THE PREDICTED ENVIRONMENTAL DISTRIBUTION OF SELECTED FLAME RETARDANT CHEMICALS

by

Semra BAYSAN

B.Sc. in Biology, Istanbul University, 1980

Submitted to the Institute for Graduate Studies in Science and Engineering in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Sciences

Boğaziçi University

To

Prof. Dr. Yüksel İNEL

ACKNOWLEDGEMENTS

I take this opportunity to express my sincere gratitude to Prof. Dr. Yüksel İnel for his helpful supervision and guidance during this study. I am especially thankful for his continued support and encouragement.

I would also like to express my sincere appreciation to Dr. Melek Türker Saçan for her help, continued support and empathy during some of the most difficult moments. Without Prof. Dr. İnel's and Dr. Saçan's encouragements, this would not have been possible.

I would like to extend my thanks to the members of the Thesis Committe: Doç. Dr. Orhan Yenigün and Doç. Dr. Dilek Çalgan for their helpful comments and valuable suggestions.

I wish to express my deepest thanks to my mother, my brother and his family for their constant encouragement and patient endurance.

I also take this opportunity to express my gratitude to Price Waterhouse for their permission to use the hardwares, to Thomas F. Marcellino for his encouraging and understanding attitude throughout this work, to Timuçin Özgeç and Leonard Vandivere for their valuable assistance in drawing the charts, and to Erol Karsan for his interest and encouragement in the completion of this study.

Finally, I wish to thank to Arlette İtken for proof reading, and to "Çağdaş Daktilo" for typing the manuscript.

ABSTRACT

The aim of this study is to calculate environmental equilibrium distributions for selected Flame Retardant Chemicals and thus to indicate where each of them goes and what relative concentrations they adopt in the enviromental compartments.

In this study, Mackay's Level I Fugacity Model, based on fugacity that characterizes the escaping tendency from a phase, is used for calculations. The fugacity calculations are applied to an evaluate environment - a "unit world" consisting of compartments of homogeneous air, soil, water, biota, suspended solids and sediment. Each compartment is assigned a reasonable volume and properties and the equilibrium distributions of those chemicals are calculated using fugacity capacities, that are calculated from physical and chemical data partition coefficients.

When the results are designed to yield priorities for each compartment, it is found that Halognated Flame Retardant Chemicals for the air compartment, Phosphorus Flame Retardant Chemicals in the Sediment and Soil compartments are priorities.

ÖZET

Bu çalışmanın amacı seçilmiş yanmayı geciktirici kimyasalların çevredeki dağılımının hesaplanması ve böylece bu kimyasalların çevrede nereye gideceklerinin çevrenin çeşitli kompartmanlarında hangi bağıl konsantrasyonlara ulaşacaklarının belirlenmesidir.

Bu çalışmada Mackay tarafından geliştirilen maddenin bir fazdan diğer faza kaçınım yatkınlığı ilkesine dayalı fugasite modelinin birinci aşaması kullanılarak, fizikokimsayal özellikler ve dağılım katsayılarından hesaplanan fugasite kapasiteleri yardımı ile ve fugasite hesaplamaları herbiri belli hacim ve özelliklere sahip homogen hava, su, toprak, biota, asılı madde ve sediment kompartmanlarından oluşan bir teorik birim çevreye uygulanarak, seçilmiş yanmayı geciktirici kimyasalların her bir departmandaki bağıl miktarları ve bağıl konsantrasyonları hesaplandı. Elde edilen sonuçlara göre halogeneted yanmayı geciktirici kimyasalların hava kompartmanı için, fosforlu yanmayı geciktirici kimyasalların ise toprak ve sediment kompartmanları için önem verilmesi gereken kimyasal maddeler oldukları belirlendi.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

APPENDIX I.

LIST OF SYMBOLS

B	Mass fraction of biota times total Biota or Lipid part.
C	Concentration of the dissolved gas
C_i	Concentration
C_A	Concentration in air
C_w	Concentraiton in water
F_i	Fugacity
F_a	Fugacity in air/f_b fugacity in biota/f_s fugacity in soild f_{sd} fugacity in sediment, /f_{ss} fugacity in suspended solids/f_w fugacity in water
H_{vb}	Heat of vaporization in Cal/mol
H	Henry's Law Constant
K_b	Bioconcentariton factor
K_d	Soil adsorption
K_f	Constant, derived from a condiretation of the dipole moments of polar and nonpolar molecules
K_{oc}	Soil sorpiton coefficient
K_{ow}	Octanol - Water partition coefficient
K_{ps}	Soil - Water partition coefficient
K_{pss}	Suspended Solids - Water partition coefficient
M_i	Amount of moles in each compartment
MT	Total amount of moles
O_1	Minimum concentration of oxygen in an oxygen-nitrogen atmosphere that is necessary to initiate and support a flame.
P	Partial pressure of the gas
R	Univerasl Gas constant in cal/mol.K (1.987 cal/mol.K)
S	Aqueous solubility
T	Absolute temperature

T_b	Normal boiling point
T1	Reference temperature
Z_i	Fugacity capacity in each phase
Z_a	Fugacity capacity of a chemical in air
Z_b	Fugacity capacity of a chemical in biota
Z_b	Figacity capacity of a chemical in soil
Z_{sd}	Fugacity capacity of a chemical in sediment
Z_{ss}	Fugacity capacity of a chemical suspended solids
Z_w	Fugacity capacity of a chemical in water Density
ρ_b	Density of biota
ρ_s	Density of soil
ρ_w	Density water
ρ_{ss}	Density of suspended solids
ρ_{sd}	Density of sediment

I. INTRODUCTION

Modern technology has brought a dramatic increase in the production and consumption of chemicals. In a few cases the benefits of chemicals have been accompanied by unexpected adverse effects. Incidents such as the mercury contamination of fresh water, the widespread distribution of the industrial group of chemicals known as PCBs, and the alleged destruction of the ozone layer in the stratosphere due to the release of aerosol propellants (chloro-fluoro-methanes) have made the public increasingly aware of the ability of some chemicals to cause unexpected results at some point far removed from where they were introduced [1].

This awareness has generated two important questions which have and will continue to motivate research in environmental science. These questions are:

1- What is the expected environmental concentration-time profile for a chemical at specific locations in various media during the manufacture, use, and dissipation of the product?

2- What are the hazards to man and his environment resulting from these environment concentrations?

It should be obvious that the second question can be asked only after the first question is answered.

