43
IL1-IA	555	31.0	17205	17.21
IL2-IA	560	29.3	16408	16.41
IL3-IA	495	30.2	14924	14.92
IL4-IA	470	29.1	13677	13.68
IL5-IA	555	29.0	16095	16.10
			Average	***15.02***

Table A-9. Nanograms (ng) of OC Pesticides in Indoor Air

Fractions:	*F1*	*F2(BA)†*	*F2*	*F2*	*F1+F2*	*F1+F2*	*F2(BA)*	*F1+F2*	*F1+F2*	*F1+F2*	*F1+F2*
Sample	**HEPT**	**HEPX+OXY**	**TC**	**CC**	**TN**	**Aldrin**	**Dieldrin**	***p,p'*-DDE**	***p,p'*-DDD**	***o,p'*-DDT**	***p,p'*-DDT**
PA1-IA	3.130	ND*	2.382	2.664	1.279	ND	7.394	4.890	0.551	5.779	ND
PA2-IA	2.568	ND	ND	ND	ND	ND	0.920	2.075	ND	1.393	ND
PA3-IA	2.898	ND	1.986	2.744	1.793	ND	3.949	8.658	2.393	15.145	ND
OH1-IA	79.046	ND	37.817	27.504	21.458	ND	22.909	4.894	0.794	1.776	ND
OH2 -IA	31.650	ND	30.669	22.991	14.577	ND	1.976	4.692	ND	3.946	ND
OH3-IA	3.351	ND	4.625	4.543	3.020	ND	3.675	1.404	ND	0.716	ND
OH4-IA	4.897	ND	2.761	2.619	1.740	ND	6.623	13.480	3.593	16.182	ND
OH5-IA	34.088	ND	17.004	12.591	7.834	ND	4.398	1.991	ND	ND	ND
OH6-IA	1.325	ND	ND	ND	ND	ND	ND	0.597	1.839	ND	ND
OH7-IA	1.893	ND	0.421	0.880	0.282	ND	ND	ND	ND	ND	ND
IN1-IA	112.575	ND	27.357	15.400	23.655	ND	2.151	ND	ND	ND	ND
IN2-IA	1393.932	77.344	1541.251	1125.712	381.264	ND	16.457	40.081	24.398	110.171	10.219
IN3-IA	123.757	5.916	100.114	76.671	71.569	ND	20.527	4.835	8.996	10.178	ND
IN4-IA	14.418	ND	6.860	5.456	5.372	ND	2.053	0.500	ND	ND	ND
IN5-IA	11.381	ND	67.450	56.171	53.592	ND	3.894	6.131	10.499	8.754	ND
IN6-IA	8.779	ND	6.470	5.582	3.707	ND	2.487	0.543	ND	ND	ND
IN7-IA	717.126	26.684	484.567	344.862	231.039	173.729	2.863	5.457	11.882	4.493	ND
IN8-IA	122.793	20.984	210.208	154.899	105.322	1261.629	521.344	122.269	14.155	169.087	73.530
IL1-IA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
IL2-IA	0.850	ND	0.257	0.704	ND	ND	12.928	1.034	ND	ND	ND
IL3-IA	176.646	8.460	47.652	17.294	12.179	ND	6.537	2.629	0.825	2.855	ND
IL4-IA	3.112	ND	1.473	1.919	0.951	ND	5.369	5.712	ND	2.037	ND
IL5-IA	8.731	ND	2.382	2.262	1.961	ND	5.255	5.714	ND	3.190	ND

†BA=Pre-Acid

*ND=Not Determined

Table A-10. Ambient Air Volumes

Volumes

Sample	Time (min)	Mag Avg.	m^3/min	L/min	Volume m^3 Air
PA1-AA	1352	32.0	0.490	490	662.48
PA2-AA	2545	23.0	0.715	715	1819.68
PA3-AA	1425	37.0	0.365	365	520.13
OH1-AA	1447	30.0	0.540	540	781.38
OH2-AA	1750	36.0	0.390	390	682.50
OH3-AA	1873	33.5	0.453	453	847.53
OH4-AA	1619	30.5	0.528	528	854.02
			Mean =	***497***	

Table A-11. Nanograms of Organochlorine Pesticides in Ambient Air

Sample	HEPT	HEPX+OXY	TC	CC	TN	Dieldrin	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT
PA2-AA	3.577	34.308	2.045	4.691	2.069	17.708	2.031	ND*	ND	ND
PA3-AA	10.577	6.816	13.681	13.895	13.566	ND	9.298	1.143	6.905	ND
OH3-AA	15.087	4.711	10.719	8.057	5.438	4.941	22.222	0.981	2.868	ND
OH4-AA	6.599	6.766	11.773	15.706	8.081	9.035	12.672	1.924	2.342	ND

Figure A-1. Standard calibration plot (linear) of *o,p'*-DDT for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

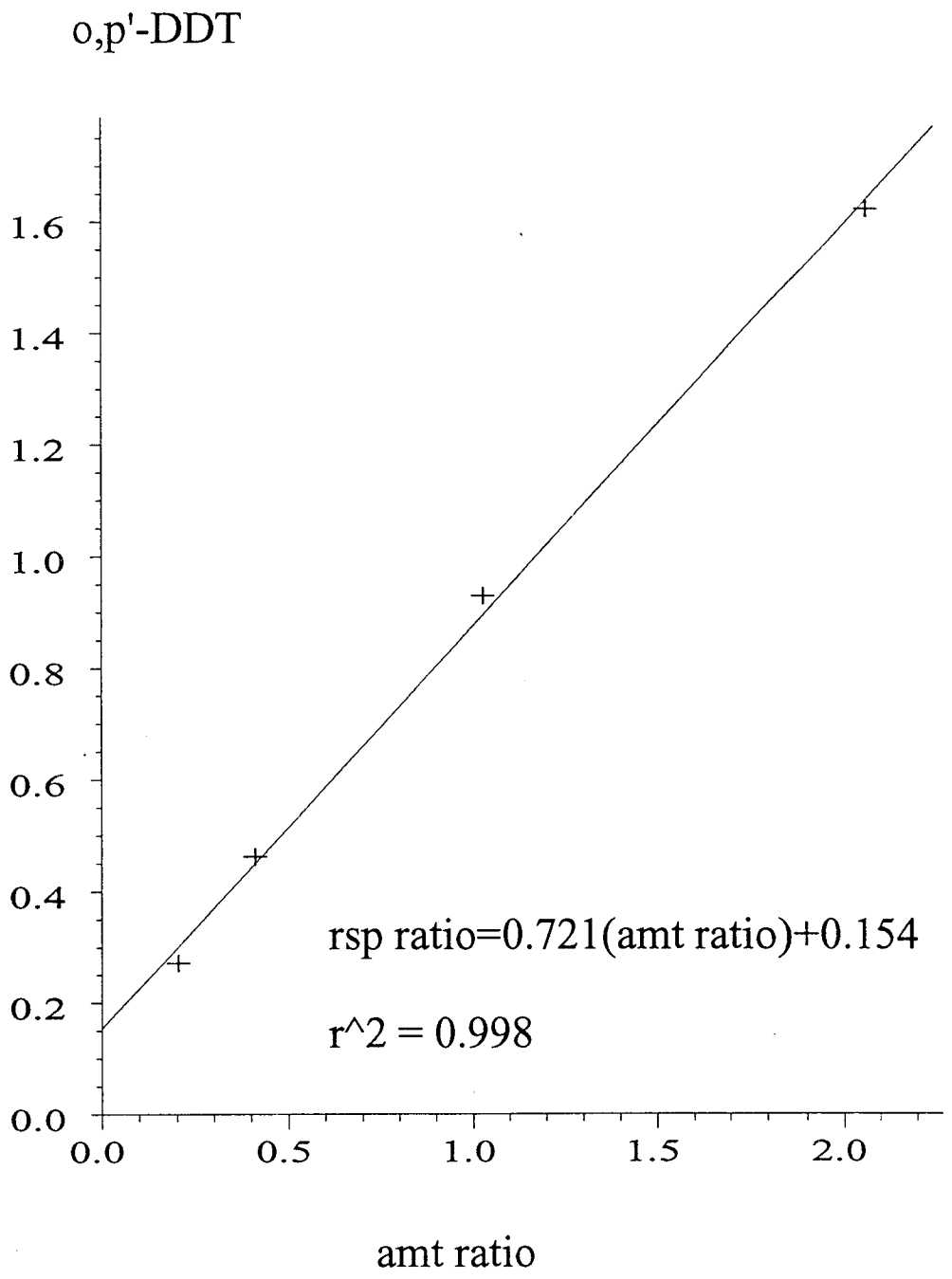


Figure A-2. Standard calibration plot (linear) of *p,p'*-DDT for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

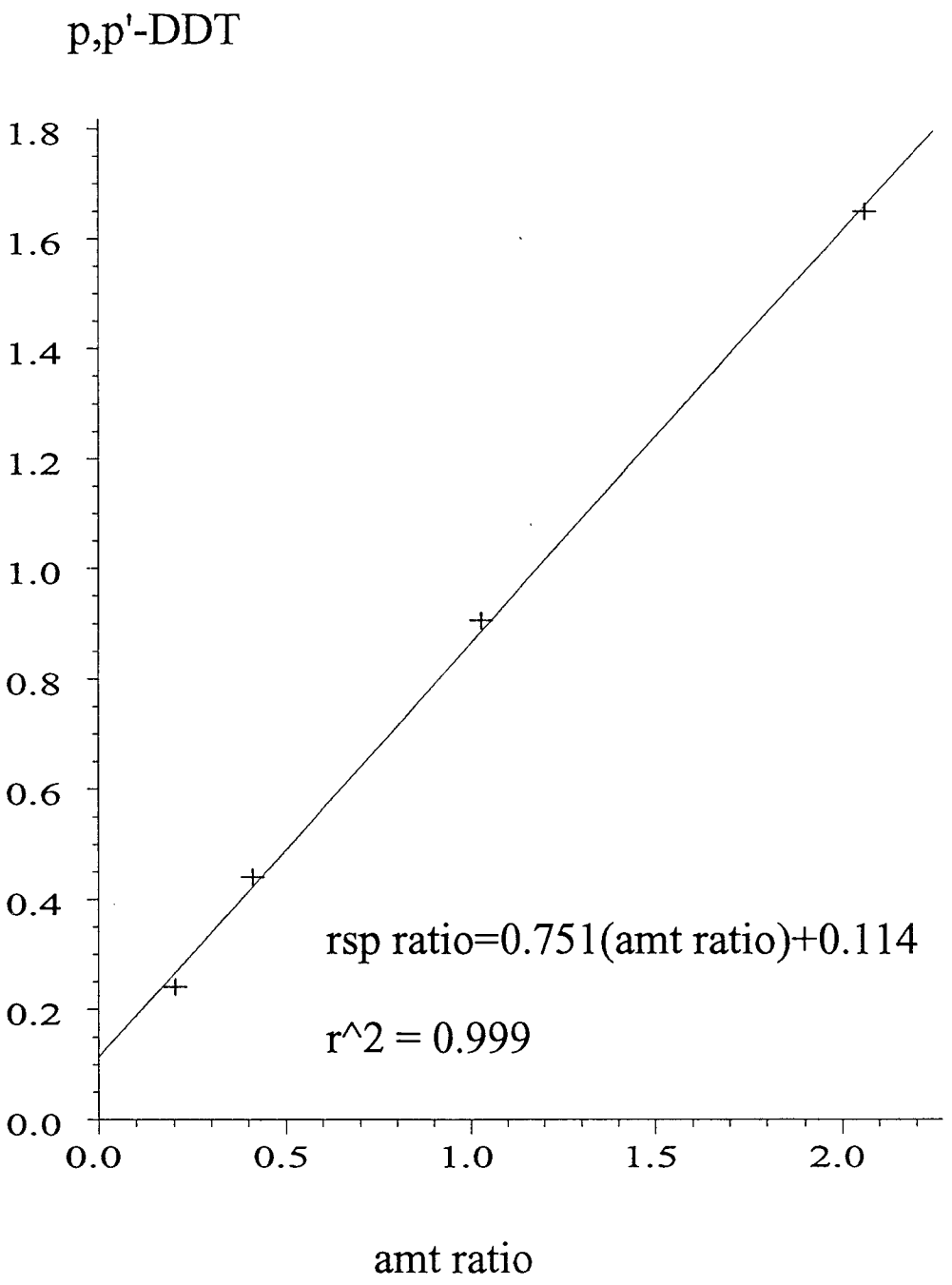


Figure A-3. Standard calibration plot (linear) of *p,p'*-DDD for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

