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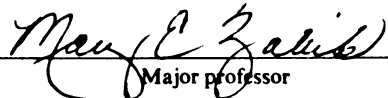
REMOVAL OF PCBs FROM WATER AND PEANUT OIL: STRUCTURAL
INTERRELATIONSHIPS OF PCB CONGENERS AND SELECTED POLYMERIC
PACKAGING MATERIALS

presented by

Melvin Arthur Pascall

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Food Science/Environmental
Toxicology


Major professor

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REDUCTION OF PCBs FROM WATER AND PEANUT OIL: STRUCTURAL
INTERRELATIONSHIPS OF PCB CONGENERS AND SELECTED POLYMERIC
PACKAGING MATERIALS

By

Melvin Arthur Pascall

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ABSTRACT

REDUCTION OF PCBs FROM WATER AND PEANUT OIL: STRUCTURAL INTERRELATIONSHIPS OF PCB CONGENERS AND SELECTED POLYMERIC PACKAGING MATERIALS

By

Melvin Arthur Pascall

The kinetic characteristics and uptake capacity of three commercially available polymer (polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS)) films for the removal of polychlorinated biphenyls (PCBs) were evaluated. Solutions of congener specific PCBs in distilled water and peanut oil were prepared. These solutions were contacted with the polymer films within sealed glass vials with no head-space and in the absence of light. Change in concentration of PCB congeners, both in the polymers/aqueous phases and the peanut oil phase alone were determined as a function of storage time. Mass balance determinations showing the ratios of PCBs in the polymeric and liquid phases were used to validate the analytical methodology. From the experimental data generated, partition coefficients, diffusion, solubility and rate loss constants were calculated for the various films and liquids.

Results indicated the sorption of PCBs by the polymers

generally followed a Fickian diffusion. Polystyrene at 35°C showed a greater sorption than at 25°C, and at an increased material thickness at 25°C. The aqueous medium displayed a greater rate loss of PCBs than that of peanut oil. Results also showed that polyethylene exhibited the highest sorption diffusion and partition coefficients when compared to the other materials at similar experimental conditions. Although PVC indicated larger sorption diffusion and partition coefficients for the lower chlorinated congeners than polystyrene, a reversal of this trend was observed for the higher congeners. Lower chlorinated congeners displayed a larger rate loss than congeners with higher chlorination for all polymers in the aqueous phase. However, in the peanut oil medium, the higher chlorinated congeners generally indicated a larger rate loss. Results from this study can be used to model possible transfer of environment contaminants from foods with polar and non polar characteristics to selected packaging materials.

DEDICATED TO THE MEMORY OF MY LOVING MOTHER

ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

Food safety is a consumer issue of the 1990's. The media often use scare tactics to state the prevalence of food safety problems. Thus, there is a need for food scientists to understand what issues consumers perceive as important so they can proactively respond and thus be viewed as a credible source of accurate food safety information. According to a 1994 national consumer survey conducted by the Food Marketing Institute (FMI), 89% of respondents said product safety was a very important or somewhat important factor in selecting foods. When shoppers were asked to rank a list of potential health hazards in the FMI survey, an overwhelming 79% said residues, such as pesticides and herbicides, are a serious health hazard if taken in with food. This was followed by antibiotics in poultry and livestock (55%), irradiated foods (35%), nitrites in food (35%), additives and preservatives (23%), and artificial coloring (19%) (Food Marketing Institute, 1994).

To many people, eating and drinking have become death-defying feats. No wonder sales of "organic" foods and bottled

waters have surged to new heights (Toufexis, 1989). This consumer anxiety is heightened by sensational stories carried by the news media. Coverage of such issues as Alar, stoked public fears of apples and pesticide use (Newton, 1990). Carpenter (1991) reported that the fear of pesticides has been exacerbated by frenzied publicity over celebrated cases, such as the "60 Minutes" report on the apple spray - alar (daminozide). In the winter of 1983-84, alarm about residues of ethylene dibromide (EDB) in grain led many states to pull cake mixes and other packaged foods from store shelves. In March 1989, panic over poisoned grapes resulted in a serious public food scare episode. This prompted the FDA to issue a recall of grapes after evidence of cyanide tampering had been discovered (Ravenswaay, 1990). While it may be desirable to shift the debate to a more scientific level, practical considerations dictate that individual processors do all they can to ensure their product's safety and their corporate reputation (Newton, 1990).

The use of synthetic pesticides has increased dramatically since World War II. According to the Environmental Protection Agency, in 1988 more than 1 billion pounds of pesticides and related products were used in the U.S.: herbicides (680 million pounds), fungicides (132 million pounds), insecticides (268 million pounds), and other related chemicals (70 million pounds). This quantity corresponds to more than 4 pounds of pesticides for each person in the U.S. (Huff and Haseman, 1991).

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Industrial contaminants have now become a serious cause of concern because of their prevalence and entry into the food chain. Billings (1991) reported that once released into the environment, these chemicals seek out the media (water, air, soil, and biota) in which they are the most soluble. For example, trichloroethylene and benzene are most soluble in air and, consequently, inhalation is the principal means of human exposure. Dichlorobiphenyl trichloroethane (DDT) and polychlorinated biphenyls (PCBs) are most soluble in organic matter and tend to be concentrated in biota and thus are transferred to humans through the food chain. PCBs, once used in a broad range of industrial products, are found at particularly high concentrations in the fatty tissue of fish feeding in polluted waters, such as Lake Michigan, and in animal products from farms with contaminated silos (Jacobson et al., 1989). They also noted that PCBs, polybrominated biphenyls (PBBs) and DDE are not readily excreted, except by lactation, and that placental passage has been documented for PCBs and PBBs, although much larger quantities are transferred to the infant postnatally in breast milk due to its high lipid content.

Dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin, TCDD) is one of the most toxic man-made compounds known. TCDD is not manufactured commercially, it is a contaminant in the manufacture of several chlorinated phenolic products including the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and hexachlorophene (Umbreit et al., 1986). TCDD have been found

at low levels in many populations around the world, according to Graham et al. (1985). Industrial accidents and environmental contamination have been suggested as possible sources of TCDD, and may be responsible for continued human exposure. Human exposure to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is a matter of great concern in many parts of the world (Svensson et al., 1991). In studies of exposure to dioxins and dibenzofurans through the consumption of fish, Svensson et al. (1991) found that fatty fish such as herring and salmon from the Baltic Sea have been found to contain high levels of some PCDDs and PCDFs. They also reported similar levels of TCDD in fish from the Great Lakes.

The Great Lakes form the world's largest body of fresh water, and the area around them is home to about 37 million people (Park, 1991). Millions of Canadians and Americans depend on the Great Lakes for bathing and drinking water, fishing and recreation, commerce and other uses. Scientists have found increasing evidence that pollutants in the water are causing insidious neurological damage, particularly in children, and infertility among adults (Park, 1991). Writing in the Chemical and Engineering News April 23, 1990, Bette Hileman quoted the International Joint Commission's (IJC) report which states that the Great Lakes Basin pose serious documented health problems - including reproductive problems, gross deformities, and behavioral and hormonal changes - in wildlife and lab animals. It also cites studies of infants

born to women who eat Lake Michigan fish on a regular basis. In these infants, the gestational period, birth weight, skull circumference, and cognitive, motor, and behavioral development seem to be adversely affected by the mothers fish consumption.

Seltzer (1989) also cited an IJC report which states that even if all current pollution is stopped, PCBs, heavy metals and other toxins lodged in the sediments by past pollution "may remain in the Great Lakes ecosystem indefinitely". Numerous measures have been taken to improve the quality of the Great Lakes Basin. However, many researchers indicate that effective relief will require substantial commitment of funds and decades of restorative action. Populations of many species of birds are recovering as a result of cleanup efforts, but problems remain for some populations in some locations (Worthy, 1989). Certain key species of fish, including lake trout, still can't establish self-sustaining populations in several lakes (Worthy, 1989).

In a more direct approach, to reduce the level of organochlorine contaminants in Great Lakes fish prior to consumption, several researchers have employed various cooking methods and the technique of fish fat trimming (Zabik et al., 1995; Voiland, Jr. et al., 1991; Sanders and Haynes, 1988). Another direct approach, which can be explored to reduce these contaminants, could be through the use of specially designed packaging made with carefully selected materials.

Presently, plastic packaging materials are widely used

because of their cost and outstanding service properties. Low-density polyethylene (LDPE) for example, the most widely used food-packaging material, is used both as a free film and as a coating in containers for such foods as bakery products, water, milk, agricultural produce, margarine and poultry. Many other types of plastics have also found similar use. These include but are not limited to polyvinyl chloride (PVC), polypropylene, polystyrene and nylons as examples. Many laminates and polyblends have been fabricated to offer specialized characteristics to meet the packaging needs of an increasing sophisticated consuming society. In addition to their role as a packaging material, several researchers have used various polymers to concentrate certain lipophilic chemical compounds within their matrix and thus reduce the levels of these compounds in water, air and soil samples.

In 1980, Byrne and Aylott patented a device consisting of a nonpolar organic solvent separated from water by semipermeable membranes (regenerated cellulose, vinyl chloride, polyvinylidene fluoride, and polytetrafluoroethylene) that concentrated organic molecules from water samples (Huckins et al., 1990^b). The September 9, 1991 issue of Chemical and Engineering News reported the use of a similar device, designed to mimic the bioconcentration of organic contaminants (like polychlorinated biphenyls and polyaromatic hydrocarbons) in lipids of aquatic organisms. Huckins et al. (1990^a) used a similar technique to separate organic contaminants from fish lipid. This was done by

placing the lipid samples into specially prepared polyethylene bags. The sealed bags were then suspended in covered cyclopentane baths in order to effect the separation of the contaminant from the lipid extract. This was achieved because the contaminants diffused through the polymeric bag and into the cyclopentane, leaving the lipid portion behind.

Zabik et al. (1992) concentrated pesticide residues in soil by filling polyethylene bags with three different types of adsorbents - liquid 2,2,4-trimethylpentane, solid C_{18} bonded-phase silica sorbent and XAD-4 resin. When buried in contaminated soil, these passive sampling devices (PSD) were found to concentrate the chemical contaminants into the polymer and the packaged adsorbents to varying degrees. Heindorf (1992) did similar studies using packages made of polyethylene, polypropylene, polyvinyl chloride, acetate and silastic[®] (a silicone elastomer) materials. These were filled with solvents such as hexane, isooctane, toluene, octanol and methylene chloride, then exposed to aqueous solutions containing contaminants such as naphthalene, lindane, aldrin, 2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene (DDE), dieldrin, methoxychlor and 2,4,5,2',4',5'-hexachlorobiphenyl. The results obtained demonstrated that the device concentrated the contaminants up to 2,400 times the normal levels expected for these chemicals in the environment.

This concept of PSDs can be extended to food packaging if selected polymeric materials can be contacted to products known to have selected chemical contaminants. Grayson et al.

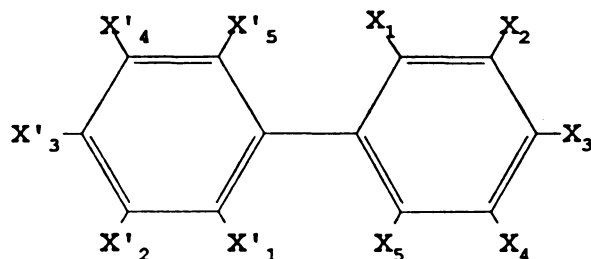
(1987) successfully showed this physicochemical phenomenon when they investigated the sorption of dimethyl chloride by poly(aryl-ether-ether-ketone) (PEEK) polymeric films of differing thicknesses, surface treatments and thermal annealings.

These proposed study will evaluate a method for the extraction, cleanup and quantification of congener specific PCB sorbed by food grade polyethylene, PVC and polystyrene films. The sorbed PCB will be removed by the polymers when they are made to contact samples of spiked PCB/water and PCB/peanut oil solutions. The studies will also investigate the sorption characteristics of each material under similar conditions of storage and dimensions. Polystyrene will be further investigated for its sorption characteristic under changing conditions of temperature and material wall thickness. The data will be compared with the stereochemistry and the chemical structure of both the PCB congeners and the polymers in order to identify related trends.

CHAPTER 2
LITERATURE REVIEW

POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (PCBs) belong to a group of chlorinated hydrocarbons synthesized by the controlled chlorination of the biphenyl molecule with anhydrous chlorine using either iron filings or iron(III) chloride and a catalyst. Presently, two hundred and nine (209) arrangements of this substitution (congeners) are theoretically possible, but in actual practice, slightly more than 100 formulations have been used (Swain, 1983). Congener is defined as a PCB compound with a specific chlorine substitution pattern. The International Union of Pure and Applied Chemistry (IUPAC) has definite rules for the nomenclature of organic chemistry, one ring system in the biphenyl ring assembly is assigned unprimed numbers and the other primed numbers (Figure 1).



POLYCHLORINATED BIPHENOL (PCB)

X or X' = Chlorines or Hydrogens

Figure 1. Basic structure of polychlorinated biphenyls with the numbered carbon atoms and possible position of substituted chlorine atoms.

Groups with the same number of chlorines in PCB congeners are called homologs, such as 2,4,6-trichlorinated biphenyls (IUPAC # is 30) and 2,4',5-trichlorinated biphenyls (IUPAC # is 31) are referred to as tri-chlorinated biphenyls (Tri-CBs) homolog.

PCBs have been manufactured and used on a world wide basis. In the United States, PCBs were produced and marketed under the trade name Aroclor® by Monsanto Chemical Co. All Aroclors are characterized by a four digit number, the first two digits representing the type of molecule. Aroclor 1254

for example, is a 12-carbon system with 54% chlorine. In other countries PCBs are sold under different trade-names from that which exist in the United States.

First synthesized in 1881, PCBs did not gain wide-spread industrial application in the United States until 1929. Until cessation of production in 1977, U.S. industry manufactured and used PCBs because of their high dielectric constant, chemical and thermal stability, non-flammability and their low cost. The industrial uses of PCBs included insulating fluids in electrical transformers and capacitors, heat transfer substances, cutting oils, hydraulic fluids, lubricating oils, and plasticizers used in plastics manufacture. Application was also found for these compounds in paints, printing inks, carbonless copy paper, sealants, adhesives, and many other industrial applications (Swain, 1983).

Although their usage is currently banned or restricted, PCBs remain in the environment at declining but still unacceptably high concentrations because of their past widespread application and chemical stability (Schmidt and Heselberg, 1992). Recent studies have shown that at least 18 and perhaps up to 36 of the 209 congeners have potential for toxicity due to their abundance in fish/animal tissue and their demonstrated enzyme induction effects (McFarland and Clarke, 1989; Tanabe, 1988). This is understandable because the highly lipophilic nature of PCBs results in adipose tissue accumulation when ingested, and thus reduces the potential for easy excretion. The identical characteristics which made them

industrially desirable, also make them persistent and allow accumulation in the environment. Indeed the chemical stability of PCBs is superior to many other chemical compounds similar to it in structure and properties. PCBs are resistant to acid-base reactions, hydrolysis, chemical oxidation, photodegradation, thermal changes, and most chemical agents (Swain, 1983). As a result, they are poorly metabolized by biological systems.

Properties of Polychlorinated Biphenyls

The average boiling point of PCBs is about 360 °C. PCBs have a yellow color in appearance but some are clear. They are hydrophobic, show low water solubility, high lipophilicity, high density, low vapor pressure, high dielectric constant and possess a high octanol/water partition coefficient. The degree of lipophilicity increases with increasing ring chlorination. The viscosity characteristics of PCBs resembles that of a liquid oil at room temperature. The vapor pressure of PCBs and their solubility in water decrease with the increased chlorination.

Table 1. Characteristics of Aroclor® 1254

Color	yellow or clear
Specific gravity	1.495-1.505
Molecular weight(average)	328.4
Boiling point (°C)	365 - 390
Density	1.53
Dielectric constant (at 25°C)	5.0
Aqueous solubility (ppb)	42
n-Octanol/water partition coefficient (K_{ow})	1,288,000
Soil sorption constant (K_{oc})	63,914

(Adapted from Waid, 1986).

Numerous researchers have reported the use of adequately suitable qualitative and quantitative techniques for the analysis of PCBs in biological specimens (Gonzalez et al., 1995; Miller et al., 1992; William and Koszdin, 1991 and Jacobson et al., 1989). Recent research has also focused on the analysis for polymeric materials used as cleanup and bioconcentration tools for the analysis for PCBs and other organic chemicals from water, soil and lipophilic media (Zabik et al., 1992; Huckins et al., 1990^a; Sodergren, 1987 and Coutant et al., 1985).

Extending this concept to food packaging, researchers can focus on issues such as the migration of PCBs from packaging materials to packaged foods or in the reverse case, the sorption of PCBs from contaminated foods by the packaging material. Thus, a useful exercise would be to develop a methodology for the determination of specific PCB congeners in

selected polymeric packaging materials used for the packaging of foods. In this study the packaging materials used are polyethylene, polystyrene and polyvinyl chloride (PVC).

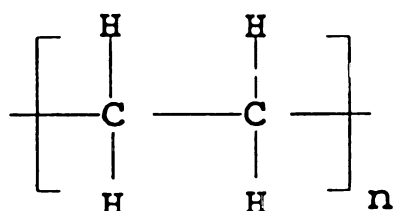
PACKAGING MATERIALS

Polyethylene

Polyethylene is the most widely used thermoplastic and continues to experience significant technological developments which promise to extend its applications dramatically. This production of all types of polyethylene will increase from 30 million tons in 1990 to 40 million tons in 1996 (Manders, 1994). At present over 300 million kg of polyethylene film is used each year. This does not include 2 million kg of heavy-gauge sheet material used for thermoforming. About 60 million kg is used for shrink and stretch packaging. About half the film is used for foods and half for nonfoods such as shipping sacks, soft goods packaging, laundry and dry-cleaning bags (Hanlon, 1992).

The polymerization of ethylene to polyethylene can be described as an addition polymerization process. Thus, polyethylene is called an addition polymer. This process involves a chain formation mechanism of (1) initiation, (2) propagation, and (3) termination (Giacin, 1993). During this process, two variants of polyethylene can be produced. These are linear chains with successive monomers (Figure 2) being added only at the ends of the growing chain, or branched

chains, where the monomers are added at multiple sites. These variants differ in structure and properties, including physical and mechanical properties. These two are characterized by high density and low density polyethylene, respectively. The first being a linear and the second a branched structure (Benning, 1983).



POLYETHYLENE (PE)

Figure 2. The monomeric structure of polyethylene.

The structural regularity of the linear chain type of polyethylene contributes to the development of crystallinity within its matrix. Since the presence of branching disrupts this regularity of structure, such regions are usually non-crystalline and are referred to as being amorphous. Branching is achieved by copolymerizing the monomeric ethylene with other olefinic comonomers such as butene and hexene as examples (Bremer, 1988).

Commercial polyethylene is a partially crystalline solid, somewhat flexible, whose properties are strongly influenced by

the relative amounts of crystalline and amorphous phases. The smallest crystalline units are called lamellae. These are interconnected by chains which pass from one lamella, through small amorphous regions, to another lamella. The lamellae form much larger spherically shaped units called spherulites, which are interconnected through amorphous regions. The crystalline phase provides rigidity and a high softening temperature, whereas the amorphous phase which is relatively soft at service temperature, provides flexibility and high impact strength. Certain properties are also affected by the size of the spherulites.

The substituent groups found within most polyethylenes not only influence a reduction in its crystallinity and melting point, but also its density. The density of the crystalline regions can approach 1.00 g/cm^3 while that of the amorphous phases is usually about 0.855 g/cm^3 , thus showing the relationship of density to crystallinity. Other important differences in the structure of polyethylene are average molecular weight and molecular weight distribution, and long-chain branching. These are known to influence the percent crystallinity and the resultant changes in properties associated with it. Commercial polyethylene can thus be divide into 5 main groups: 1. high pressure, low density polyethylene (LDPE), 2. linear low density polyethylene (LLDPE), 3. high density polyethylene (HDPE), 4. ultra-high molecular weight polyethylene, and 5. modified polyethylene. Modern manufacturing modifications have given rise to certain

sub-groupings of these different types of polyethylene. Orientation of the semi molten polymers during processing has been shown to improve its mechanical properties as compared to unoriented analogues. Studies by Choy et al. (1984) confirms this to be so when they showed a decrease in toluene diffusion in oriented polypropylene as compared to unoriented polypropylene. Thus, one can find references to names such as oriented HDPE.

Crystallographic studies of polyethylene show the crystal system to be of three types - orthorhombic, monoclinic and triclinic. Beach and Kissin (1986) reported that the C-C bond length is 0.154 nm, a C-C-C angle is 112° , and an ethylene unit length of 0.254 nm. The volume occupied by these units of polyethylene will be dealt with later when the pore spacing/diffusion relationship is discussed.

Unsubstituted polyethylene (high density polyethylene) has a density of $0.96\text{--}0.97\text{ g/cm}^3$ and crystallinity of 70-90%. The crystalline phase usually has a melting point as high as 135°C . Polyethylene with such properties is called high density homopolymer, and represents a small proportion of commercially used polyethylene. Blow-molding products are the single largest use of HDPE. This represents 41% of the total HDPE consumption (Beach and Kissin, 1986). Products manufactured by this process include milk and juice jugs, drums, tanks, toys and other similar products. Injection molding accounts for approximately 30% of the HDPE consumption (Beach and Kissin, 1986). This provides products such as food

containers, pails, crates, cases and toys as examples. Other minor uses of HDPE include products such as pipes, conduits and film applications such as bags.

LDPE is synthesized at 250°C, and high pressure (1000 to 3000 atm). The process utilizes a free-radical process which causes the formation of alkyl substituents or short-chain branches onto its backbone chain. This produces a highly branched structure usually containing 2-8 carbon atoms. Since the alkyl groups cannot fit properly into the crystalline lattice of the polyethylene chain, its melting point, crystallinity, and thus its density is reduced. Commercial LDPE usually has a density of 0.916-0.93 g/cm³, a percent crystallinity of 45-55% and melting points of 105-115°C.

Over half the LDPE produced is used as sheets and mono and multilayered films. Other uses include extrusion coatings for paper, metals, and other plastics; wire and cable coating; injection molding; blow molding; adhesives; and pipe extrusion. The homopolymer film applications include containers and bags of various sizes, packaging for food and clothing, industrial liners, vapor barriers, agricultural film, house-hold uses, and shrink-and stretch-wrap film (Doak, 1986).

LLDPE has a linear structure but with some controlled level of branching. The number and length of the branch chains are much less than those associated with LDPE. It also has a narrower molecular weight distribution than that of conventional LDPE. Linearity contributes to the polymer's

mechanical strength, while branching increases toughness. The combination of the two in the LLDPE results in physical properties that are improved over conventional LDPE. Compared to LDPE, LLDPE is superior in tensile, elongation, impact, puncture resistance and low-temperature properties. The trash-bag market exceeds 4.5×10^5 t/yr and is its largest single market (Beach and Kissin, 1986). As a result, less resin is used while necessary properties are provided in applications where it is substituted for LDPE.

Ultra low-density polyethylene (ULDPE) and very low-density polyethylene (VLDPE) are the new categories of LLDPE. The lower density limit for such resins are between 0.88 and 0.89 g/cm³ (Cady and Ratter, 1988). ULDPE exhibits properties far superior to that of conventional LLDPE in areas of strength, sealability, flexibility, and optical properties.

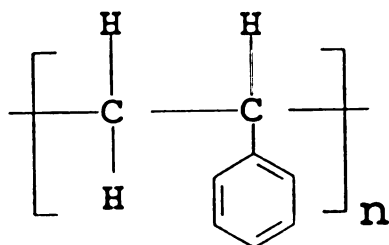
VLDPE products are used in many applications where toughness, impact strength, puncture and dart-drop resistance, in combination with softness and flexibility are important desirable characteristics. This combination of properties makes them suitable for film, blow and injection molded parts, flexible sheets, and extruded profiles and tubing (Rundlof, 1994). Applications of VLDPE include meat packaging, stretch film, bag-in-box, shrink film, medical packaging, and heavy duty shipping sacks. This material is also suitable for use as soft flexible films for disposable gloves, upholstery film, diaper film, and health care products (Rundlof, 1994).

Polystyrene

Polystyrene is a thermoplastic resin used in many applications because of its low cost and easy processability. It is available as a homopolymer called crystal polystyrene, or a toughened graft or blend with elastomers called impact polystyrene. This designation of polystyrene as crystal, only refers to its clarity and not to its molecular order. Copolymers are also available that give enhanced physical and thermal properties. These uses as disposables (single use packaging), in automobiles, packaging, toys, construction, electronics, and housewares.

General purpose polystyrene, also referred to as crystal polystyrene, the parent of the styrene plastics family, is a high-molecular-weight linear polymer consisting of about 2000-3000 styrene units. It is formed by combining benzene with ethylene gas to form ethylbenzene. This is dehydrogenated to make the styrene monomer. When this is polymerized, we have the long chain polymer as shown in Figure 3. Monomeric styrene is known to act either as an electron-donating or an electron-withdrawing center. Therefore, in addition to free-radical polymerization, it can be polymerized by all other primary propagation mechanisms such as anionic, cationic and coordination. Currently, all commercially produced polystyrene is atactic and is produced by free-radical polymerization. There are three common commercial grades of

general-purpose polystyrene. These are easy flow, medium flow and high heat grades. High heat polystyrene is used mostly for extrusion applications such as films, whereas the other types are mainly used for injection molding (Hahnfeld and Sugden, 1994).



POLYSTYRENE (PS)

Figure 3. The monomeric structure of polystyrene.

One should not confuse the term crystal polystyrene with the crystalline property of polystyrene. Crystal polystyrene is an amorphous polymer. It is clear and colorless with excellent optical properties and high stiffness. It is brittle until biaxially oriented, at which time it becomes comparatively flexible and durable. Typical properties of high heat general purpose polystyrene include the following:

Table 2. Properties of polystyrene.

Properties	Measured values
Specific gravity	1.0865 g/cm ³
Tensile strength	56.6 MPa
Flexural strength	82.75862 MPa
Typical shrinkage	0.01143 cm/cm
Boiling temperature (T_b)	145°C
Glass transition temp. (T_g)	108°C
Izod impact strength notch	24 J/m

(Hahnfeld and Dalke, 1986)

This type of polystyrene has several advantages over the other types of polystyrene. Most of its advantages are due to its amorphous nature, which results in its excellent clarity and fabrication ease. This polymer needs little energy input for its fabrication because it has no crystalline melting point, and as such no heat of crystallization. Thus, its transition from glass to a viscous liquid is gradual.

Crystal polystyrene finds many uses, especially where clarity is desirable. Applications for high heat polystyrene include foam extrusion for consumer electronics, expanded cushioning and food packaging - egg cartons, meat and poultry packaging trays; sheet extrusion and thermoforming for lighting, construction and decoration; film extrusion for oriented food packaging; injection molding for tape reels; and injection blow molding for packaging containers (Hahnfeld and Sugden, 1994).

Impact polystyrene is an amorphous polymer made from the

graft polymerization of styrene monomer with an elastomer, or a physical blend of polystyrene with an elastomer (typically polybutadiene). The resulting polymer is tough, usually white, and quite easily extruded and molded. The percentage of the elastomeric phase in such cases directly influences the toughness of the resulting resin. Therefore, the properties of impact polystyrene can vary significantly. For this reason, it is typically divided into three categories - medium impact (Izod <80.07 J/m); high impact (Izod 80.07 J/m); and super-high impact (Izod 138.788 to 266.9 J/m). Typical properties include flexural and tensile strength of 13.7931 to 48.27586 MPa, elongation of 10 to 60%, gloss of 5 to 100%, contact clarity from very good to poor, shrinkage of about 0.0152 cm/cm, and coefficient of thermal expansion in the same range as crystal polystyrene. It has a viscous softening of 102.3°C (Hahnfeld and Dalke, 1986).

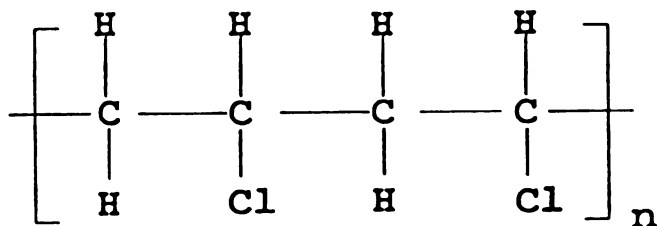
Impact polystyrene has found many applications and industrial uses because of its ease of processing, low cost and performance. Its major uses are for packaging and disposables, appliances, consumer electronics, toys, recreation and buildings materials. Its major food packaging uses are for dairy containers, vending and portion cups, kits, plates and bowls, and disposables such as flatware, closures, safety razors and pens (Poloso, 1994).

The most common form of expandable polystyrene is made by blowing pentane gas into crystal polystyrene beads. This results in a foamed product. It finds many uses from coffee

cups to automobile bumpers. Generally, its major end uses are for disposable drinking cups, cushioned packaging and in thermal insulation (Klepik, 1994).

Polyvinyl chloride

The initial step in the industrial production of PVC begins with the reaction of chlorine with ethylene gases to produce ethylene dichloride. This is then dehydrohalogenated to yield vinyl chloride monomer, which is then polymerized to produce polyvinyl chloride, shown below in Figure 4.



POLYVINYL CHLORIDE (PVC)

Figure 4. The monomeric structure of polyvinyl chloride.

Commercial PVC is produced by an addition polymerization. In this process, a free radical is formed by decomposition of an initiator. This free radical then forms an active center with the vinyl chloride monomer and thus initiates the

polymerization process. This continues until the chain is terminated. The average number of molecules in a typical chain has been estimated to be between 950 at a polymerization temperature of 122°F and 480 at a temperature of 158°F (Gabbett, 1994). The polymeric structure of PVC is partly crystalline (approximately 15%), this is mainly due to the regularity of its structure. The chlorine molecules are usually bonded in a head-to-tail alignment and is referred to as being syndotatic. The higher the processing temperature, the higher the level of irregularity of the polymeric structure, and thus the lower its percent crystallinity.

In its pure form, PVC is very stiff and rigid (Brittleness - 20 elongation at break point in percent length) with little impact resistance (Izod 8 ft.-lb). To be made soft and pliable, plasticizers must be incorporated within its structure during its manufacture. Liquid plasticizers presumably gather in pockets between adjacent amorphous chain segments, giving them mobility to produce softness and flexibility. The use of plasticizers in PVC manufacture accounts for approximately 70% of the total plasticizer market (Deanin, 1978). Thus, PVC is seldom used in its pure form. The proportion of plasticizers used directly relates to the characteristics of the finish polymer. Although the plasticizers increase its machinability, this is at the expense of its cohesive density, and thus result in a reduction of its barrier properties. Collins and Daniels (1975) reported that the percent plasticizers in PVC can range

between 25.9 - 39.4%.

PVC is a good barrier for oils, alcohols and petroleum solvents so long as a judicious use of plasticizers was employed in its manufacture. Rigid PVC has been known to retain odors, flavors, oxygen, moisture, and gases in general to a desirable extent, but may react with halogenated hydrocarbons. PVC has a glass-transition temperature (T_g) of 87°C and a Melt temperature (T_m) of 212°C. Incorporation of plasticizers can lower these temperatures in proportion to the percentage and type incorporated.

TRANSPORT PROPERTIES THROUGH A MEMBRANE

Factors affecting the uptake of a compound by an adsorbent include: (1) the physical and chemical nature of the adsorbent, (2) the physical and chemical nature of the compound, (3) the concentration of the compound in contact with the adsorbent, (4) the characteristics of the phase in contact with the adsorbent, and (5) the resident time of the system.