In order to estimate the environmental exposure of a chemical it is necessary to understand how materials are transported and transformed as they move from their point of entry to their final resting place.

There are four major components to every ecosystem being perturbed by an outside influence. The perturbations are as follows:

INPUT: The system must have a source of perturbation. This could vary from a dosage schedule for a pesticide applied to a field or to the waste load in the effluent being discharged to a receiving body of water. In every case, before an estimate of concentration can be made, there must be some knowledge as to how much chemical has been added to the system under investigation.

KINETIC PROCESSES: The ultimate fate of the added chemical is represented by kinetic reactions specific for the chemical. Biodegradation and hydrolysis are examples of such processes.

TRANSPORT PROCESSES: Within the ecosystem there are several natural processes by which the chemical moves across the various interfaces.

OUTPUT: In order to complete the mass balance there must be suitable sinks by which the chemical leaves the ecosystem such as burial in the bottom sediments of a pond.

Once the data have been collected it becomes necessary to integrate the individual pieces into a holistic picture. Mathematical models have the unique ability to handle this integration operation. One of the first questions to be addressed is how will the chemical partition among the major environmental compartments? The answer can be given by model building.

By using basic physical and chemical properties of a chemical such as water solubility, vapor pressure, n-octanol-water partition coefficient and molecular weight, the partitioning of that chemical between the major environmental compartments can be quickly assessed.

Further, the percentage of the chemicals which will be located in the air, soil, water, biota, suspended solid and sediment compartments can be estimated. The results are not meant to be absolute but are designed to show the rank of importance. If further tests are needed, they can be designed in a logical and sequential manner.

It is hoped that such assessments will bring prior warning of potential impacts of toxic substances. By being aware of the potential environmental problems before they occur, greater precautionary measures can be taken in both manufacture and distribution of the chemical, and such action will minimise the effect on the various ecosystems.

In this thesis the potential concentrations and equilibrium distributions in and between the compartments of an evaluated environment are calculated for selected flame retardants, using Mackay's Level I fugacity model. They are ordered with respect to their potentials to contaminate each compartment.

As a result, the equilibrium partitioning and concentrations of selected flame retardants in various compartments of the environment are calculated.

II. FLAME RETARDANT CHEMICALS

Most of the materials in our immediate surroundings are combustible clothes, furnishings, many of the construction materials in dwelling and work places, the interiors of cars, buses, airplanes, etc. Wood, paper, textiles, and synthetic polymers all burn under the right conditions; many burn vigorously and ignite readily. Humans have always been plagued by unwanted fire. So it is not surprising that they have sought ways to reduce the combustibility of their surroundings.

Hazards associated with the ready combustibility of cellulosic materials were recognized as early as the 4th century BC, when Neneas is said to have recommended treatment of wood with vinegar to impart fire resistance.

The technique of imparting flame resistance to textile fabrics is relatively new. Among the earliest references is an article by Sabattini published in 1638. Recognizing a need to prevent fire, he suggested that clay or gypsum pigments be added to the paint used for theater scenery to impart some flame resistance.

By the 19th century, enough was understood to enable Gay-Lussac to make a systematic study of available flame retardant chemicals. He found that ammonium salts of sulfuric, phosphoric, and hydrochloric acids were effective as well as certain mixtures of these with borax [2].

The first successful, launder resistant, flame retardant finish for fabric was based on the work of Perkin, who precipitated stannic oxide within the fiber. This fabric was flame resistant but afterglow was severe and persistent enough to completely consume the fabric.

In 1930s the effect of mixing antimony oxide with organic halogen compounds was discovered. These three efforts represent the major discoveries on which modern flame-retardant chemicals are based. The technology has become far more sophisticated in recent years.

2.1 TERMINOLOGY

The application of such terms as fireproof, flameproof, self-extinguishing, non-burning, noncombustible, etc, has often led to ambiguity about the relative flammabilities of different materials.

The term fire retardant (flame retardant) is used to describe polymers whose basic flammability has been reduced by some modification as measured by one of the accepted test methods.

A fire retardant chemical denotes a compound or mixture of compounds that when added to, or incorporated chemically into a polymer serve to slow up or hinder the ignition or growth of fire.

A textile that is flame resistant or fire resistant does not continue to burn or glow once the source of ignition has been removed, although there is some change in its physical and chemical characteristics. Fireproof or flameproof, on the other hand, refer to material that is totally resistant to fire or flame. No appreciable change in the physical or chemical properties is noted. Asbestos is an example of a fireproof material.

Terms such as self-extinguishing, non burning, and noncombustible are no longer used by the fire research community because they have been found to be misleading.

2.2 THE NEED FOR FLAME RETARDANCY

Hydrocarbon polymers such as ethylene-propylene copolymer and polyethylene belong to a class of the most flammable polymers [3]. Because of their excellent electrical and mechanical properties, they are used largely as insulators for wires and cables and are often required to be given flame retardancy. The increased emphasis on the safety of nuclear power plants, where wires and cables are used in an ionizing radiation environment, produces the novel need for additional stable flame retardants.

Poly (ethylene terephthalate) (PET) and polyester fibers [4], because of their outstanding characteristics of high strength, resistance to shrinkage and stretch, good dyeability and chemical resistance, are used extensively in carpets, furnishings, and apparel. The flammability characteristics of polyester textiles are usually described as average. When a flame is applied to a polyester fabric, it usually melts and shrinks away from the impinging flame; hence, unless the flame is allowed to follow the shrinking fabric, or the fabric is fed into the flame, the material will not usually ignite and continue burning.

However, if the fabric is prevented from moving away from the ignition flame, the polyester may be ignited and burnt. Such is the case when, for example, fibers are used in conjuction with cotton in polyester/cotton blends. In this situation, the carbonised cellulose formed when the cotton portion burns provides a supporting framework which allows the molten polyester to burn in much the same way as a candle burns on a wick. In order to reduce this enchanced burning characteristic associated with these polyester/cotton blends, a substantial amount of research effort has been directed towards identifying economical, effective and practical flame-retardant chemicals.

2.3 ACHIEVING FIRE RESISTANCE

The materials to be made resistant to fire are invariably polymers-natural and synthetic. Some are inherently more difficult to ignite and burn than others. Graphite is very difficult to burn, whereas nitrocellulose burns explosively. One way to reduce fire hazard is to use polymers especially tailored to resist burning. By making a polymer rich in ring structures and low in readily oxidisable side groups, low flammability may be achieved. An example is an aromatic polyimide that contains no hydrogen atoms.