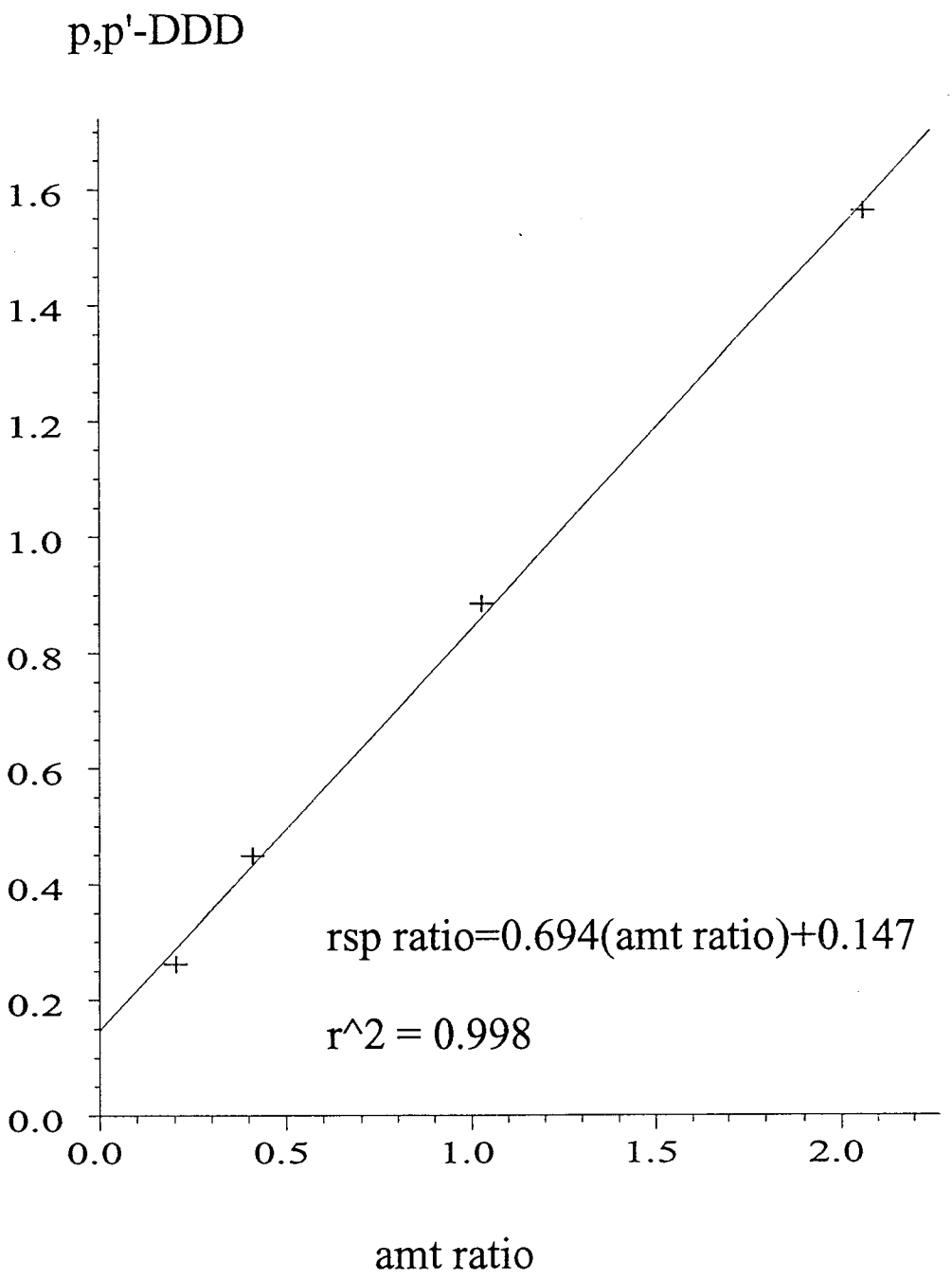


Figure A-4. Standard calibration plot (linear) of *p,p'*-DDE for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

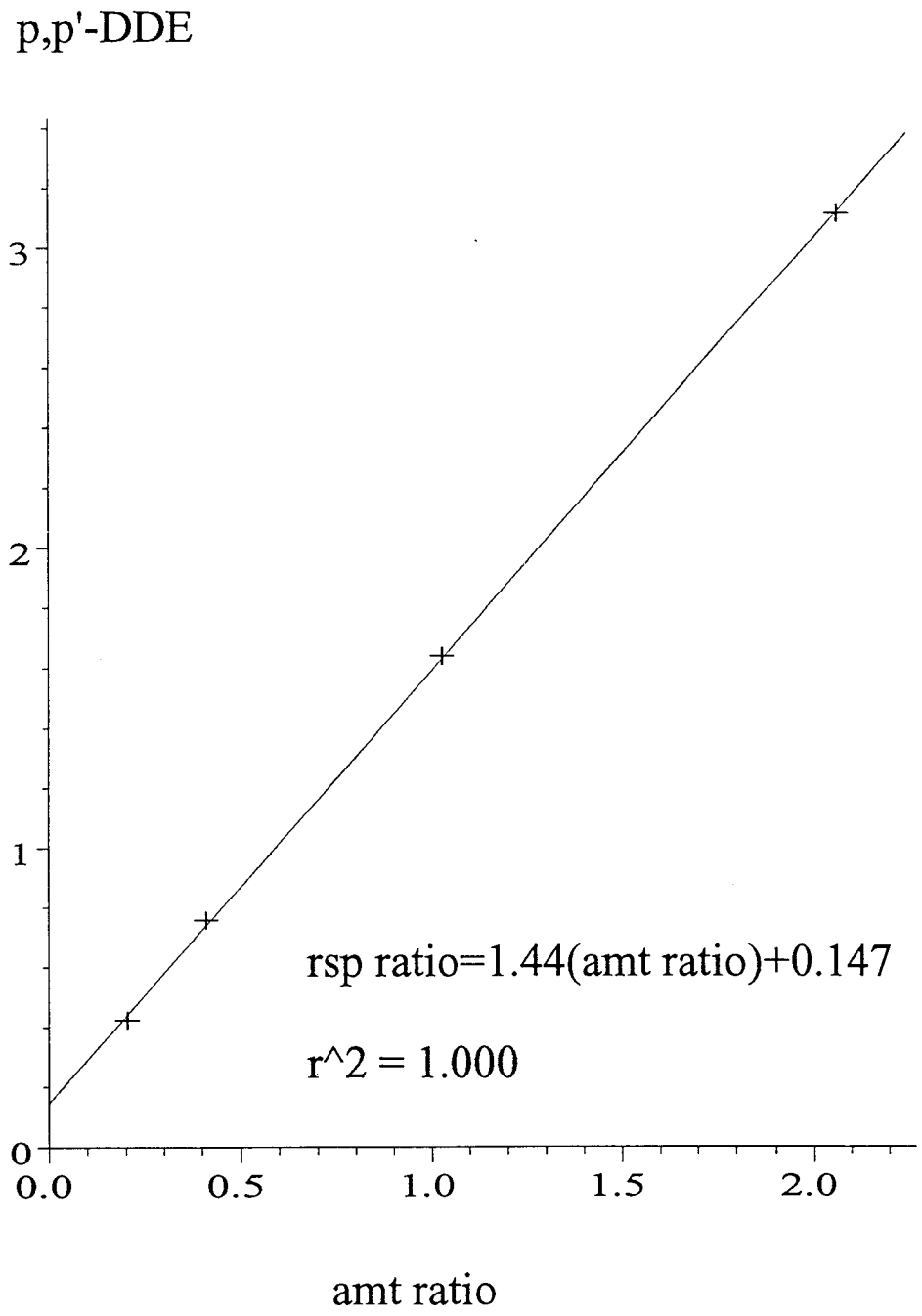


Figure A-5. Standard calibration plot (linear) of Dieldrin for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

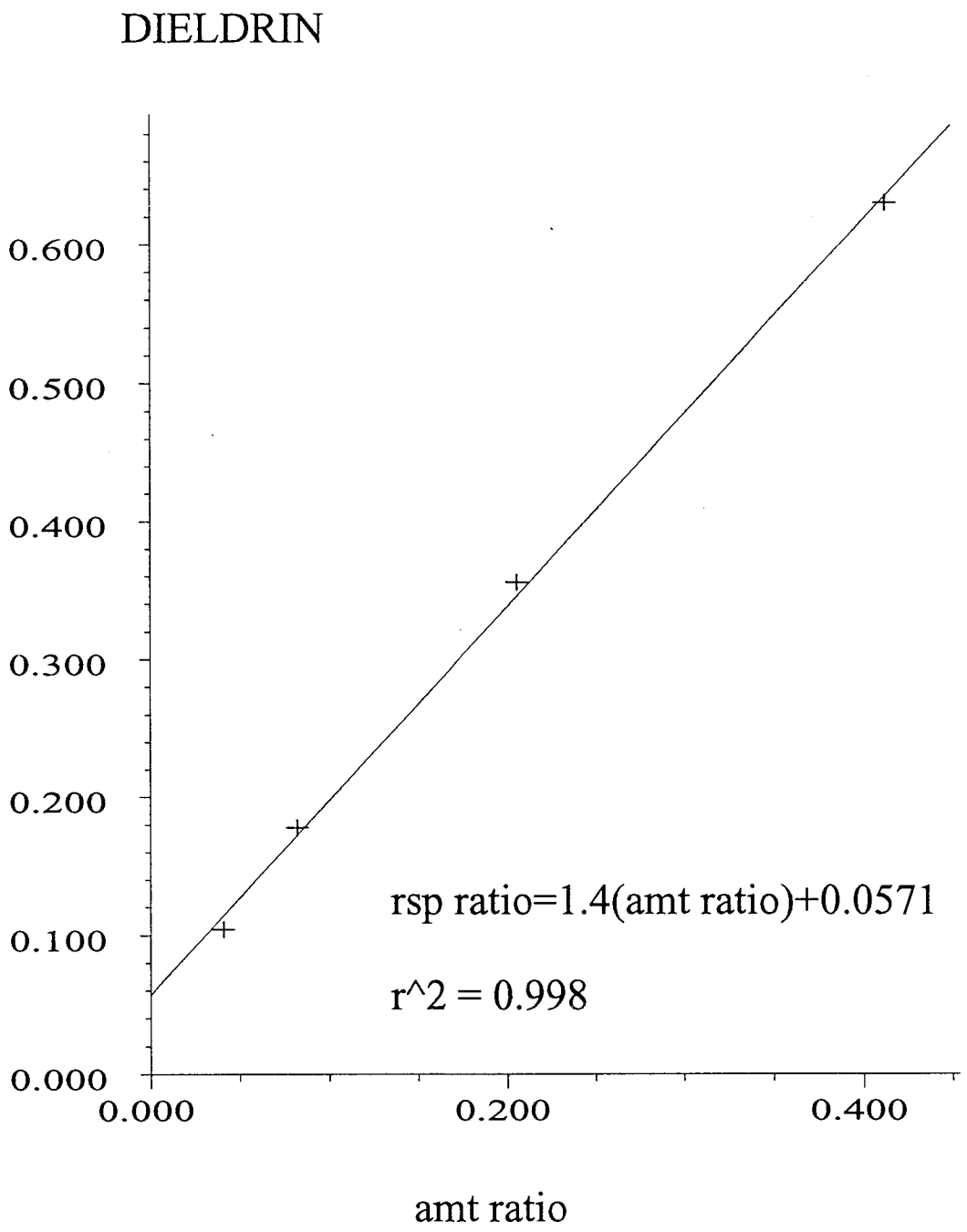


Figure A-6. Standard calibration plot (linear) of TC for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