Pore and solute size

The pore size of a polymer together with the size and shape of the solute will influence the passage of molecules through the membrane. The mobilities of the polymer's segments and the penetrant molecules in a polymer-penetrant mixture are primarily determined by the amount of free volume in the system. This can be described by the following:

$$M_A = A_d \exp\left[\frac{-B_d}{v_f}\right] \quad (1)$$

Where M_A is the mobility of the penetrant, v_f is the average fractional free volume of the system, and A_d and B_d are empirical free-volume parameters that are assumed independent of penetrant concentration and temperature. The parameter A_d depends on the size and kinetic velocity of the penetrant, while B_d is equivalent to the critical hole free volume necessary for a penetrant to make a diffusive jump (Cohen and Turnbull, 1959). This expression can be modified by arguing that crystalline material reduces the free volume in direct proportion to the amount of crystalline material present (Kreituss, 1981). Thus, the equation in (1) above will become:

$$M_A = A_d \exp\left[\frac{-B_d}{\Phi_a v_f}\right] \quad (2)$$

where Φ_a is the amorphous volume fraction of the penetrant free polymer at zero pressure and the temperature of the system. Other factors that also influence pore size include the flexibility of the polymer chain, the amount of membrane swelling, the extent of cross-linking and the temperature. Bixler and Sweeting (1971) studied this phenomenon by investigating the linear relationship between the infinite dilution solubility coefficient and the amorphous fraction in

polyethylene at 25°C for various gases and organic vapors. The results from this study supported the notion of the impenetrability of crystalline regions even by gas molecules. Bixler and Sweeting (1971) also showed that the solubility coefficient S_i of the gases and organic vapors are proportional to the volume fraction of the amorphous region ϕ_a and the intrinsic solubility coefficient of the totally amorphous material S_a where:

$$\frac{S}{S_a} = \phi_a \quad (3)$$

After the molecule passes through a pore in the membrane surface it must negotiate passage through channels in the membrane. This is referred to as the tortuosity factor. The tortuosity of the corridor is influenced by the density of chain packing, which is decreased by the presence of bulky functional groups. The twofold effect of chain motion analogous to chemical cross-linking and tortuous barrier property has been studied by Michaels and Bixler (1961) who showed that both increase with increasing crystallinity of the membrane. This can be expressed mathematically to show the relationship of tortuosity θ to diffusion:

$$D = \frac{D_a}{\theta\beta'} \quad (4)$$

where D and D_a are the diffusion coefficients in the actual sample and in a totally amorphous sample, respectively and where β' is the immobilization factor.

As mentioned earlier, the size of the penetrant molecules can also affect passage through membranes. In the case of non-spherical compounds, the cross-sectional area and volume may be limiting factors. Hwang and Kamermeyer (1975) reported that molecular weight is not an effective description of molecular size and parameters such as the parachlor, permachlor, the space factor or molar volume can be used to correlate molecular properties with passage through a membrane. Heindorf (1992) reported that the parachlor (P_c) is an empirical relationship between density and surface tension and is defined as:

$$P_c = \left(\frac{M}{D-d}\right)\tau = \sum P_{ca} \quad (5)$$

where τ is the surface tension, D is the density in a liquid phase and d is the density of the molecule when in the gas phase, which is often negligible. The parachlor is also

phase, which is often negligible. The parachlor is also estimated by summing atomic parachlors (P_{ca}) (Banerjee et al., 1995; Tulp and Hutzinger, 1978). Leman (1981) stated that since d in (5) above is much smaller than D , equation (5) can be rewritten as:

$$P_c = \left(\frac{M\sigma^{1/4}}{D} \right) \quad \text{or} \quad P_c = V\sigma^{1/4} \quad (6)$$

where σ is surface tension and V is the molar volume. Parachlor values, in units of $\text{g}^{1/4} \cdot \text{cm}^3 / (\text{sec}^{1/2} \cdot \text{mol})$, are generally in the range of 100-600.

The permachlor concept that relates the polymers structure to its permeability by using a scheme of additive (+/-) structural components descriptive of the polymer was developed by Salame (1962) and Malachowski (1971). In experiments performed by them, they obtained good correlation between membrane permeability and the permachlor values for homologous series of penetrant compounds. The space factor concept was also derived by Malachowski (1971) to allow for the effects of temperature on the polymer. This space factor Q_{sf} can be derived from the following:

$$\ln Q_{sf} = a + b \frac{T_c}{T} + c \frac{d}{T^n} \quad (7)$$

where T_c is the critical absolute temperature for the permeant, d is the molecular diameter of the solute and is temperature dependent, n is the space factor, T is the absolute temperature that contributes to the solubility of the permeating species in the polymer and a , b , and c are constants that depend on the polymer.

The molar volume (V) alluded to by Leman (1981) above, can be used to estimate the size of an organic compound (except organophosphates) from its chemical structure. Tables 3 and 4 list the contributions of selected atoms to the gaseous molar volumes which can be applied to a given chemical structure.

Table 3. Gaseous Molar Volume (V_g) of selected atoms in aromatic and heterocyclic rings structures.

Atom	Increment (cm^3/mol)	Ring size	Increment
C	16.5	Aromatic & heterocyclic rings	-20.2
H	1.98		
O	5.48		
Cl	19.5		

(Adapted from Leman, 1981)

Table 4. Gaseous Molar Volume (V_g') of selected atoms in heterocyclic rings structures.

Atom	Increment (cm^3/mol)	Ring size	Increment
C	14.8	3-membered	-6.0
H	3.7	4-membered	-8.5
O	9.1	5-membered	-11.5
Cl	24.6	6-membered	-15.0
		Naphthalene	-30.0

(Adapted from Leman, 1981)

From Leman's proposals as shown above, the gaseous molar volumes of the PCB congeners used in this study can be determined. This determination was done and is shown in Table 5. The size of the congeners increase with increasing chlorination of the biphenyl ring from tri-chloro to deca-chlorinated.

Table 5. Calculated molar volumes V_B and V_B' for PCB congeners used in this study.

Biphenyl Compound	Calculated V_B Leman molar vol (cm ³ /mol)	Calculated V_B' Leman molar vol (cm ³ /mol)
2,4',5-		
Trichlorobiphenyl	229.96	245.00
2,2',4,4'-		
Tetrachlorobiphenyl	247.48	265.90
2,2',4,5',6-		
Pentachlorobiphenyl	265.00	286.80
2,2',3,3',4,4'-		
Hexachlorobiphenyl	282.52	307.70
2,2',3,3',4,4',6-		
Heptachlorobiphenyl	300.04	328.60
2,2',3,3',4,5',6,6'-		
Octachlorobiphenyl	317.56	349.50
2,3,4,5,6,2',3',4',5'-		
Nonachlorobiphenyl	335.08	370.40
2,3,4,5,6,2',3',4',5',6'-		
Decachlorobiphenyl	352.60	391.30

(Adapted from Leman, 1981)

Similar values were also obtained by Spurlock and Biggar (1994) for a range of organic compounds including similar PCB congeners.

Crystallographic data on polyethylene, PVC and polystyrene reported by Brandrup and Immergut (1975) in Table 6, is a useful guide to the volumetric space occupied by the polymeric structures of these materials. Due to the presence of the benzene rings in polystyrene, a tightly packed molecular structure is impossible, hence the reason why polystyrene is relatively permeable to gases and vapors usually encountered in food packaging and processing. When compared to PVC or HDPE for example, the regularity, crystallinity and dipole/dipole moments (induced in PVC due to

the chlorine atoms) result in a closely packed polymeric structure that is much less permeable than polystyrene to the same penetrants under similar conditions.

Table 6. Crystallographic data for polystyrene, PVC and polyethylene polymers used in this study.

Polymer	Crystal System	Unit Cell Parameter (Å)		
		a	b	c
polyethylene	orthorhombic	7.40	4.93	2.53
	monoclinic	8.09	2.53	4.79
	triclinic	4.29	4.82	2.54
Polyvinyl chloride	orthorhombic	10.60	5.40	5.10
polystyrene		21.90	21.90	6.63

(Brandrup and Immergut, 1975)

One can thus see that a unit monomeric cell of polystyrene occupies more space than polyethylene and PVC. Even though polyethylene occupies less space, one must remember that commercially used polyethylenes are usually less than 100% crystallinity. Thus, the introduction of amorphous regions are expected to greatly increase its permeability to the usual penetrants which normally come into contact with it.

Temperature

In cases where temperature is increased, volume dilation and thus an increase in free volume occurs. As a result, the

diffusion coefficient increases with temperature. The free-volume fraction may be represented as a linear addition of several variables (Stern et al., 1972; Fang et al., 1975):

$$v_f(T, p, \phi_1) = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) + \gamma\phi_A \quad (8)$$

where v_f is the fractional free volume of the pure, penetrant-free, amorphous polymer at some reference temperature T_s , usually the glass-transition temperature, and pressure p_s , usually 101.3 kPa. The penetrant volume fraction is ϕ_A and the coefficients α , β , and γ are positive constants for thermal expansion, compressibility and concentration, respectively. These constants characterize the role temperature, pressure and penetrant concentration play in affecting the free volume in the amorphous phase. They can be derived from the following equations:

$$\alpha = \left(\frac{\partial v_f}{\partial T} \right)_s \quad \beta = \left(\frac{\partial v_f}{\partial p} \right)_s \quad \gamma = \left(\frac{\partial v_f}{\partial \phi_1} \right)_s \quad (9)$$

where s denotes some reference state.

The effect of temperature on the rate of diffusion can also be explained by the Activated State Theory. This is based on the assumption that holes covering a spectrum of

different volumes and involving segments of several polymer molecules are continuously formed and destroyed due to thermal fluctuations. The rate of diffusion depends on the concentration of transient holes that are sufficiently large to accept diffusing molecules. Assuming a Boltzmann distribution, the concentration of a given set of holes decreases exponentially with the energy associated with its formation. Vergnaud (1986) reported that the activation energy of diffusion generally decreases with increasing temperature above the glass-transition temperature T_g , of the polymer. The activation energy is thus related to the amount of energy required to form the transient voids necessary for the process of diffusion. The temperature dependence of the diffusion coefficient based on the activated state theory can be described by Arrhenius law and is expressed as:

$$D = D_0 \exp\left(\frac{-E_d}{RT}\right) \quad (10)$$

where D_0 is the pre-exponential factor and E_d is the energy of activation for diffusion.

Temperature may also affect the thickness of the boundary layer at the membrane surface by altering the strength and number of hydrogen bonds in clusters of water or other polar

molecules if they are the penetrant under study. In this case, the concentration of this stagnant layer may become elevated through increased random movement of the solute molecules and a resultant decrease in its internal hydrogen bonding. Therefore individual penetrant molecules encounter less self attraction and find it easier to migrate towards the polymer.

Clustering effect

Clustering in itself can be considered as a factor that can affect the mobility of a polar penetrant through a polymeric matrix. Clustering could reduce the effective mobility of the penetrant since the size of the diffusing group increases. A similar effect has been reported for Kapton by Yang et al. (1985). Koros and Hellumus (1986) reported that if the diffusion process involves primarily jumps by a monomeric, unassociated penetrant, energy must be available both to make a gap to allow the penetrant to jump in or to cause the dissociation of one of the penetrants in a local region adjacent to the gap. As a result, higher activation energies for diffusion and, thus, a lower diffusion coefficient at activities above which clustering occurs are expected. A cluster integral G_A proposed by Zimm and Lundberg (1956) can be used to discuss the sorption behavior of clustering systems in terms of the partial molar volume V_A , the activity a_A , and the volume fraction of penetrant ϕ_A :

$$\frac{G_{AA}}{V_A} = -(1 - \phi_A) \left(\frac{\partial(a_A + \phi_A)}{\partial a_A} \right)_{p,T} - 1 \quad (11)$$

When G_{AA}/V_A is greater than -1, the solute is expected to cluster. G_{AA} can be obtained from equilibrium sorption data as a function of the penetrant partial pressure. Thus, $(\phi_A G_{AA}/V_A)$ equals the excess number of 'A' molecules above the number that would exist in the neighborhood of an arbitrarily chosen type 'B' molecule if the mixing were totally random, that is, no clustering (Koros and Hellum, 1986).

Polarity and charge

In considering a situation where an aqueous liquid is in contact with a polymer, it should be visualized as an immiscible organic layer in contact with an aqueous phase. Molecules from the bulk water diffuse and form a thin, highly structured layer at the membrane surface. Partitioning into and through the membrane can only occur if passage through this structured layer is successful. In situations where highly hydrophobic polymers such as polyolefin, vinyl plastics, nylons, epoxy resins, elastomers and other similar materials, are in contact with polar penetrants such as water, alcohols (methanol, ethanol, n-propanol, isopropanol, etc.), and acetic acid, clustering is expected to take place, form a less dense liquid layer at the boundary, and thus decrease the

equilibrium concentration of the liquid phase on the membrane surface (Lee et al., 1989; Hermann, 1972). Heindorf (1992) reported that for some molecules, variations in pH may influence water solubility, alter the diffusion constant from the bulk phase and the membrane solubility. The presence of dissolved substances such as humic materials may affect partitioning properties in a similar fashion. She also reported that interactions between the molecule and the membrane include dipole/dipole, dipole/induced dipole, and London dispersion interactions can also affect diffusion constants.

Derjaguin and Churaev (1981) reported that polymers such as polyolefins have long hydrocarbon segments and therefore are expected to have a strong dispersive character. Thus, if a hydrophobic contaminant in an aqueous phase contacts such polymers, its uptake by the membrane should be expected to be easily facilitated. The dispersive character is greater for saturated hydrocarbons than for similar unsaturated ones, and greater for cyclic than for aliphatic analogs (Derjaguin and Churaev, (1981). Adamson (1990) reported that a polar (nonpolar) adsorbent will preferentially adsorb the more polar (nonpolar) component of a nonpolar (polar) solution. Polarity is used here in the general sense of ability to engage in hydrogen bonding or dipole-dipole type interactions as opposed to nonspecific dispersion interactions. As an extension of this, the Traube's rule states that the adsorption of organic substances from aqueous solutions increases strongly and

regularly as we ascend the homologous series of a given compound. Adamson (1990) quoting Holmes and McKelvey (1928), showed that Traube's rule can be modified to show that a reversal of order should occur if a polar adsorbent and a nonpolar solvent were used. Wheeler and Levy (1959) reported that aromatic ring compounds tend to adsorb preferentially to aliphatic ones on carbon. As an explanation for this, they speculated that this may be due to the presence of the π electron interactions within the benzene ring structure, or alternatively, because of the higher polarizability of such rings. Bulky substituents reduce this preference, perhaps because of their preventing a close approach of the ring to the adsorbent surface.

Concentration

The interaction at the interface between two phases involving the transition of a molecule from one phase to another and driven by different concentration values, can be considered as the sorption of the molecule (Kovach, 1978). Sorption can be divided into two categories, adsorption and absorption. Adsorption is the concentration or accumulation of a penetrant at the surface of a membrane. Absorption on the other hand, is the process by which the molecules of the penetrant interpenetrate almost uniformly within the membrane, forming a solution-like relationship with that of the membrane.

The fundamental difference between adsorption and

absorption is illustrated in Figure 5 for the reaction in which the molecules of a liquid move towards a solid surface (Weber, 1972).

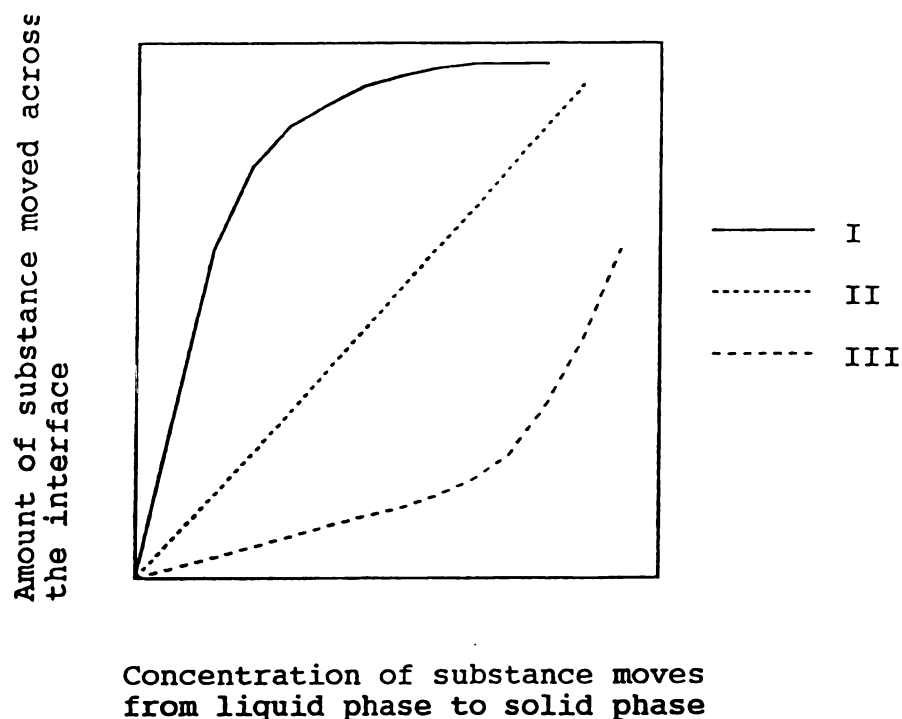


Figure 5. Types of sorption curves for three penetrants by a given sorbent material (Weber, 1972).

Takashi (1994) reported that curves I and III indicate curvilinear dependence of the amount concentrated at the solid surface on the amount remaining in the solution phase for favorable and unfavorable separation patterns, respectively. On the other hand, curve II shows linear adsorption and an absorption which occurs in direct proportion to concentration. He also noted that the adsorption is described by a Langmuir

type of isotherm, while the absorption is described by Henry's Law. In certain cases the Flory-Huggins equation instead of Henry's Law can be used to describe an absorption phenomenon (Hernandez, 1989).

The adsorption of a penetrant by a membrane, for example, can be described as either physical or chemical in nature. In physical adsorption, the molecules are physically attached to the membrane surface and may be multilayered, where each molecular layer forms on top of the previous layer with the number of layers being proportional to the penetrant's concentration. Thus, the higher the concentration of the penetrant, the greater the number of molecular layer formed. The point should be made that this multilayer diminishes with increasing distance from the membrane due to the inverse relationship that exists between the attractive force of the membrane for the penetrant molecules and/or vice versa. Increases in turbulence increase the number of penetrant molecules that arrive at the boundary layer and thus increase the probability of adsorption. Heindorf (1992) reported that if the concentration of an aqueous boundary layer is too great, concentration polarization will limit the efficiency of the transfer.

Chemical adsorption occurs when a chemical compound is produced between the adsorbed organic molecule and the adsorbent. This is a one-molecular layer system and is quasi-irreversible. This process requires energy in its formation and so energy would be required for its reversal or desorption.

Diffusion is a macroscopic manifestation of a random walk or Brownian motion of individual additive molecules within the polymer lattice (Limm and Hollifield, 1995). Generally, a reference velocity such as mass, molar, or volume average bulk velocity is selected, and movement of the component of interest (gases, vapors, liquids, and solutes) relative to this reference velocity is defined to be true diffusion (Koros and Hellumus, 1986). This mode of molecular transport has been shown in most cases to obey Fick's laws of diffusion (Crank, 1975) which states:

$$\text{Fick's first law: } F = -D_p \frac{\partial C_p}{\partial x} \quad (12)$$

$$\text{Fick's second law: } \frac{\partial C_p}{\partial t} = D_p \frac{\partial^2 C_p}{\partial x^2} \quad (13)$$

where F is the rate of transfer of a penetrant per unit area of polymer expressed as mass, molar or bulk volume as described above. D_p is the diffusion coefficient in $(\text{length})^2/\text{time}$, t is elapsed time and c_p is the concentration of the penetrant in the polymer expressed in the same units as the diffusant per unit of volume or mass of polymer. One can thus see that Fick's first law is concentration dependent while the second law is independent of concentration. If the diffusion coefficient is time-dependent, the diffusion process

is said to be non-Fickian. Chainey (1989) reported that in the steady state, the diffusion flow is constant, and where the diffusion coefficient is independent of concentration, Fick's first law may be integrated to give:

$$J_s = \frac{D(C_1 - C_0)}{L} \quad (14)$$

where C_1 and C_0 are the concentrations of penetrant at the high and low concentration faces of the film, respectively. J_s is the steady-state flow and L is the film thickness.

Chainey (1989) also reported that it is the pressures or partial pressures, p , of gas or vapor above the faces of the film, rather than the surface concentrations, C , which are usually known. These quantities are related by Henry's law, which states that:

$$C = S p \quad (15)$$

where S is the solubility coefficient. This relationship is obeyed only at low penetrant concentrations. It is often found that where the diffusion is concentration dependent, the solubility coefficient also exhibits a concentration or pressure dependence, although the magnitude of this effect is usually less. It can be seen that a combination of equations

14 and 15 can give the permeation equation:

$$J_s = \frac{DS(p_1 - p_0)}{L} \quad (16)$$

where DS is the permeability coefficient P. Thus, J_s , the steady-state flow can be rewritten as:

$$J_s = \frac{P(p_1 - p_0)}{L} \quad (17)$$

Since J_s is the amount of penetrant Q, which has passed through the film in time t, the equation can be written as:

$$J_s = \frac{Q}{t} \quad (18)$$

Surface area (dimensional changes)

As mentioned above in Fick's laws, the flux or rate of transfer of the penetrant is dependent on the exposed area of the membrane. Indeed, the diffusion coefficient itself is expressed in units of area (cm²) per unit time (sec). Gases

and vapors can permeate through materials by macroscopic or microscopic pores and pinholes or they may diffuse by a molecular mechanism, known as activated diffusion. In activated diffusion, the gas is considered to dissolve in the membrane at one surface, to diffuse through the packaging material by virtue of a concentration gradient, and to reevaporate at the other surface of the packaging material. This phenomenon is referred to as permeability. The permeability constant (P) of a membrane to a given penetrant can be expressed as:

$$P = \frac{J_s \times L}{A \times \Delta P} \quad (19)$$

where A is the exposed surface area and ΔP is the partial pressure gradient across the membrane. Here again we see the dependence of transport of a penetrant through a membrane on the thickness and surface area of the membrane. One can also see that the dependence of concentration on diffusion, solubility and now permeability coefficients has been dealt with under equations 15 and 17, and the fact that $P = DS$.

An alternative diffusion equation

In cases where the membrane sample is immersed in the penetrant, such that both faces are exposed simultaneously to

the same concentration, the penetrant enters the film and diffused towards its center. Chainey (1989) reported that in such cases, the sorption method for the measurement of transport properties should be used. He also stated that the bulk and surface concentrations are usually rapidly attained when compared to the rate of diffusion, and that such conditions are usually satisfied by polymers at temperatures well above their glass-transition temperature. In such situations the diffusion coefficient is usually independent of concentration and the extent of sorption at time t into the membrane is given by:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{L^2} \right)^{1/2} \left\{ \frac{1}{\sqrt{\pi}} + 2 \sum_{n=2}^{\infty} (-1)^n \operatorname{ierfc} \left[\frac{nL}{2(Dt)^{1/2}} \right] \right\} \quad (20)$$

where M_t and M_∞ are the masses sorbed at time t and at equilibrium, respectively, and ierfc is the inverse complementary error function. For short times, this equation simplifies to:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{L^2} \right)^{1/2} \quad (21)$$

A plot of M_t/M_∞ vs $\sqrt{t}$ will give D , the diffusion coefficient, as the initial linear slope. In a case of a concentration dependent diffusion coefficient, the initial slope of M_t vs $\sqrt{t}/L$ gives an average diffusion coefficient D_y over the concentration range of the experiment. Crank (1975) showed that a good approximation of the average diffusion coefficient can be obtained by:

$$D_y = \frac{1}{C_0} \int_0^{C_0} D(C) dC \quad (22)$$

In addition to exposing a liquid penetrant to a polymeric membrane in sorption experiments and determining its sorption by spectroscopy and chromatographic techniques, the sorption of a gas or vapor penetrant can be analyzed by the gravimetric technique. Takashi (1994) reported that this can be done by recording continually the gain or loss of weight of the membrane as a function of time using an electrobalance. Hernandez (1986) reported that the diffusion equation appropriate for the sorption of penetrants by a polymer sample in sheet or film form can be determined from Crank (1975) where:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \left[\exp\left(\frac{-D \times \pi^2 \times t}{L^2}\right) + \frac{1}{9} \exp\left(\frac{-9D \times \pi^2 \times t}{L^2}\right) \right] \quad (23)$$

Hernandez et al. (1986) also reported that the sorption diffusion coefficient (D_s) can be calculated from equation 23 by setting M_t/M_∞ equal to 0.5 and solving to give D_s ,

$$D_s = \frac{0.049 L^2}{t_{0.5}} \quad (24)$$

where $t_{0.5}$ is the "half-sorption- time" or the time required to attain the value $M_t/M_\infty = 0.5$.

Crank (1975) also described a similar equation for the sorption of a similar penetrant by a polymer in spherical or powdered form. In this case, L the thickness of the film is replaced by d the diameter of the penetrant particles

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \left[\exp\left(\frac{-4D \times \pi^2 \times t}{d^2}\right) + \frac{1}{4} \exp\left(\frac{-16D \times \pi^2 \times t}{L^2}\right) \right] \quad (25)$$

In this case, the sorption diffusion coefficient (D_s) can be obtained as follows:

$$D_s = 7.45 \times 10^{-3} \frac{d^2}{t_{0.5}} \quad (26)$$

the transport of limonene, ethyl acetate and toluene in polyethylene. Choy et al. (1984) and Vergnaud (1986) also used similar techniques when studying the sorption of toluene in polypropylene and benzyl alcohol by plasticized PVC, respectively.

PARTITIONING STUDIES

Bioconcentration factor

Bioconcentration factor (BFC) is defined as the ratio between the concentration of an analyte in an organism and the concentration of the same analyte in the environment. This can be expressed mathematically as:

$$BFC = \frac{\eta g \text{ compd. / g wet wt. organism}}{\eta g / ml \text{ water}} \quad (27)$$

This term has been widely used by environmental biological researchers to correlate the chemical and physical properties of xenobiotics to the tendency of biomonitors to accumulate a particular chemical contaminant. As is evident from the equation, BFC can be influenced by the aqueous solubility of the contaminant, the design of the experiment and the

biochemical ramifications of the organism involved.

Octanol/water partition coefficient

The concept of octanol/water partition coefficient (K_{ow}) was first proposed by Fujita et al. (1964). The octanol/water partition coefficient (K_{ow}) is defined as the ratio between the concentration of a chemical in octanol and the concentration of the same chemical in an aqueous phase. Expressed mathematically, this is describes as:

$$K_{ow} = \frac{\text{conc. } \epsilon \text{ the octanol phase}}{\text{conc. } \epsilon \text{ the aqueous phase}} \quad (28)$$

where ϵ represents in.

This expression was first used to describe the distribution of drugs in a variety of biological systems (Heindorf, 1992). Octanol was used as a standard substance to describe lipophilicity or the potential of the chemical to favor the non polar environment when in an immiscible solution of two polar/non-polar solutions.

Equilibrium partition coefficient (K_e)

Instead of using the terms K_{ow} and BCF, researchers working with polymers express the ratio between the

equilibrium concentration of a chemical in the polymeric phase and the equilibrium concentration of the same chemical in an aqueous phase as the equilibrium partition coefficient (K_e). This is expressed as:

$$K_e = \frac{[C_p]_{eq}}{[C_{aq}]_{eq}} \quad (29)$$

where $[C_p]_{eq}$ is the equilibrium concentration of the compound in the plastic film, and $[C_{aq}]_{eq}$ is the equilibrium concentration of the compound in the aqueous solution (Kwapong and Hotchkiss, 1987). The resulting K_e values can thus be an important parameter in determining the extent of sorption, since it is an indicator of the affinity of the compound for the plastic film.

CHAPTER 3

EXPERIMENTAL

EXPERIMENTAL DESIGN

The molecular structure, size, uptake capacity, physical, chemical, and kinetic characteristics of commercially available polyethylene, polyvinyl chloride and polystyrene were studied. These characteristics were studied in relation to the ability of these materials to remove or reduce the concentration of PCBs in an aqueous and peanut oil systems. A total of eight (8) PCB congeners, ranging from tri-chlorinated to deca-chlorinated were selected based on their differential molecular size and structural arrangement. After consultation (J. Gill, Department of Animal Science, Michigan State University, 1993, personal communications) it was determined that three replicates would be sufficient to distinguish differences in total concentrations of PCBs in the materials and the liquid phases.

Firstly, the relationships between the three materials and each PCB congener in an aqueous system were studied at the same environmental conditions. For the analysis involving the peanut oil, only the polyethylene material was used. In this case the ability of the material to remove the PCB from the oil was compared to its ability to remove the congeners from the aqueous system.

The study for the polystyrene was repeated but with a material thickness five (5) times that of the original material. This was repeated a third time, but with the original material at an elevated temperature. The results from this part of the study were also compared in order to determine the effect of temperature and material thickness on the potential of the material to remove the different PCB congeners from the aqueous system.

The mathematical basis for uptake of the congeners from polymeric phases, was the calculation of sorption diffusion coefficients and partition coefficients for each congener by all materials at all treatment conditions. Rate loss calculations were performed to mathematically compare the loss of the PCBs from the liquid phases.

To evaluate the results obtained in this study, and to measure its success against the initial objectives, five hypotheses were postulated. Testing of these hypotheses by analysis of variance using SPSS statistical software (1988), assisted in arriving at logical conclusions based on the calculated results. These hypotheses are:

1. there are no significant differences between the three polymeric materials in their uptake potential for the PCB congeners;
2. there are no significant differences in the removal of the PCBs from water as compared to oil by polyethylene;
3. there is no significant difference in the effect of thickness on the potential of polystyrene to remove PCBs

- from water;
4. there is no significant difference in the effect of temperature on the potential of polystyrene to remove PCBs from water;
 5. there are no significant affinity differences between the congeners for the polymeric materials.

MATERIALS

Glassware

All glassware (Erlenmeyer flasks, beakers, Turbo-Vap tubes, chromatographic columns, Soxhlet condensers, separatory funnels, boiling flasks, 1 mL and 5 mL volumetric flasks) were washed with detergent, rinsed with tap water, distilled water, acetone, and finally with hexane. The glassware was then oven dried.

Polymers

- Polyvinyl Chloride (PVC) - transparent film with a thickness of 1.778×10^{-3} cm (1 ply PVC thickness) and supplied by Reynolds Metals (Grottoes, VA).
- Polystyrene - transparent film with a thickness of 3.048×10^{-3} cm (1 ply) and supplied by Dow Chemical (Midland, MI). (Reference to 1 ply polystyrene is equivalent to 3.048×10^{-3} cm thick. Reference to 5 ply equals 15.24×10^{-3} cm thick.)
- Polyethylene - resin supplied as pellets by Dow Chemical (Midland, MI). The polyethylene pellets were extruded using a single screw 4 zone Killion model KLB-100 extruder, with

a 76.2 cm diameter barrel attached. It was interfaced with a Killion chill roll attached to a model 8412-A sterico steritronic temperature control console. The temperature zones 1 - 4 were set to operate at 110, 121, 132, and 149°C, respectively, while the die temperature was set at 143°C. The screw speed was set to operate at 15 rev/min., the 20.32 cm wide and 15.24 cm diameter chill roll at the dial speed of 100 (xx rpm), with a cooling temperature of 120°C. The percent crystallinity of the polyethylene, after extrusion, was calculated to be 53.56%. It had a thickness of 2.286×10^{-3} cm (1 ply polyethylene thickness).

Solvents

All solvents were analytical HPLC grade quality.

- Hexane - 85.04%, EM Science (Gibbstown, NJ).
- Acetone - 99.8%, Mallinckrodt Chemicals (Paris, KT).
- Isooctane - 99.91%, Mallinckrodt Chemicals (Paris, KT).
- Petroleum ether - 99.99% EM Science (Gibbstown, NJ).
- Toluene - 99.99%, Mallinckrodt Chemicals (Paris, T).
- Diethyl ether - 99.99%, Mallinckrodt Chemicals (Paris, KT).
- Acetonitrile - 99.8%, Mallinckrodt Chemicals (Paris, KT).

Chemicals

All chemicals were analytical grade quality.

- Sodium sulfate Na_2SO_4 - (activated by storing overnight at 130°C), Mallinckrodt Chemicals (Paris, KT).

- Florisil, 60-80 mesh - (activated by storing overnight at 130°C), Mallinckrodt Chemicals (Paris, KT).
- Silica gel 60, 70-230 mesh - (activated by storing 16 hrs overnight at 130°C), Mallinckrodt Chemicals (Paris, KT).
- Polychlorinated biphenyl congeners - Accustandard Inc. (New Haven, CT) are shown in Table 8 below:
- Sodium chloride NaCl - Mallinckrodt Chemicals (Paris, KT).

Table 8. Systematic names of the PCB congeners used in this study.