The atomic polyimides have excellent fire resistance, but they are expensive and therefore are limited to specialty uses such as aerospace applications. The more common approach to obtain fire resistance is to add one or more of the commonly used fire retardant elements to a flammable polymer system. This may be done either with an inert additive (eg. surface treatment of fibers and films or unreactive admixtures to molding or extrusion mixes) or by copolymerising a moderate amount of a monomer containing the requisite element. Occasionally, a polymer can be treated reactively after polymerisation as in chlorinating polyethylene. There are many ways to incorporate the elements antimony, boron, chlorine, bromine, phosphorus and mixtures of these into polymer systems, sometimes with other metals or with certain nitrogen compounds. Often the most difficult task is to achieve the desired safety level and to retain the functional properties of the parent polymer, properties for which the system is sold. Achieving good fire resistance often requires 10-20 wt % of the fire retardant element in the compound containing that element.

2.4 REQUIREMENTS FOR FIRE RESISTANCE

Nearly all markets for fire-retardant chemicals are created by fire regulations. The markets are as varied as the regulations. Textile products are covered by federal standards for apparel, carpets, and mattresses, as well as by local building codes for textile coverings used in places of public assembly. The building codes control the flammability of wall or ceiling coverings for the public parts of most buildings; in some areas of the United States the codes are extended to furnishings, eg, the seat coverings in airport waiting rooms.

Traditionally in the United States fire test methods have been written by consensus standard groups in the private sector. After a particular hazard has been identified, a committee, usually in the National Fire Protection Association, (NFPA), prepares and publishes a method of testing. For building products the next step is incorporation of the method in a model building code. The method becomes law when the model code is adapted by municipalities. In recent years the federal government has played an increasing role in establishing standards. The Department of Housing and Urban Development (HUD) has authority to set minimum performance standards for its insured housing. In 1974, it was given authority over all mobile homes manufactured or sold in the United States. The U.S. now has fire standards on materials and products for housing, automobile interiors, buses, trains, aircraft interiors, mines, etc.

A survey by Kirk and Othmer provides estimates of the market for chemicals used as fire retardants in plastics and related products. About two thirds of these chemicals are used in plastics [2].

Chemical Types	**Estimated Volume** 1976	**Estimated Volume Thousands of Metric Tons** 1986
Phosphate esters	23	32
Halogenated phosphate esters	10	20
Chlorinated hydrocarbons	20	32
Brominated hydrocarbons	13	20
Antimony trioxide	14	22
Borates	4	7
Polyols containing phosphorus	5	12
Brominated bisphenol A	5	7
Others	5	7

2.5 EFFECTS OF FIRE-RETARDANTS

The amount of char (a carbonaceous residue) formed upon the thermal degradation of a polymer is a measure of its flame resistance. A high char-forming polymer usually produces fewer combustible products with the simultaneous protection of the remaining material by the heat-shielding effect of the resulting surface residue.

High char yields appear to be connected with possible cross-linking and ring-forming reactions that occur during thermal degradation processes [5].

2.6 FIRE TESTING

Flammability of the polyamides can be measured by the oxygen index (OI) method.

OI is defined as the minimum concentration of oxygen in an oxygen-nitrogen atmosphere that is necessary to initiate and support a flame.

$$OI = \frac{\text{volume of } O_2}{\text{volume of } O_2 + \text{Volume of } N_2} \times 100 \qquad [5]$$

There is no doubt that flame-retardant additives affect the response of many materials to fire. However materials rich in carbon will burn, despite the presence of additives, if the exposures to heat and oxidizer are severe enough. The product developer and users should realize that the flammability of the material is decreased but not eliminated. Still fire-retardant materials will continue to play an important role in fire-safety engineering.

2.7 INORGANIC FLAME RETARDANTS

2.7.1 ANTIMONY COMPOUNDS

2.7.1.1 ANTIMONY TRIOXIDE

Among the antimony compounds, the most favored one is Sb_2O_3. It has been used along with some halogen-containing compounds, such as chlorinated hydrocarbons, octaphenylene dioxide, dimers of hexachlorocyclopentadiene, hexa-and tetrachlorophthalimides, tetrabromobisphenol A-bis (dibromopropyl ether) and decabromodiphenyl ether [6].

Antimony trioxide is manufactured by oxidizing molten antimony sulfide and/or antimony metal in air at 600-800 C. Antimony trioxide can be used as a flame retardant in cellulosic materials. The addition of antimony trioxide to vinyl formulations significantly increases the flame resistance. In these substrates, it reacts endothermically with the hydroxyl groups and forms a variety of products. The endothermic reaction absorbs heat needed to propagate the flame. The products formed are difficult to ignite and shield the underlying cellulose from the flame, minimising pyrolytic and oxidative degradation.

2.7.1.2 ANTIMONY PENTOXIDE

Antimony pentoxide is manufactured by the oxidation of antimony trioxide with nitrates or peroxides. When the pentoxide is heated above 380°C, it disproportionates into antimony tetroxide with the evolution of oxygen. Commercially, antimony pentoxide is primarily available as a stable colloid or as a redispersible powder. It is significantly more expensive than antimony trioxide and is designed primarily for highly specialised applications.

2.7.1.3 SODIUM ANTIMONATE

Sodium antimonate is a free-flowing white powder made by the oxidation of antimony trioxide in a basic medium.

2.7.1.4 MIXED METAL ANTIMONY COMPOUNDS

Recent development in inorganic flame-retardant synergists has centered on mixed products that contain antimony and other metals which reportedly give excellent performance at reduced cost.

2.7.1.5 ANTIMONY-HALOGEN MECHANISMS

Antimony trioxide is used almost exclusively with heat-labile halogen compounds. Most of the mechanisms proposed indicate that antimony trioxide is activated by reaction with halogens, forming antimony trihalides or antimony oxyhalides.

This can be shown simply by the following reactions.

$Sb_2O_3 + 6HCl \dashrightarrow 2SbCl_3 + 3H_2O$

$Sb_2O_3 + 2HCl \dashrightarrow 2SbOCl + H_2O$

Antimony trichloride and antimony oxychloride work primarily as flame phase flame retarders. The type of antimony halide formed depends on the concentration of the hydrogen halide and the temperature of the reaction.