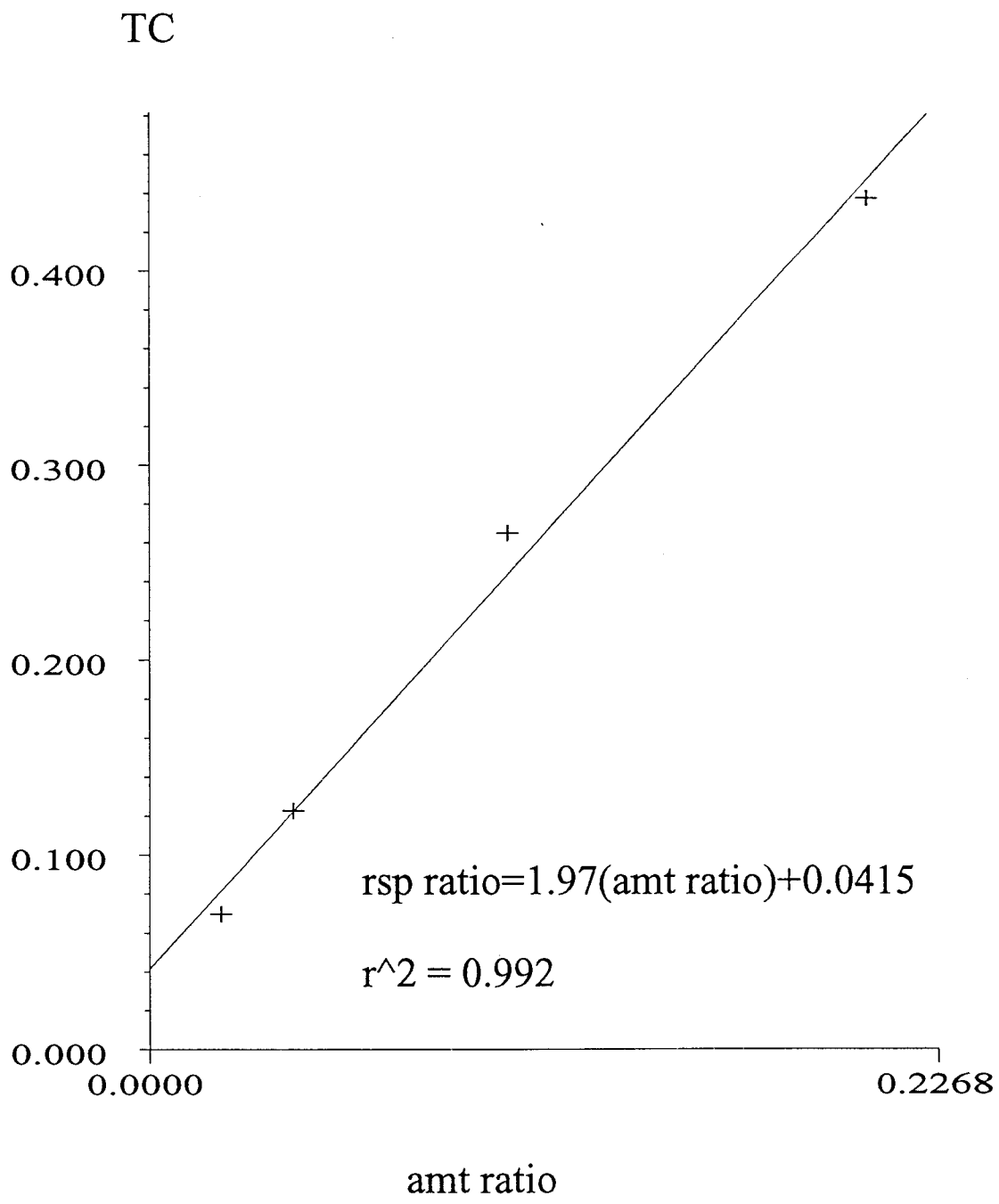


Figure A-7. Standard calibration plot (linear) of CC for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

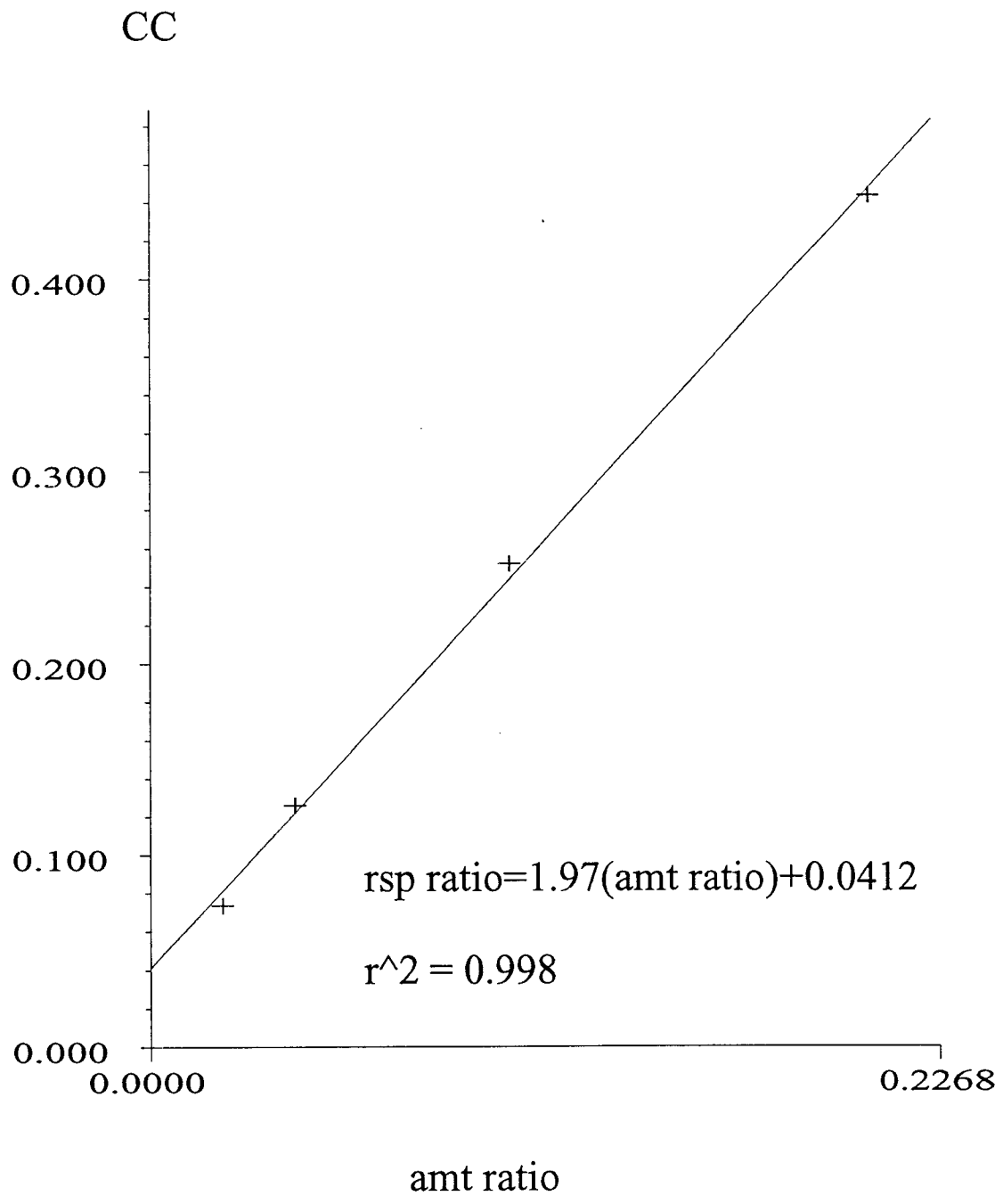


Figure A-8. Standard calibration plot (linear) of TN for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