IUPAC No.		Chlorobiphenyl systematic names
Internal Standard	#30	2,4,6-Trichlorobiphenyl
Isomer #		Biphenyl Compound
31		2,4',5-Trichlorobiphenyl
47		2,2',4,4'-Tetrachlorobiphenyl
103		2,2',4,5',6-Pentachlorobiphenyl
128		2,2',3,3',4,4'-Hexachlorobiphenyl
171		2,2',3,3',4,4',6-Heptachlorobiphenyl
200		2,2',3,3',4,5',6,6'-Octachlorobiphenyl
206		2,3,4,5,6,2',3',4',5'-Nonachlorobiphenyl
209		2,3,4,5,6,2',3',4',5',6'Decachlorobiphenyl
(Ballschmitter and Zell, 1980)		

These are based on the occurrence of the congeners in Aroclor 1254 (Ballschmitter and Zell, 1980).

EXPOSURE OF FILM TO PCB CONGENERS

Deionized distilled water was spiked with a mixed PCB

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standard solution to produce a 10 ppb solution of each congener. This was done by initially dissolving equal concentrations of the 8 PCB congeners using acetone as a solvent. After adding the desired quantity to give the 10 ppb solution, the system was heated at 40°C for 1 hr with frequent shaking, to evaporate any residual acetone. After cooling 25°C, the solution was ready for contact with the polymeric materials.

A 0.1 ppm stock solution of spiked peanut oil with PCBs was also prepared. This was made by dissolving 1 mL of a 50 ppm mixed PCB in hexane solution in approximately 5 mL of peanut oil in a glass tube. The hexane in this solution was then evaporated for 30 min under nitrogen using a N-Vap Model III instrument (Organomation Assoc., Shrewsbury, MA). The resulting solution was then made up to 500 mL in a volumetric flask. This solution was then ready for contact with the polyethylene material.

Approximately 0.160 g of each polymeric film, except the 5 ply thick polystyrene, was prepared by cutting into longitudinal strips approximately 4 x 1.5 cm. The average weight of the 5 ply polystyrene strips was approximately 0.70 g, but the dimension was similar to that of the other samples. All sample numbers, actual weights and duration of exposure are recorded in Tables 9 - 13.

Table 9. Weights of PVC samples & storage times in water at 25°C.

Exposure time (hrs)	Replicate #	PVC Sample wt. (g)
0.083	1	0.1565
0.083	2	0.1790
0.083	3	0.1778
0.167	1	0.1534
0.167	2	0.1478
0.167	3	0.1510
0.25	1	0.1540
0.25	2	0.1425
0.25	3	0.1584
0.333	1	0.1648
0.333	2	0.1516
0.333	3	0.1556
0.5	1	0.1665
0.5	2	0.1622
0.5	3	0.1672
0.75	1	0.1710
0.75	2	0.1611
0.75	3	0.1560
1.0	1	0.1597
1.0	2	0.1512
1.0	3	0.1541
1.5	1	0.1425
1.5	2	0.1431
1.5	3	0.1762
2.0	1	0.1453
2.0	2	0.1539
2.0	3	0.1762
4.0	1	0.1476
4.0	2	0.1498
4.0	3	0.1633
8.0	1	0.1581
8.0	2	0.1476
8.0	3	0.1488
12.0	1	0.1582
12.0	2	0.1754
12.0	3	0.1631

Table 10. Weights of Polystyrene samples & storage times in water at 25°C.

Exposure time (hrs)	Replicate #	PS sample wt. (g)
0.083	1	0.1514
0.083	2	0.1754
0.083	3	0.1576
0.167	1	0.1821
0.167	2	0.1723
0.167	3	0.1567
0.25	1	0.1449
0.25	2	0.1406
0.25	3	0.1641
0.333	1	0.1703
0.333	2	0.1526
0.333	3	0.1601
0.5	1	0.1600
0.5	2	0.1462
0.5	3	0.1476
0.75	1	0.1391
0.75	2	0.1528
0.75	3	0.1698
1.0	1	0.1575
1.0	2	0.1685
1.0	3	0.1446
1.5	1	0.1507
1.5	2	0.1380
1.5	3	0.1363
2.0	1	0.1367
2.0	2	0.1434
2.0	3	0.1710
4.0	1	0.1526
4.0	2	0.1446
4.0	3	0.1427
8.0	1	0.1491
8.0	2	0.1344
8.0	3	0.1448
12.0	1	0.1375
12.0	2	0.1461
12.0	3	0.1422

Table 11. Weights of Polyethylene samples & storage times in water at 25°C.

Exposure time (hrs)	Replicate #	PE sample wt. (g)
0.083	1	0.1634
0.083	2	0.1427
0.083	3	0.1643
0.167	1	0.1641
0.167	2	0.1678
0.167	3	0.1898
0.25	1	0.1565
0.25	2	0.1583
0.25	3	0.1466
0.333	1	0.1529
0.333	2	0.1419
0.333	3	0.1589
0.5	1	0.1878
0.5	2	0.1953
0.5	3	0.1800
0.75	1	0.1767
0.75	2	0.1612
0.75	3	0.1663
1.0	1	0.1828
1.0	2	0.1955
1.0	3	0.1853
1.5	1	0.1848
1.5	2	0.1921
1.5	3	0.1802
2.0	1	0.1835
2.0	2	0.1796
2.0	3	0.1855
4.0	1	0.1575
4.0	2	0.1704
4.0	3	0.1525
8.0	1	0.1456
8.0	2	0.1449
8.0	3	0.1465
12.0	1	0.1608
12.0	2	0.1634
12.0	3	0.1629

Table 12. Weights of Polystyrene samples & storage times in water at 35°C.

Exposure time (hrs)	Replicate #	PS sample wt. (g)
0.083	1	0.1419
0.083	2	0.1499
0.083	3	0.1463
0.167	1	0.1476
0.167	2	0.1534
0.167	3	0.1630
0.25	1	0.1546
0.25	2	0.1527
0.25	3	0.1534
0.333	1	0.1727
0.333	2	0.1546
0.333	3	0.1759
0.5	1	0.1627
0.5	2	0.1710
0.5	3	0.1631
0.75	1	0.1598
0.75	2	0.1776
0.75	3	0.1434
1.0	1	0.1680
1.0	2	0.1627
1.0	3	0.1595
2.0	1	0.1471
2.0	2	0.1603
2.0	3	0.1560
4.0	1	0.1470
4.0	2	0.1726
4.0	3	0.1482
8.0	1	0.1741
8.0	2	0.1459
8.0	3	0.1523
12.0	1	0.1628
12.0	2	0.1772
12.0	3	0.1691

Table 13. Weights of 5 ply polystyrene samples & storage times
in water at 25°C.

Exposure time (hrs)	Replicate#	PS sample wt. (g)
0.083	1	0.6907
0.083	2	0.7161
0.083	3	0.6336
0.167	1	0.7215
0.167	2	0.7791
0.167	3	0.7588
0.25	1	0.6898
0.25	2	0.7798
0.25	3	0.7064
0.333	1	0.7614
0.333	2	0.7825
0.333	3	0.7784
0.5	1	0.6882
0.5	2	0.7108
0.5	3	0.6839
0.75	1	0.7374
0.75	2	0.7009
0.75	3	0.7186
1.0	1	0.6773
1.0	2	0.6815
1.0	3	0.7142
2.0	1	0.6437
2.0	2	0.7496
2.0	3	0.6576
4.0	1	0.6936
4.0	2	0.6320
4.0	3	0.6203
8.0	1	0.6803
8.0	2	0.7176
8.0	3	0.7694
12.0	1	0.7282
12.0	2	0.6916
12.0	3	0.6779

Each sample was then inserted in a 76 mL serum vial supplied by Wheaton Inc., Millville, NJ. Each vial was then brim-filled with the spiked aqueous PCB congener solution, sealed, and stored at 25°C in the absence of light. At given time intervals for a total of 12 hrs for polystyrene and PVC and a total of 72 hrs for polyethylene, samples were removed for PCB congener quantification. The analysis for polystyrene was repeated twice, once at 35°C, then again with a film 5 times thicker (5 ply) than the polystyrene used in the initial analysis. The thickness of the 5 ply material was determined to be 16.51×10^{-3} cm. This thicker material was manufactured from the same stock as the original one. The polyethylene exposed to the peanut oil was prepared similarly to that of the polyethylene exposed to the water and also stored at 25°C for maximum time of 72 hrs.

PCB CONGENER ANALYSIS

The PCB analytical method, including the clean-up procedures used in this study, was adapted from electron capture gas chromatographic analyses for PCB as outlined by Price et al. (1986). All samples in this study were extracted in triplicates and subsequently quantified for PCBs.

PCB EXTRACTION PROCEDURES

Extraction of PCB from polymers

After exposure of the samples for the specified time, the

polymers were immediately removed from the spiked water. The PCBs were extracted from the materials by Soxhlet extraction using 120 mL hexane as the solvent for 18 hrs. A 1 mL aliquot of a 5 ppm PCB congener 2,4,6 tri-chlorobiphenyl (IUPAC #30) solution was used as an internal standard for determination of concentrations and recoveries of PCBs. This solution was added to each sample prior to extraction. This PCB congener was selected as an internal standard because it does not occur in commercial Aroclor® mixtures nor has it been detected in environmental samples (Williams and Giesy, 1992). After the extractions were performed, each extract was collected into a 200 mL volumetric flask. These were subsequently reduced in a Turbo-Vap evaporator (Zymark) to approximately 0.5 mL volume at ambient temperature. Care was taken to avoid reducing the extracts to dryness.

Extraction of PCB from oil solution

After exposure of the oil to the polyethylene, the PCBs were extracted from the oil by first adding 25 mL acetonitrile (saturated with hexane) to it in a 250 mL separatory funnel. This was shaken for approximately 2 min, then the lower acetonitrile layer drained into a 500 mL separatory funnel. The remaining oil in the 250 mL separatory funnel was extracted two times more, each time with a fresh aliquot of 25 mL acetonitrile. In each case the acetonitrile layer was drained and combined in the 500 mL flask. To this combined solution was then added 100 mL hexane and 100 mL of a 10%

aqueous sodium chloride solution. After shaking for 2 min, three layers were observed. The bottom layer was discarded then the remaining solution was shaken again with fresh 100 mL aliquots of hexane and the 10% aqueous sodium chloride solution. If three layers appeared after this second extraction, a third 100 mL aliquot of each of the hexane and sodium chloride was again added then extracted. However, if only two layers were observed, the lower layer was discarded and the upper layer collected into a 200 mL volumetric flask. In cases where three extractions were performed, this upper layer was also collected while the lower was discarded, after it became clear that only two layers were present within the flask. To the solution collected in the 200 mL volumetric flasks 8 g of anhydrous sodium sulfate was added. After allowing half hour for the drying action of the Na_2SO_4 , the extracts were reduced in the Turbo-Vap evaporator to approximately 1.0 mL volume at ambient temperature. Care was taken to avoid reducing the extracts to dryness. Each sample was then reduced to approximately 0.1 mL by nitrogen evaporation using the N-Vap Model III instrument then made up with isooctane to exactly 0.5 mL in a volumetric flask.

Extraction of PCB from aqueous solution

The water solutions were also analyzed for their PCB concentrations. After the polymers were removed from the vials, the spiked water which remained was transferred to 250 mL separatory funnels. To each sample, a 30 mL aliquot of

hexane was added and vigorously shaken for approximately 30 sec. After standing for several minutes, the hexane layer rose to the top. This was drawn off and transferred to a 100 mL flask fitted with a stopper. This extraction procedure was repeated 2 more times on the same water sample, using 30 mL of hexane on each occasion. The extracts were combined, then a 10 g quantity of granular anhydrous Na_2SO_4 (activated by storing overnight at 130°C), was added to each flask to remove any traces of water in the extract. After allowing 30 min for drying with Na_2SO_4 , the extracts were reduced in the Turbo-Vap evaporator to approximately 1.0 mL volume at ambient temperature. Care was taken to avoid reducing the extracts to dryness. Each sample was then reduced to approximately 0.1 mL by nitrogen evaporation using the N-Vap Model III instrument then made up with isooctane to exactly 0.5 mL in a volumetric flask.

PCB's CLEANUP PROCEDURES

Gel Permeation Chromatography (GPC)

Cleanup by GPC resulted in removal of plasticizers, antislip agents, antistatic agents, flame retardants, monomers, dimers, dissolved polymers, antioxidants, light absorbers, and any other compound removed by the hexane during the Soxhlet extraction, without alteration of residual PCBs. The automated GPC system (Waters 712 WISP, Milford, MA) provided for unattended operation with a timed control system to remove the non PCB compounds. Each sample was diluted to 4 mL with

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HPLC grade hexane and transferred to a 6 mL GPC vial. After the contaminant as well as PCB fractions were collected, an automated washing device would flush the system prior to the next injected sample. This system was used to cleanup the concentrated extracts of polyvinyl chloride (PVC) and polyethylene from the Turbo-Vap evaporator.

The following procedure of cleanup by GPC was: a 2 mL aliquot of each extract was injected into the GPC column (Waters 19 x 300 mm Ultrastyrigel 500 Å) at a solvent flow rate of 5 mL/min. The solvent used was hexane. This was attached to a Waters/590 Programmable HPLC pump (Milford, MA) and a Waters fraction collector using a UV detector set at 254 nm. This was interfaced with a Hewlett Packard 3390A integrator (Avondale, PA). The contaminant portion was discarded, while the PCB portion collected, then reduced in the Turbo-Vap evaporator to approximately 1.0 mL. Each sample was reduced to approximately 0.1 mL by nitrogen evaporation using a N-Vap Model III instrument (Organomation Assoc., Shrewsbury, MA), after which the sample was made up with isooctane to exactly 0.5 mL in a volumetric flask.

Florisil/silica gel

The polystyrene and oil extracts were cleaned up using florisil followed by silica gel low pressure chromatography. The concentrated extracts from the Turbo-Vap were initially eluted through the florisil column with a 6% (by volume) of diethyl ether in petroleum ether solvent. The column (1 cm

i.d. x 51 cm), was prepared by placing 1 cm of granular anhydrous Na_2SO_4 on a glass wool plug, followed by 5 g of 60-80 mesh florisil (activated by storing overnight at 130°C), then another 1 cm of granular anhydrous Na_2SO_4 .

The prepared column was then washed by allowing the elution of a 20 mL portion of hexane. When the hexane reached the top of the upper layer of Na_2SO_4 , the Turbo-Vap concentrate was transferred to the column and allowed to drain onto the florisil bed. A 40 mL aliquot of elution solvent (6% diethyl ether in petroleum ether) was then added to the column. Care was taken not to allow the florisil bed to go to dryness. The collected eluent was then reduced to approximately 1 mL volume in the Turbo-Vap evaporator.

The silica gel column was prepared similar to that described for the florisil columns, but with silica gel 60 (70-230 mesh) activated at 130°C for 16 hours. A 50 mL quantity of 0.5% toluene in hexane was used as elution solvent. The concentrated eluent from the florisil column was eluted through this silica gel column, collected, then reduced to approximately 1.0 mL volume in the Turbo-Vap and to approximately 0.1 mL by nitrogen evaporation using the N-Vap Model III instrument. Each polystyrene sample was then made up with isooctane to exactly 0.5 mL in a volumetric flask. The oil samples were made up to 1 mL in a volumetric flask.

PCB QUANTIFICATION

The concentration of individual PCB congeners in each

extract was determined by gas chromatography (GC) with a ^{63}Ni electron capture detector (Hewlett Packard 5890 series II, Avondale, PA), and equipped with DB-5 capillary column (60 m x 0.25 mm i.d.). PCBs would generally elute in order of chlorination: $\text{C}_{12}\text{H}_9\text{Cl}$ first, $\text{C}_{12}\text{Cl}_{10}$ last.

The separated peaks from the GC column were detected at different times (retention times). The retention time of each PCB congener was confirmed by comparing the individual peaks with the retention time of the 12 PCB congeners mixed standard. These 12 congeners are found in Arochlor 1254[®] and run under the same conditions used for Arochlor 1254[®] quantitation. The standard PCB congeners used were all the same concentration and are listed in Table 8.

All quantification was based on peak areas relative to the area of individual congener standards and congener #30. A standard curve was constructed for each PCB congener from different concentrations of the standard mixture. The GC conditions for peak separation and quantification were as follows:

Detector temperature: 300°C
Inject temperature: 160°C
Inject volume: 3 μL
Carrier gas: Helium
Flow rate: 1 mL/min
Detector makeup gas: Nitrogen

The oven was programmed at an initial temperature of 160°C. The total run time was 60 min with 2 temperature/time levels.

Level 1 was set at 8°C/min. to a maximum of 200°C held for 5 min. Level 2 was set at 2°C/min. to a maximum of 280°C held for 10 min. The data were recorded on a HP Level Four integrator.

The PVC and polyethylene samples were quantified by comparison of peak area using the following equations:

$$\text{Recovery \%} = \frac{(\text{RA of sample soln internal std.})}{(\text{RA of 5ppm std. No. 30 PCB})} \times 100 \quad (30)$$

$$\text{Conc. (ppm) inj. vol.} = \frac{\text{GPC dil. factor} \times \text{LS of congener} \times \text{RA of congener}}{\text{Recovery \%}}$$

(31)

$$\text{Wt. PCB (mg) in sample} = \frac{\text{Conc. inj. vol.} \times 0.5\text{mL} \times 0.076\text{L}}{0.003\text{mL}} \quad (32)$$

GPC vol.: Gas Permeation Chromatography volume = 2 mL

GLC vol.: Gas Chromatography injected volume = 3 μ L

LS: Line Slope

RA: Retention Area

Sample wt.: Sample weight (g)

The polystyrene and the water samples were quantified by comparison of peak area using the following equations:

$$\text{Conc. (ppm) inj. vol.} = \frac{\text{LS of congener} \times \text{RA of congener}}{\text{Recovery \%}} \quad (33)$$

$$\text{Wt. PCB (mg) in sample} = \frac{\text{Conc. inj. vol.} \times 0.5\text{mL} \times 0.076\text{L}}{0.003\text{mL}}$$

DATA ANALYSIS

Mass balance determination

A mass balance of the weights of PCBs in the liquid and the polymeric phases were performed. The results of this

determination can be used to validate the effectiveness of the method used to quantitate the PCB congeners in the aqueous systems before and after the contact with the polymers and for PCBs in the three polymeric materials. These ratios were obtained by taking the sum of the PCB concentrations in the water and in the plastic and dividing by the initial PCB concentration in the water. This is expressed in the following equation:

$$\text{Mass bal. ratio} = \frac{(\text{Wt. PCB in H}_2\text{O at time}_t) + (\text{Wt. PCB in plastic at time}_t)}{\text{Wt. PCB in H}_2\text{O at time}_0}$$

(35)

In an ideal system, the mass balance ratio should be equal to one (1). In such cases, the concentration of the penetrant removed by the polymer would be equal to the concentration lost from the surrounding medium. However, due to experimental errors one might get small fluctuations above and below this ideal.

Sorption diffusion coefficient determination

The determination of the sorption diffusion coefficients for each material was obtained using Crank (1975) model for the sorption of penetrants by a polymer sample in sheet or

film form where:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \left[\exp\left(\frac{-D\pi^2 \times t}{L^2}\right) + \frac{1}{9} \exp\left(\frac{-9D\pi^2 \times t}{L^2}\right) \right] \quad (36)$$

The sorption diffusion coefficient (D_s) was calculated from equation 4-2 by setting M_t/M_∞ equal to 0.5 and solving to give D_s where:

$$D_s = \frac{0.049 L^2}{t_{0.5}} \quad (37)$$

where $t_{0.5}$ is the "half-sorption-time" or the time required to attain the value $M_t/M_\infty = 0.5$. The values obtained from these calculations provided a mathematical estimate of the equilibrium sorption coefficients for each congener by the polymeric materials.

Equilibrium partition coefficient (K_e)

The equilibrium partition coefficient (K_e) expresses the ratio between the equilibrium concentration of a given congener in the polymeric phase and the equilibrium concentration of the same congener in an aqueous phase of a

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unit sample system. This is expressed as:

$$K_e = \frac{[C_p]_{eq}}{[C_{aq}]_{eq}} \quad (38)$$

where $[C_p]_{eq}$ is the equilibrium concentration of the compound in the plastic film, and $[C_{aq}]_{eq}$ is the equilibrium concentration of the compound in the aqueous solution. The K_e values obtained were used to determine the extent of sorption, since they are indicators of the affinity of the PCB congeners for the plastic films.

Statistical calculations

The statistical significance of the relationships between the materials, liquid phases, the PCB congeners, and environmental conditions used in this study, were tested using a one-way analysis of variance (ANOVA) model. This was calculated using SPSS Release 4.1 for IBM (1988) statistical software. The criteria for statistical significance was chosen as 0.05. Where significant differences were found, a contrast analysis was performed. Tukey range test was used to determine the pairs of means which were statistically significant at 0.05 level.

CHAPTER 4

RESULTS

VALIDITY OF THE PCB ANALYTICAL METHODOLOGY

Tables 14, 15 and 16 show the mass balance ratios for PCB congeners concentrations in the polyethylene, polystyrene and PVC, respectively, and the water to which they were exposed. These results can be used to validate the effectiveness of the method used to quantitate the PCB congeners in the aqueous systems before and after the contact with the polymers and for PCBs in the three polymeric materials. In an ideal system, the mass balance ratio should be equal to one (1). In such cases, the concentration of the penetrant removed by the polymer would be equal to the concentration lost from the surrounding medium. However, due to experimental errors, small fluctuations above and below this ideal might occur. One factor contribution to errors may be the fact that the internal standard used to determine the percent recovery is a tri-chlorinated PCB congener. Since the electron capture detector in the GC instrument is sensitive to chlorine atoms, its sensitivity to the higher chlorinated congeners would be greater than to the lower analogues. Another factor likely to contribute to these errors may be the low concentration of the PCB analyte. These factors may account for the low ratios

obtained for the penta-chlorinated congeners shown in Tables 15 and 16, and the high ratios obtained for the tri-chlorinated analogues.

Table 14. Mass balance ratios for PCB congeners in polyethylene/water stored at 25°C.

Time (hrs)	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.08	1.46	1.20	1.00	1.21	1.20	0.94	0.99	1.12
0.17	1.34	1.23	0.98	1.23	1.21	0.97	0.86	0.95
0.25	1.13	1.19	0.95	1.08	1.21	0.94	0.80	0.88
0.50	1.15	1.04	0.88	1.09	1.08	0.94	0.77	0.75
0.75	1.21	1.04	0.85	0.96	1.12	0.98	0.84	0.89
1.00	1.21	1.06	0.91	0.99	1.12	1.10	0.88	1.01
1.50	1.25	1.21	1.09	1.14	1.24	1.23	0.96	1.12
2.00	1.26	1.21	1.05	1.06	1.40	1.16	0.92	1.08
4.00	1.23	0.98	0.95	0.97	1.09	1.12	1.16	1.09
8.00	1.36	0.95	0.88	0.88	1.10	1.07	1.06	1.13
12.00	0.98	0.97	0.95	0.91	1.05	1.05	1.06	1.32
24.00	1.83	1.22	1.08	1.17	1.17	1.16	0.84	1.20
48.00	1.74	1.53	1.51	1.30	1.39	1.40	1.00	1.39
72.00	1.84	1.45	1.13	1.19	1.66	1.23	0.90	1.26

Table 15. Mass balance ratios for PCB congeners in polystyrene/water stored at 25°C.

Time (hrs)	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.08	1.49	0.99	0.97	1.50	1.58	1.46	1.37	1.30
0.17	1.31	1.01	0.99	1.49	1.56	1.46	1.33	1.26
0.25	1.51	0.94	0.91	1.53	1.55	1.49	1.35	1.23
0.33	1.18	0.85	0.77	1.54	1.59	1.50	1.46	1.24
0.50	1.29	0.86	0.80	1.36	1.40	1.35	1.22	1.18
0.75	1.24	0.80	0.68	1.41	1.47	1.36	1.26	1.19
1.00	1.09	0.75	0.67	1.49	1.56	1.47	1.30	1.28
1.50	1.11	0.68	0.57	1.23	1.38	1.29	1.19	1.16
2.00	0.95	0.67	0.51	1.64	1.69	1.62	1.47	1.43
4.00	1.01	0.56	0.43	1.37	1.44	1.35	1.28	1.26
8.00	1.04	0.54	0.39	1.43	1.48	1.45	1.52	1.35
12.00	1.04	0.55	0.40	1.53	1.56	1.46	1.58	1.42

Table 16. Mass balance ratios for PCB congeners in PVC/water stored at 25°C.

Time (hrs)	Tri	Tetra	Penta	Hexa	Hepta	Octa
0.00	1.00	1.00	1.00	1.00	1.00	1.00
0.08	1.19	1.28	0.87	1.16	1.20	1.01
0.17	1.24	1.27	0.84	1.14	1.37	1.00
0.25	1.51	1.02	0.79	0.92	1.02	0.95
0.33	1.63	1.10	0.73	0.93	1.00	0.83
0.50	1.65	1.03	0.78	1.01	1.14	0.94
0.75	1.27	0.86	0.62	0.86	1.09	0.91
1.00	1.52	0.92	0.66	0.83	0.96	0.92
1.50	1.37	0.65	0.47	0.73	0.91	0.88
2.00	1.39	0.95	0.65	0.96	1.15	1.14
4.00	1.13	0.83	0.52	0.88	1.15	1.08
8.00	0.97	0.80	0.52	0.88	1.16	1.00
12.00	0.87	0.87	0.52	0.90	1.04	0.98

A chromatograph of a standard 10 ppm solution of the ten (10) PCB congeners is shown in Figure 6. Beginning at retention time 9.443 min through retention time 53.402 min, prominent peaks for the mono chlorinated congener to the deca chlorinated congener are seen respectively. These retention times were used as a reference in identifying the PCB congener peaks in sample solutions' chromatographs for all materials and at all storage times.

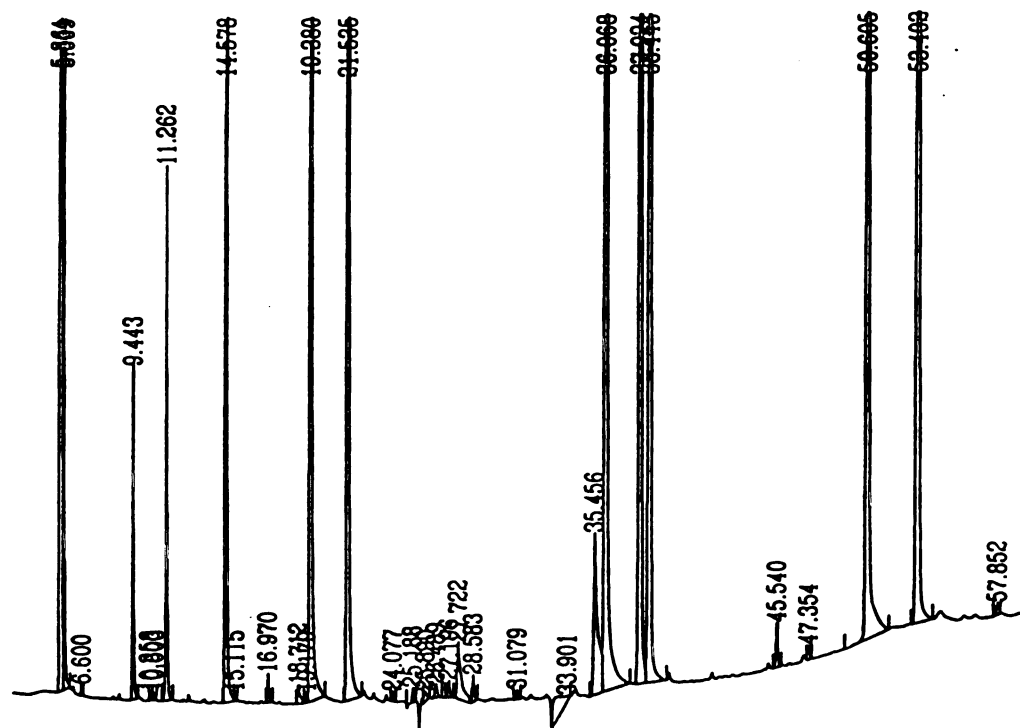


Figure 6. Gas chromatogram of standard PCB congeners mono(9.443), di(11.262), tri(14.578), tetra(19.380), penta(21.535), hexa(36.068), hepta(37.924), octa(38.445), nona(50.605) and deca(53.402).

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The efficiency of the cleanup procedure for polyethylene is shown in Figure 7 and 8. The chromatograph shown in Figure 7 is that of a polyethylene extract with no cleanup applied. This can be compared with Figure 8 which shows a chromatograph of a cleanup sample of the same polyethylene extract.

A chromatograph of polystyrene/10 ppm PCB without cleanup is seen in Figure 9, while that of polystyrene/10 ppm PCB after the cleanup procedure is seen in Figure 10. The polystyrene cleanup was not done by the GPC method because it contained chemical compounds with the same retention time as the PCBs congeners used in this study. Thus, it was unable to separate the PCBs from the other extraneous chemical compounds.

These same sequence of presentations are also seen in Figures 11 and 12 for PVC/10ppm PCB without cleanup, and PVC/10ppm PCB after cleanup, respectively. Like the chromatographs of the other materials, the cleanup procedure for PVC shows a reduction of the extraneous materials extracted from the polymers together with that of PCB during the soxhlet extraction.

Since hexane, the solvent used, is very non-polar, it is expected that all extracted compounds were also non-polar in nature. The presence of chlorinated functional groups in any of these extracts would therefore be detected by the electron capture detector of the GC, and thus would create identification problems alluded to earlier. GPC is a form of liquid chromatography in which solute molecules are separated

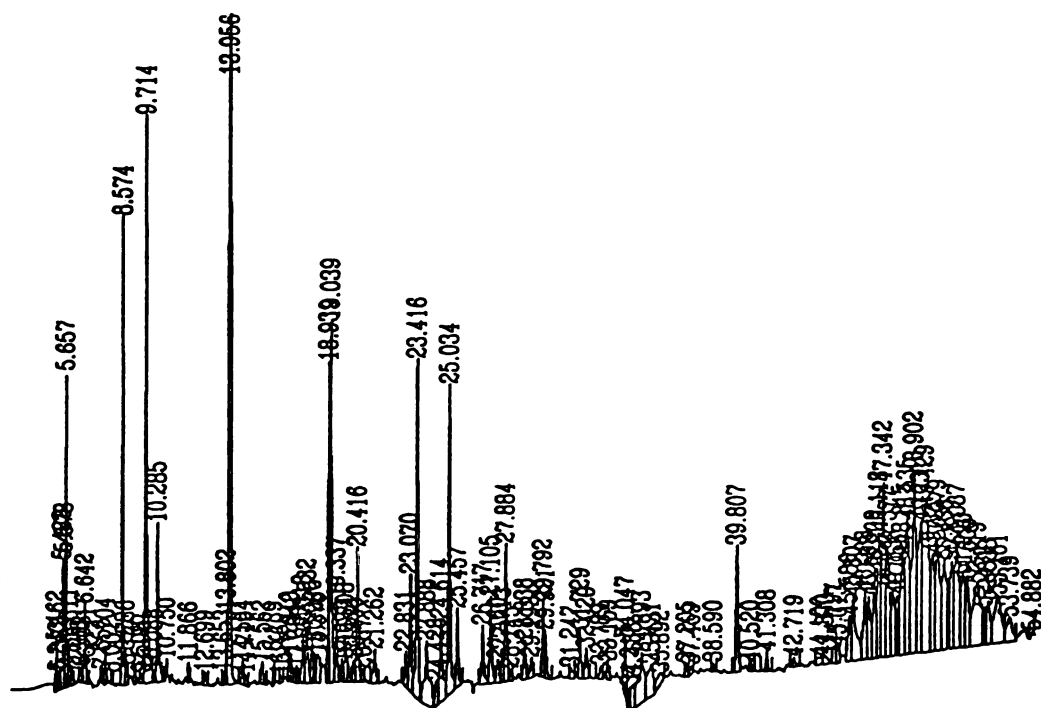


Figure 7. Gas chromatogram of polyethylene/PCB extract before cleanup.