Antimony trihalides are the flame retarding species whether they are generated directly from the starting antimony-halogen mixture or from antimony oxyhalide. They inhibit combustion by altering the manner and type of decomposition products formed by the plastic and by modifying the reactions in the flame to make them less exothermic. In the condensed phase or molten polymer just beneath the flame, antimony trihalide promotes reactions that form carbonaceous chars instead of highly volatile reactive gases. The chars act as heat shields, which deflect the heat of the flame, and slow down the thermal and oxidative decomposition of the polymer. The chars also form a seal around the polymer preventing potentially flammable gas from escaping and entering the flame.

The effect of halogenated organoantimony compound based flame retardants upon the melting behavior and on the flammability and thermal behavior of polypropylene has been discussed by Bajaj et al [7].

2.7.2 BORON COMPOUNDS

Borates are used as flame retarders for poly(vinyl chloride), cellulosics and unsaturated halogenated polyesters. Zinc borates are the most widely used compounds of this class.

2.7.2.1 BORIC ACID-SODIUM BORATE

Boric acid and sodium borate are two of the oldest known flame retardants. They are used primarily to flame-retard cellulosics such as cotton and paper. Both products are inexpensive and fairly effective in these applications. Their use is limited to products for which nondurable flame retardancy is acceptable, since both are very water soluble.

Boron compounds function as flame retardants in both the flame and condensed phases. Flame-phase-active boron compounds are generated from a combination of borates and halogenated organic compounds.

Boric acid and borax are effective especially in cellulosic fibers. When these compounds are exposed to a flame, they melt and form a glasslike coating around the fibers. Prolonged exposure causes the coating to dehydrate, generating water which cools the flame and causes it to extinguish. The boron residue also reacts with the hydroxyl groups of the cellulose to generate additional quantities of water and form an inorganic char that is difficult to ignite and burn. The char is an insulator that slows down the rate of polymer degradation and fuel formation.

2.7.2.2 AMMONIUM FLUOROBORATE

Ammonium fluoroborate NH_4BF_4 is another boron-containing compound that has some utility as a flame retardant. Flame retardant plastic formulations recently published suggest that ammonium fluoroborate should be used primarily in combination with antimony trioxide.

2.7.3 ALUMINA HYDRATES

Alumina trihydrate (ALTH) can be used to flame-retard unsaturated polyesters and foam carpet backings. Alumina trihydrate is the only aluminum compound of commercial significance used as a flame retardant. It functions as a flame retardant in both the condensed and flame phases. When alumina trihydrate is exposed to temperatures above 250 °C, it forms water and alumina.

$$Al_2(OH)_6 \text{ -----> } Al_2O_3 + 3H_2O$$

The evolution of water absorbs heat, then cools the flame and dilutes the flammable gases and oxidants in the flame. The alumina residue, an excellent heat conductor, increases the removal of heat from the flame zone.

The major application areas for ALTH are filled thermoses polyesters and styrene-butadiene rubber latex rug backing.

Alumina trihydrate is also used as a secondary synergist to improve the flame retardance of polymer systems that already contain antimony trioxide, zinc borate or some phosphorus flame retardants.

2.7.4 MOLYBDENUM OXIDES

Molybdenum compounds have been used as flame retardants of cellulosics for many years. Recently, they have found some use in other polymers. Molybdenum trioxide (MoO_3) acts to change the normal thermal degradation pattern of PVC and promotes the formation of a thermally stable char which acts as a physical barrier to oxidation and combustion. The change in the thermal degradation pattern of PVC, which is promoted by MoO_3, inhibits the formation of volatile aromatic hydrocarbons. In the absence of a condensed phase smoke retarder, such as MoO_3, the formation of benzene and other volatile aromatic hydrocarbons quickly follow the onset of dehydrochlorination. It is generally accepted that the combustion of these aromatic hydrocarbons gives rise to much of the smoke which is released during the flaming combustion of PVC.

In the presence of MoO_3 the generation of volatile aromatic hydrocarbons is greatly reduced. In the same way, the MoO_3 acts to greatly diminish the quantity of smoke generated when PVC is forced to undergo flaming combustion [8].

The most expeditious flame retardant for polyolefins is a combination of antimony trioxide and a halogen-containing additive. The amount of antimony oxide necessary depends upon the polymer (polypropylene or polyethylene, etc.) and the type of halogen (chlorine vs. bromine, aromatic vs. alphatic).

2.8 HALOGENATED FLAME RETARDANTS

Halogenated or phosphorus-containing compounds are widely used as fire retardants for synthetic polymers. Although these new polymers are not necessarily more flammable than natural polymers, they are more readily used in forms, (eg, foams, electrical applications, etc.) that can result in an increased fire control problem.

In general, the halogenated compounds influence the flammability by producing hydrogen halides which act as radical traps at high temperatures or by depressing the flammable gas mixture available for burning. Phosphorus-containing compounds are in a position to reduce the flammability, because they can promote char formation and inhibit the glowing reaction.

The fire retardants used in industry are almost all bromine-containing organic compounds, such as tetrabromobisphenol A, decabromodiphenyl ether, and octabromoctiphenyl ether [9], because these bromine-containing compounds have better compatibility with polymer. Most of the phosphorus containing compounds are incompatible with the polymeric system and have high manufacturing cost.

Along with the development of many synthetic polymer systems during the 1930s and 1940s, a significant advance in the science of imparting flame resistance occurred. For example halogenated organic materials were used to impart ignition resistance to these new polymer systems.

In early plastics applications, the small size and relative scarcity of fabricated articles made fire retardancy a secondary consideration. Advances in plastics technology have led to increasingly large-scale applications, especially in the construction industry. Since many polymers have fuel values (heat of combustion) comparable to common fuels, eg, wood, oil, alcohol, etc, it is readily understandable that they contribute to the burning process in a typical fire.

2.8.1 PRINCIPLES OF DEVELOPING FLAME-RETARDANT POLYMERS

Any discussion on the principles of developing flameretardant polymer systems must acknowledge the chaotic situation that exists at present. This situation has arisen for a variety of reasons: technical, economic, legal, and semantic.

The semantic problem is the worst in that it is at the root of most of the other problems and is caused by the fact that the term fire or flame retardant may be perceived in a variety of ways depending upon the user's viewpoint. The term, as defined above, means simply that some change has been made in a polymer system so that it will pass one or more of at least a hundred different flammability tests. These tests are normally designed to minimise, but not eliminate, the fire risk associated with the use of a polymer in some specific use or product. As a consequence, a modification of a polymer that makes it suitable for one used does not necessarily make it suitable for others. There is no single fire-retardant chemical or method that is applicable to all polymer systems or even to all uses of a single polymer.