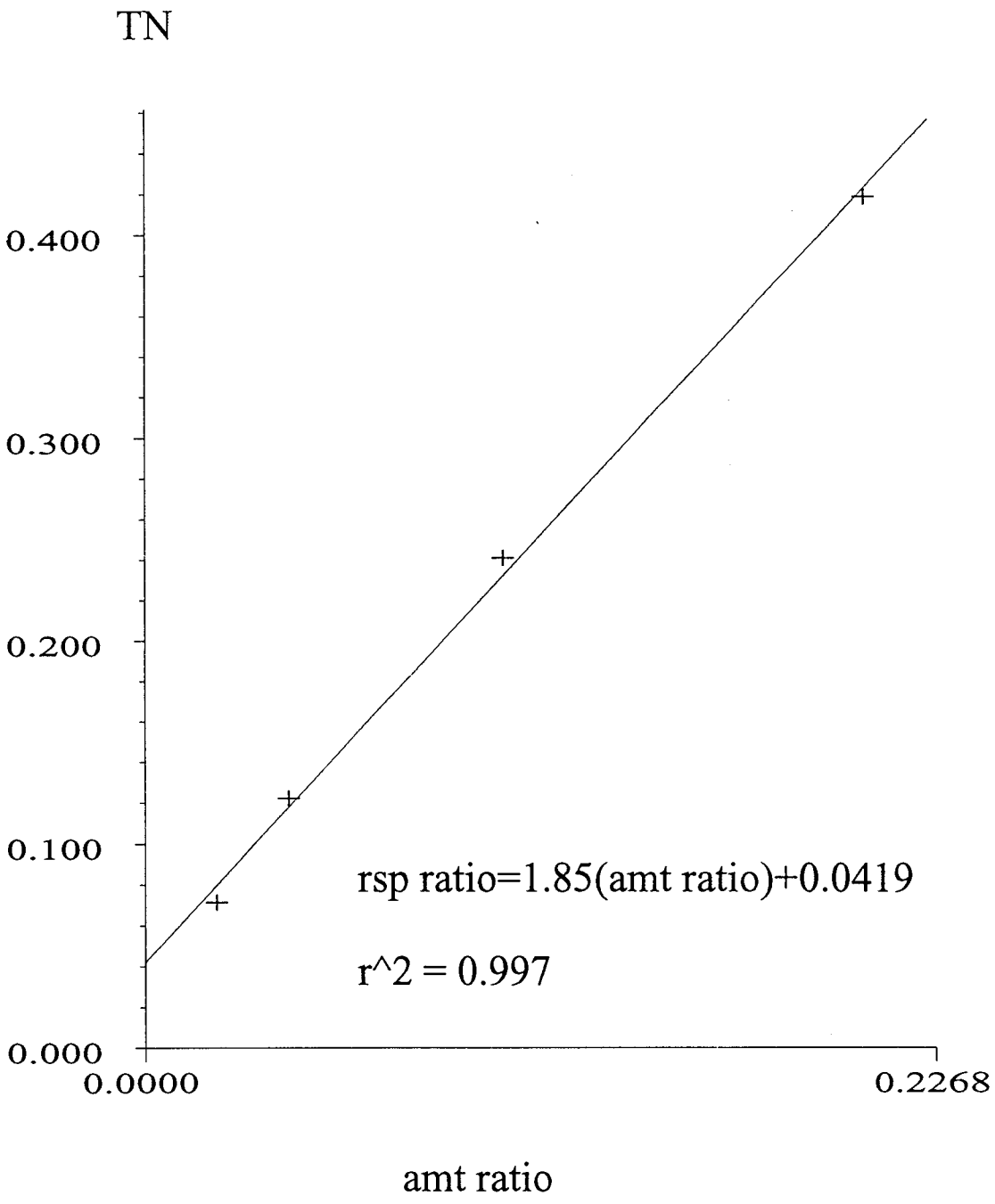


Figure A-9. Standard calibration plot (linear) of HEPT for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

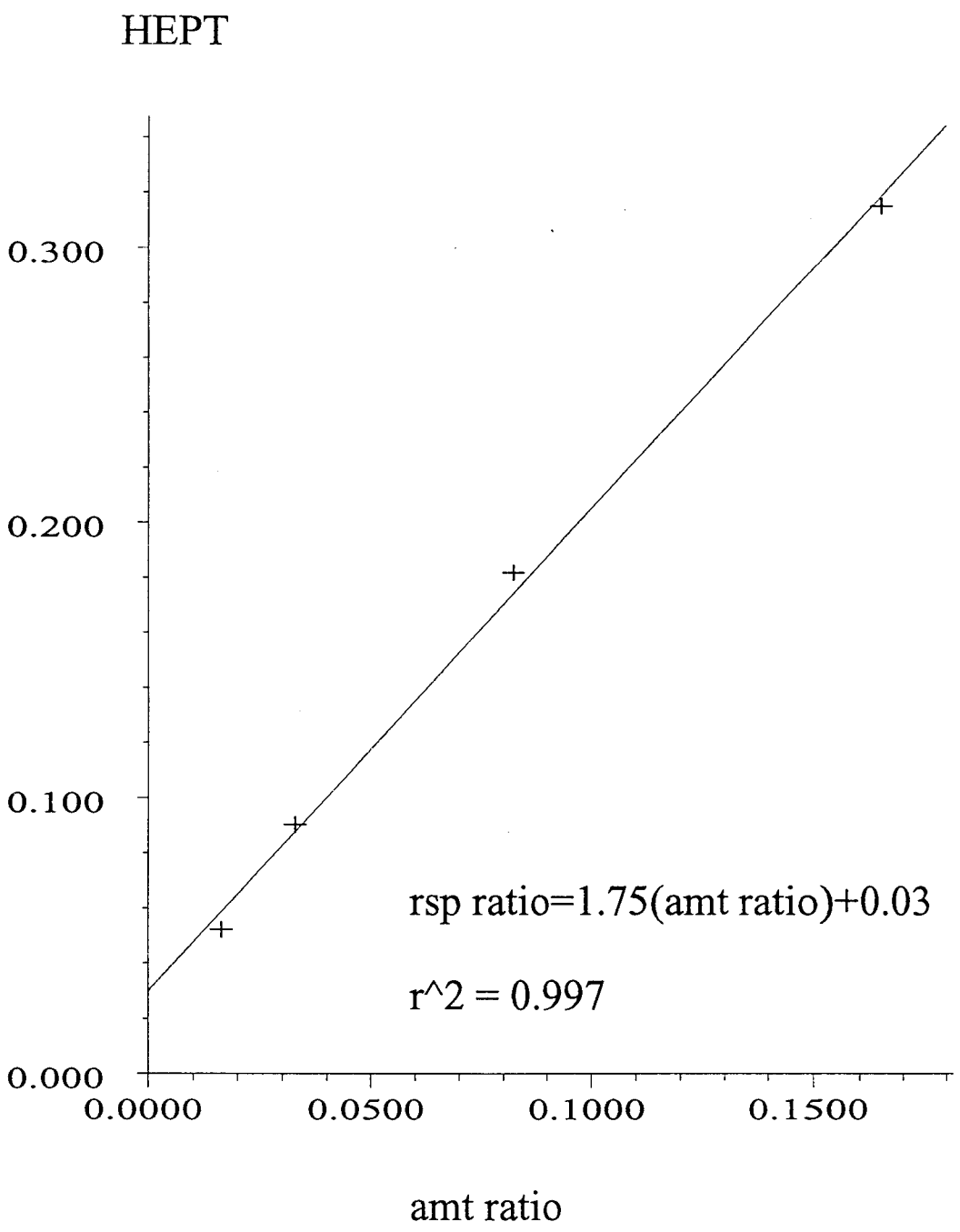


Figure A-10. Standard calibration plot (linear) of HEPX for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

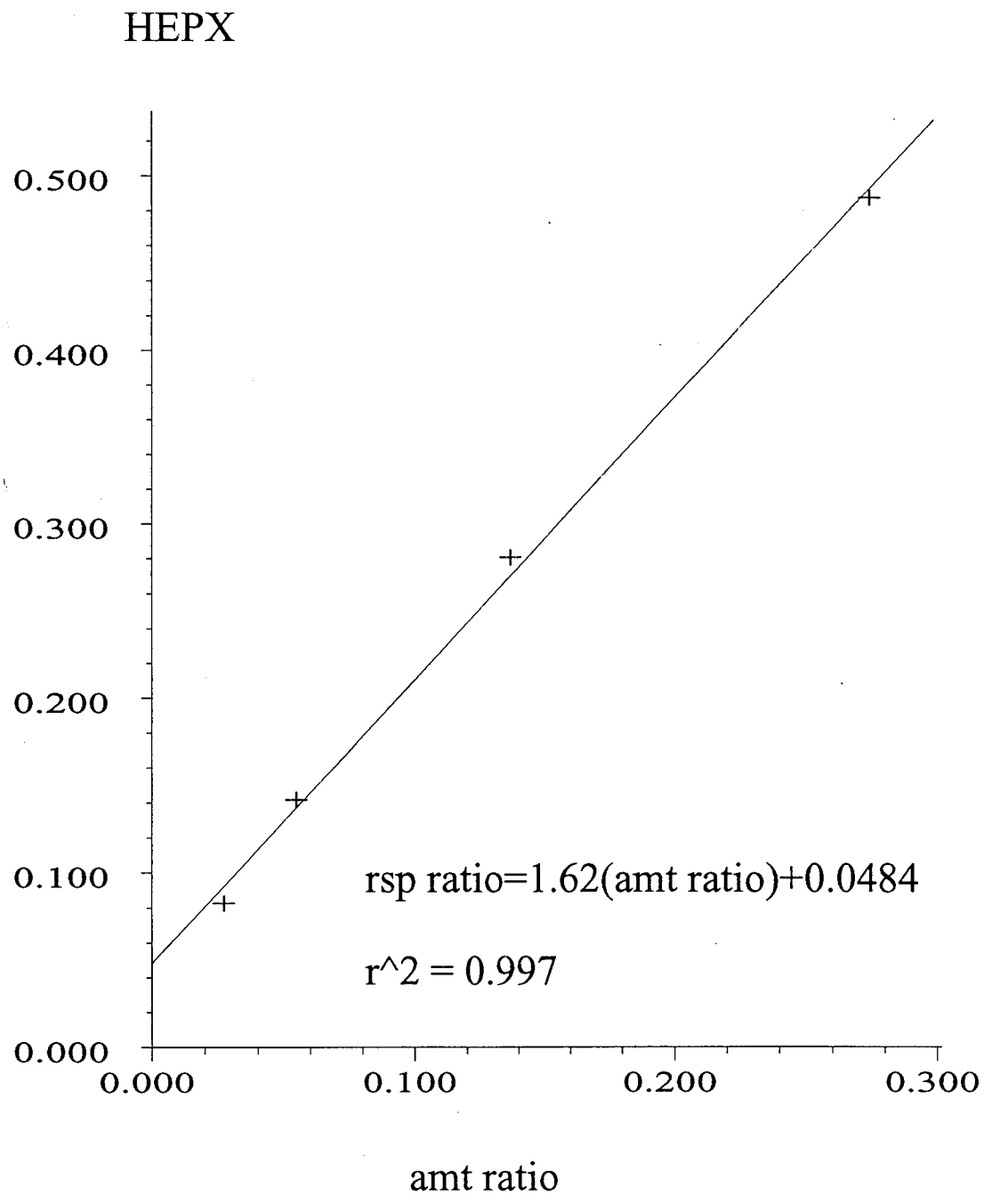


Figure A-11. Standard calibration plot (linear) of α-HCH for soil. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