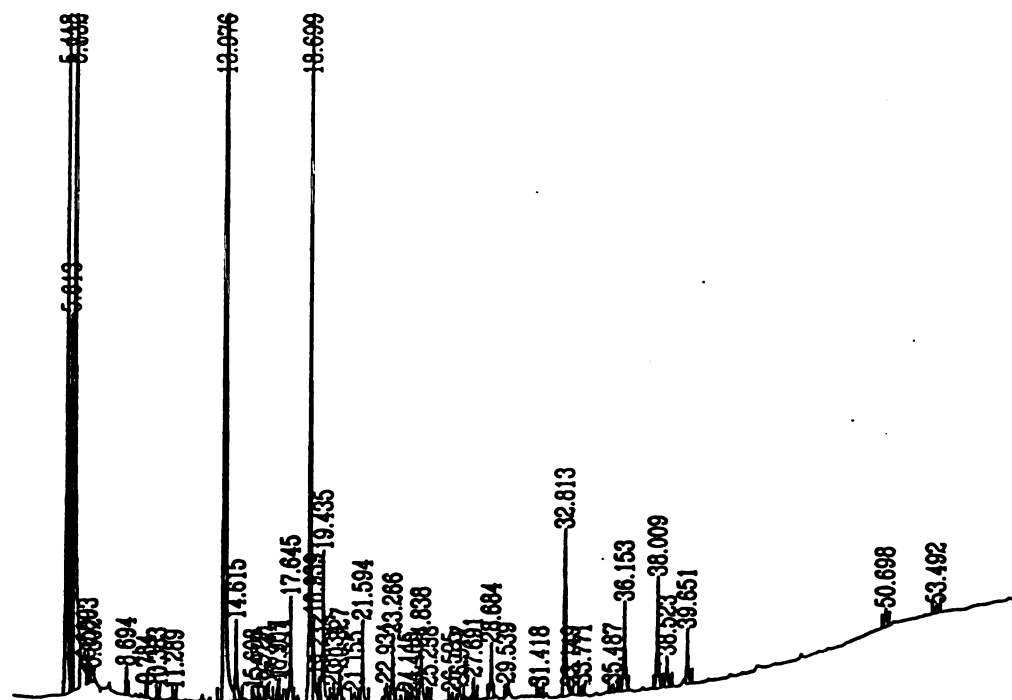


Figure 8. Gas chromatogram of polyethylene/PCB extract after cleanup.

Figure

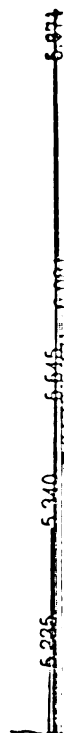
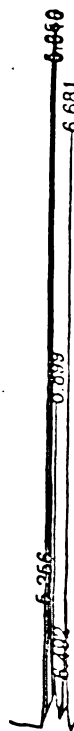


Figure 1



Mass spectrum of the sample showing relative intensity versus m/z. The base peak is at m/z 41.988. Other significant peaks are labeled with their m/z values.

m/z	Relative Intensity (approx)
5.266	Low
5.402	Low
5.588	Low
5.681	Low
9.417	Low
10.584	Low
11.240	Low
12.489	Low
15.109	Low
16.560	Low
17.552	Low
18.905	Low
19.188	Low
20.274	Low
22.881	Low
23.282	Low
24.095	Low
24.786	Low
26.861	Low
27.220	Low
28.594	Low
28.804	Low
31.384	Low
31.861	Low
33.718	Low
35.441	Low
41.988	100 (Base Peak)
43.554	Low
46.280	Low
47.426	Low
56.661	Low
56.662	Low
56.663	Low
57.889	Low
59.081	Low

Figure 10. Gas chromatogram of polystyrene/PCB extract after cleanup.

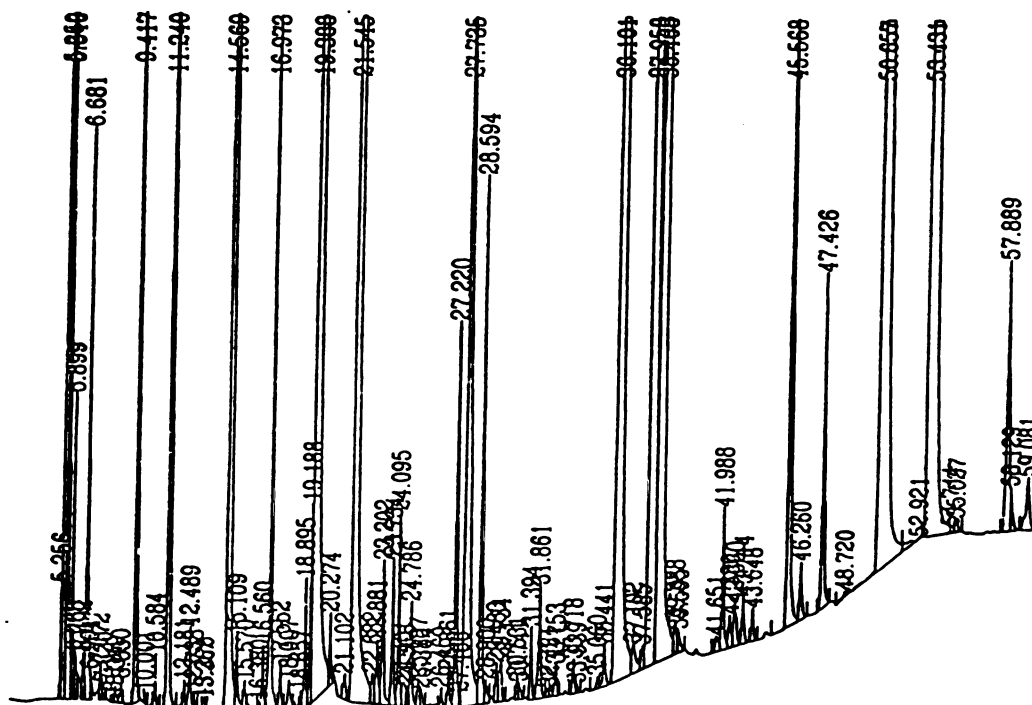


Figure 11. Gas chromatogram of PVC/PCB extract before cleanup.

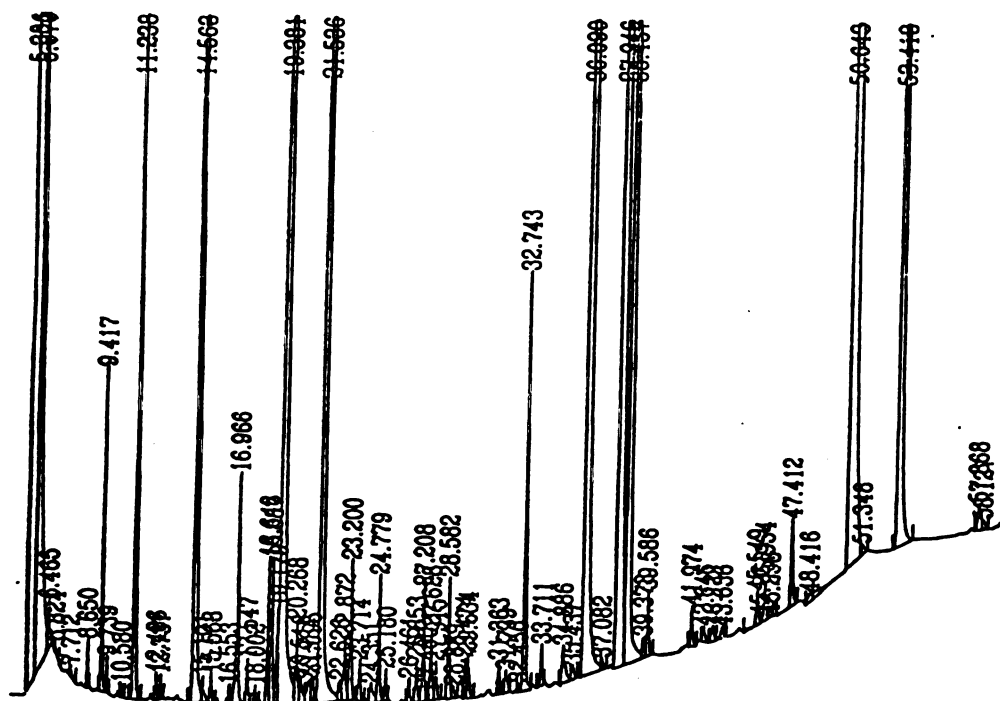


Figure 12. Gas chromatogram of PVC/PCB extract after cleanup.

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selectively as they permeate the pores in the column packing. The solution molecules larger than the largest pores of the gel are excluded from the pores because of their size. Smaller particles penetrate the gel particles to a varying extent, depending on their size and shape. The solution molecules are therefore eluted from the gel bed in the order of decreasing molecular size. The florisil and silica gel columns on the other hand, used the principle of adsorption in order to effect separation of the eluted compounds. Separation in this ion exchange method depends on differing affinities of the eluting compounds for the chromatographic packing material. The use of the different elution solvents facilitated the subsequent removal of the PCBs while leaving most of the extraneous compounds still adsorbed to the florisil and or silica gel.

The cleanup procedures used in this study were necessary in order to aid identification of the PCB peaks, and to reduce the chances of overlapping of these peaks with that of the extraneous compounds. If indeed this were to occur, errors in the integration of the peak areas would result, and thus errors in the interpretation of the results.

POLYMERIC MATERIALS

POLYETHYLENE

The weights of PCB congeners (μg) in the water exposed to the polyethylene as a factor of time (hours) are presented graphically in Figures 13 and 14. Figure 13 indicates the

Weight of PCB congeners in water exposed to 1 ply thick polyethylene stored at 25 degrees C.

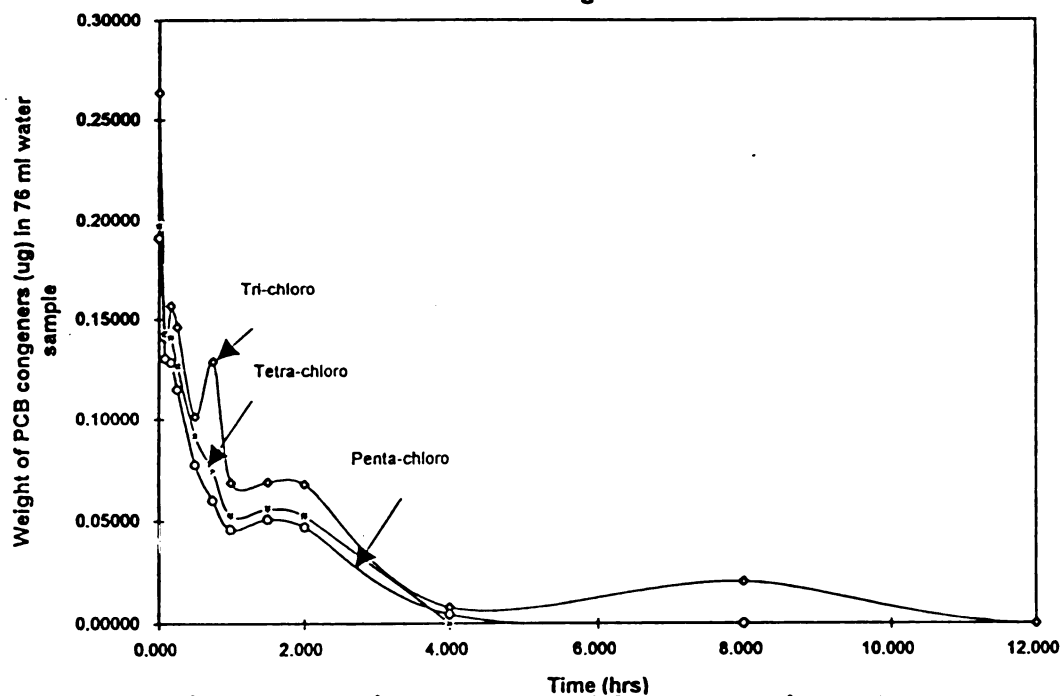


Figure 13. Weight of Tri to penta-chloro PCB in water exposed to 1 ply PE stored at 25° C.

Weight of PCB congeners in water exposed to polyethylene film stored at 25 degrees C.

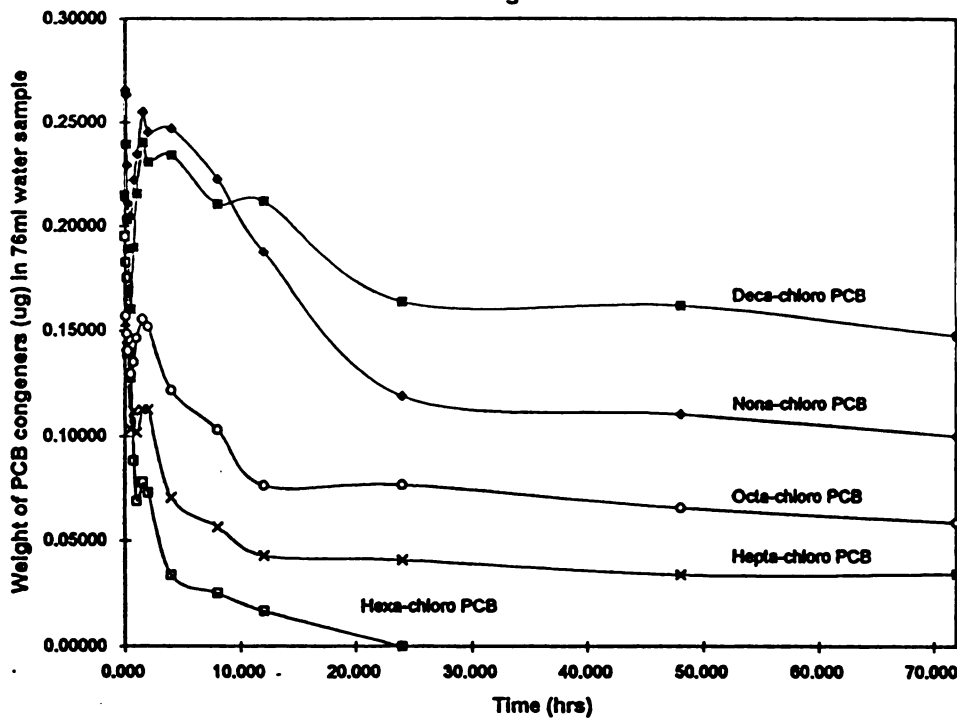


Figure 14. Weight of hexa to deca-chloro PCB in water exposed to 1 ply PE stored at 25° C. weights for tri-chloro

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to penta-chlorinated PCBs while hexa-chloro to deca-chlorinated PCBs are depicted in Figure 14. The weights of these congeners in the polyethylene material are similarly shown in Figures 15 and 16. The graphs showing the uptake of PCBs by the polymer seem to be an inverted mirror image of the graphs showing the weight loss of PCBs from the water. This is not surprising since the mass shows total amount recovered minus original. Therefore, mass balance demonstrates good recovery of original and data used in mass balance shows us that the analyte in the water moved into the plastic.

Figures 17 and 18 show the calculated isotherms and the experimental concentrations for the congeners tri-chloro to hexa-chloro and hepta-chloro to deca-chloro, respectively. These sorption diffusion coefficients are summarily presented as a bar graph in Figure 19. These results show that the lower chlorinated congeners were sorbed to a greater extent by the polyethylene than the higher chlorinated molecules. As should be expected, the lower chlorinated congeners seen in Figure 20 showed a greater rate loss from the water than the higher chlorinated congeners.

The percent PCB congeners retained in the peanut oil are graphically depicted in Figures 21 and 22. These figures show relatively little loss of PCB from the oil. The rate loss of PCBs from the water and from the oil is presented in Figure 23. Comparison of each curve shows that the rate loss of PCBs from water is greater than that from the oil. The lower chlorinated congeners showed a larger rate loss than the

congeners with higher chlorination in the aqueous medium. In the oil a reverse trend is observed, where the higher chlorinated congeners generally show a larger rate loss.

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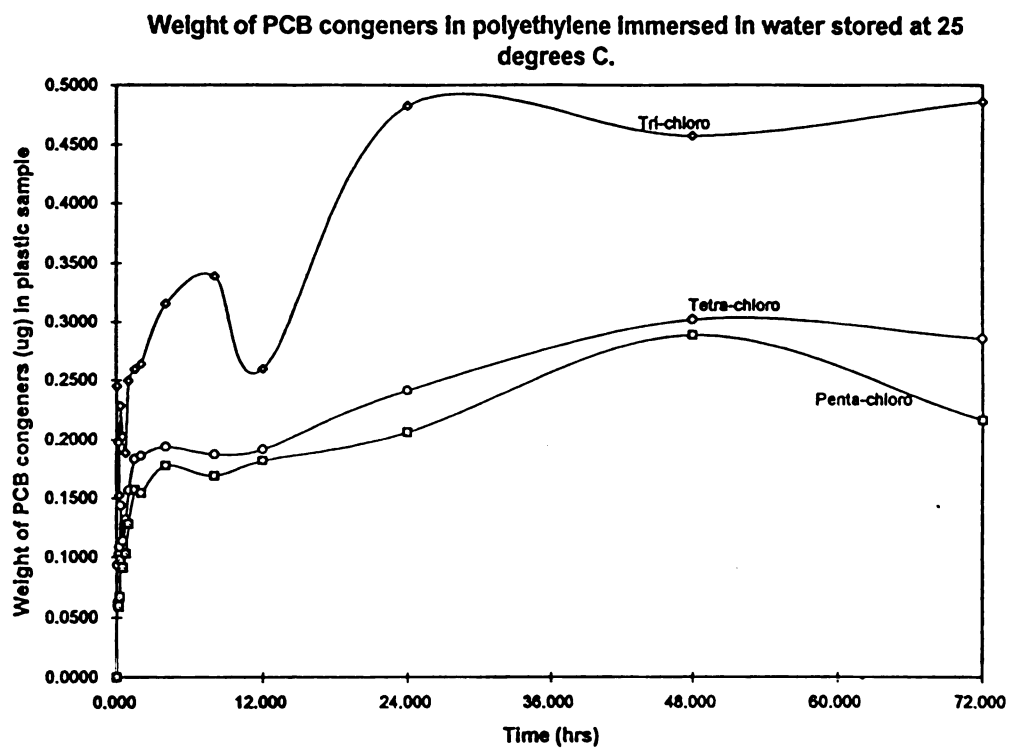


Figure 15. Weight of tri to penta-chloro PCB uptake by 1 ply PE stored at 25° C.
Weight of PCB congeners in 1 ply thick polyethylene Immersed in water stored at 25 degrees C.

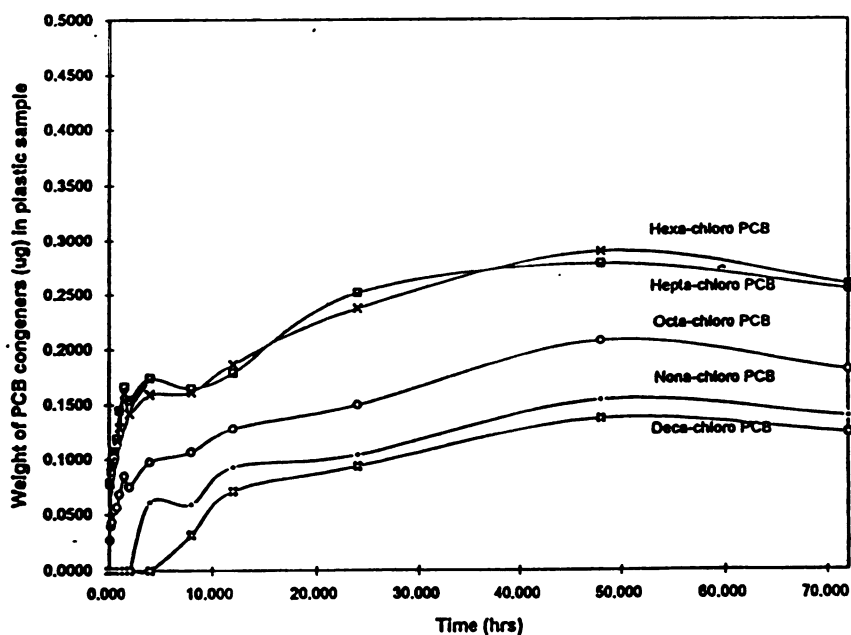


Figure 16. Weight of hexa to deca-chloro PCBs uptake by 1 ply PE stored at 25° C.

Plot of M_t/M_{inf} vs time for PCBs sorption by 1 ply thick polyethylene film exposed to water at 25 degrees C.

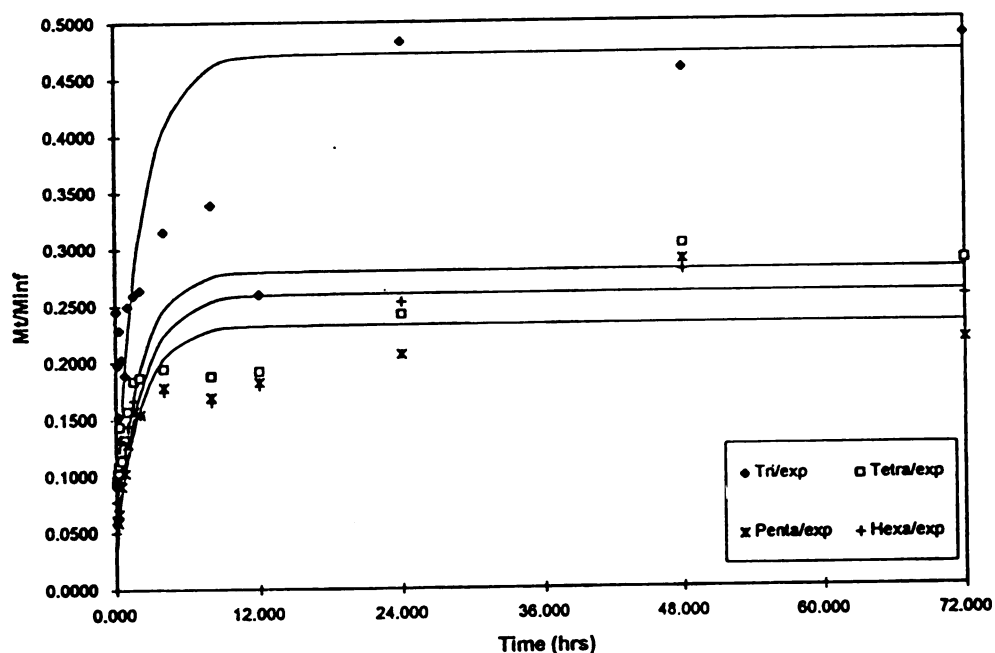


Figure 17. Calculated and experimental isotherm for tri to hexa-chloro PCB uptake by 1 ply PE stored at 25° C.

Plot of M_t/M_{inf} vs time for PCBs sorption by 1 ply thick polyethylene film exposed to water at 25 degrees C.

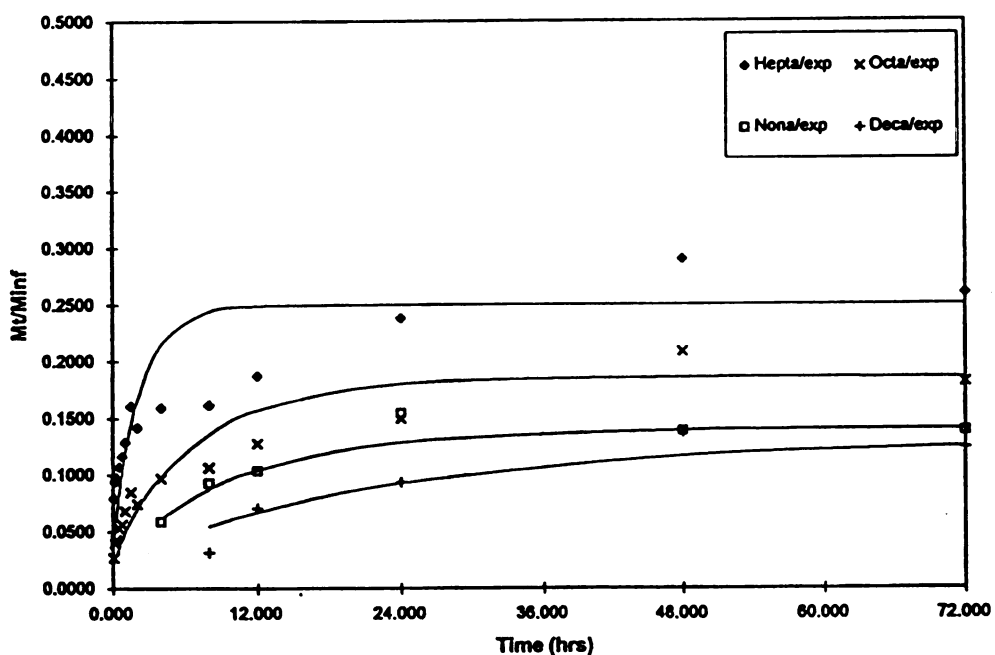


Figure 18. Calculated and experimental isotherm for hepta to deca-chloro PCB uptake by 1 ply PE stored at 25° C.

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Fig

Sorption diffusion coefficient (Ds) for PCBs by 1 ply polyethylene immersed in water at 25 degrees C.

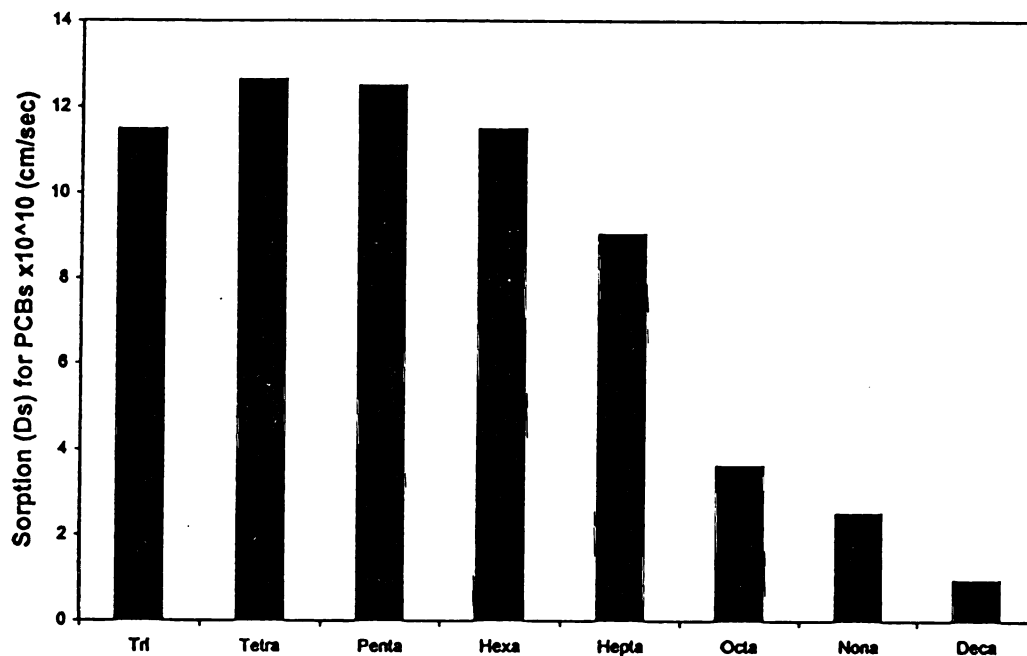


Figure 19. Comparison of diffusion coefficients for all congeners by 1 ply PE stored at 25° C.

Rate loss of PCB congeners from water exposed to 1 ply polyethylene stored at 25 degrees C.

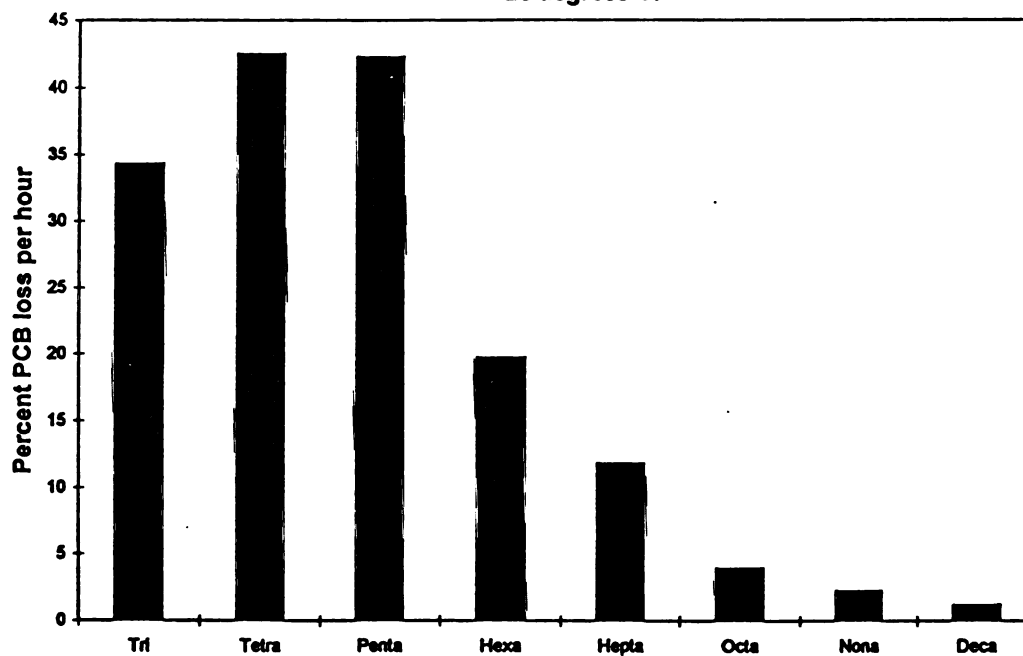


Figure 20. Comparison of rate loss for all congeners from water exposed to 1 ply PE stored at 25°C.

Percent PCB congeners retained in peanut oil exposed to polyethylene film

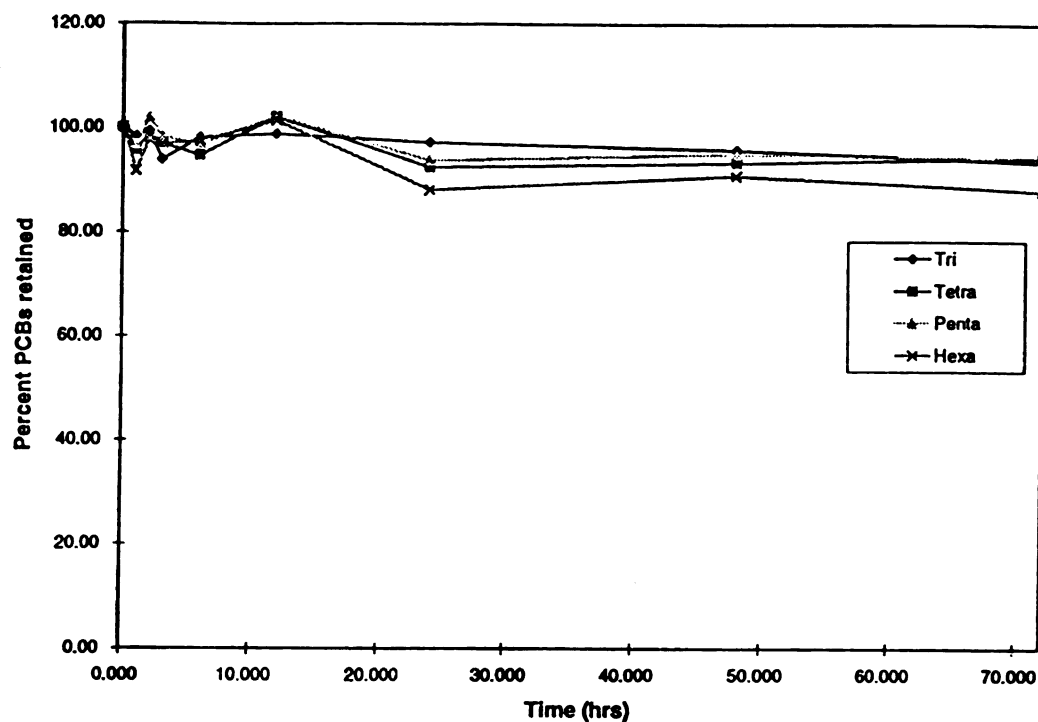


Figure 21. Percent tri to hexa-chloro PCBs retained in oil exposed to 1 ply PE stored at 25°

Percent PCB congeners retained in peanut oil exposed to polyethylene film

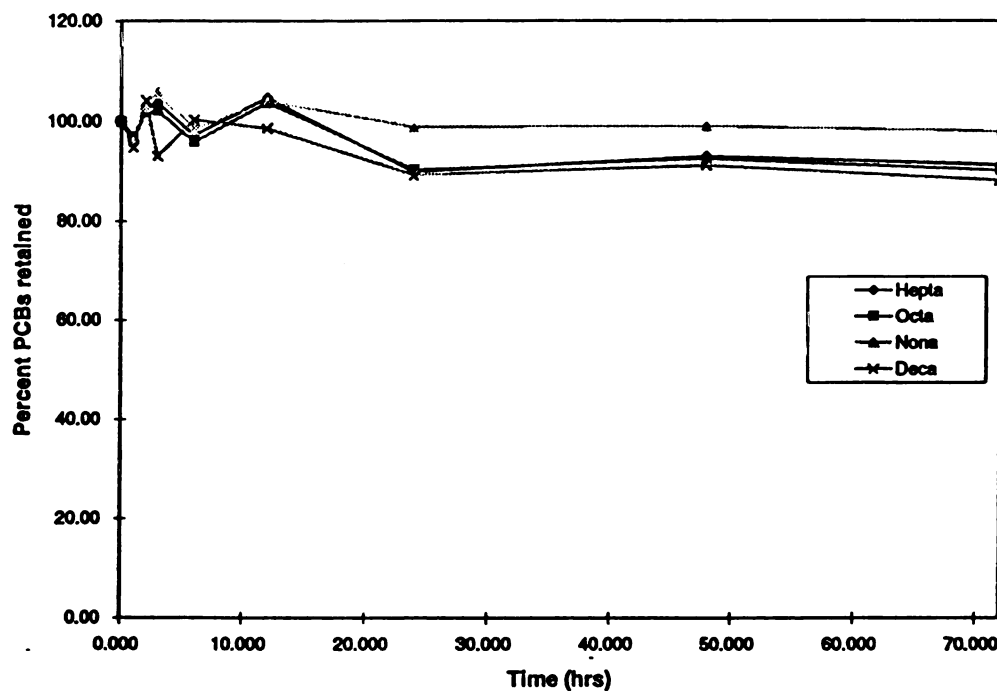


Figure 22. Percent hepta to deca-chloro PCB retained in oil exposed to 1 ply PE stored at 25°C.