It is, therefore, necessary that early in the development of a flame-retardant polymer system the question

"Why?" is answered before much effort is put into answering the question "How?"

Chlorine and bromine compounds are the only halogenated compounds commercially significant as flame retardant chemicals. Fluorine compounds are expensive, and except in special cases, ineffective. Iodine compounds, although effective, are expensive and too unstable to be used.

The number of chlorinated compounds used as flame retardants has decreased in recent years, and most of the newest agents are based on bromine. This shift has occurred at least partially, as a result of the increasingly severe flammability standards imposed on plastic products.

These standards normally require levels of chlorine that are difficult to obtain without destroying the desirable properties of a polymer. In addition the decreased use of lead in gasoline has freed large quantities of bromine that were previously used in the production of ethylene dibromide. The anticipated large excess in bromine capacity prompted new uses for bromine, among them a number of flame-retardant chemicals has been developed.

The bromine concentration in the fuel tends to peak at certain temperatures. When this effect is combined with variations in composition of the pyrolytic fuel, a situation can arise where a high bromine concentration coincides with a fuel particularly sensitive to flame quenching by bromine. Such a combined effect may be the reason why some brominated flame retardants are far more effective than others [10].

The use of brominated aromatics as flame retardants is a new potential source of environmental contamination. Many of these compounds have close structural relationship to PCBs and other known persistent organic pollutants or pesticides. In a review article by Hutzinger [11] on flame retardants published in 1976, it can be seen that from a knowledge of the manufacture and use of textiles and polymers one may conclude that leaching of flame retardants from technical processes or simple laundering [12] are possible sources of contamination. Pentabromotoluene was found in a sewage plant in Sweden as a result of leaching from a technical process [13]. PBT is used as a flame retardant in textiles, polyester resins and paint emulsions.

Some of these compounds are reported to be non-toxic. On the other hand mixtures of polybrominated biphenyls (PBBs) were synthesized commercially as fire-retardant chemicals and were sold under the trade name fireMaster. These products were of minor commercial importance but gained national attention after an accident that occurred in 1973 [14], in which the commercial PBB mixture fireMaster FF-1 was unintentionally substituted for nutriMaster, a magnesium oxide cattle feed supplement. The direct addition of fireMaster into feeds resulted in a major pollution disaster primarily confined to the state of Michigan (Robertson and Chynoweth, 1975; Kay, 1977). The initial high-level contamination of feed and livestock (11,000 cattle, 2,000 hogs, 393 sheep, 1,5 million chickens and 4.6 million eggs had been burried [15]) ultimately resulted in the widespread contamination of the food chain, and PBB residues were detected in wildlife, and in the general population of Michigan. PBBs are stored in the adipose tissue and have been identified in human blood, fat and breast milk.

The toxicity and persistance of PBBs dictate that the analytic or synthetic chemist use extreme care while handling these compounds. A number of reviews and comparative studies have indicated that polychlorinated and polybrominated biphenyls elicit toxic and biological responses that are similar to those produced by 2,3,7,8-tetrachlorodibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [16].

In order to get more information about the influence of structure on the high-pressure liquid chromatography (HPLC) retention behavior of polyhalogenated biphenyls, some selected compounds were synthesized by Höfler, et al. [17], The analysis of these compounds enabled scientists to make a good guess about the structures of unknown compounds.

Like other halogenated aromatics, commercial PBBs cause weight loss [18], thymic atrophy, liver damage, endocrine disorders, and various skin lesions in exposed animals. They are also potent inducers of a variety of drug-metabolizing enzymes. FireMaster can apparently act as both a genotoxic and epigenetic carcinogen. Administration of the commercial PBB to rats causes hepatocellular carcinomas and enhances the carcinogenicity of diethylnitrosamine, whereas topical application of the PBB mixture to hairless mice pretreated with specific carcinogens results in skin tumor promotion. Further, the effects of treatment with twelve different halogenated biphenyls on relative body weight, liver weight, thymus weight in mice were demonstrated by Robertson et al. [16].

In another study Kohli, et al, dealt with the metabolism of several isomeric PBBs and two additional bromoaromatics, 1,4dibromobenzene and 1,4-dibromonaphthalene by the preparation of an emulsion and further injection to a young female pig housed in a metabolic cage [19].

In recent years there has been considerable interest in graft polymerisation as a tool for achieving flame proofing of textiles with special attention given to radiation grafting. It was pointed out that the radiation grafting method had two useful characteristics: being a low energy consumpting process, and having a potential for good fixation of flame retardants.

It is well known that bromine-bearing compounds are effective agents in suppressing the combustion burning of a variety of polymers. Several comparative studies of the effectiveness of aromatic vs. aliphatic brominated compounds have been published [20]. It should be noted that the flame retardancy mechanism of the aromatic compounds is not yet fully understood.

Owing to environmental and toxicity problems as well as the tendency for additives to be fugitive, several excellent halogenated flame retardants have been abandoned during the development stage or have been removed from the market. Notable examples include polychlorobiphenyls, tris (2,3-dibromopropyl) phosphate and several derivatives of hexachlorocyclopentadiene.

Among the first of the halogenated organics to be developed as flame retardants were the resinous chlorinated paraffins which reached commercial importance during World War II as a treatment for cotton duck for the military. They are still by far the biggest sales item of the halogen compounds in the flame-retardant chemicals market.

The chlorination is controlled to yield mainly liquid products containing 20-70 wt % chlorine. Several solid resinous products containing 70wt % chlorine are also available. The products are available in a variety of formulations, ranging from neat oils and solids to water-based emulsions.

The polychlorinated paraffins are classified as nontoxic, both dermally and by ingestion, according to the Federal Hazardous Substances Labelling Act of 1961.

Even though they are known as nontoxic, different methods have been published by Laham et al. [21], to determine in human and animal blood, and also it has been understood that dichloromethane can produce an important reduction of blood pressure accompanied by a decrease in hemoglobin.

All polychlorinated paraffins are somewhat biodegradable and insoluble in water. According to Zitko et al [22], accumulation factors of Dechloranes are low to intermediate, the accumulation factor of mirex is relatively high.

2.9. PHOSPHORUS COMPOUNDS

Organophosphorus compounds have been widely studied as flame retardants for cellulose. The results from many of these studies (Lawler, et al [23], indicate that most phosphorusbased retardants act by phosphorylation of cellulose at the primary hydroxyls, thus blocking the formation of levoglucosan and reducing the production of flammable gasses by the pyrolyzing cellulose.