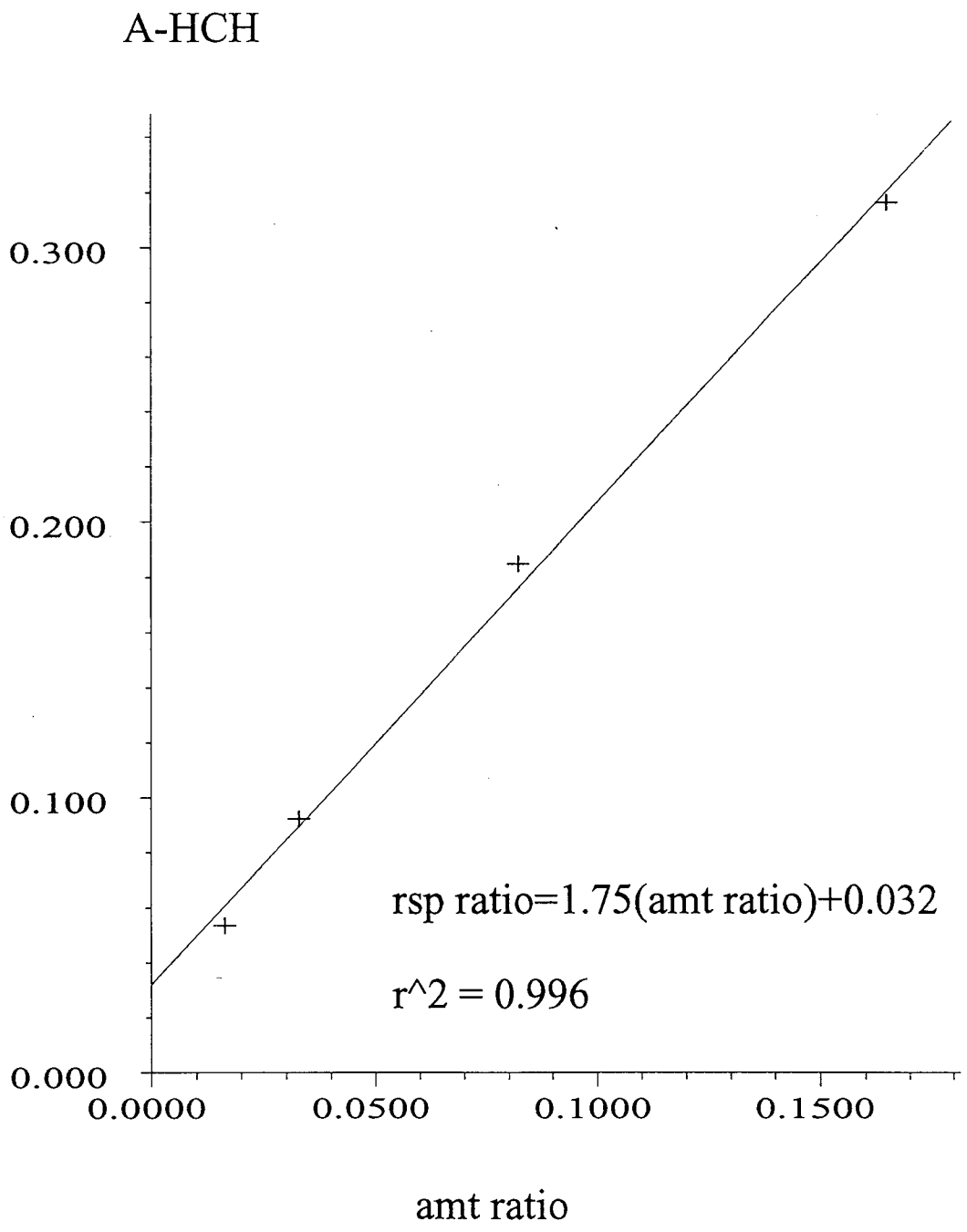


Figure A-12. Standard calibration plot (power curve) of *o,p'*-DDT for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

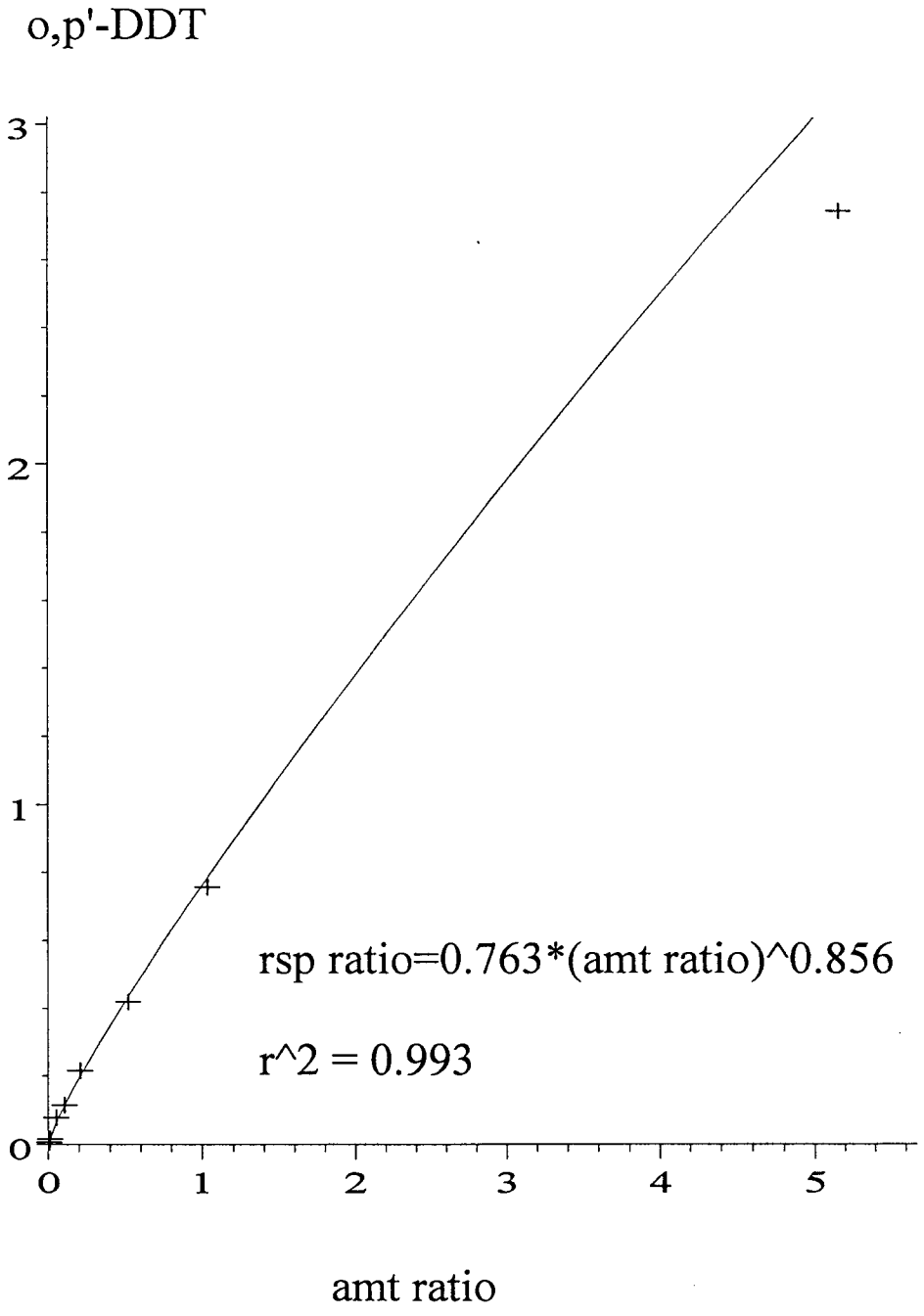


Figure A-13. Standard calibration plot (power curve) of *p,p'*-DDT for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

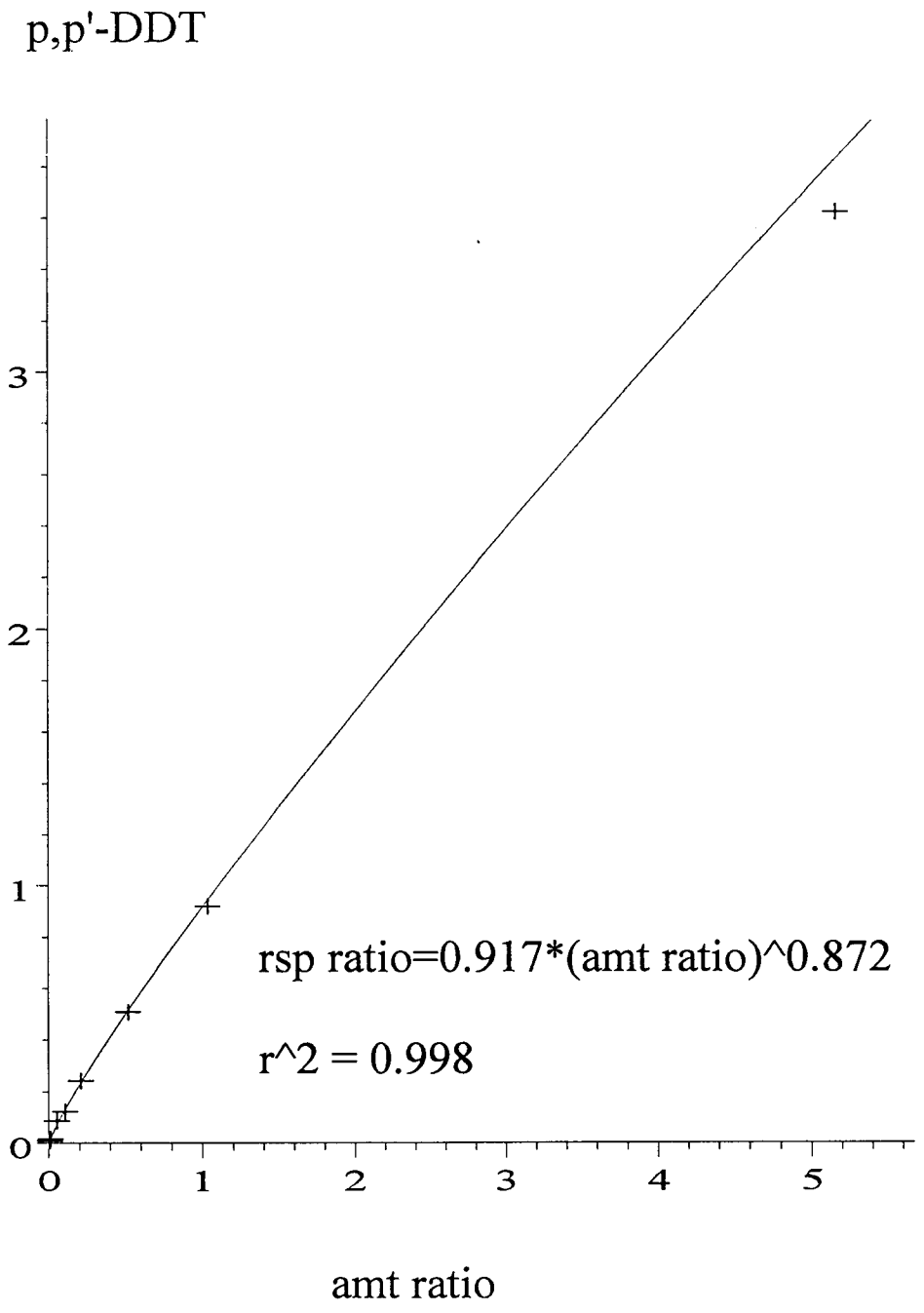


Figure A-14. Standard calibration plot (power curve) of *p,p'*-DDD for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