Rate loss of PCB congeners from peanut oil and water exposed to polyethylene film stored at 25 degrees C.

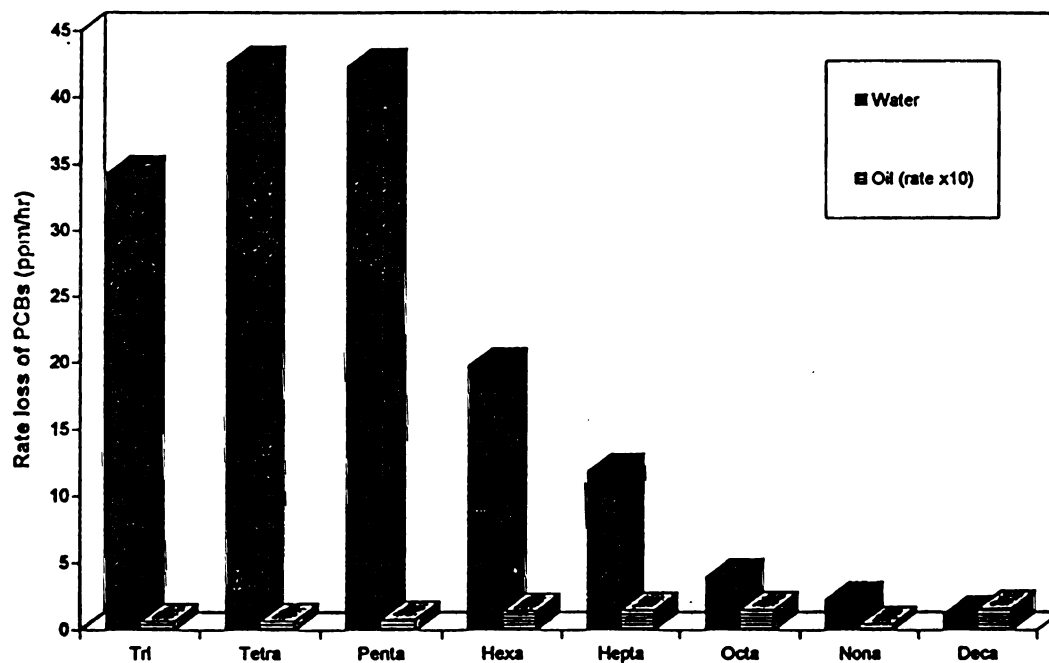


Figure 23. Comparison of rate loss for all congeners in water and oil exposed to 1 ply PE stored at 25° C.

POLYSTYRENE

Graphical representations of the weights of PCB congeners retained in the water at 25°C and exposed to polystyrene as a factor of time (hours) are presented graphically in Figures 24 and 25. Figure 24 shows the weights for tri-chloro to hexa-chlorinated PCBs while hepta-chloro to deca-chlorinated PCBs are demonstrated in Figure 25. The weights of these congeners in the polystyrene material are similarly shown in Figures 26 and 27. A comparison of the graphs showing the uptake of PCBs by polystyrene and the loss of PCBs from the water, shows a similar inverse pattern like those obtained for polyethylene. These results are also corroborated by the results of the mass balance ratios of these analyses shown in Table 15.

Calculations of the sorption diffusion coefficients for polystyrene were also performed using the same mathematical models as for polyethylene. Comparisons of these graphic results with the experimental PCB concentrations were also plotted and are shown in Figures 28 and 29. The sorption diffusion coefficients are summarily presented as a bar graph in Figure 30. These results also show that the lower chlorinated congeners were sorbed to a greater extent by the polyethylene than the higher chlorinated molecules. The lower chlorinated congeners showed a greater rate loss from the water than the higher chlorinated congeners. This is displayed graphically in Figure 31.

Repeated at 35°C, the graphical representations of the concentrations of PCBs in the water and in the polystyrene are

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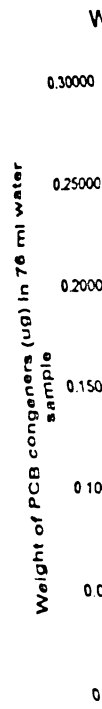
loss of PCBs

is seen in P

similarly shown in Figures 32, 33, 34 and 35, respectively. The results for the sorption diffusion coefficients compared with the experimental concentrations are shown in Figures 36 and 37 and are similarly presented as for the polystyrene at 25°C.

Results for polystyrene at 5 ply thickness are represented in the same format as for the polystyrene stored at 25°C and 35°C. Results of the analysis for PCBs in water and in the film can be seen in Figures 38 to 41, while that for the sorption diffusion coefficients and the experimental concentration in the polystyrene can be seen in Figures 42 and 43, respectively.

A comparison of the sorption diffusion coefficients for the polystyrene exposed to the water under the three conditions mentioned, is shown in Figure 44. A comparison of the rate loss of PCBs from the water associated with these conditions is seen in Figure 45.



Figure

congeners (ug) in 76ml water

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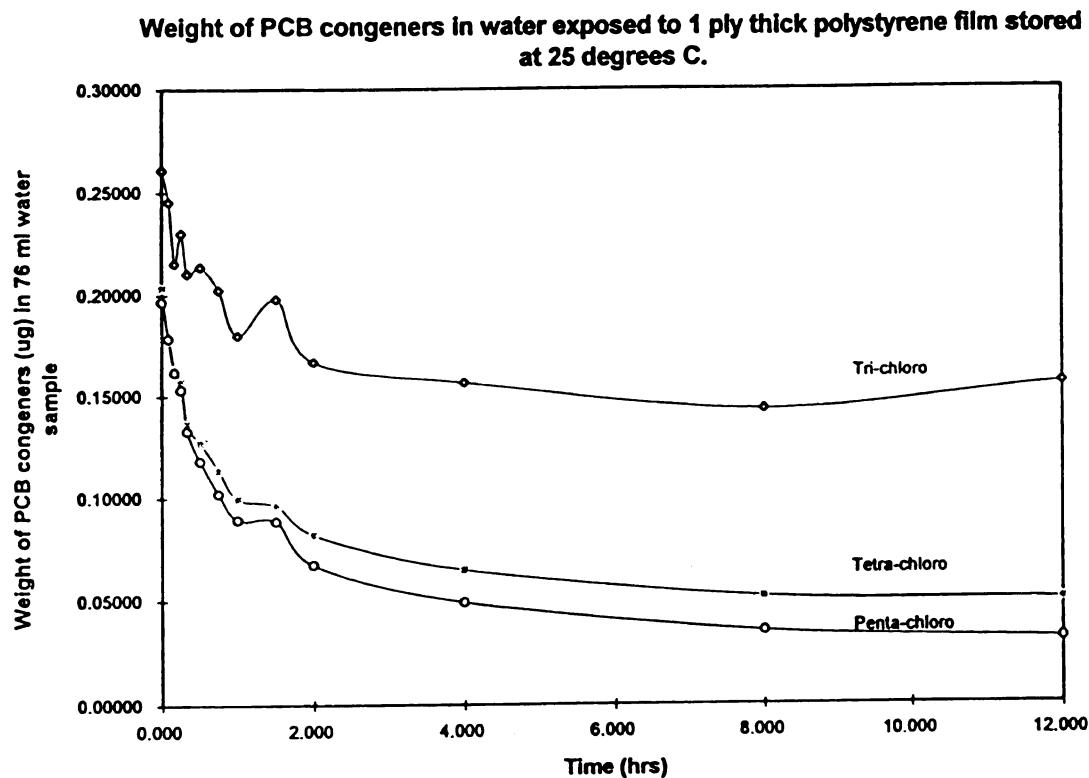


Figure 24. Weight of tri to penta-chloro PCB in water exposed to 1 ply PS stored at 25° C.

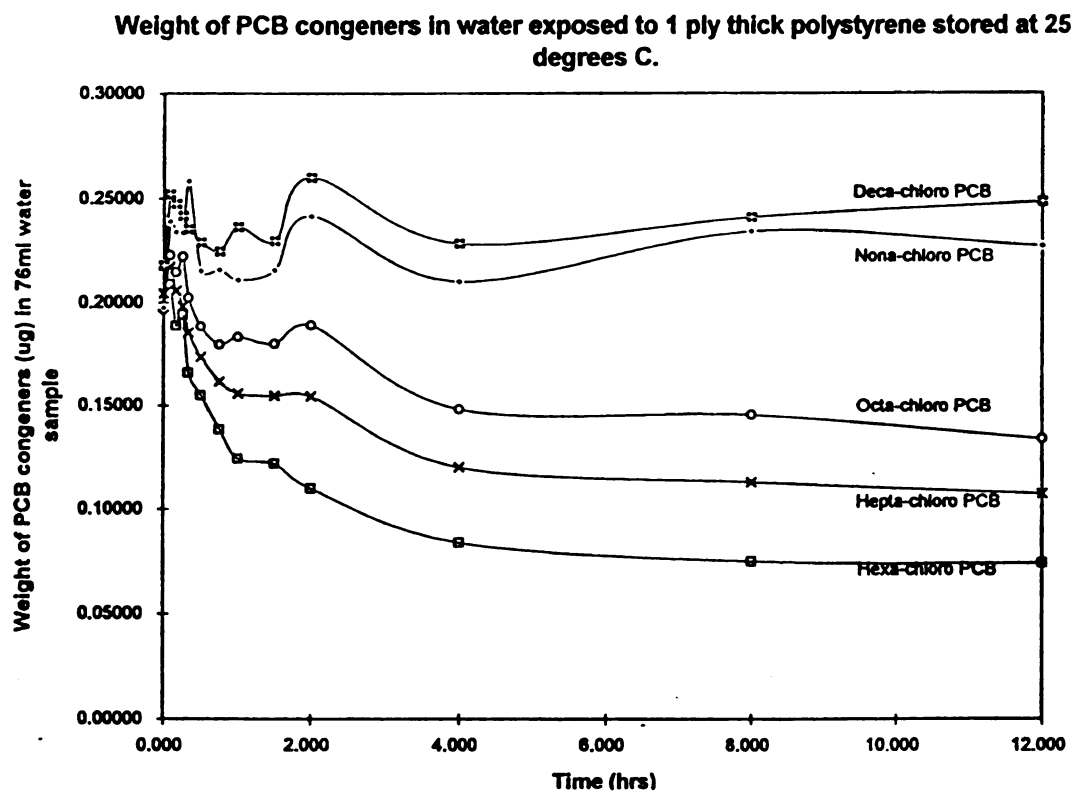


Figure 25. Weight of hexa to deca-chloro PCB in water exposed to 1 ply PS stored at 25° C.

Figure

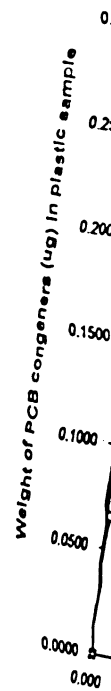


Figure 27. We
PS

Weight of PCB congeners in 1 ply thick polystyrene film immersed in water stored at 25 degrees C.

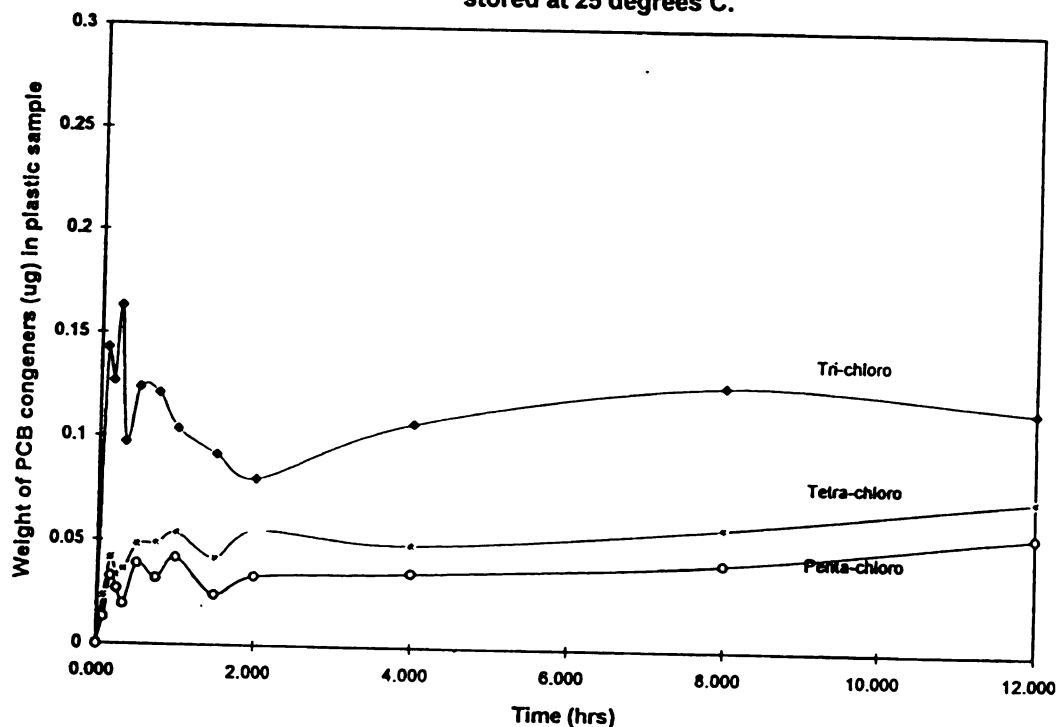


Figure 26. Weight of tri to penta-chloro PCB uptake by 1 ply PS stored at 25° C.

Weight of PCB congeners in water exposed to 1 ply thick polystyrene at 25 degrees C.

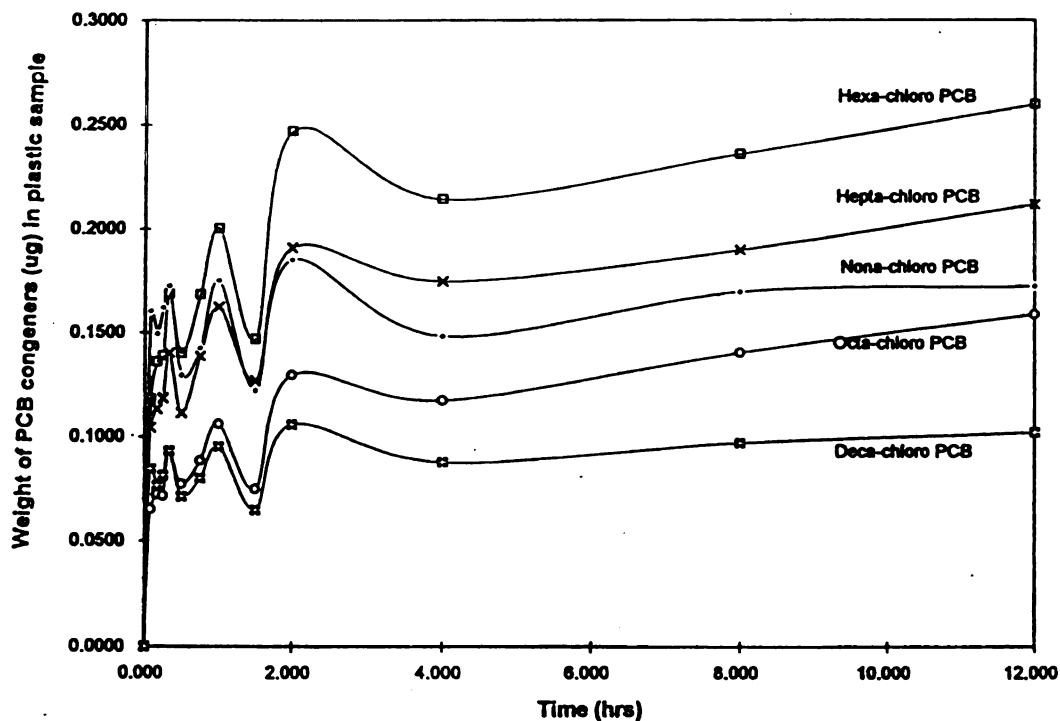


Figure 27. Weight of hexa to deca-chloro PCB uptake by 1 ply PS stored at 25° C.

Figure 2
hexa-chl

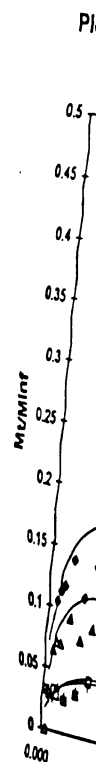


Figure 29. Calc
deca

Plot of M_t/M_{inf} vs time for PCBs sorption by 1 ply thick polystyrene film exposed to water at 25 degrees C.

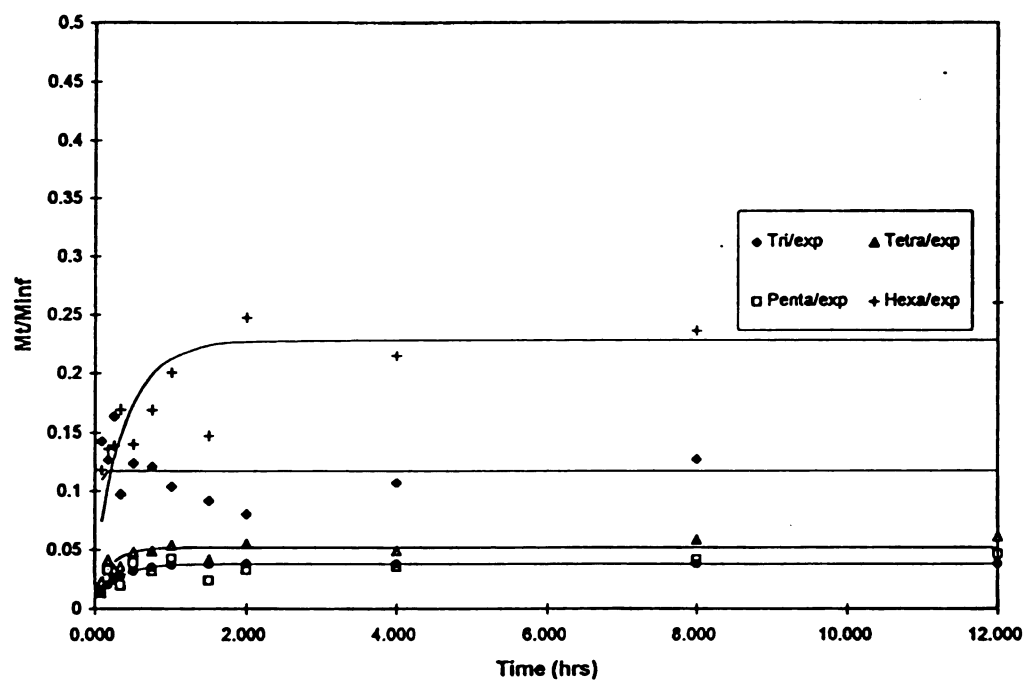


Figure 28. Calculated and experimental isotherm for tri to hexa-chloro PCB uptake by 1 ply PS stored at 25° C.

Plot of M_t/M_{inf} vs time for PCBs sorption by 1 ply thick polystyrene film exposed to water at 25 degrees C.

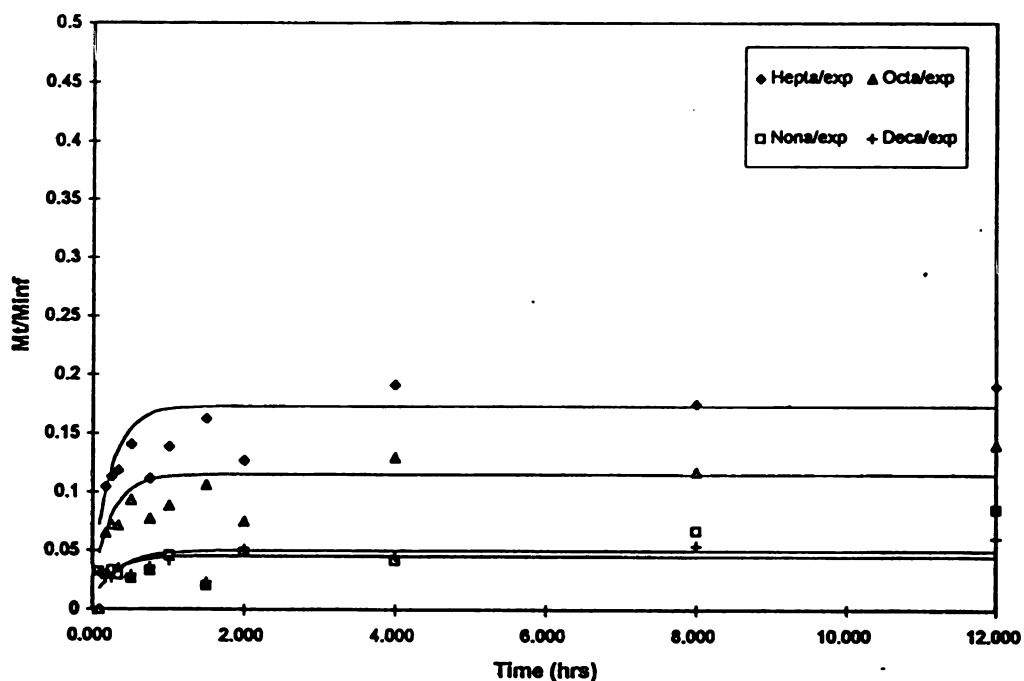


Figure 29. Calculated and experimental isotherm for hepta to deca-chloro PCB uptake by 1 ply PS stored at 25° C.

Sorption (Ds) for PC

Figure



Figure 31.

Sorption diffusion coefficient (D_s) for PCBs by 1 ply polystyrene immersed in water at 25 degrees C.

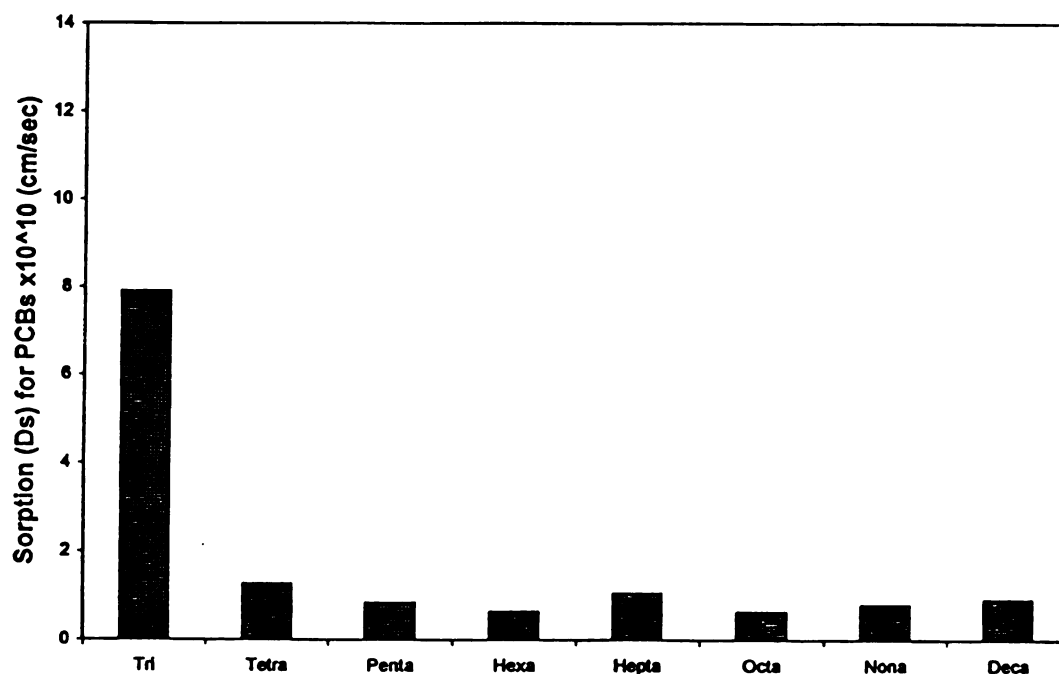


Figure 30. Comparison of diffusion coefficients for all congeners by 1 ply PS stored at 25° C.

Rate loss of PCB congeners from water exposed to 1 ply polystyrene stored at 25 degrees C.

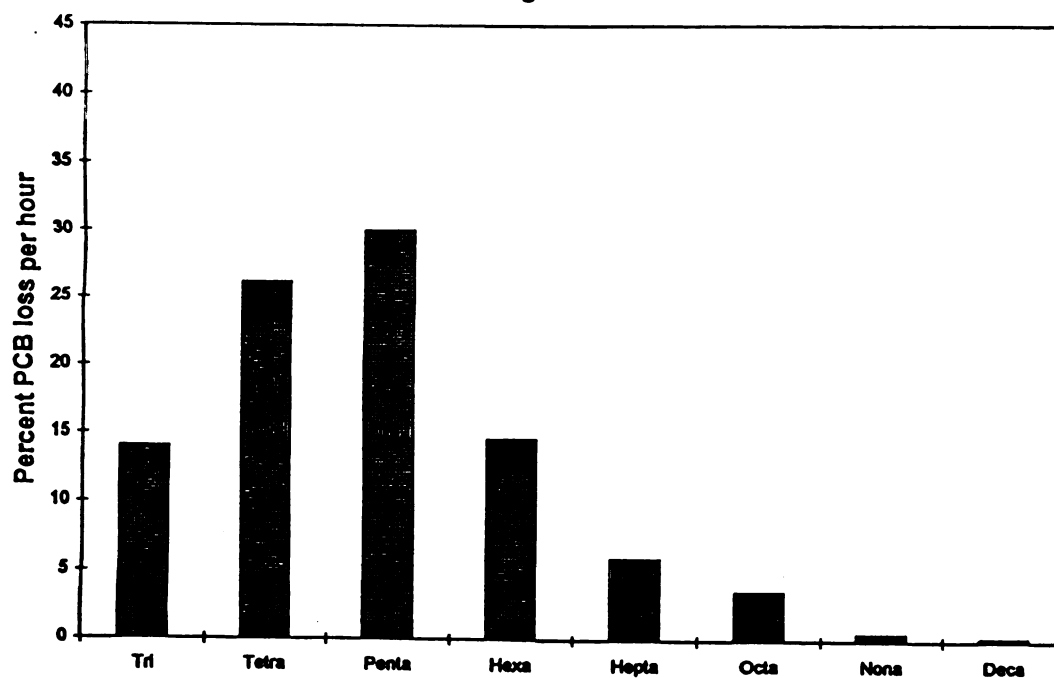


Figure 31. Comparison of rate loss for all congeners from water exposed to 1 ply PS stored at 25°C.

Figure

Percent PCBs retained
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Figure 33.

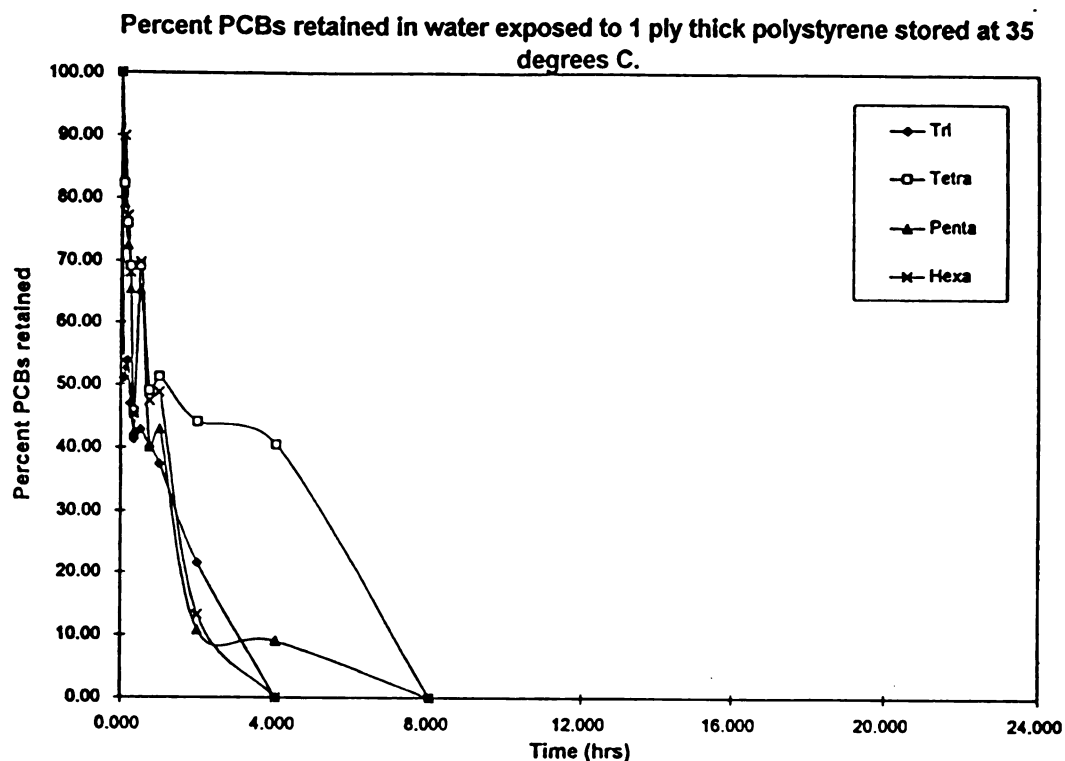


Figure 32. Percent tri to hexa-chloro PCB congeners retained in water exposed to 1 ply PS stored at 35° C.