2.9.1. PHOSPHORUS-BASED FLAME RETARDANTS IN COMMERCIAL USE

Since the original report of ammonium phosphate as a flame retardant by Gay-Lussac in 1821 and the commercial introduction of tricresyl phosphate as a flame-retardant plasticiser for cellulose early in the present century, many thousands of phosphorus compounds have been described as having the flame-retardant utility.

2.9.2. INORGANIC PHOSPHORUS COMPOUNDS

2.9.2.1. RED PHOSPHORUS

This allotropic form of phosphorus is relatively nontoxic and, unlike white phosphorus, is not spontaneously flammable. In Europe it has found commercial use in molded nylon electrical parts. Handling hazards, such as flammability, odor, partial reversion to toxic white phosphorus, and the imparting of color, have deterred broader usage.

2.9.2.2. AMMONIUM PHOSPHATES

These salts were recommended for treating theater curtains in 1821. Their use in forest-fire control is well established. Monoammonium phosphate and diammonium phosphate, or mixtures of the two, which are water soluble and almost neutral, are still used in large amounts for nondurable flame-retarding of paper, textiles, disposable nonwoven cellulosic fabrics, and wood products. Their advantage is high efficiency and low cost. Ammonium phosphate finishes are not resistant to laundering or even to leaching by water, they are however resistant to organic solvents such as dry-cleaning solvents.

The crystalline nature of ammonium phosphates may produce a gritty texture on the surface of some substrates.

Ammonia/P_2O_5 products: Staufers Victamide is known to be a complex mixture. Victamide, as an aqueous solution, can be applied to paper, cotton cloth, cotton matting, and nonwowens. When dry, it produces a smoother surface texture than that produced by the crystalline ammonium phospates. When Victamide is applied to a cellulosic substrate and heated, it yields a semidurable flame-retardant finish that stands several aqueous washes.

2.9.3. ORGANIC PHOSPHORUS COMPOUNDS

Triethyl Phosphate is a colorless liquid boiling at 209-218 °C and containing 17 wt % phosphorus. It is manufactured from diethyl ether and phosphorus pentoxide. Triethyl phosphate has been used commercially as an additive for polyester laminates and in cellulosics.

Triaryl/alkyl phosphate esters are widely used as fire-resistant hydraulic fluids and plasticizers. Entry of phosphate esters into aquatic environments is thought to occur via leakage from machinery and subsequent loss to sewers as well as by leaching from plastics. The low water solubility and high specific gravity of most phosphate esters suggest that they will partition into bottom sediments following the entry into aquatic systems, (Muir et al [24]) Muir et al [25], also showed that, triphenyl phosphate (TPP) and 2-ethylhexyldiphenyl phosphate (EHDPP) esters have half-lives of about 15 hours in the water column and show rapid absorption to bottom sediment.

Phosphate additives are used commercially in polyurethane and polyisocyanurate foams, carpet backing, flame-laminated polyurethane foam, flame-retardant paints and lacquers, epoxy resins, phenolic resins, amino resins, poly(vinyl acetate) coatings and adhesives, urethane coatings, cast acrylic sheet, polyester resins, and wood-resin composites such as particle board.

According to the findings by Bellet, et al, [26], bicyclic phosphorus compounds should be handled with great care because of their high toxicity to mammals. Their toxicity is generally attributed to inhibition of acetylcholinesterase (ACHE) in the nervous system of Swiss Webster mice.

In 1972 the United States established flammability standards for children's sleepwear to reduce burn injuries. To comply with these standards, manufacturers began to use chemical additives (usually organic halogens or phosphate esters or both) to confer flame-resistant properties to the fabric [27].

About 50 million children were exposed to these chemicals before they were banned from use in childrens' clothing in April 1977. A child wearing sleepwear treated with Tris-BP absorbed a considerable daily dose and the presence of Tris-BP was indicated in the child's urine. A quite high exposure was likely for children who put their sleepwear into their mouths [28].

Compared to Tris-BP, less information has been available for assessing possible toxic effects of human exposure to Tris-CP. To further study the relative genotoxic potential of Tris-CP and Tris-BP, the Salmonella test was used by Soderlund et al, and Nakamura, et al [29, 30]. On the other hand Nakamura et al, reported a feasible means of determining Tris (2,3-dibromo propyl) phosphate (TDP) by using a gas chromatographic column packed with [31]. Moreover, pure samples of mono-BP, bis-BP, and their magnesium and ammonium salts were tested for mutagenicity against Salmonella again by Nakamura et al [32].

III. PARAMETERS USED FOR MODELLING AND PREDICTING ENVIRONMENTAL PARTITIONING OF CHEMICALS

3.1 PHYSICOCHEMICAL PROPERTIES

Some progress has been made in using physical and chemical contaminats [33].

The measurement of physical and chemical properties is considerably easier and less expensive than conducting laboratory or field studies on environmental fate. The fundamental physicochemical properties used for modelling and prediction purposes are water solubility, vapor pressure, n-octanol-water partition coefficient and molecular weight.

3.2 INPUT DATA

The fundamental physical properties of selected flame retardant chemicals such as water solubility, vapor pressure, n-octonal/water partition coefficient are complied in Table 3.1.

3.2.1 Water Solubility

Water solubility is the saturation concentration of a substance in distilled water. It is a function of temperature. It can influence the wider distribution of a substance. The maximum amount of a chemical in the water compartment is governed by the water solubility. Many organic compounds that cause environmental problems have a very low solubility in water.

In this study all the solubility values were taken from the literature. In the cases of availability of more than one value, mean values were calculated. For example in Table 3.1 the mean value for trichloromethane is logs= -1.190. (In the Appendix I)

On the other hand the solubility values not found in the literature can be derived using the octanol-water partition coefficents (Figure 3.1).

The solubility of organic compounds in water can easily be influenced by several factors.

3.2.2 Vapor Pressure

One of the most important data items in assessing the environmental partioning and transport of a chemical is its vapor pressure. More often than not, reliable vapor pressure data for temperatures near ambient are not available. Prediction of vapor pressures as a function of temperature thus becomes necessary.

Numerous equations and correlations for estimating vapor pressure are presented in the literature. In general, they require information on at least three of the following properties: (1) the critical temperature, T_c, (2) the critical pressure, P_c (3) the heat of vaporization, ΔH_v, and / or (4) the vapor pressure (P_{vp}) at some reference temperature.

Figure 3.1 shows selected roots for the estimation of water solubility, vapor pressure, and Henry's law constant [1].