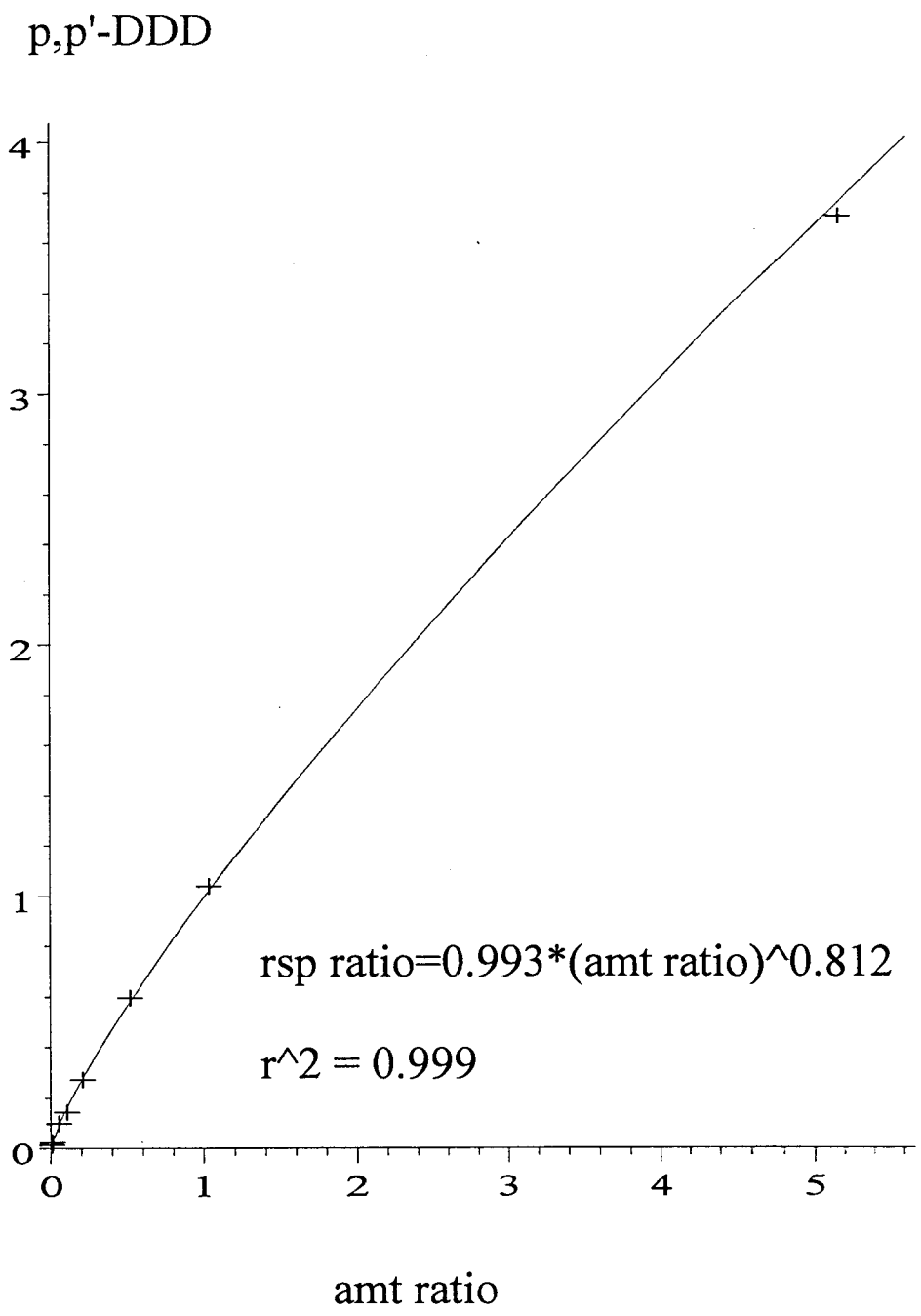


Figure A-15. Standard calibration plot (power curve) of *p,p'*-DDE for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

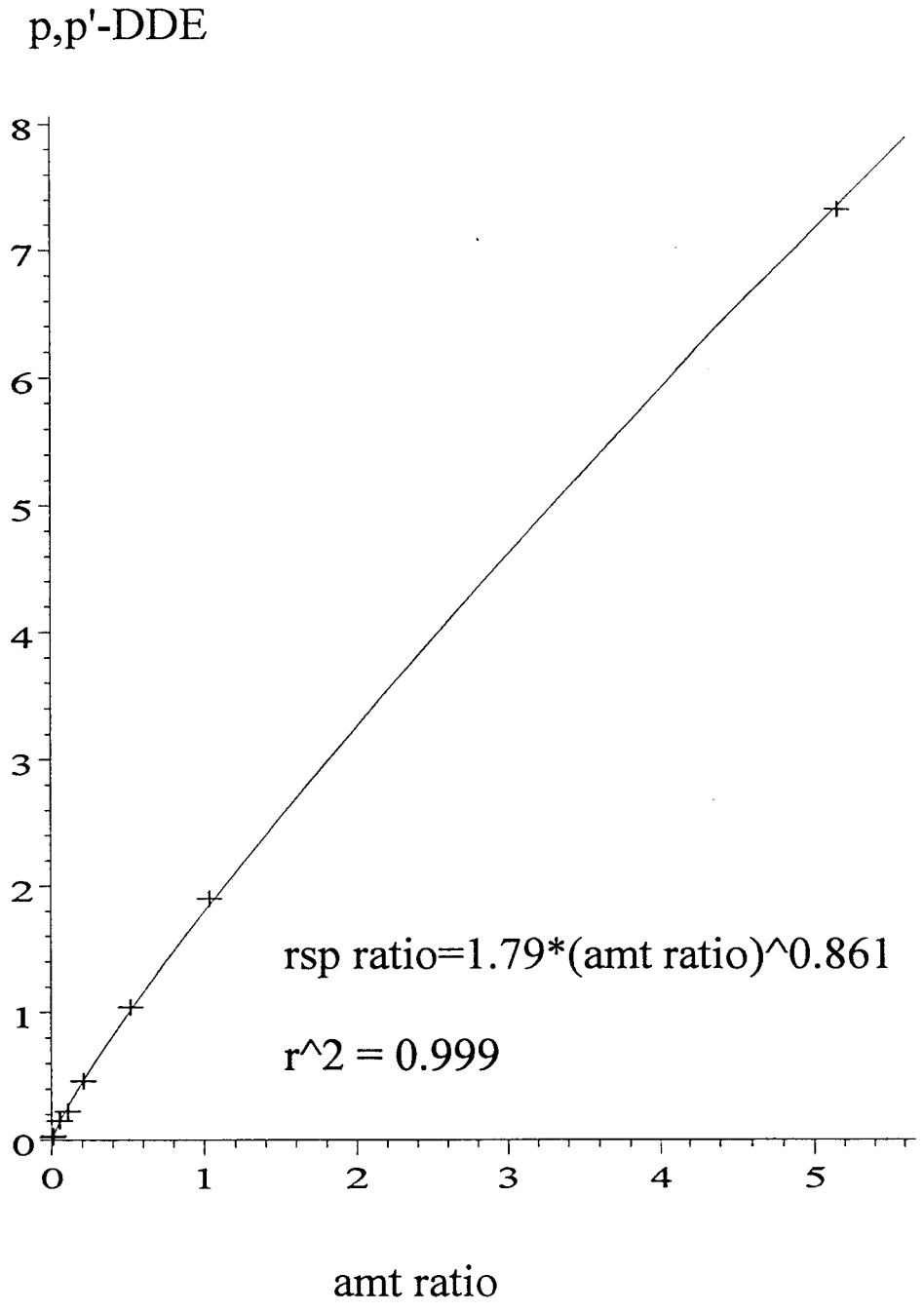


Figure A-16. Standard calibration plot (power curve) of Aldrin for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

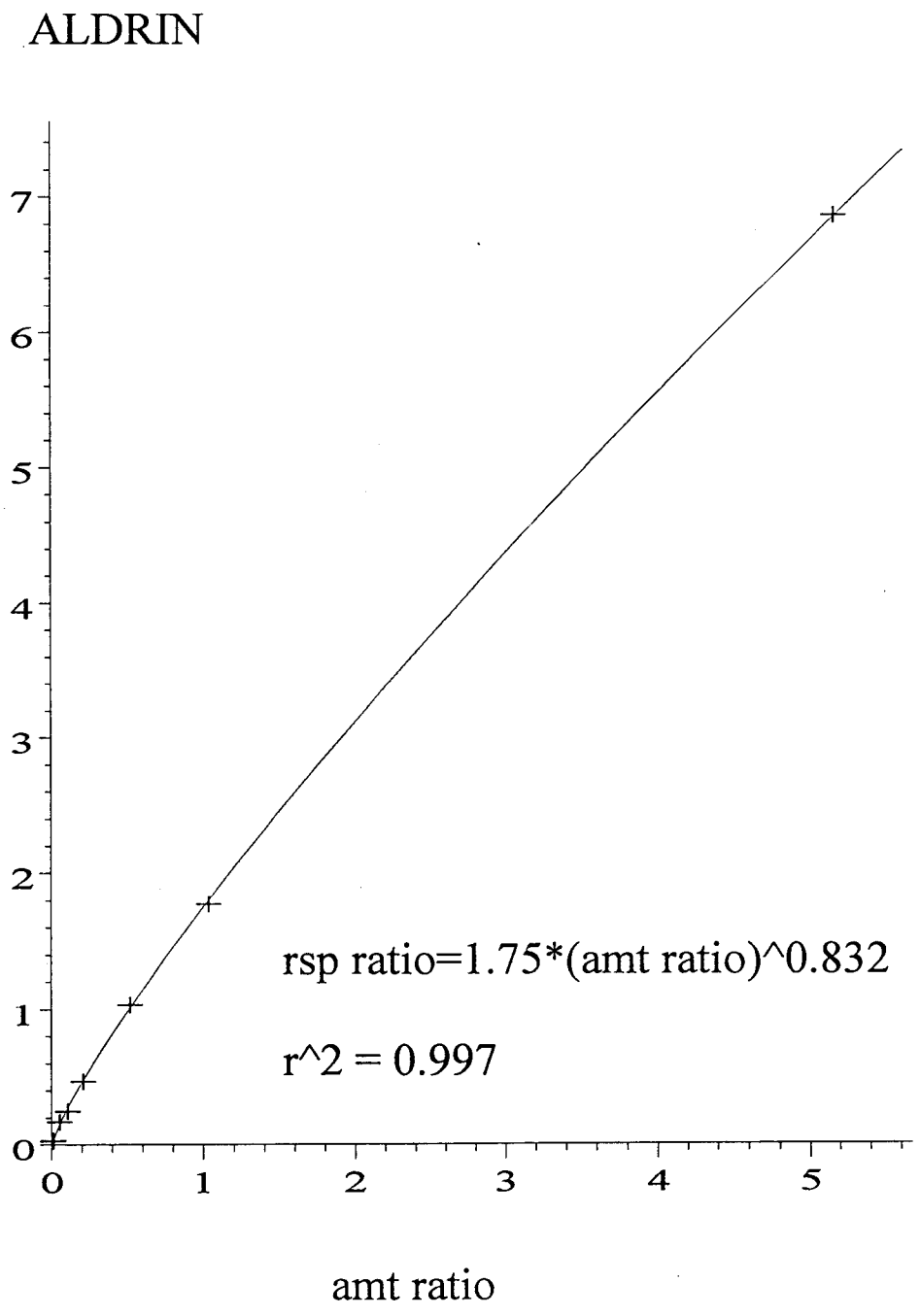


Figure A-17. Standard calibration plot (power curve) of Dieldrin for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