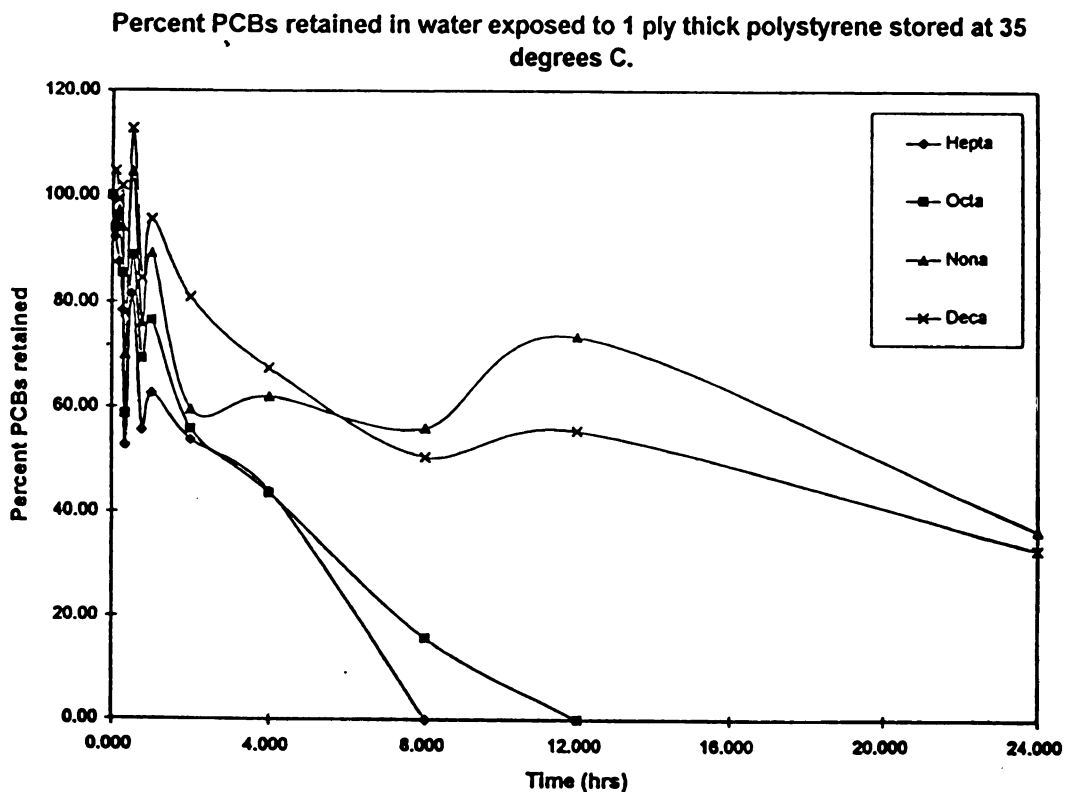


Figure 33. Percent hepta to deca-chloro PCB congeners retained in water exposed to 1 ply PS stored at 35° C.

Weight

Figure

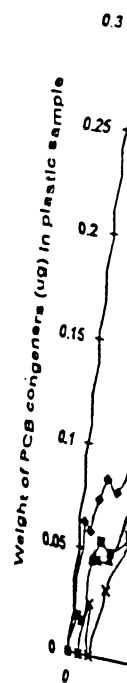


Figure 35.

Concentration PCBs in 1 ply thick polystyrene immersed in water at 35 degrees C.

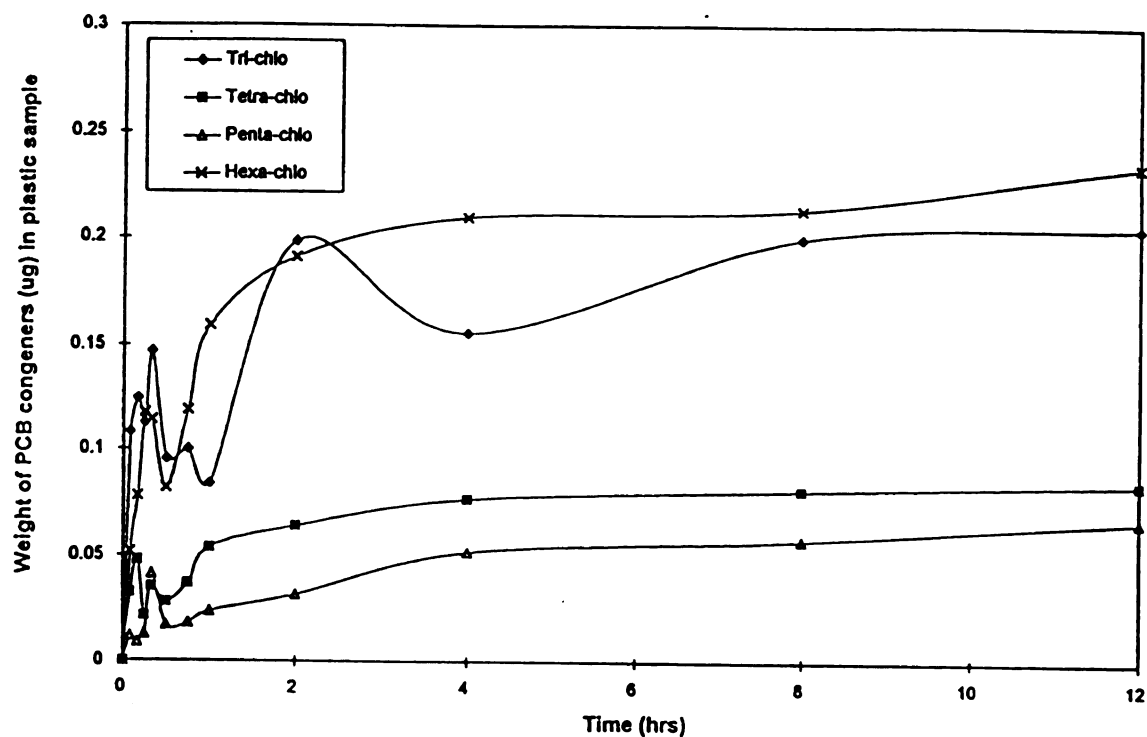


Figure 34. Weight of tri to hexa-chloro PCB uptake by 1 ply PS stored at 35° C.

Concentration PCBs in 1 ply thick polystyrene immersed in water at 35 degrees C.

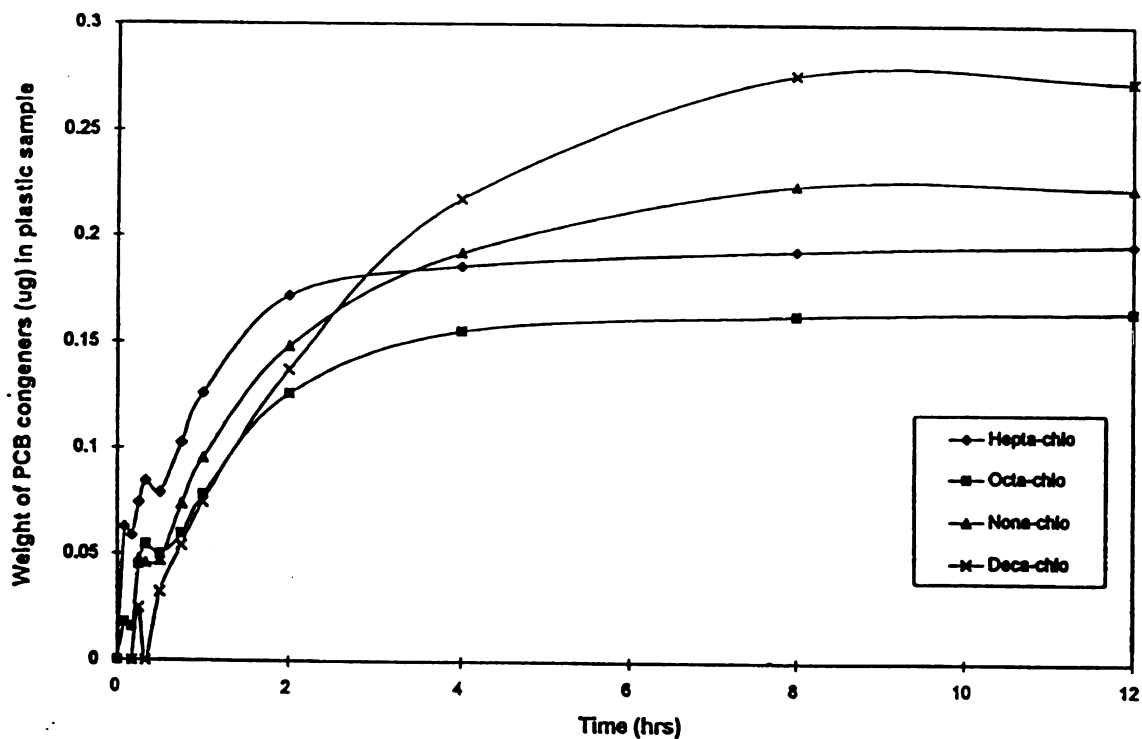


Figure 35. Weight of hepta to deca-chloro PCB uptake by 1 ply PS stored at 35° C.

Figure 3

Figure 37

Plot of M_t/M_{∞} vs time for PCBs sorption by 1 ply thick polystyrene exposed to water at 35 degrees C.

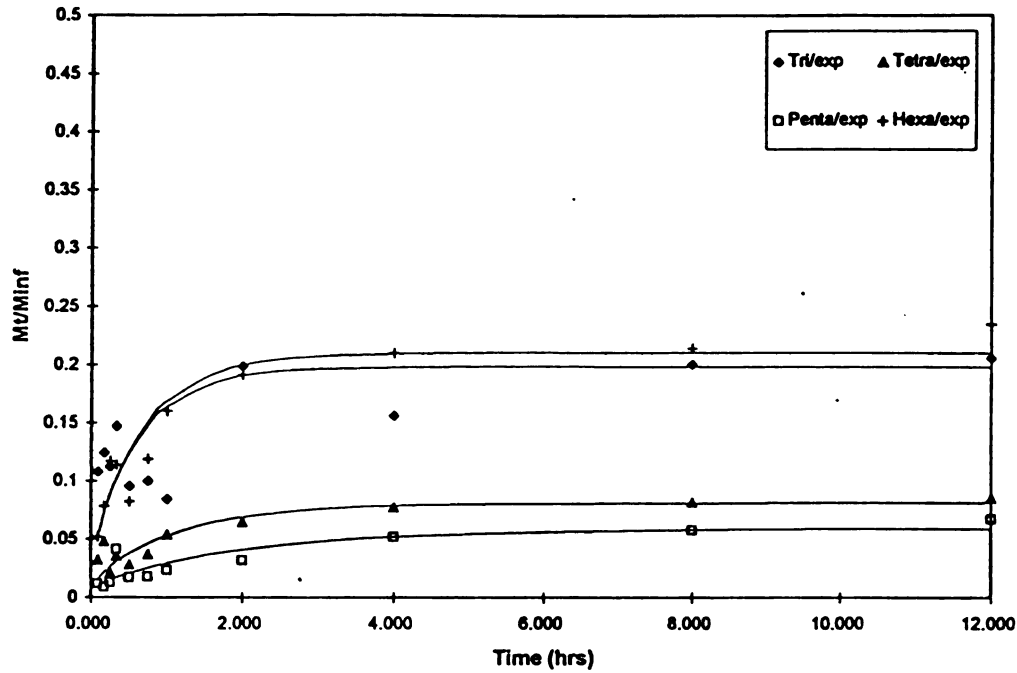


Figure 36. Calculated and experimental isotherm for tri to hexa-chloro PCB uptake by 1 ply PS stored at 35° C.

Plot of M_t/M_{∞} vs time for PCBs sorption by 1 ply thick polystyrene exposed to water at 35 degrees C.

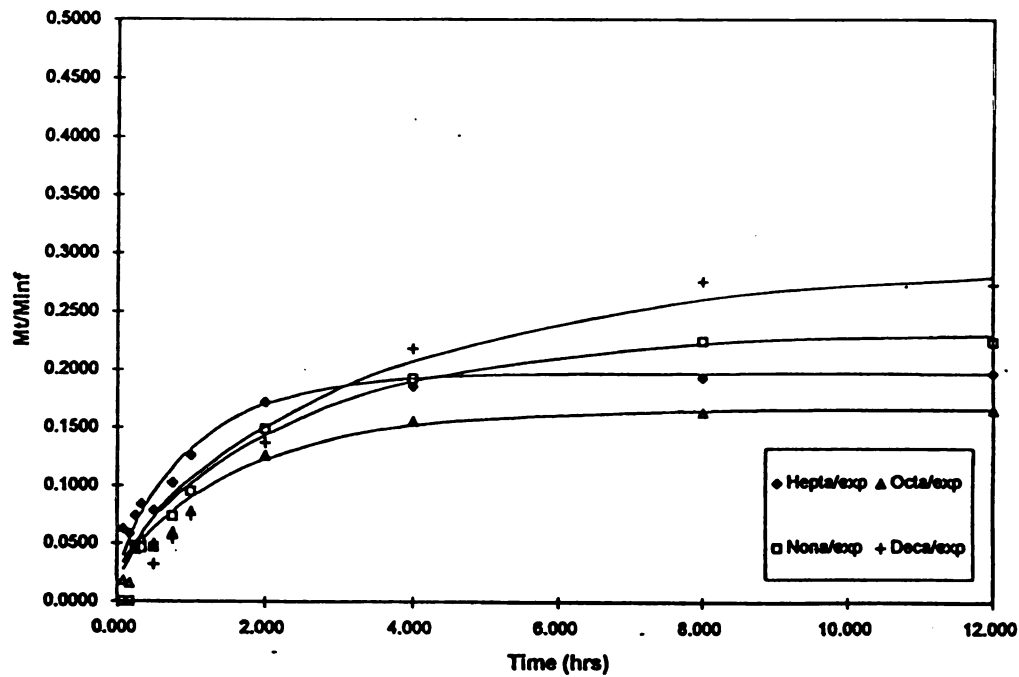


Figure 37. Calculated and experimental isotherm for hepta to deca-chloro PCB uptake by 1 ply PS stored at 35° C.

Percent PCBs retained in water exposed to 5 ply thick polystyrene film at 25 degrees C.

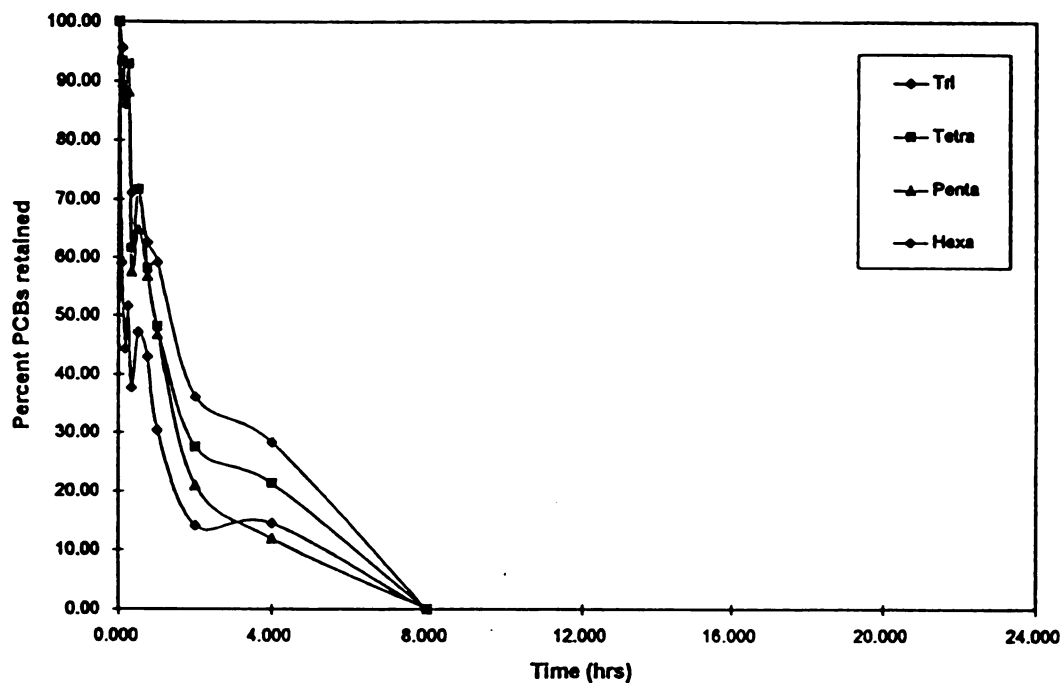


Figure 38. Percent tri to hexa-chloro PCB congeners retained in water exposed to 5 ply PS stored at 25° C.

Percent PCBs retained in water exposed to 5 ply thick polystyrene film at 25 degrees C.

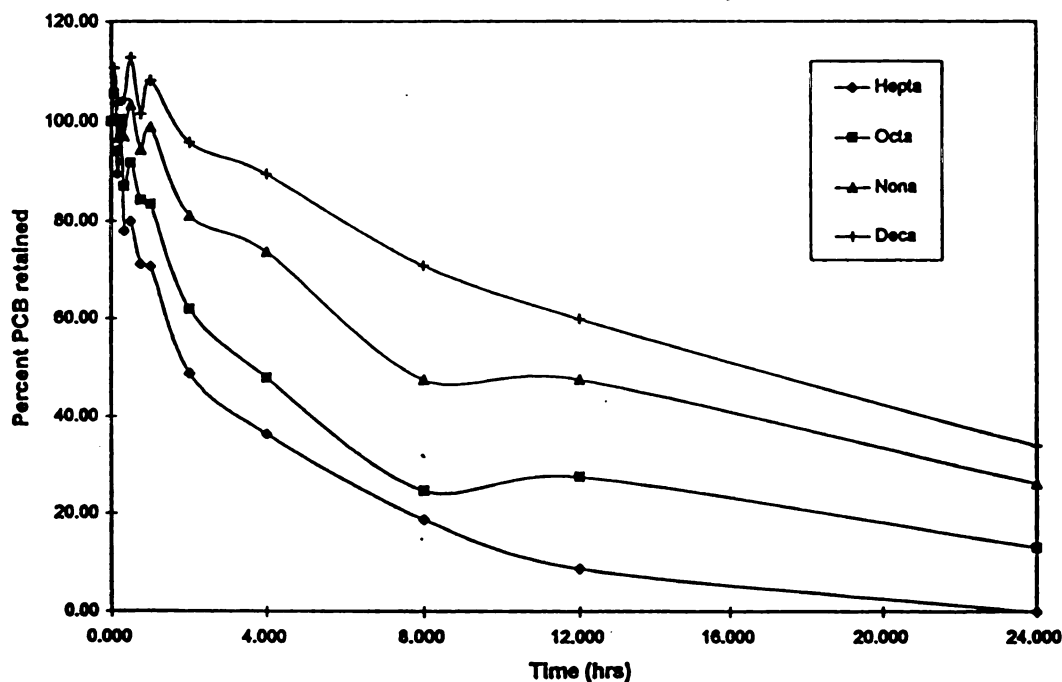


Figure 39. Percent hepta to deca-chloro PCB congeners retained in water exposed to 5 ply PS stored at 25° C.

Weight of PCBs in 5 ply thick polystyrene Immersed in water at 25 degrees C.

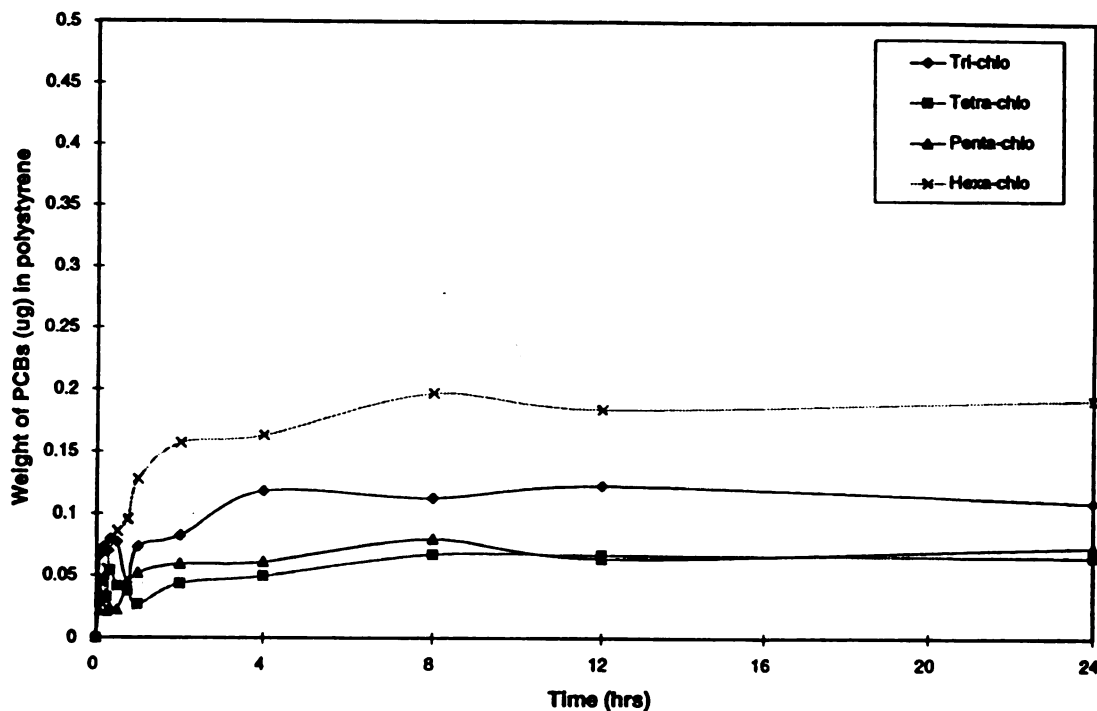


Figure 40. Weight of tri to hexa-chloro PCB uptake by 5 ply PS stored at 25° C.

Weight of PCBs in 5 ply thick polystyrene Immersed in water at 25 degrees C.

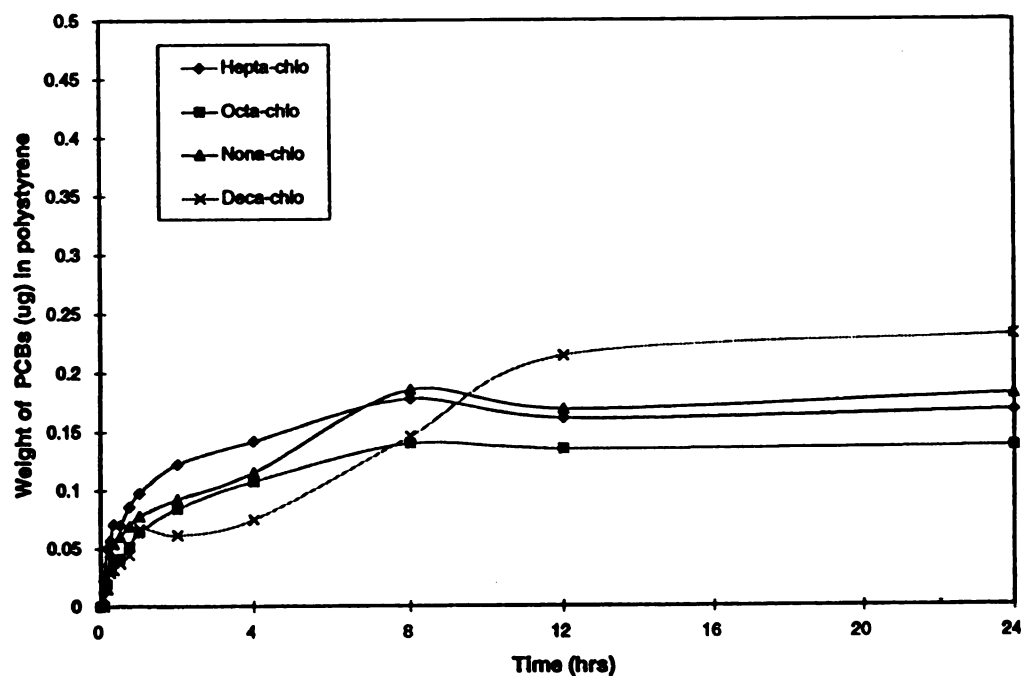


Figure 41. Weight of hepta to deca-chloro PCB uptake by 5 ply PS stored at 25° C.

Plot of M_t/M_{inf} vs time for PCBs sorption by 5 ply polystyrene film exposed to water at 25 degrees C.

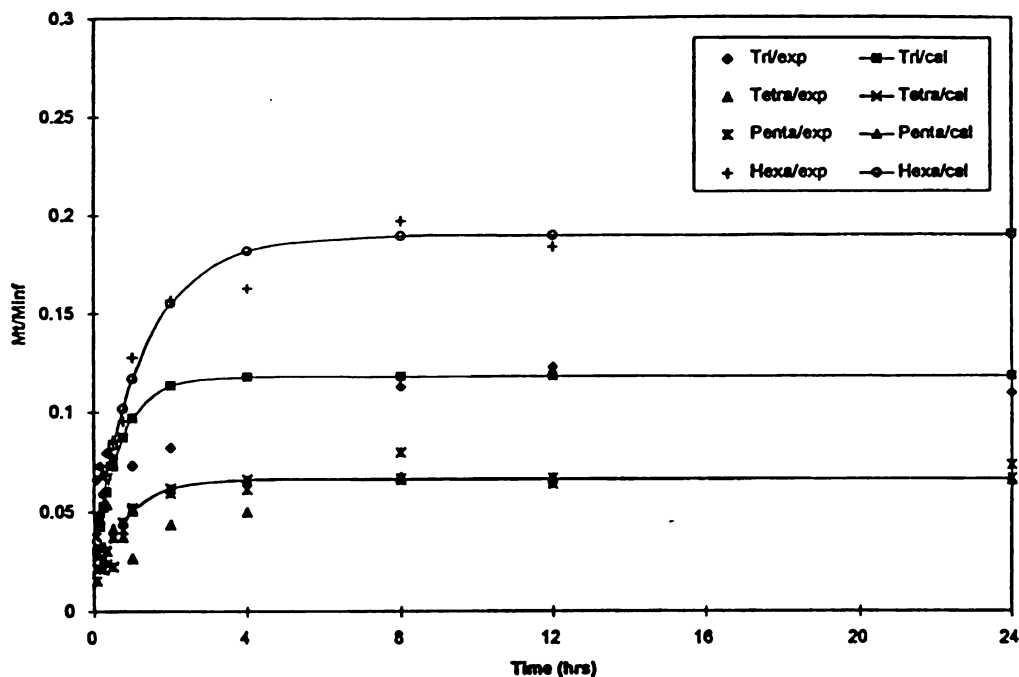


Figure 42. Calculated and experimental isotherm for tri to hexa-chloro PCB uptake by 5 ply PS stored at 25° C.

Plot of M_t/M_{inf} vs time for PCBs sorption by 5 ply polystyrene film exposed to water at 25 degrees C.

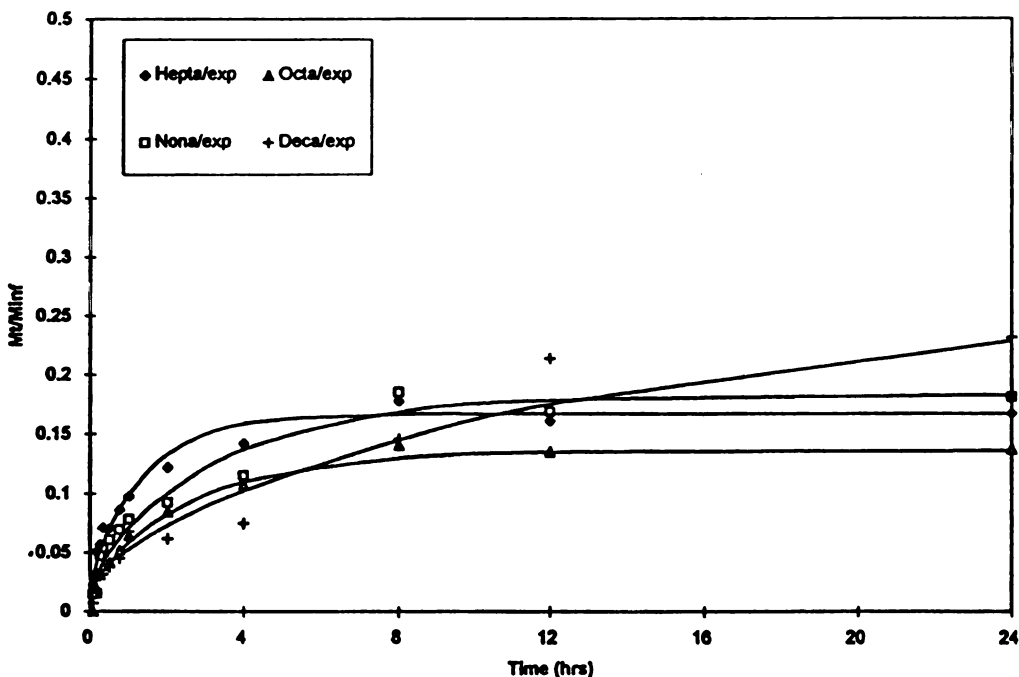


Figure 43. Calculated and experimental isotherm for hepta to deca-chloro PCB uptake by 5 ply PS stored at 25° C.

Fi

Figur

Sorption diffusion coefficient (Ds) for PCBs by polystyrene films of various thicknesses and exposed to water at 25 and 35 degrees C.

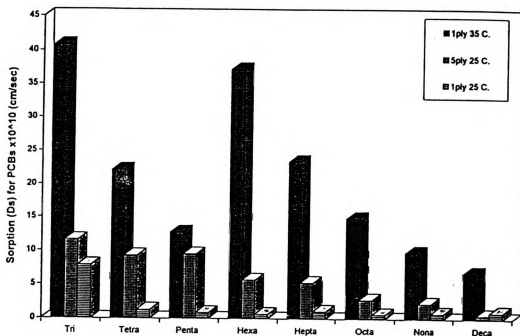


Figure 44. Comparison of sorption coefficients for all congeners by 1 and 5 ply PS stored at 25° C. and 1 ply PS stored at 35° C.

Rate loss of PCB congeners from water exposed to polystyrene films of various thicknesses at 25 and 35 degrees C.

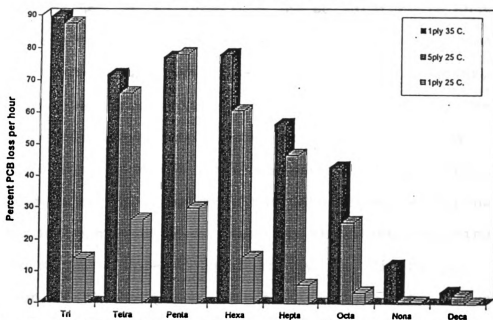


Figure 45. Comparison of rate loss for all congeners exposed to 1 and 5 ply PS stored at 25° C. and 1 ply PS stored at 35° C.

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Figure 5

POLYVINYL CHLORIDE

The graphical representations of the analysis for PCBs in the water and exposed PVC at 25°C are shown similarly to that of the polyethylene and polystyrene plastics. Figures 46 and 47 show the weights of tri-chloro to hexa-chlorinated and hepta-chloro to deca-chlorinated PCB, respectively, in the water, while Figures 48 and 49 similarly show the weights of the same congeners in the polymer. Calculations of the sorption diffusion coefficients for PVC were also performed using the same mathematical models as for polyethylene and polystyrene. Comparisons of these graphic results with the experimental PCB concentrations were also plotted and are shown in Figures 50 and 51. The bar graph shown in Figure 52 summarized the sorption diffusion coefficients for the PCB congeners in the PVC material. These results are also similar to those obtained for polyethylene and polystyrene in showing that the lower chlorinated congeners were sorbed to a greater extent than the higher chlorinated molecules. However, in this case, the presence of the nona-chloro and deca-chlorinated congeners were not detected in the material.

The rate loss from the water was similar to polyethylene and polystyrene in showing that the lower chlorinated congeners had a greater rate loss than the higher chlorinated ones. This is displayed graphically in Figure 53. A comparison of the sorption diffusion coefficients for each congener exposed to the different polymers can be seen in Figure 54. The corresponding rate loss from the exposed water

can be viewed in Figure 55.