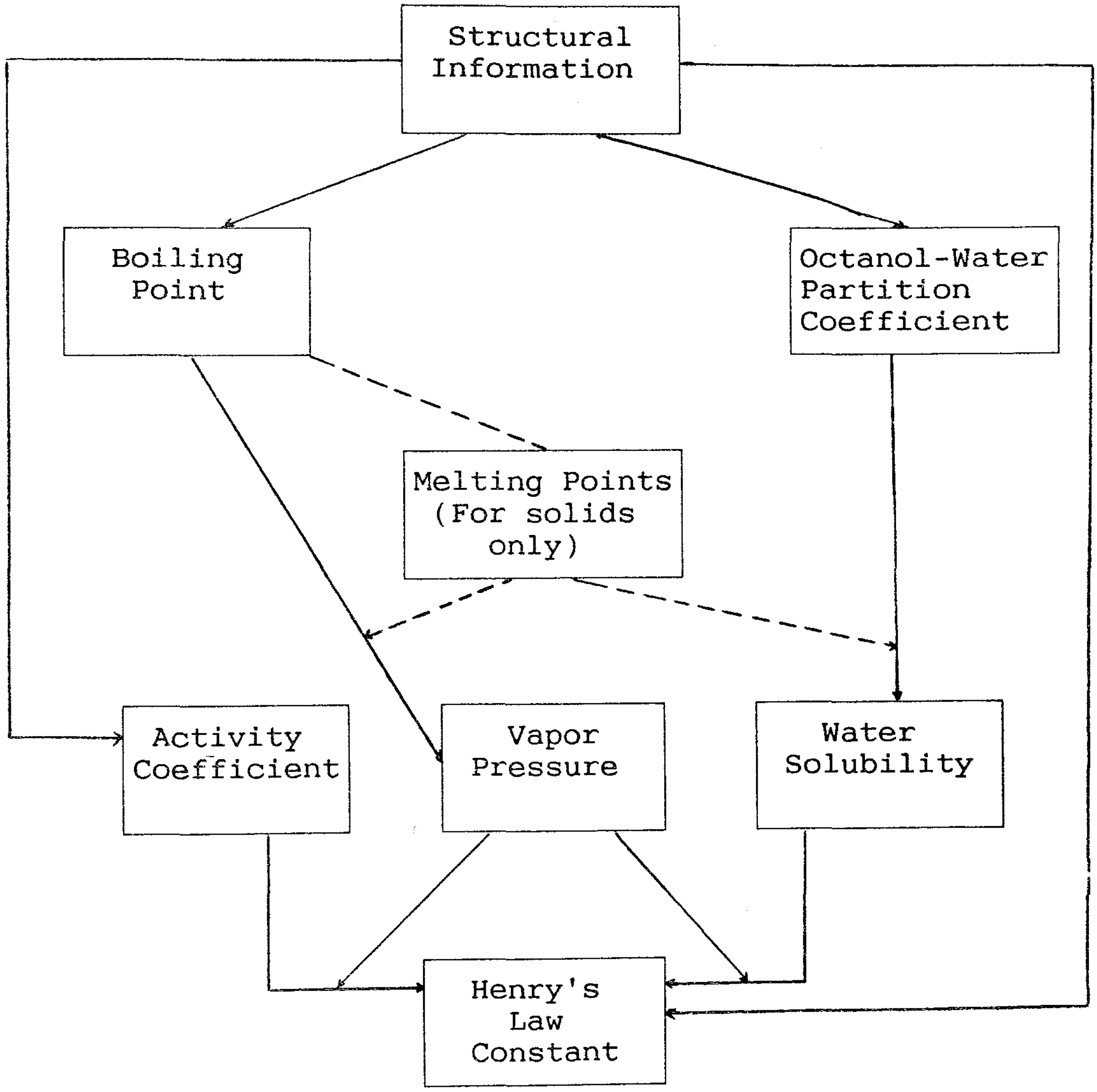


Figure 3.1 Selected routes for the estimation of Water Solubility, Vapor Pressure, and Henry's Law Constant.

Method 1.

Method 1 is generally applicable over the pressure range from 760 mm to 10^{-3} mm.

The method uses the Antoine equation, and can be written as follows [43]:

$$\ln P_{vp} = \frac{\Delta H_{vb} (T_b - C_2)^2}{\Delta Z_b R T_b^{\,2}} \left[\frac{1}{(T_b - C_2)} - \frac{1}{(T - C_2)} \right] \quad (3.1)$$

where

P_{vp} is the vapor pressure in atmosphere
ΔH_{vb} is the heat of vaporization in cal/mol
R is the gas constant in cal/mol.k (1.987 cal/mol.k)
T is the temperature in k
T_b normal boiling point
ΔZ_b is assumed to have the value of 0.97
C_2 is estimated via Thomson's rule, such that

$$C_2 = -18 + 0.19\, T_b \quad (3.2)$$

The heat of vaporization at the boiling point H_{vb}, is evaluated using a simple method introduced by Fishtine, who modified the Kistiakovskii equation to obtain

$$\frac{\Delta H_{vb}}{T_b} = \Delta S_{vb} = K_F\,(8.75 + R \ln T_b) \quad (3.3)$$

where K_F is derived from a consideration of the dipole moments of polar and nonpolar molecules. Table 3.2 lists values of K_F for various compound classes. Thus the only input data needed is the normal boiling point, T_b.

This method is applicable only over the normal liquid range. Thus, it was used to estimate the vapor pressure of selected flame retardant chemicals that are either in the liquid or vapor state at the temperature of interest.

TABLE 3.2

K_F Factors for Aliphatic and Alicyclic[a] Organic Compounds

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group 1	2	3	4	5	6	7	8	9	10	11	12-20
Hydrocarbons												
n-Alkanes	0.97	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkane isomers				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Monc-and diolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.00
Cyclic saturated hydrocarbons			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Halides (saturated or unsaturated)												
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Monoiodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.01
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Compounds Containing the Keto Group												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Aldehydes	-	1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Nitrogen Compounds												
Primary amines	1.16	1.13	1.12	1.11	1.10	1.10	1.09	1.09	1.08	1.07	1.06	1.05[b]
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03[b]
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles	-	1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01

(Continued)

TABLE 3.2 (Continued)

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group											
	1	2	3	4	5	6	7	8	9	10	11	12-20
Sulfur Compounds												
Mercaptans	0.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulfides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Alcohols												
Alcohols (single-OH group)	1.22	1.31	1.31	1.31	1.31	1.30	1.29	1.28	1.27	1.26	1.24	1.24[b]
Diols (glycols or condensed glycols)		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols (glycerol, etc.)			1.38	1.38	1.38							
Cyclohexanol, cyclohexyl methyl alcohol, etc.						1.20	1.20	1.21	1.24	1.26		
Miscellaneous Compounds												
Esters (aliphatic only)		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

a. Carbocyclic or heterocyclic compounds having aliphatic properties.

b. For N= 12 only; no prediction is made for K_r where N>12.