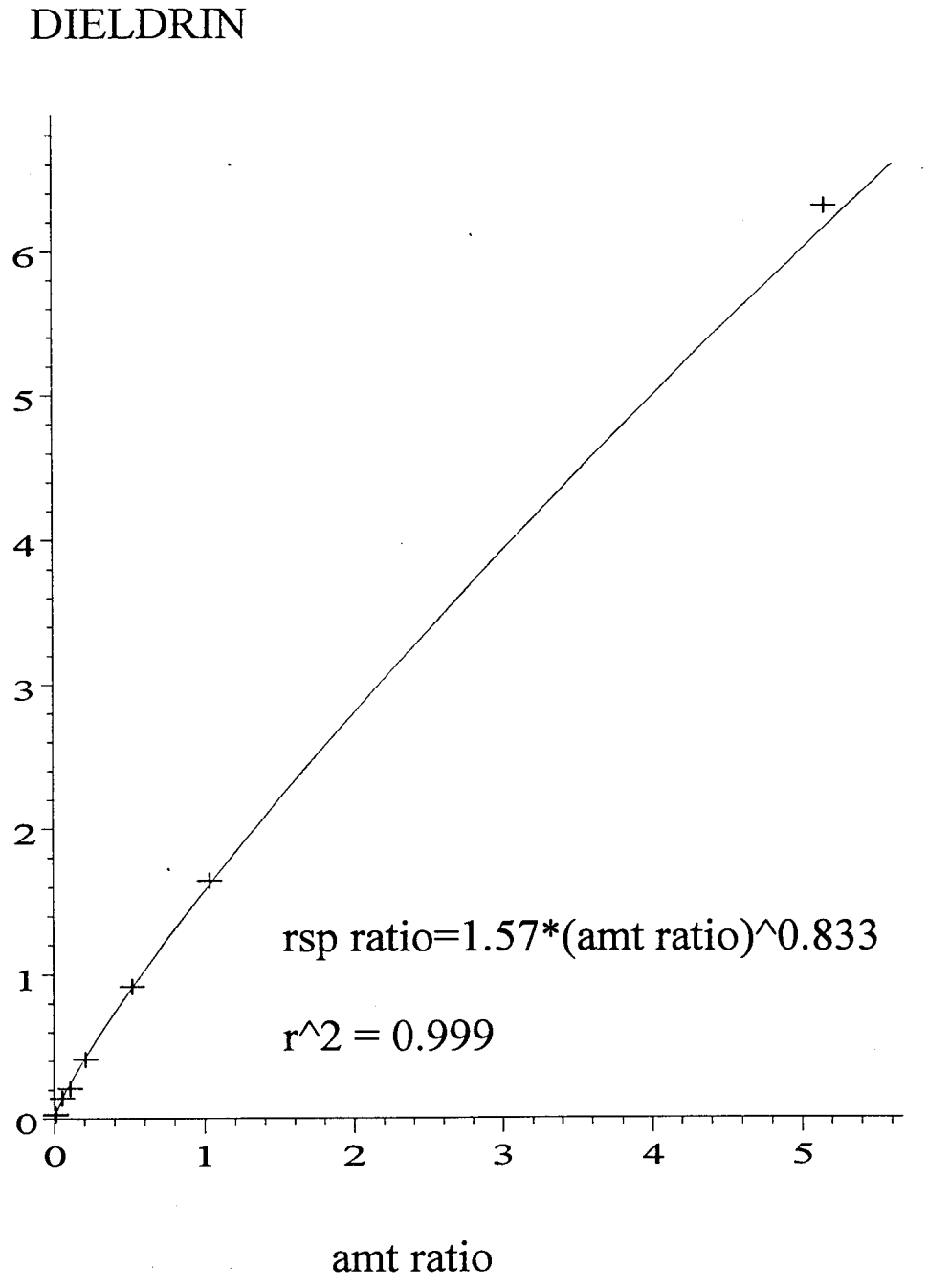


Figure A-18. Standard calibration plot (power curve) of TC for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

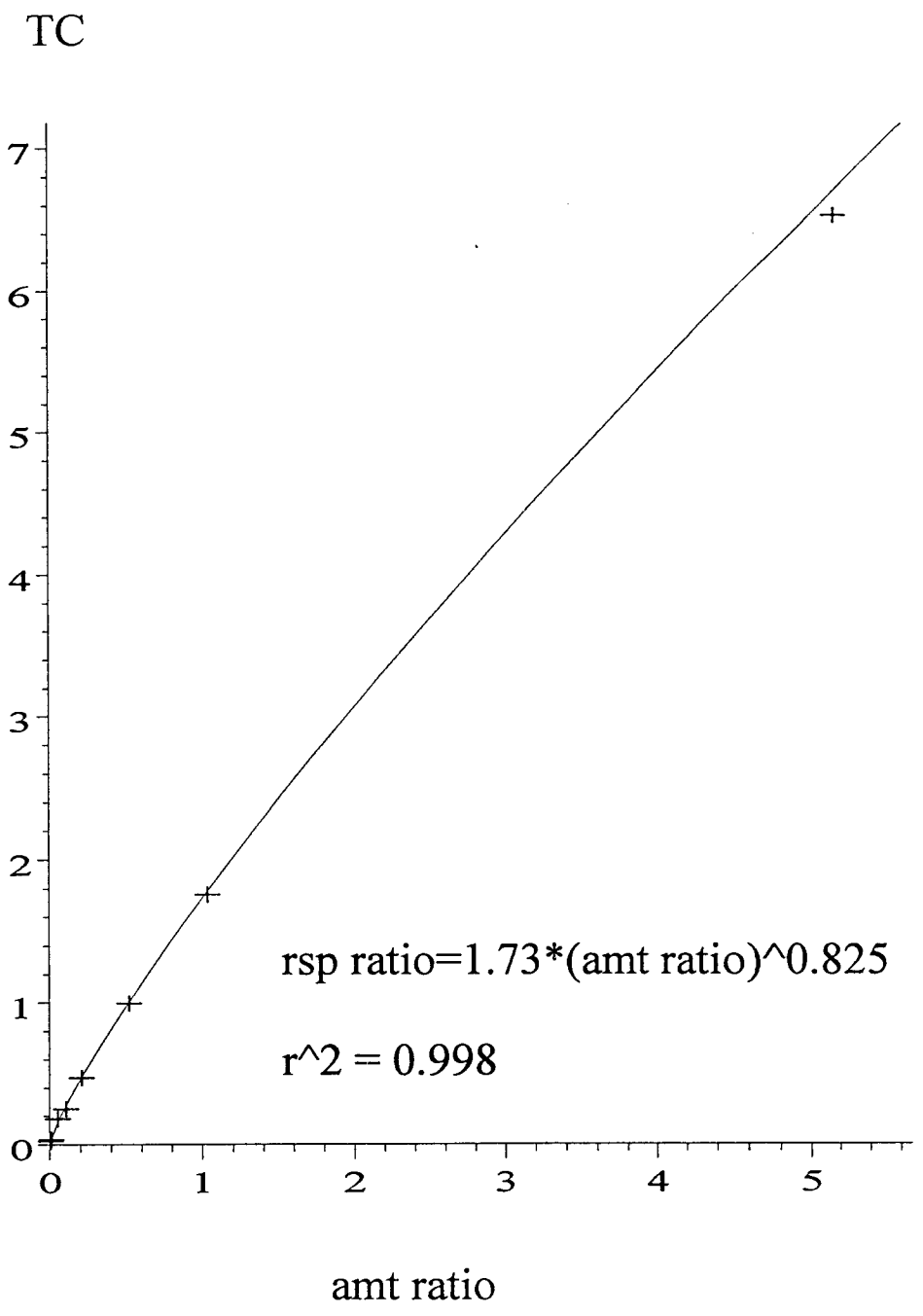


Figure A-19. Standard calibration plot (power curve) of CC for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

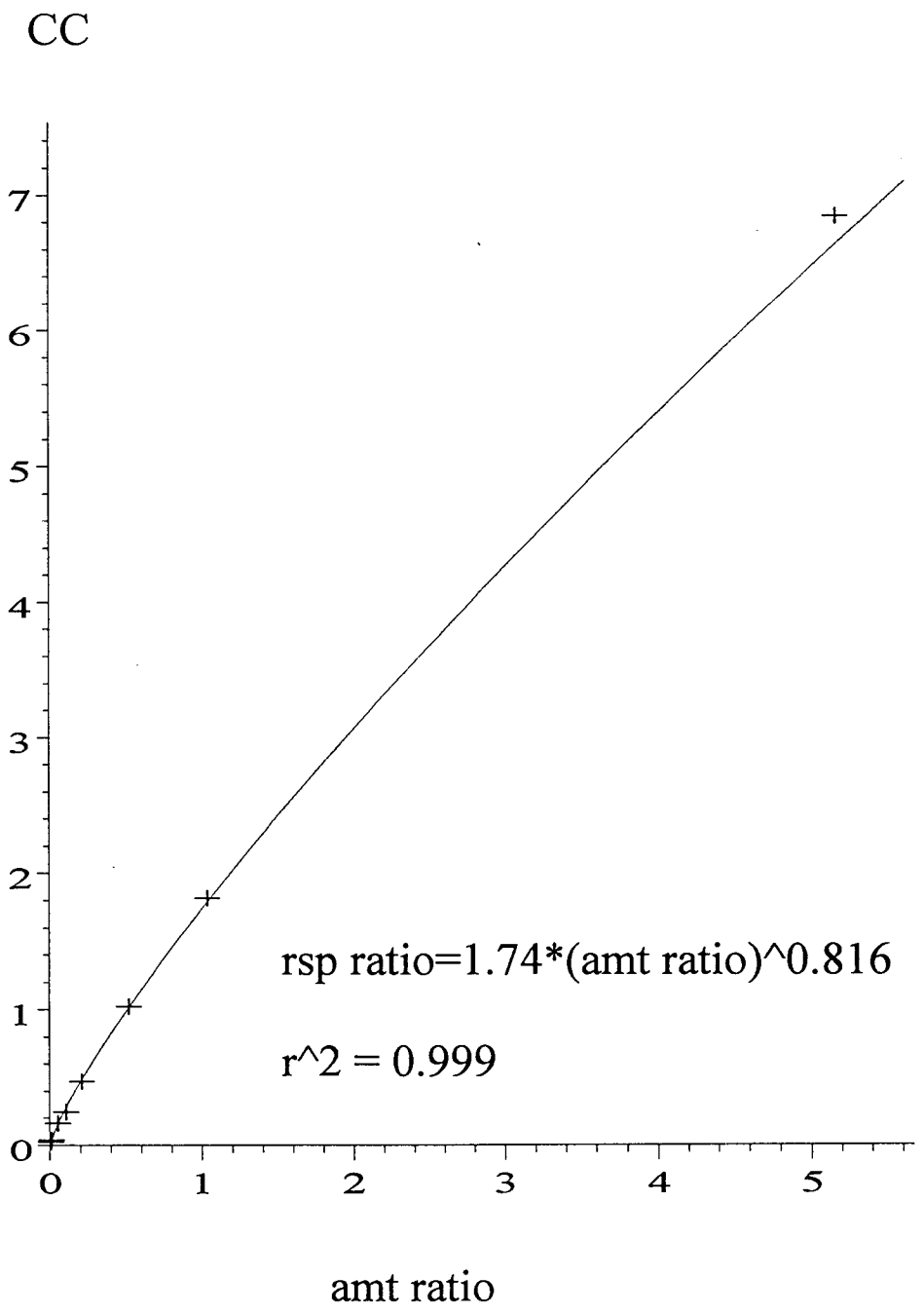


Figure A-20. Standard calibration plot (power curve) of TN for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