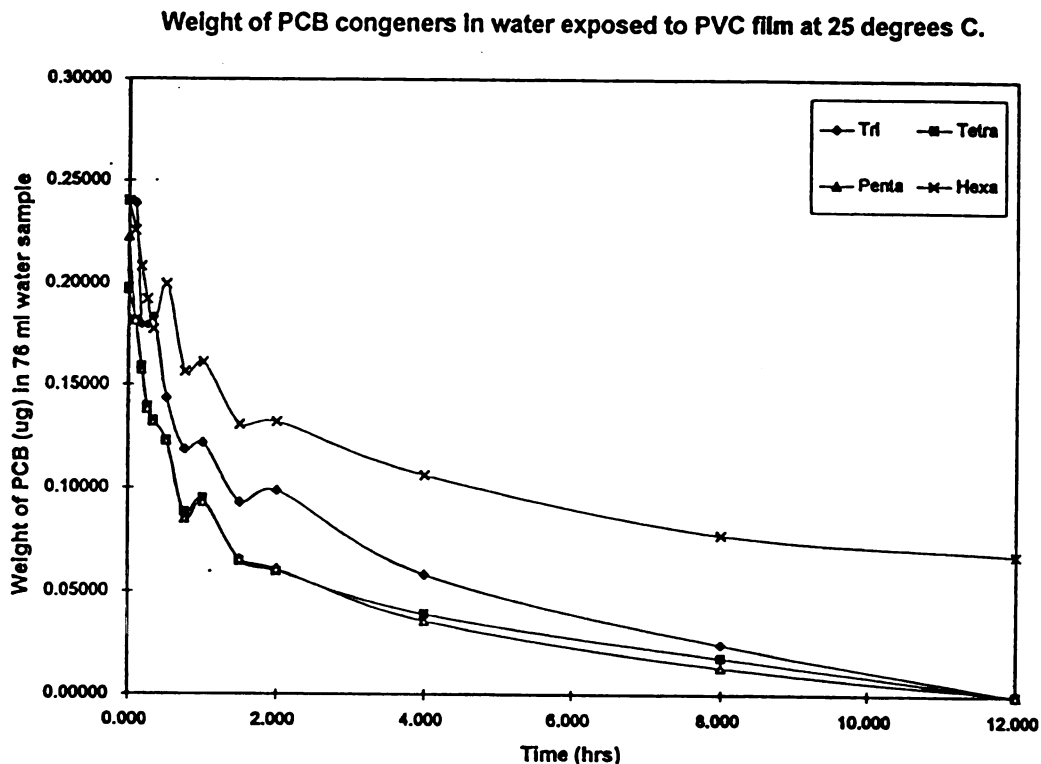


Figure 46. Weight of tri to hexa-chloro PCB in water exposed to 1 ply PVC stored at 25° C.

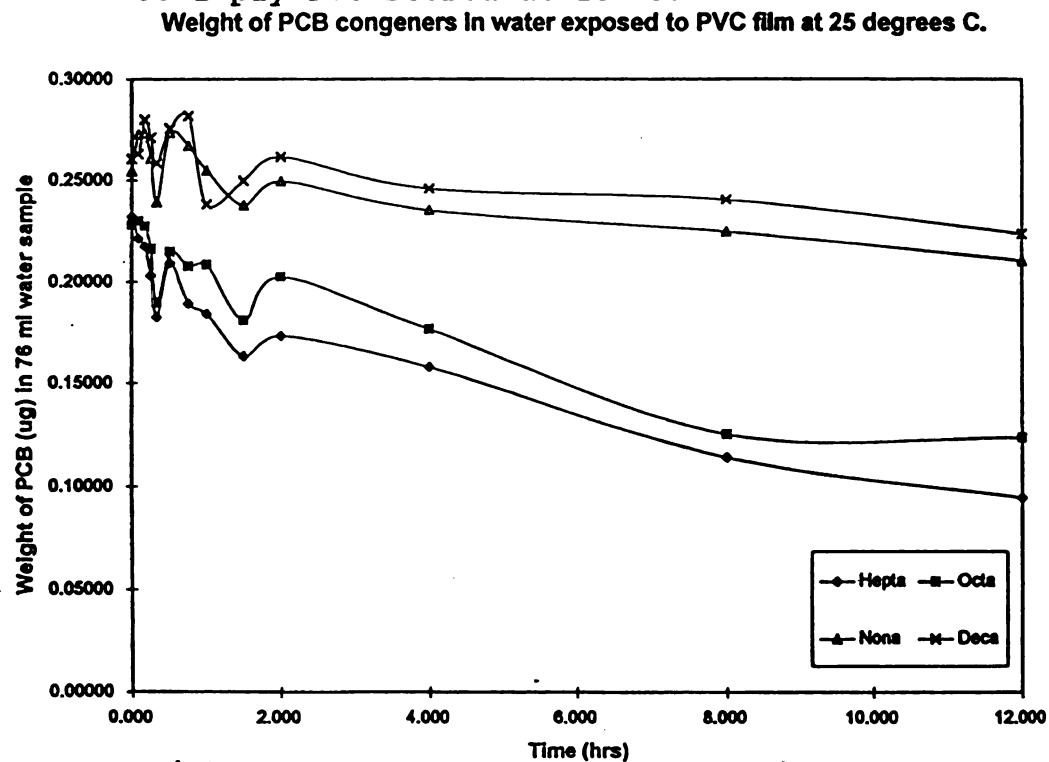


Figure 47. Weight of hepta to deca-chloro PCB in water exposed to 1 ply PVC stored at 25° C.

Weight of PCB congeners in polyvinyl chloride (PVC) immersed in water at 25 degrees C.

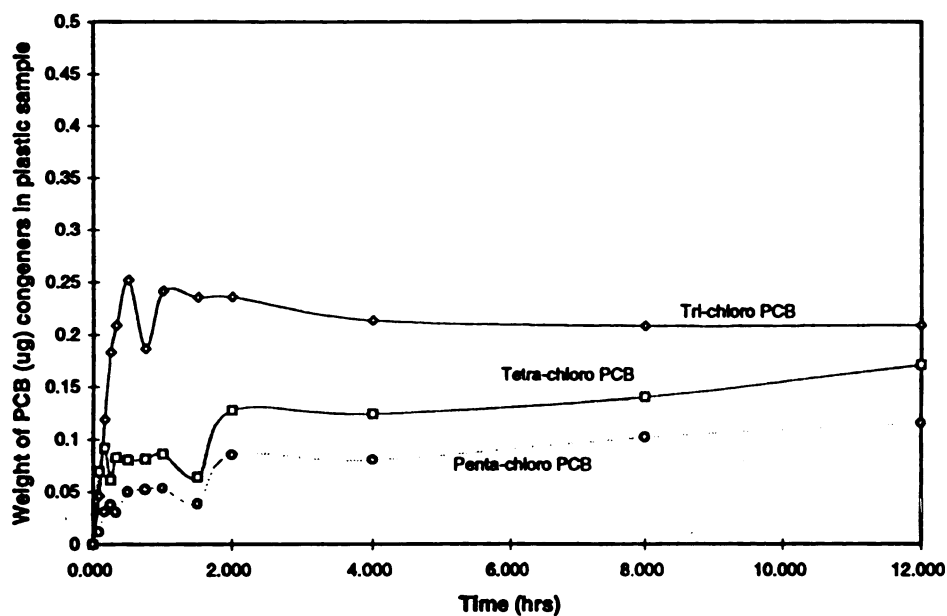


Figure 48. Weight of tri to penta-chloro PCB uptake by 1 ply PVC stored at 25° C.

Weight of PCB congeners in polyvinyl chloride (PVC) immersed in water at 25 degrees C.

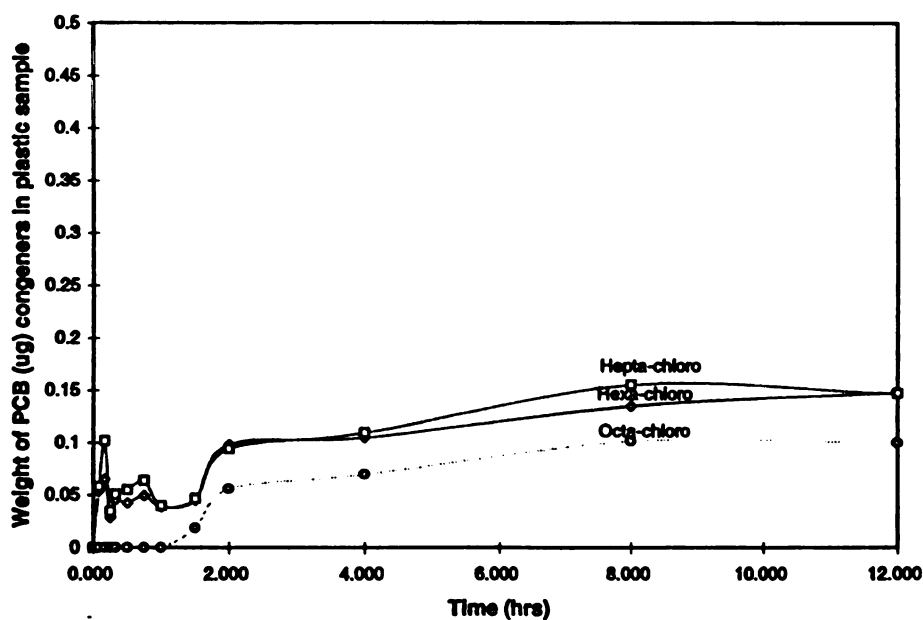


Figure 49. Weight of hexa to deca-chloro PCB uptake by 1 ply PVC stored at 25° C.

MuMInf

Figure

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0.2

0.15

0.1

0.05

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MuMInf

Figure 51

Plot of M/M_{inf} vs time for PCBs by PVC exposed to water at 25 degrees C.

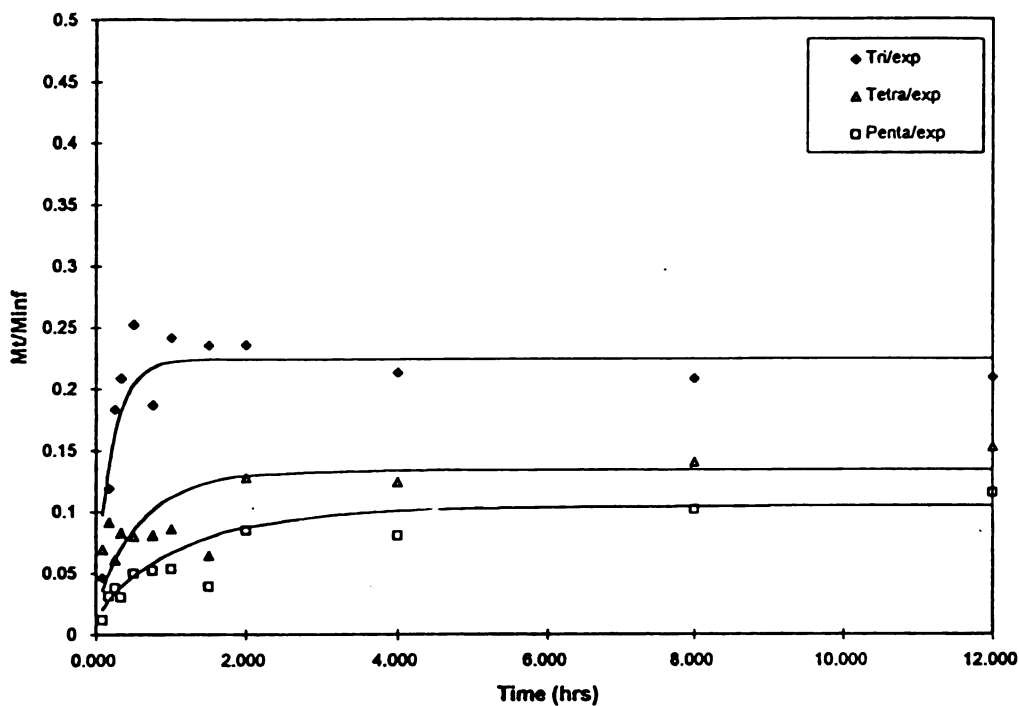


Figure 50. Calculated and experimental isotherm for tri to penta-chloro PCB uptake by 1 ply PVC stored at 25° C.

Plot of M/M_{inf} vs time for PCBs by PVC exposed to water at 25 degrees C.

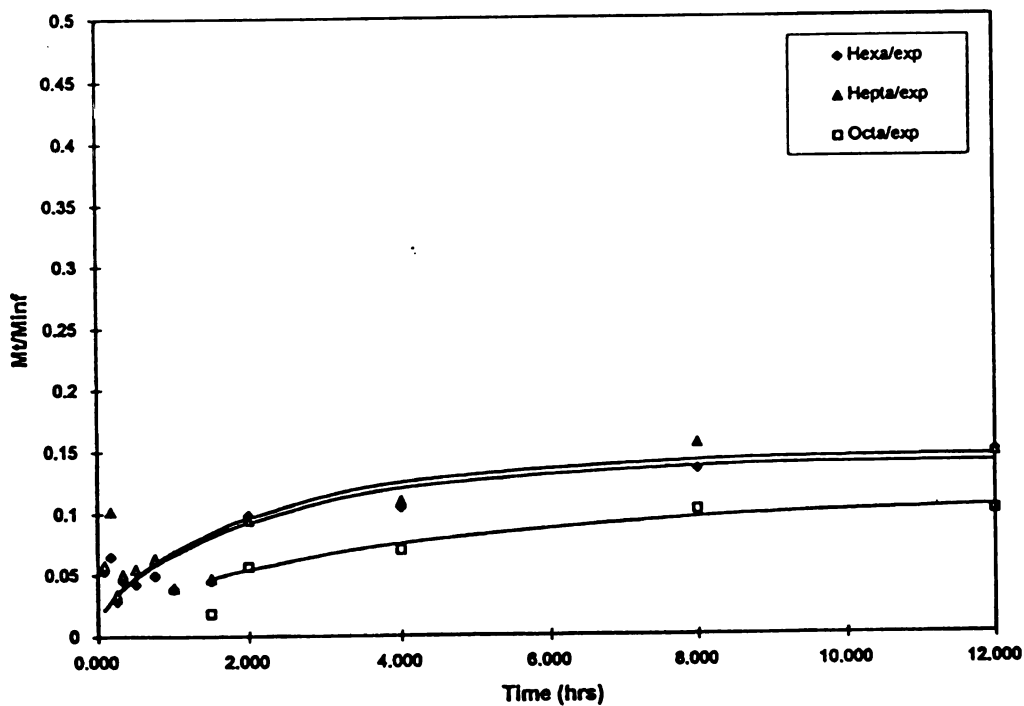


Figure 51. Calculated and experimental isotherm for hepta to octa-chlor PCB uptake by 1 ply PVC stored at 25° C.

Sorption (Ds) for PCBs x10⁻¹⁰ (cm/sec)

Figure

4

4

3

3

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Percent PCB loss per hour

Figure

Sorption diffusion coefficient (Ds) for PCBs by 1 ply PVC immersed in water at 25 degrees C.

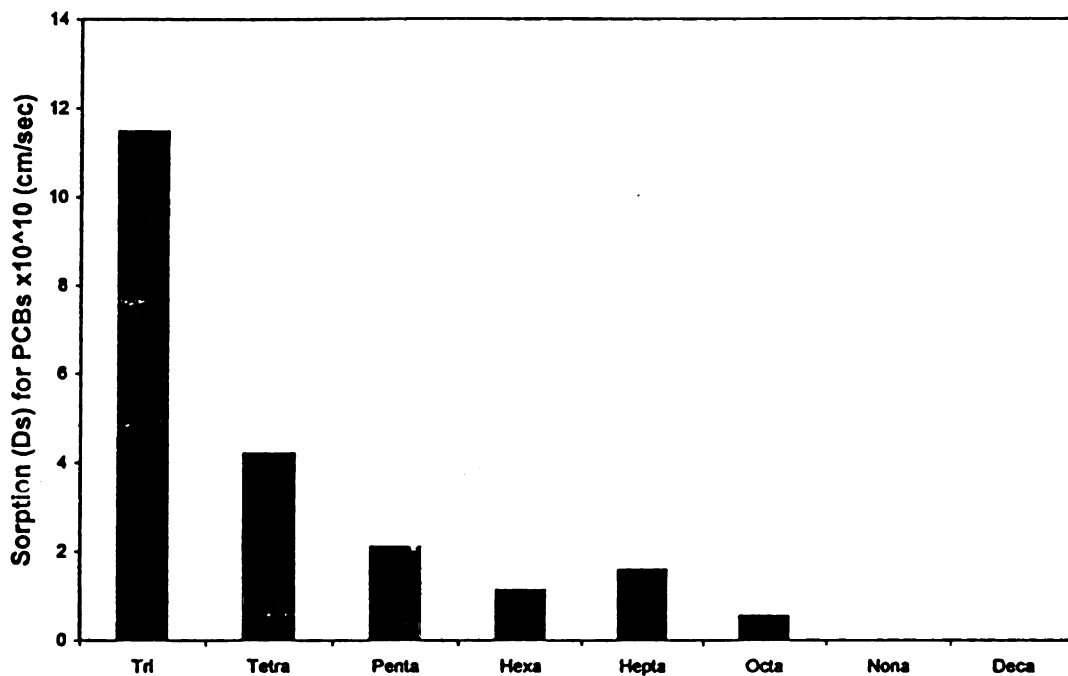


Figure 52. Comparison of diffusion coefficients for all congeners by 1 ply PVC stored at 25° C.

Rate loss of PCB congeners from water exposed to 1 ply PVC stored at 25 degrees C.

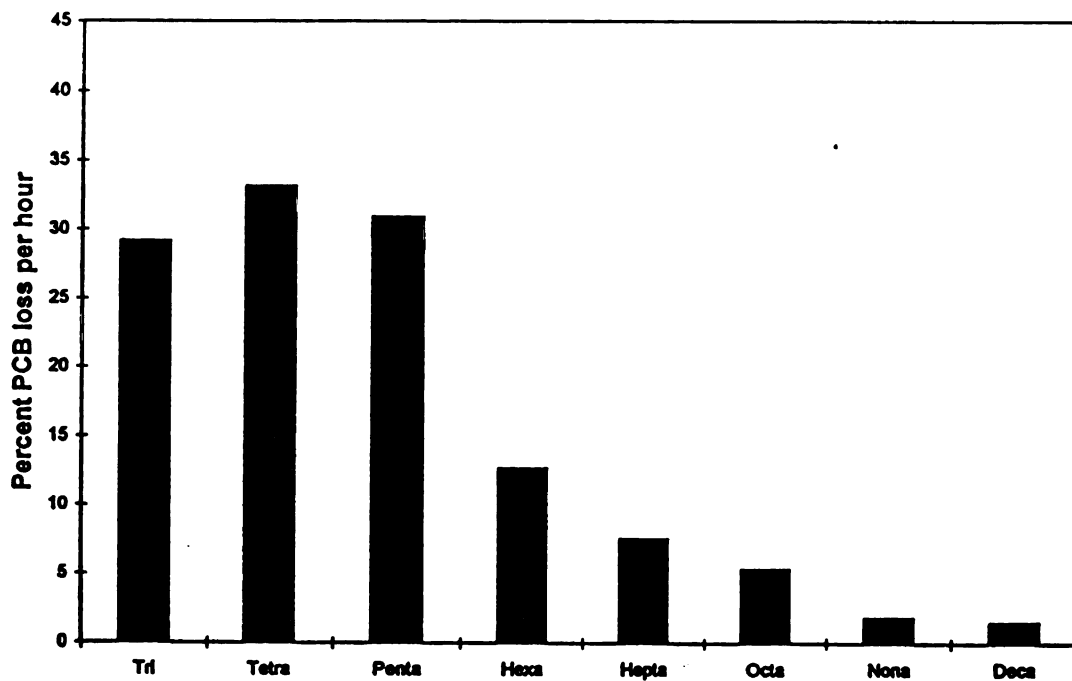


Figure 53. Comparison of rate loss for all congeners exposed to 1 ply PVC stored at 25° C.

Sorption (D_s) for PCBs $\times 10^{10}$ (cm/sec)

Figure

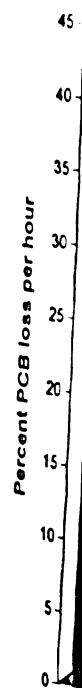


Figure 55

Sorption diffusion coefficient (Ds) for PCBs by 1 ply plastic materials immersed in water at 25 degrees C.

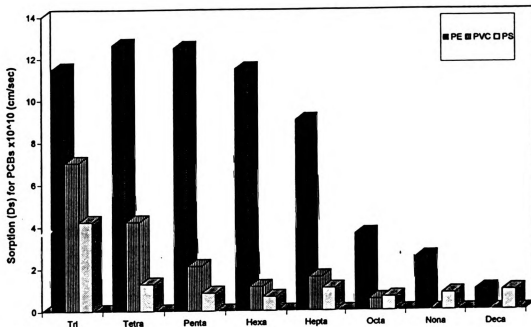


Figure 54. Comparison of sorption coefficients for all congeners by 1 ply PE, PVC and PS stored at 25°

Rate loss of PCB congeners from water exposed to 1 ply plastic films stored at 25 degrees C.

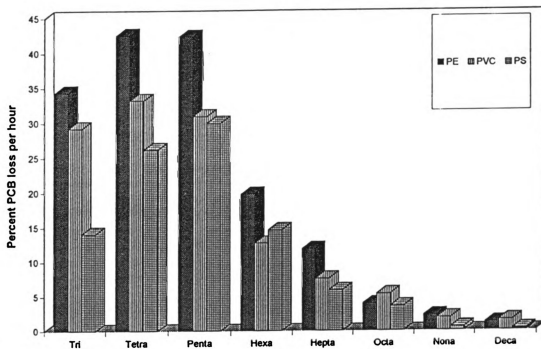


Figure 55. Comparison of rate loss for all congeners exposed to 1 ply PE, PVC and PS at 25° C.

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EQUILIBRIUM PARTITION COEFFICIENT (k_e)

The results for the partition coefficient determination for each material is shown in Tables 17 and 18. Table 17 shows the results for the polyethylene, PVC and the 1 ply polystyrene stored at 25°C. Table 18 shows the results for the 1 ply polystyrene at 25°C and 35°C, and the 5 ply polystyrene at 25°C.

Table 17. Partition coefficient (K_e) for all congeners exposed to all 1 ply materials stored at 25°C.

Congeners	Materials		
	Polyethylene	PVC	Polystyrene
Tri	115	61	10
Tetra	57	61	13
Penta	53	44	13
Hexa	87	16	39
Hepta	83	12	21
Octa	31	7	12
Nona	12	N/A	10
Deca	11	N/A	5

N/A - not applicable

Table 18. Partition coefficients (K_c) for polystyrene stored at 25°C and 35°C, and different thicknesses.

Congeners	Materials		
	1 ply PS 25°C	1 ply PS 35°C	5 ply PS 25°C
Tri	10	222	10
Tetra	13	33	16
Penta	13	92	26
Hexa	39	325	17
Hepta	21	40	8
Octa	12	31	5
Nona	10	15	3
Deca	6	14	1

A comparison of the results for the three different materials in Table 17 shows that polyethylene has the greatest partition coefficient, followed by PVC then polystyrene for congeners tri through penta. For the hexa through octa, the polyethylene still shows the greatest values, but polystyrene shows larger values than that of PVC. Since the nona and deca congeners were not detected in the PVC, no calculations were reported for them. However, the polyethylene also showed a higher partition coefficient than the polystyrene for these congeners. In general, the lower chlorinated congeners showed a higher partition coefficient than the higher analogues. The results for the polystyrene at the different treatments shown

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in Table 18, also show the general trend where the lower chlorinated congeners have a larger partition coefficient than the higher chlorinated analogues. The polystyrene exposed at 35°C shows a higher coefficient than the 5 ply and the 1 ply stored at 25°C. The 5 ply polystyrene shows higher coefficients for tri through penta chlorination, but lower values for hexa through deca chlorination when compared to the 1 ply polystyrene stored at 25°C.

The partition coefficients for the PCB congeners exposed to polyethylene, PVC and polystyrene at 25°C was plotted versus the Lemay's molar volume range for these congeners. This plot can be seen in Figure 56. The results of this relationship confirms the principle alluded to earlier, that the potential of the larger chlorinated congeners to penetrate the polymers diminishes with increasing size when in the aqueous medium. It can be seen in Figure 56 that the curve generally decreases with increasing molar volume.

A plot of the partition coefficients for the congeners exposed to 1 and 5 ply polystyrene immersed in water at 25 and 35°C, is indicated in Figure 57. Except for the sharp increase in partition coefficient of the hexa-chlorinated congener at 35°C, the relationship is similar to that in Figure 56, where the trend is a decrease in partition coefficients as the molar volume increases.

The average percent recovery of the PCB congeners after extraction from the polyethylene, PVC and the polystyrene stored at 25°C was determined to be 69.41%. This was

calculated from the area response obtained for the internal standard added to each sample prior to the extraction process, and the area response of the same internal standard injected directly into the GC at the time when the samples were been analyzed. The average percent recovery for the PCBs extracted from the water exposed to the polymeric materials was similarly determined to be 114.80%.

The higher percentage observed in the recovery for the congeners in the water phase may be due to errors in measuring the internal standard prior to its addition to the sample, or errors introduced by the automatic sampler of the GC. The lower percentages seen in the polymeric phase may also be due to errors similar to those mentioned for the higher percentages. However, in the case of the lower percentages, the higher partitioning of the congeners for the polymers, increases the difficulty of extracting the PCBs from materials. Thus, this may also be a factor in increasing the errors introduced into the analytical process. This problem is also confirmed by the relatively low recovery for the congeners in the oil which was calculated to be 23.43%.

Comparison of Leman's molar volume with partition coefficients for all congeners exposed to polystyrene, PVC and polyethylene at 25 degrees C.

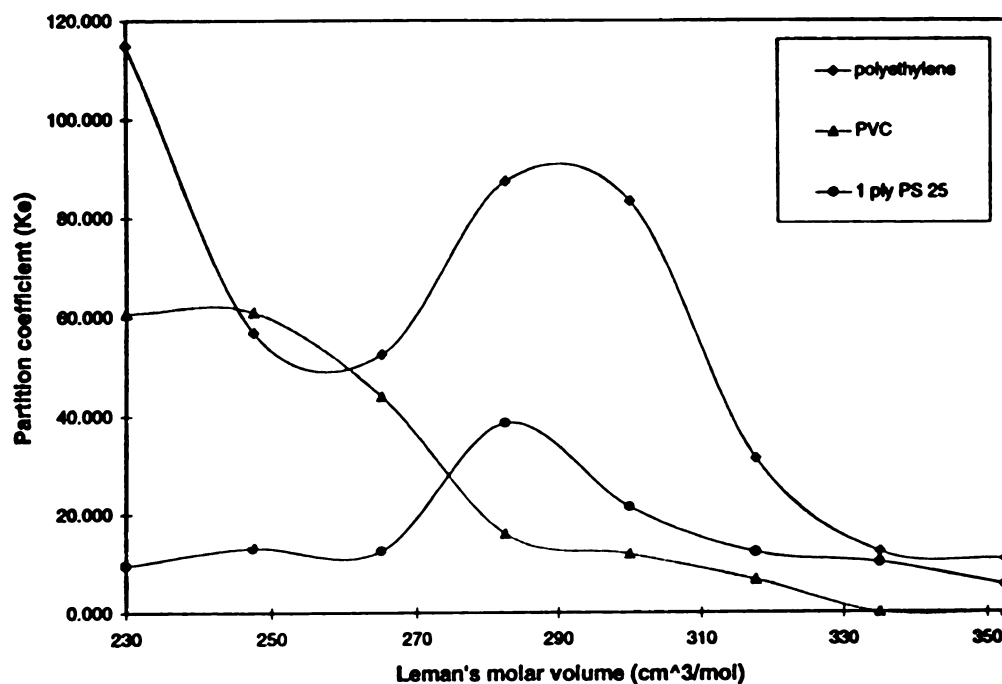


Figure 56. Plot of partition coefficient vs molar volume of the PCB congeners exposed to PE, PVC and PS stored at 25°C.

Comparison of Leman's molar volume with partition coefficients for all congeners exposed to polystyrene at 25 & 35 degrees C.

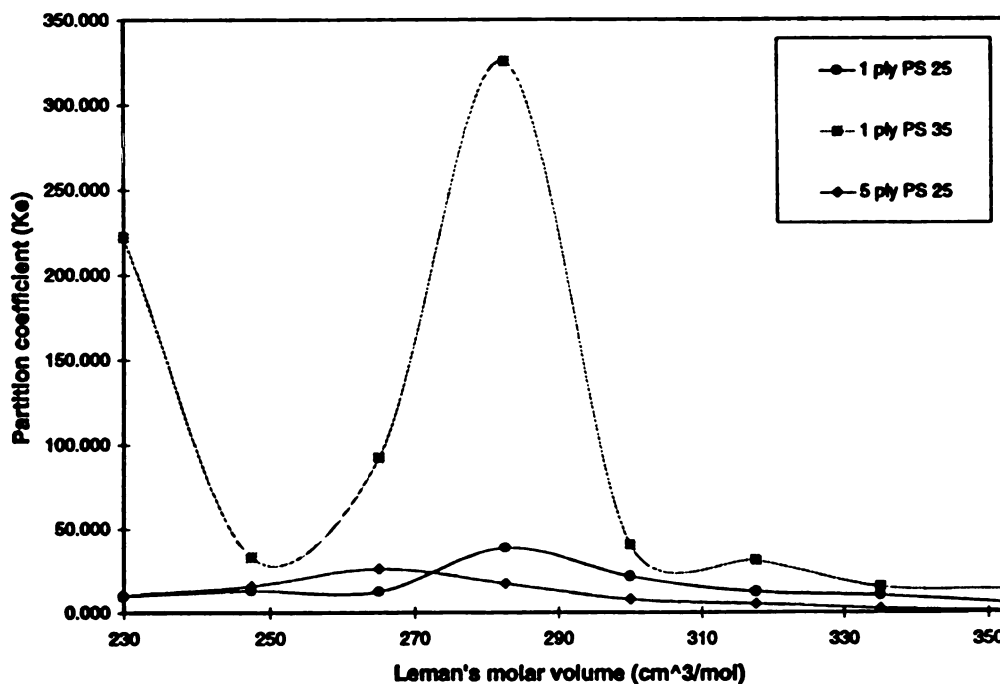


Figure 57. Plot of partition coefficient vs molar volumes of the PCB congeners exposed to 1 and 5 ply PS stored at 25 and 35°C.

STATISTICAL ANALYSIS

Full one-way ANOVA tables of all the statistical analyses performed in this study can be seen in appendix 1. A summary of these ANOVA results for the steady state concentrations of the PCB congeners in the three materials (PE, PVC, and PS) stored at 25°C can be seen in Table 19. This table shows the means and standard deviations of these concentrations, the statistical F-test values and the calculated probabilities (p) for each congener exposed to each material. No data are shown for nona and deca for PVC since the concentrations of these congeners were below the detection limit of the GC. A similar summary for all congeners exposed to 1 and 5 ply polystyrene stored at 25°C and exposed to 1 ply polystyrene at 35°C, can be seen in Table 21.

Table 19. Summary of means, std. dev., statistical F and p data for PCBs in water exposed to polyethylene, PVC and polystyrene stored at 25°C.

Congeners	PVC		polyethylene		polystyrene		F	p
	means	SD	means	SD	means	SD		
Tri	0.2164	0.05	0.4213	0.12	0.1078	0.03	53.52	0**
Tetra	0.1357	0.05	0.2551	0.05	0.0560	0.01	111.7	0**
Penta	0.0953	0.02	0.2232	0.04	0.0391	0.01	135.9	0**
Hexa	0.1212	0.07	0.2412	0.04	0.2392	0.05	17.41	0**
Hepta	0.1261	0.09	0.2436	0.04	0.1910	0.04	11.72	0**
Octa	0.0816	0.06	0.1664	0.03	0.1351	0.03	12.26	0**
Nona	N/A		0.1221	0.03	0.0607	0.02	32.90	0**
Deca	N/A		0.1059	0.03	0.0527	0.02	30.24	0**

** significant at 0.001 level,
N/A - not applicable.
n=37

Table 20. Summary of statistical data showing areas of significant uptake differences between congener for polyethylene, PVC and polystyrene in water stored at 25°C.

Tri, tetra and penta-chloro

	polystyrene	PVC
PVC	*	
polyethylene	*	*
* significantly different		

Hexa, hepta and octa-chloro

	polystyrene	PVC
PVC	*	
polyethylene		*
* significantly different		

Nona and deca-chloro

	polystyrene	PVC
PVC	N/A	
polyethylene	*	N/A
* significantly different		

Table 21a. Summary of means, std. dev., statistical F and p data for PCBs in water exposed to 1 ply PS stored at 25°C and exposed to 1 ply PS at 35°C.