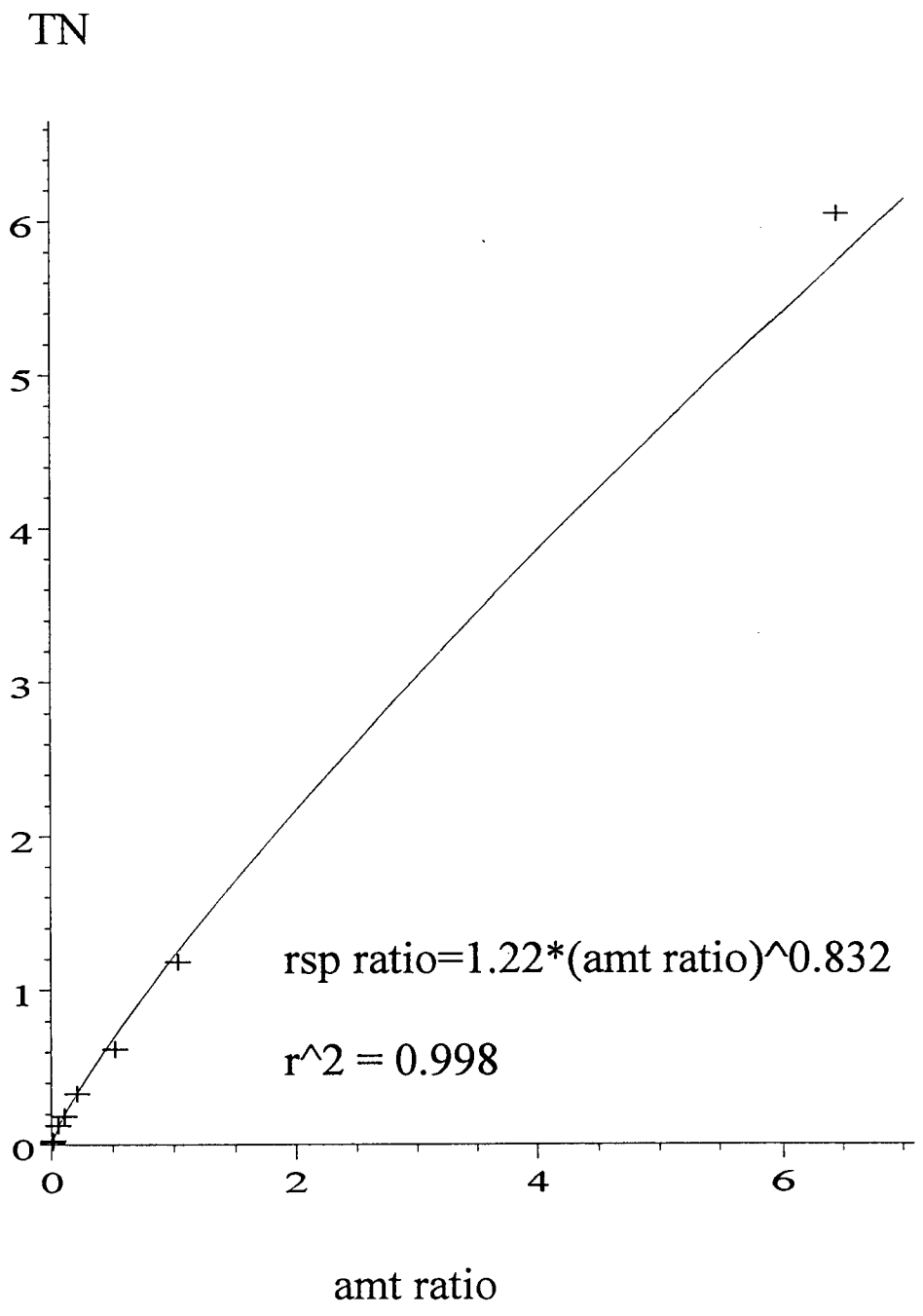


Figure A-21. Standard calibration plot (power curve) of HEPT for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

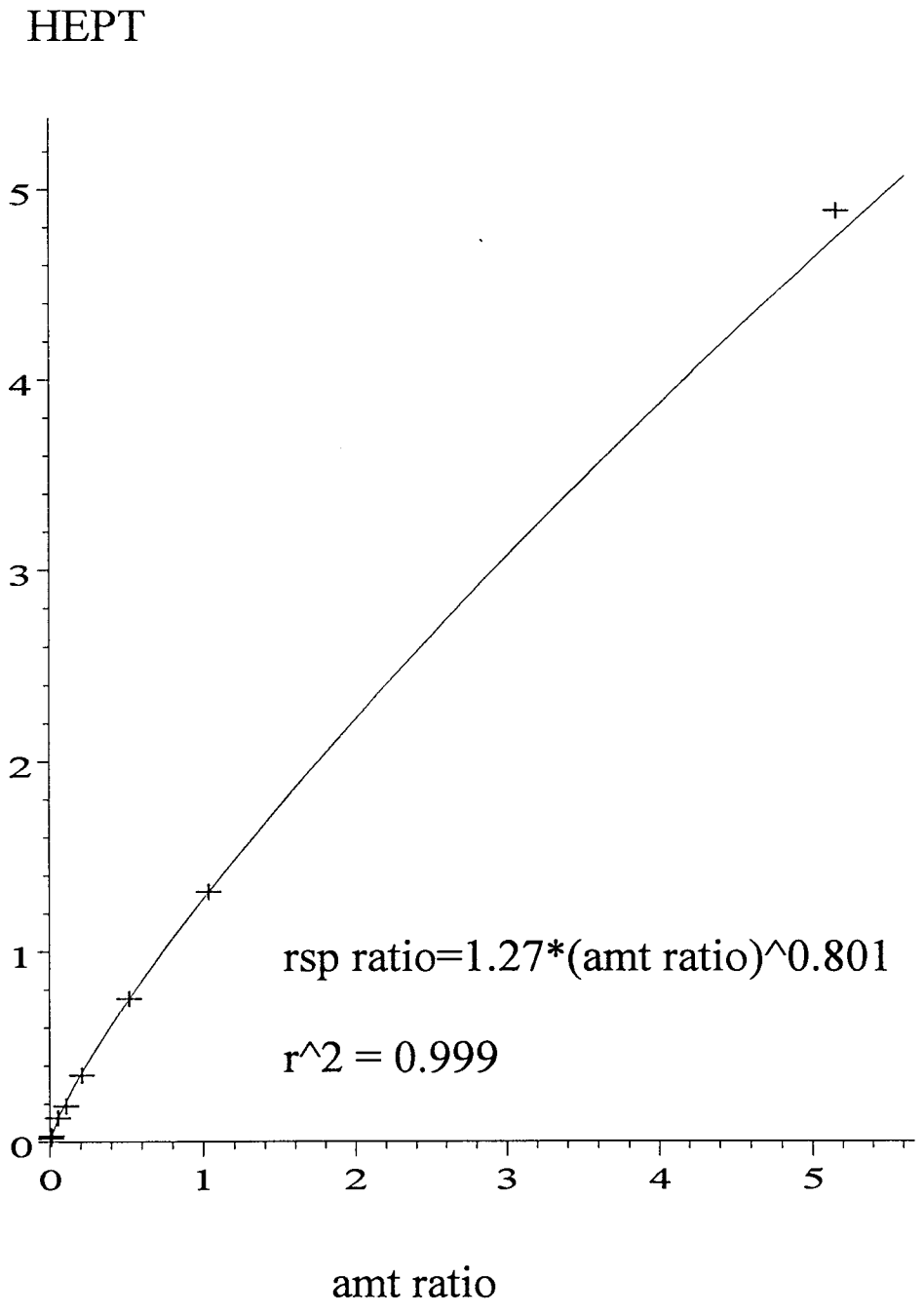


Figure A-22. Standard calibration plot (power curve) of HEPX for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.

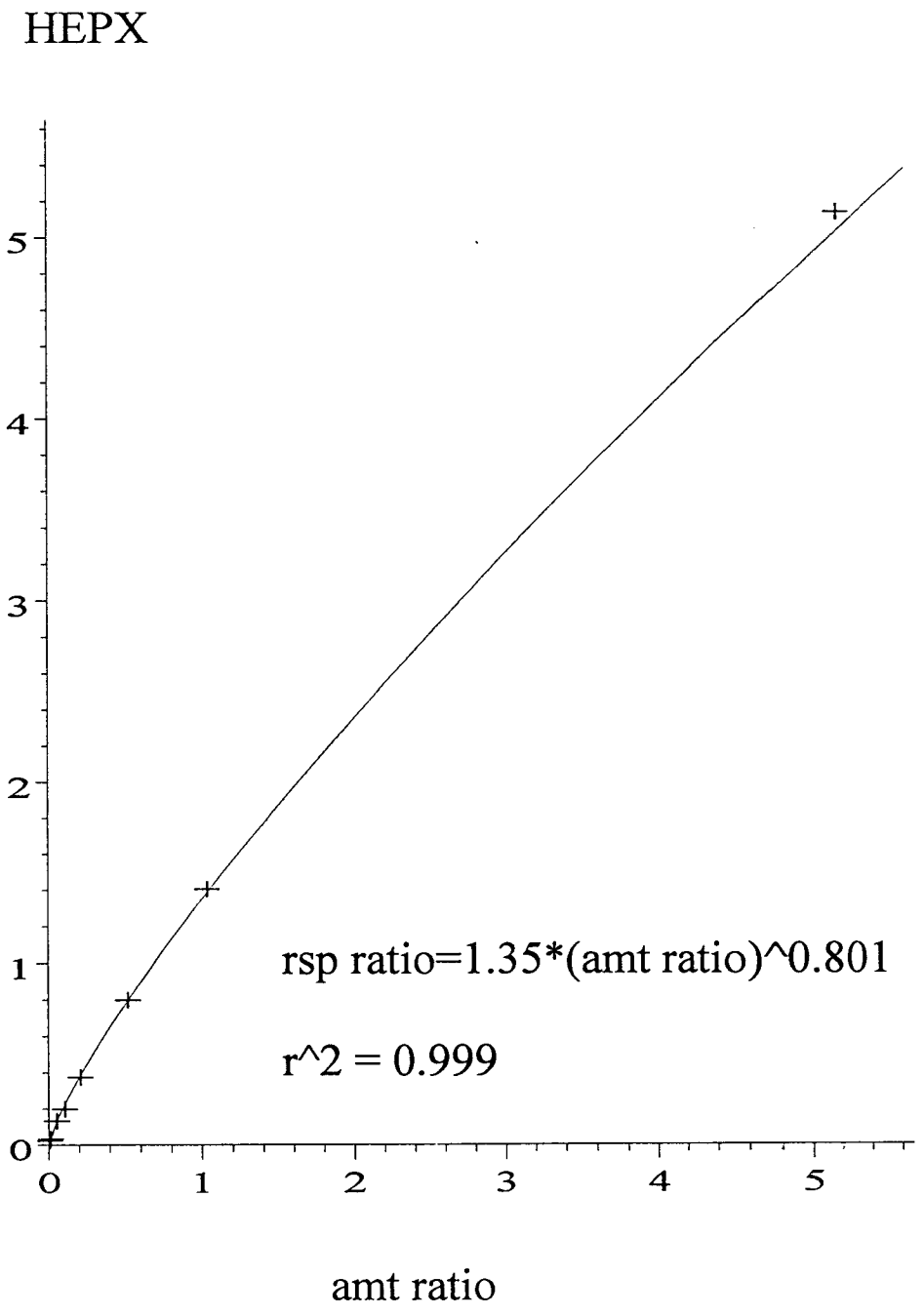


Figure A-23. Standard calibration plot (power curve) of α-HCH for air. Amt Ratio equals concentration (ng) x 10. Rsp ratio equals response factor used for calculation of sample concentrations. r^2 values for curve are given.