Congeners	25 degrees C		35 degrees C (polystyrene)		F	p
	means	SD	means	SD		
Tri	0.108	0.028	0.1901	0.034	45.95	0.0**
Tetra	0.056	0.013	0.0770	0.010	18.37	0.0**
Penta	0.039	0.009	0.0522	0.015	5.944	0.02
Hexa	0.239	0.049	0.2124	0.019	4.137	0.05
Hepta	0.192	0.039	0.1870	0.014	0.190	0.666
Octa	0.135	0.029	0.1524	0.018	2.941	0.096
Nona	0.061	0.024	0.1972	0.034	97.91	0.0**
Deca	0.053	0.017	0.2262	0.066	57.11	0.0**

** significant at 0.001 level;

* significant at 0.005 level.

n=37

Table 21b. Summary of means, std. dev., statistical F and p data for PCBs in water exposed to 1 and 5 ply PS stored at 25°C.

Congeners	1 ply thick		5 ply thick (polystyrene)		F	p
	means	SD	means	SD		
Tri	0.108	0.028	0.1089	0.027	0.008	0.929
Tetra	0.056	0.013	0.0570	0.013	0.035	0.852
Penta	0.039	0.009	0.0660	0.014	25.16	0.0**
Hexa	0.239	0.049	0.1753	0.019	23.47	0.0**
Hepta	0.192	0.039	0.1506	0.025	13.41	0.001**
Octa	0.135	0.029	0.1165	0.026	3.372	0.075
Nona	0.061	0.024	0.1403	0.041	33.27	0.000**
Deca	0.053	0.017	0.1238	0.070	9.607	0.004*

** significant at 0.001 level;

* significant at 0.005 level.

n=37

Table 22. Summary of statistical data for PCB congeners in water and peanut oil exposed to polyethylene at 25°C.

Congeners	peanut oil		Water		F	p
	means	SD	means	SD		
Tri	2.575	0.097	0.081	0.075	15351	0**
Tetra	1.680	0.071	0.069	0.065	9952	0**
Penta	1.716	0.075	0.063	0.061	10705	0**
Hexa	1.819	0.123	0.081	0.074	5820	0**
Hepta	1.050	0.071	0.096	0.051	4545	0**
Octa	0.790	0.052	0.121	0.042	3769	0**
Nona	0.478	0.039	0.202	0.059	474	0**
Deca	0.430	0.031	0.190	0.049	524	0**

** significant at 0.001 level.
n=74

The results for the three materials at the same environmental conditions show that there are significant differences ($P < 0.05$) between the steady state concentration of PCBs in the materials for each congener. The contrasts using the Tukey range test shows where the differences are once significant differences are detected by the ANOVA. These results for the three materials at the same environmental conditions can be seen in Table 20. Significant differences were observed for each material for congeners tri to penta-chlorinated. No differences were obtained for the polyethylene and polystyrene for congeners hexa to octa-chlorinated, while significant difference were detected for the these materials with PVC. Since nona and deca-chlorinated PCBs were not detected in the PVC, only the interrelation of the polyethylene and the

polystyrene were tested. Significant differences ($P < 0.05$) were obtained between these materials.

Results for the polystyrene at the different temperatures show that there are significant differences ($P < 0.05$) between the steady state concentration of PCBs in the materials for tri, tetra, nona and deca-chlorinated congeners. There were no significant differences between the other congeners. This trend is also the same for the congeners exposed to polystyrene at the different thicknesses. Since only two variables were tested in each case, the Tukey range test was not necessary.

ANOVA for the comparing the means for the congeners exposed to polyethylene in the peanut oil medium compared to the water can be seen summarized in Table 22. Significant differences ($P < 0.05$) were obtained for each congener between these liquid media.

DISCUSSION

EFFECTS OF POLYMER TYPE, TEMPERATURE & THICKNESS ON PCB UPTAKE FROM AQUEOUS AND OIL MEDIA

In this study, the polymeric samples were completely immersed in the penetrant, such that both faces were exposed simultaneously to the same concentration. It was assumed that the penetrant entered the film and diffused towards its center. Diffusion behavior differs from polymer to polymer and this paper focuses on two descriptions of this behavior - Fickian and non-Fickian diffusion systems. Fickian behavior is usually associated with rubbery polymers such as polyethylene, while non-Fickian behavior is usually exhibited by glassy polymers such as the PVC and polystyrene used in this study.

Polymers in the rubbery state respond rapidly to changes in their condition. A change in temperature for example, causes an almost immediate change to a new equilibrium volume. Glassy polymers on the other hand, tend to be time-dependent. In this case, a change in condition produces an immediate but partial response, followed by a slow, asymptotic approach to equilibrium. Crank (1975) reported that deviations from Fickian behavior are considered to be associated with the finite rates at which the polymer structure may change in response to the sorption or desorption of penetrant molecules.

Increasing concentrations of many penetrants act similar to that of temperature by increasing the motion of the polymer segments and decreasing relaxation times of the molecular structure. In the case of rubbery polymers such as polyethylene, well above their glass temperature, the polymer chains adjust so quickly to the presence of the penetrant that they do not cause diffusion anomalies (Crank, 1975).

In an attempt to classify the diffusion behavior in the different polymeric systems, Alfrey et al. (1966) proposed three descriptive classes:

1. Case I which they referred to as Fickian diffusion. In this instance, the rate of diffusion is less than the rate of relaxation of the polymeric chains to the approaching front. In this case, it would be obvious that the process is concentration dependent;
11. Case II in which the rate of diffusion is quicker than the relaxation process. One can see that in this case the diffusion process will be dependent on the relaxation rate of the polymeric chains or as was mentioned above, will be time dependent;
111. Non-Fickian or anomalous diffusion. In this case the diffusion and relaxation processes are described as comparable.

Crank (1975) summarizes these behaviors by reference to the types of sorption and desorption curves one should expect for penetrants with Fickian and non-Fickian systems, these curves are shown in Figure 58.

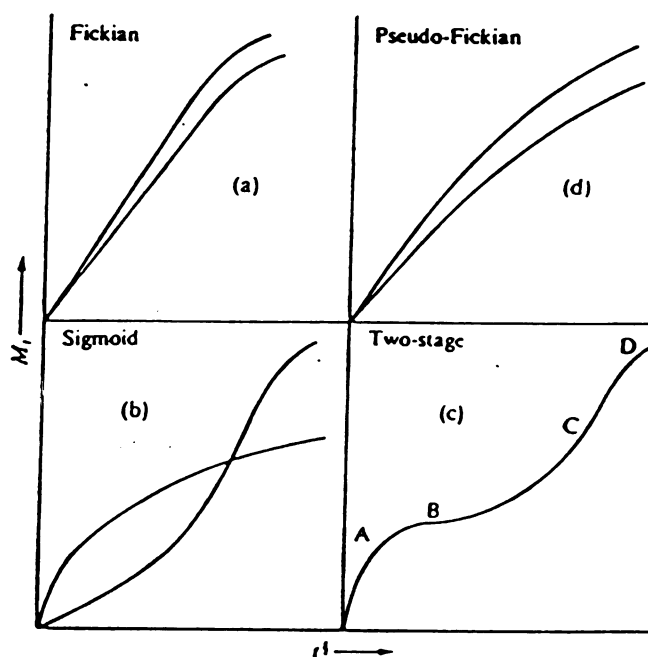


Figure 58 Fickian and Non-Fickian sorption and desorption type curves.

A comparison of the results obtained for the concentration of PCBs in the polyethylene film exposed to water as a function of time, shows that they appear to be Fickian in nature, similar to those in Figure 58 (a) and (b) above. This is not surprising since we know that polyethylene is rubbery at 25°C, the temperature of the study. The departure from an almost perfect Fickian curve by that obtained for the tri-chlorinated congener in Figure 5 may be

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due to experimental errors. Thus, one should expect that the diffusion process for polyethylene exposed to water was concentration dependent. Similar results were obtained by Stannett and Yasuda (1963) for cyclohexane and benzene through polyethylene. The presence of the PCBs in an aqueous medium also sets up certain conditions which should not be ignored. Water differs from the PCBs and other similar organic compounds in that its molecular size is comparatively small. It can also be described as being in a condensed state with the formation of hydrogen bonds (Chainey, 1989). Thus, in contact with the polyethylene, one should expect clustering of the water molecules to occur. This has been shown in experiments performed by Thornton et al. (1958). This clustering will be expected to hinder the transport of the PCBs through the polymer, since only the monomeric species are small enough to diffuse. As a result, these must detach themselves from a cluster before a diffusive jump into the polymers matrix is possible. These processes are by no means simple and clear cut. Chainey (1989) reported that further complications can arise depending on the polymer type exposed to the water, and that the heat of sorption can be large, producing temperature rises of several degrees, and thus can lead to errors in the interpretation of the data.

In the case of the polyethylene exposed to the oil, it can be reasonably assumed that both PCB and the oil would have a high partition coefficient for the non-polar polymer. Thus, extensive swelling of the polymer should be expected to occur,

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In the case of the polyethylene exposed to the oil, it can be reasonably assumed that both PCB and the oil would have a high partition coefficient for the non-polar polymer. Thus, extensive swelling of the polymer should be expected to occur, and both the PCBs and the oil would exert a plasticizing effect on the material. Since the partitioning of PCBs for the oil is also expected to be relatively high, it is not surprising that the rate loss of PCBs from the oil (Figure 23) was quite low for the duration of the study, when compared to that for PCBs in the aqueous phase.

Excluding the other complicating phenomena, two major factors can be sighted as influencing the differential sorption diffusion coefficients obtained for the PCB congeners tri to deca chlorinated by all plastic materials used in this study. The first is the molecular size increase of the congeners as we go from tri ($229.96 \text{ cm}^3/\text{mol}$ Lemman gaseous volume) to deca ($352.60 \text{ cm}^3/\text{mol}$ Lemman gaseous volume) chlorinated. The larger the molecular size of a penetrant, the more difficult it is to diffuse through the matrix of a polymeric material (see Table 5 for all congener volumes). Chern (1985) reported that for large non-spherical compounds, the cross-sectional area and volume may be the most important factors that determine the contaminant's ability to pass through an adequately-sized gap. Heindorf (1992), referred to the use of the parachlor and permachlor concepts in showing that an inverse correlation exists between the size of a penetrant and its diffusion rate through a given polymer.

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The second major factor influencing diffusion of the PCB congeners is the change in polarity of the biphenyl rings as we go from tri to deca chlorination. Hutzinger et al. (1974) reported that the solubility of PCBs decrease in water with increasing chlorination. This is indeed so because the influence of chlorination disrupts the π electron cloud within the biphenyl rings and thus introduces greater non-polar influences. This may well be the reason why a small, but increasing rate loss of the congeners from tri to deca-chlorination in the oil was obtained when exposed to the polyethylene (Figure 23). In addition, the synergistic swelling or plasticizing effect of both the oil and the PCBs on the material would increase the ease in which the higher chlorinated congeners could diffuse into the polymer. In this case, these higher chlorinated congeners exhibited a greater partitioning for the polyethylene than the oil. This pattern was not seen in the case of the polymer/water exposures (Figure 23). This may be due to the effect of increasing molecular size, mentioned above, and its limiting effect on the diffusion of the larger size congeners.

This effect is most pronounced when one examines the results obtained for the PVC/water exposure. In this case, the presence of the nona and deca-chlorinated congeners were not detected in the PVC film (Figures 48 and 49). One should also consider the effect of the tightly packed molecular structure of PVC as compared to both polyethylene and polystyrene. This rigidity and reduced flexibility of its

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structure is also increased by the chain to chain bonding (increased cohesive density) introduced by the presence of the chlorine atoms within the PVC backbone. In addition to these factors, PVC is a glassy polymer with a glass-transition above that of room temperature (25°C). This factor is expected to decrease the potential for uptake of the PCB congeners, especially the higher chlorinated ones.

This result is confirmed by the partition coefficients obtained for the PCB in water exposed to the PVC. Table 4 shows that the lower chlorinated congeners exhibit a higher partitioning for the plastic than the higher analogues. Legett and Parker (1994) obtained similar results for the partitioning of *cis*-dichloroethane, *trans*-dichloroethane, 1,1,2-trichloroethane, tetrachloroethane, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, and *p*-dichlorobenzene between groundwater and PVC in one instant, and for polytetrafluoroethylene (PTFE) in another instant. They showed that as the size and geometry of these penetrants changed, the partition coefficients for the PVC and PTFE increased with increasing size of the penetrants molecule.

Since the use of plasticizers is an essential ingredient in the processing of PVC, its presence introduces further complications to the diffusion process in this study. Vergnaud (1978) reported the diffusion of the penetrant occurs simultaneously with a diffusion of the plasticizer from the polymer towards the liquid environment. He also showed that this phenomenon restricts the diffusion of the penetrant

towards the polymer since a loss of the plasticizer induces a tightening and rigidity to the polymeric chains. Thus, time related sorption curves obtained from his results showed an initial uptake of benzyl alcohol by plasticized PVC, which eventually equilibrated but at a lower subsequent concentration value. A similar result for the uptake of the tri-chlorinated congener by PVC was obtained in this study (see Figure 46). Since this is a dynamic process, the net result in a given situation will depend on the plasticizing effect of the penetrant compared to the loss of the migrating initial resident plasticizer within the material.

An examination of the results for the uptake of the other congeners by PVC shows some small deviations from a true Fickian diffusion. This is understandingly so because PVC is a glassy polymer and thus is expected to behave differently from that of polyethylene. Unlike the relatively rapid isotropic swelling response to penetrants by rubbery polymers, glassy polymers exhibit a differential swelling at different geometric parts of the material. Petropoulos and Roussis (1974) reported that during absorption in glassy polymers, the network can open up immediately only to a limited extent since only very small polymer segments can move practically instantaneously. Further opening up of the polymeric structure will occur gradually until the final swelling equilibrium is attained. Fujita and Kishimoto (1958) reported two possible explanations for the molecular structural relaxation caused by the penetrating molecules. One is the

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scission of interchain bonds by a chemical action of the penetrant, while the second is the so called "plasticizing effect" already alluded to above. Thus, if we assume that the fast and slow changes proceed independently of each other, the total change in diffusion coefficient D will be the sum of the two. Crank (1953), on the basis of this assumption, assumed a first-order approach to the equilibrium and expressed the total change in diffusion coefficient by the equation:

$$\left(\frac{\partial D}{\partial t}\right)_x = \left(\frac{\partial D_i}{\partial C}\right) \left(\frac{\partial C}{\partial t}\right)_x + \alpha (D_e - D) \quad (39)$$

where D_i is the part of D which can change instantaneously, and is a function of concentration only. D_e is the equilibrium diffusion coefficient and α is the rate parameter controlling the approach to equilibrium. Other approaches and mathematical models explaining this phenomenon have also been postulated by Petropoulos and Roussis (1974), and Long and Richman (1960).

This correction for the diffusion in the glassy PVC and polystyrene were not performed in this study because of the relatively low concentration of the PCB congeners. The low concentration was necessary due to the low solubility of the PCBs in water, being only approximately 12 ppb (Hutzinger,

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1974). The use of such low concentrations is expected to complicate the situation even further, since it amplifies any experimental errors introduced during the extraction, cleanup and quantification processes for the PCBs. The shapes of the curves for this study are similar to those shown previously by Heindorf (1992), Huckins et al., (1990) and Vergnaud (1986). Vergnaud (1986) reported that curves with such shapes are non Fickian in nature. Since the concentration of the PCBs in this study is so low, they may not result in true non Fickian behavior.

Since polystyrene is also a glassy polymer, one should expect similar results to that obtained for the PVC. This can be corroborated by reference to Park (1968) who stated that it is not unusual to see an inflection in such non-Fickian curves. This is indeed so for the exposure of the polystyrene to the aqueous PCBs at 25°C and at 1 ply thickness. In the case of the tri-chlorinated congener (Figure 4-14), the deviation from Fickian diffusion is most pronounced when compared to the other congeners. It appears that the tetra and penta-chlorinated congeners which were lower in concentration in the polymer is more Fickian in behavior than the other congeners which were at a higher concentration (Figures 26 and 27).

When the results for the concentration of the PCBs in the polystyrene exposed to the water at 35°C are examined (Figures 34 and 35), one sees a more Fickian type diffusion behavior. This is understandable so because the increased temperature,

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in addition to influencing other factors, would indeed facilitate an increased diffusion rate by lowering the activation energy, and increasing the penetrant molecular motion and thus increasing its concentration at the liquid/polymer boundary. This is also mirrored by the increased rate of loss of PCBs from the water (Figure 45) as compared to that obtained at 25°C. This result is confirmed by the increased partition coefficient obtained for 35°C as compared to the lower value obtained at 25°C (Table 18). This shows that the PCBs favor polystyrene to a higher extent at 35°C than at 25°C in an aqueous system. Kwapong and Hotchkiss (1987) obtained similar results for the partitioning of limonene in an aqueous system for LDPE at temperatures of 6, 23 and 38°C, showing the highest coefficient at the elevated temperature of 38°C.

Although the results obtained for the PCB concentration in polystyrene at the increased thickness of 5 ply show an increase diffusion coefficient, the curves (Figures 43 and 44) are not as Fickian in nature when compared to the those at 35°C (Figures 36 and 37). Chainey (1989) reported that any change in shape of the material due to swelling will be resisted by the unswollen part in glassy polymers. Thus, increasing thickness should not be expected to ameliorate this situation, at least during the initial diffusion process. This is also alluded to by (Chainey 1989) who mentioned that the initial swelling in the material allows further penetrant molecules to enter. Plasticizing effect of these molecules

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allows viscous creep to occur more rapidly, thus, the rate of entry of penetrant molecules increases, and so on until equilibrium is reached. Thus, as was expected, the increased thickness did not result in a relatively large diffusion coefficient increase by polystyrene when compared to the effect of the increased temperature from 25 to 35°C (Figure 45). This is also confirmed by the results for the partitioning of the PCBs between the 5 ply material and the water as seen in Table 18. One even sees in the case of the hexa to deca chlorinated congeners that the partition coefficient is higher in the 1 ply as compared to the 5 ply material.

This result should be considered carefully because there seems to be conflict between it and the results obtained for the sorption diffusion coefficient for the 5 ply and the 1 ply polystyrene. One should remember that the dimensions of the material pieces were approximately the same. However, by using pieces that were 5 ply (5 times the thickness of the 1 ply), an increase in the weight per piece was obtained. Thus, unless the increase in concentration of the PCBs in the 5 ply material is sufficiently large, errors could be introduced in the interpretation of the result. This could be so because the greater the weight of material per unit volume, the lower would be the weight of PCB per gram (concentration) of material, when compared to the same weight of PCB in a thinner material.

A comparison of the sorption diffusion coefficients for

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all the congeners exposed to all the materials under the same environmental conditions, shows that the polyethylene has the largest coefficient and polystyrene the least (see Figure 55). A similar result was obtained for the partitioning of the PCBs between the aqueous environment and these materials (see Table 4). This confirms the fact that polyethylene is more favorable towards the PCB than the other materials under the same environmental conditions. This should not be surprising due to the fact that polyethylene is a rubbery polymer with approximately 55% crystallinity. The fact that the PVC showed a higher diffusion coefficient than polystyrene may be a result of the extent of its plasticization during processing. One should expect that at a relatively low plasticizer concentration, PVC would be expected to show a low rate of diffusion to most penetrants, even lower than polystyrene. It should be noted that the polystyrene seem to sorb the higher chlorinated congeners almost as well as the polyethylene and indeed better than that of PVC. In this case, the larger pore spaces within the polystyrene matrix is better able to accommodate the larger molecules than the other more restrictive materials.

In summary, one can see that polyethylene removes the lower chlorinated congeners from the water much better than either PVC or polystyrene. However, polystyrene removes the higher chlorinated analogues as well as does the polyethylene; and better than PVC which cannot remove detectable concentrations of these congeners. The polystyrene exposed to

the water at 35°C is more efficient in removing the PCBs than polystyrene at 25°C at 1 or 5 ply thickness. It is extremely difficult to remove the PCBs from an oil environment as compared to an aqueous one when exposed to polyethylene at 25°C.

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CHAPTER 5

SUMMARY AND SIGNIFICANCE OF THE STUDY

This study investigated the kinetic characteristics and uptake capacity of commercially available polyethylene, polyvinyl chloride and polystyrene films for the removal of polychlorinated biphenyls from aqueous and lipid solutions. The major results of the study indicated that polyethylene removed the lower chlorinated congeners from the water much better than either PVC or polystyrene. However, polystyrene removed the higher chlorinated analogues as well as did the polyethylene, and better than PVC which could not remove detectable concentrations of these congeners. Exposed to water at 35°C, polystyrene was more efficient in removing PCBs than was polystyrene at 25°C at 1 or 5 ply thickness. The rate of removal of PCBs from an oil environment as compared to an aqueous one, is much lower when exposed to polyethylene at 25°C.

These results support the initial prediction that the techniques used in this research can facilitate removal of PCBs in media with properties similar to those investigated.

Thus, the results from this study can be used to model possible transfer of environmental contaminants from foods with polar and non polar characteristics to selected packaging materials.

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The use of capillary gas chromatography associated with electron capture detection, in conjunction with the use of PCB isomers as reference analytical standards, is a viable analytical technique for the analysis of commercial PCB formulations present found in plastic packaging materials. Prior to this quantitation step, extracts of the PCBs can be effectively cleaned up by the use of high pressure gel permeation chromatography and florisil/silica gel ion exchange chromatography. Future efforts can address the modification of this technique for quantification of PCBs in other types of packaging materials.

Since 209 congeners of PCBs are presently known to exist, and several researchers have reported on the differential toxicity, bioconcentration potential and bioavailability of these congeners both individually and sub-grouped according to number of chlorination, one congener from each such subgroup was selected for this study. Since data exist showing usage of huge annual quantities of several types of polymeric packaging materials, the ones selected were done on the basis of their variabilities in terms of structural, physical and chemical properties. A variety of liquid foods, ranging widely in polarity are daily consumed, thus the water and edible oil selected as the PCB solvents, represent the daily potential real life situation that we are likely to encounter in the types of food we eat. Yes we should consume contaminant free food, but in reality this is not always the case. Should we do any thing about it? Yes, we should do

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whatever we can in order to minimize the risk to the ingestion of toxic contaminants.

One obvious application of this study is its use in water purification. Since the PCBs possess a higher partition coefficient for plastic than for water as a solvent, engineering applications of selected plastics for use as adsorbent and absorbent materials in water treatment plants can be investigated for possible use as a purification tool. This technology can be used in public water treatment plants, in commercial bottled water processing facilities, and in other situations where water in its purest form is desirable.

Another application of the techniques used in this study is in the reduction of contaminants in foods. Since the nature of the penetrant is an essential factor for the success of good diffusion, solubility, and permeation rates, one would obviously select a product that lends itself to intimate contact with the polymer. Thus liquids, vapors and gases would be products of choice for this technology. The chemical composition of these contacting products would of course be an important factor influencing their uptake by the sorbent material. For example, non-polar compounds would be more easily removed than polar ones if the polymeric material is a non-polar material such as polyethylene. With these facts in mind, many solid products can be modified in order to increase their contact with that of the polymeric packaging material. Packaging techniques such as vacuum packaging can be used to accomplish this goal, especially if the product is solid of

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semi-solid in nature. Other techniques such as gas flushing can also be used. In this case, a gas or vapor could be selected which has a high solubility for the contaminant of interest. Thus, if the packaged product is a powder for example, this gas could be used to dissolve the contaminant, then be absorbed by the polymer, thus reducing the concentration of the contaminant in the food under study. For liquid foods, the design of the packaging can be considered with a view to increasing the product/package contact. Applications such as the use of ribs, increase product compartmentalization, the use of smaller packages and selective decorative designs can be considered to achieve the desired end point.

The use of this technology can also be adapted for use as a cleanup tool in various analytical laboratory procedures. To increase the sorptive capacity of selected polymers, the use of highly adsorbent fillers, copolymers, laminates or polyblends can be considered. This technique can be modified in the laboratory for use as a concentration step in a given analysis. If for example the concentration of a compound of interest is too low for accurate analysis, exposure of the solution to an absorbent polymer followed by extraction of the compound from the polymer, can be a solution to such analytical problems.

Additional studies are needed for the investigation of other variables that were not considered during this study. Some of these can include factors such as:

1. Exposure of the samples to several temperatures both above and below room temperature.
2. The use of agitation to increase the arrival of the penetrant species at the sorbent contact surface.
3. A selection of several other liquid contact media with varying polarities, surface tensions and with PCBs of varying concentrations and congener types.
4. The use of solid, semi solid, vapor or gas solvents for contact with the polymer.
5. The use of polymers different from those used in this study.
6. The use of copolymers, polyblends and laminates as sorbent materials.
7. Exposure of the same polymers to other types of contaminants.

APPENDIX

APPENDIX 1.

- 1a. Analysis of variance for aqueous solution of tri-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable TRI
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.6084	.3042	53.5236	.0000
WITHIN GROUPS	33	.1875	.0057		
TOTAL	35	.7959			

- 1b. Analysis of variance for aqueous solution of tetra-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable TETRA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.2410	.1205	111.6893	.0000
WITHIN GROUPS	33	.0356	.0011		
TOTAL	35	.2766			

- 1c. Analysis of variance for aqueous solution of penta-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable PENTA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.2136	.1068	135.8970	.0000
WITHIN GROUPS	33	.0259	.0008		
TOTAL	35	.2395			

- 1d. Analysis of variance for aqueous solution of hexa-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable HEXA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.1134	.0567	17.4070	.0000
WITHIN GROUPS	33	.1075	.0033		
TOTAL	35	.2208			

- 1e. Analysis of variance for aqueous solution of hepta-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable HEPTA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.0832	.0416	11.7232	.0001
WITHIN GROUPS	33	.1171	.0035		
TOTAL	35	.2002			

- 1f. Analysis of variance for aqueous solution of octa-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable OCTA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.0441	.0221	12.2571	.0001
WITHIN GROUPS	33	.0594	.0018		
TOTAL	35	.1036			

- 1g. Analysis of variance for aqueous solution of nona-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable NONA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	1	.0226	.0226	32.9020	.0000
WITHIN GROUPS	22	.0151	.0007		
TOTAL	23	.0377			

- 1h. Analysis of variance for aqueous solution of deca-chloro PCB exposed to 1 ply polyethylene, PVC and polystyrene at 25°C.

Variable DECA
By Variable PLASTIC

ANALYSIS OF VARIANCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	1	.0170	.0170	30.2418	.0000
WITHIN GROUPS	22	.0124	.0006		
TOTAL	23	.0294			

- 1i. Analysis of variance for aqueous solution of tri-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by TRI
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.053	2	.027	30.237	.000
TEMP	.041	1	.041	45.953	.000
THICK	.000	1	.000	.008	.929
Explained	.053	2	.027	30.237	.000
Residual	.029	33	.001		
Total	.083	35	.002		

- 1j. Analysis of variance for aqueous solution of tetra-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by TETRA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.003	2	.002	11.734	.000
TEMP	.003	1	.003	18.370	.000
THICK	.000	1	.000	.035	.852
Explained	.003	2	.002	11.734	.000
Residual	.005	33	.000		
Total	.008	35	.000		

- 1k. Analysis of variance for aqueous solution of penta-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by PENTA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.004	2	.002	12.582	.000
TEMP	.001	1	.001	5.944	.020
THICK	.004	1	.004	25.158	.000
Explained	.004	2	.002	12.582	.000
Residual	.006	33	.000		
Total	.010	35	.000		

11. Analysis of variance for aqueous solution of hexa-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by HEXA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.025	2	.012	11.835	.000
TEMP	.004	1	.004	4.137	.050
THICK	.025	1	.025	23.469	.000
Explained	.025	2	.012	11.835	.000
Residual	.034	33	.001		
Total	.059	35	.002		

- 1m. Analysis of variance for aqueous solution of hepta-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by HEPTA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.012	2	.006	8.002	.001
TEMP	.000	1	.000	.190	.666
THICK	.010	1	.010	13.410	.001
Explained	.012	2	.006	8.002	.001
Residual	.025	33	.001		
Total	.037	35	.001		

- 1n. Analysis of variance for aqueous solution of octa-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by OCTA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.008	2	.004	6.309	.005
TEMP	.002	1	.002	2.941	.096
THICK	.002	1	.002	3.372	.075
Explained	.008	2	.004	6.309	.005
Residual	.020	33	.001		
Total	.028	35	.001		

10. Analysis of variance for aqueous solution of nona-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by NONA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.113	2	.056	49.403	.000
TEMP	.112	1	.112	97.909	.000
THICK	.038	1	.038	33.272	.000
Explained	.113	2	.056	49.403	.000
Residual	.038	33	.001		
Total	.150	35	.004		

- 1p. Analysis of variance for aqueous solution of deca-chloro PCB exposed to 1 and 5 ply polystyrene at 25°C. and 1 ply at 35°C.

*** ANALYSIS OF VARIANCE ***

by DECA
TEMP
THICK

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	.182	2	.091	28.861	.000
TEMP	.181	1	.181	57.107	.000
THICK	.030	1	.030	9.607	.004
Explained	.182	2	.091	28.861	.000
Residual	.104	33	.003		
Total	.287	35	.008		

1q. Analysis of variance for peanut oil and aqueous solutions of tri-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable TRI
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	70	2.5753	.0974	.2466	27
2.00	WATER	4	.0808	.0751	.2648	48
Within Groups Total		73	.9788	.0837	.5113	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	107.5228	1	107.5228	15351.0827	.0000
Within Groups	.5113	73	.0070		
Eta = .9976		Eta Squared = .9953			

1r. Analysis of variance for peanut oil and aqueous solutions of tetra-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable TETRA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	45	1.6798	.0707	.1300	27
2.00	WATER	3	.0688	.0651	.1990	48
Within Groups Total		49	.6487	.0671	.3289	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	44.8453	1	44.8453	9952.4116	.0000
Within Groups	.3289	73	.0045		
Eta = .9964		Eta Squared = .9927			

1s. Analysis of variance for peanut oil and aqueous solutions of penta-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable PENTA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	46	1.7158	.0752	.1469	27
2.00	WATER	3	.0625	.0611	.1752	48
Within Groups Total		49	.6577	.0664	.3221	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	47.2352	1	47.2352	10704.7163	.0000
Within Groups	.3221	73	.0044		
Eta = .9966 Eta Squared = .9932					

1t. Analysis of variance for peanut oil and aqueous solutions of hexa-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable HEXA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	49	1.8192	.1232	.3949	27
2.00	WATER	4	.0814	.0743	.2596	48
Within Groups Total		53	.7070	.0947	.6545	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	52.1817	1	52.1817	5820.4383	.0000
Within Groups	.6545	73	.0090		
Eta = .9938 Eta Squared = .9876					

1u. Analysis of variance for peanut oil and aqueous solutions of hepta-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable HEPTA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	28	1.0500	.0712	.1317	27
2.00	WATER	5	.0955	.0508	.1212	48
Within Groups Total		33	.4392	.0589	.2529	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	15.7440	1	15.7440	4544.8321	.0000
Within Groups	.2529	73	.0035		
Eta = .9921 Eta Squared = .9842					

1v. Analysis of variance for peanut oil and aqueous solutions of octa-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable OCTA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	21	.7901	.0517	.0696	27
2.00	WATER	6	.1209	.0413	.0803	48
Within Groups Total		27	.3618	.0453	.1499	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	7.7395	1	7.7395	3768.5408	.0000
Within Groups	.1499	73	.0021		
Eta = .9905 Eta Squared = .9810					

1w. Analysis of variance for peanut oil and aqueous solutions of nona-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable NONA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	13	.4777	.0387	.0390	27
2.00	WATER	10	.2022	.0589	.1632	48
Within Groups Total		23	.3014	.0526	.2022	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	1.3119	1	1.3119	473.6661	.0000
Within Groups	.2022	73	.0028		
Eta = .9308		Eta Squared = .8665			

1x. Analysis of variance for peanut oil and aqueous solutions of deca-chloro PCB exposed to 1 ply polyethylene at 25°C.

- - Analysis of Variance - -

Dependent Variable DECA
By levels of LIQUID

Value	Label	Sum	Mean	Std Dev	Sum of Sq	Cases
1.00	PEANUT OIL	12	.4299	.0313	.0254	27
2.00	WATER	9	.1907	.0489	.1122	48
Within Groups Total		21	.2768	.0434	.1376	75

Source	Sum of Squares	d.f.	Mean Square	F	Sig.
Between Groups	.9885	1	.9885	524.4161	.0000
Within Groups	.1376	73	.0019		
Eta = .9369		Eta Squared = .8778			

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