Notes:

1. Consider any phenyl group as a single carbon atom.

2. K_r factors are the same for all aliphatic isormers of a given compound. For example, K_r= 1.31 for n-butyl alcohol, i-butyl alcohol, t-butlylalcohol, and s-butyl alcohol.

3. In organometallic compounds, consider any metallic atom as a carbon atom.

4. For compounds not included in this table, assume K_r= 1.06.

Specimen Calculation

Estimation of vapor pressure of

1,1,1- Trichloroethane at 25° C, given $T_b = 74.1\ ^{\circ}C$

$$\ln P_{vp} = \frac{\Delta H_{vb}\ (T_b - C_2)^2}{\Delta Z_b\ \ RT_b^{\ 2}} \left[\frac{1}{(T_b - C_2)} - \frac{1}{(T - C_2)} \right] \qquad (3.1)$$

$T_b = 74.1^{\circ}C$

$T_b = 347.26\ K$

$K_F = 1.05$ (Table 3.2)

$$\frac{\Delta H_{vb}}{T_b} = \Delta S_{vb} = K_F\ (8.75 + R \ln Tb) \qquad (3.3)$$

$R = 1.987$ cal/mol. K.

$$\frac{\Delta H_{vb}}{T_b} = 1.05\ (8.75 + 1.987 \ln (347.26))$$

$$= 1.05\ (8.75 + (1.987 * 5.85))$$

$$= 1.05\ (8.75 + 11.62)$$

$$= 1.05 * 20.37$$

$$\frac{\Delta H_{vb}}{T_b} = 21.39 \text{ cal/ mol. K.}$$

$C_2 = -\ 18.00 + 0.19\ T_b$ from equation (3.2)

$C_2 = -\ 18.00 + 0.19\ (347.26)$

$C_2 = -\ 18.00 + 65.98$

$C_2 = 47.98$

Rearrangement of equation (3.1)

$$\ln P_{vp} = \left[\frac{\Delta H_{vb}}{T_b}\right] \frac{(T_b-C_2)^2}{\Delta Z_b\ RT_b} \left[\frac{1}{(T_b-C_2)} - \frac{1}{(T-C_2)}\right]$$

T_b-C_2 = 347.26 - 47.98

= 299.28 K

$T-C_2$ = 298 - 47.98

= 250.02 K.

ΔZ_b = 0.97

$$= \frac{21.39\ (299.28)^2}{0.97*1.987*347.26} \left[\frac{1}{299.28} - \frac{1}{250.02}\right]$$

= -1.856

P_{vp} = antilog (-1.856)*760= 118.69 mm Hg

P_{vp} = 118.69 mm Hg

The experimental value is 124 mm Hg hence the deviation is 4.8 %. (Table 3.1, Log P = 2.093)

Method 2

Quite often, data are available in which a boiling point at reduced pressure is given. A simple but adequate approximation may be obtained by considering the origin of the Kistiakovskii equation [43].

The boiling points of selected flame retardants are given in Table 3.3. (In the Appendix I)

It seems reasonable that an approximate value of $\Delta H_{v1}/T_1$ can be obtained at other temperatures by writing

$$H_{v1} = K_F P_1 V_{v1} \ln V_{v1} \qquad (3.4)$$

Using the ideal gas law, we obtain

$$\frac{\Delta H_{v1}}{T_1} = K_F R \left[\ln \frac{RT_1}{P_1} \right] \qquad (3.5)$$

where R, outside the parentheses, has the value of 1.987 cal/mol. K. and a value of 82.05 cm^3 atm/K, inside the parentheses. Equation 3-5 can be rearranged to yield

$$\frac{\Delta H_{v1}}{T_1} = K_F [\, 8.75 + R\, (\ln T_1 - \ln P_1)] \qquad (3.6)$$

With this modification, the reference temperature, T_1 can be substituted directly for T_b in Equation 3-1 (Method 1) to yield

$$\ln P_{vp} = \ln P_1 + \frac{\Delta H_{v1} (T_1 - C_2)^2}{Z_b R T_1^{\;2}} \left[\frac{1}{(T_1 - C_2)} - \frac{1}{(T - C_2)} \right] \qquad (3.7)$$

where T_1 is the reference temperature and,

P_1 is the vapor pressure of the substance, at the temperature T_1.

This method is applicable to liquids and solids and was used to calculate the vapor pressure of phosphate ester.

Specimen Calculation

Estimation of the vapor pressure of DBPP (Dibutyl phenyl phosphate) at 25° C, given that P_1 = 20 mm Hg, T_1 = 200° C (Table 3.1)

$$P_1 = \frac{20}{760} = 0.0263 \text{ atm.}$$

$$\ln P_1 = -3.637$$

$$\frac{\Delta H_{v1}}{T_1} = K_F\ (8.75 + R\ (\ln T_1 - \ln P_1)) \qquad (3.6)$$

$$= 29.90 \text{ cal/mol. K.}$$

$$C_2 = -\ 18+0.19\ (473) \qquad \text{from equation} \qquad (3.2)$$

$$C_2 = 71.87$$

$$T_1 - C_2 = 473-71.87 = 401.13$$

$$T - C_2 = 298-71.87 = 226.13$$

$$\ln P_{vp} = -3.637 + \frac{29.90*(401.13)^2}{0.97*1.987*473}\left[\frac{1}{401.13} - \frac{1}{226.13}\right] \qquad (3.7)$$

$$\ln P_{vp} = -13.822$$

$$P_{vp} = \text{antilog } (-13.822)*760 = 7.54*10^{-4} \text{ mm Hg.}$$

Because there are no experimental vapor pressure data for DBPP at 25 °C no comparison could be made between calculated and experimental values.

3.2.3 Octanol Water Partition Coefficient

The n-octanol/water partition coefficient has proved useful as a means to predict soil adsorption, biological uptake, and biomagnification [44].

The partition coefficient expresses the equilibrium concentration ratio of an organic chemical partitioned between an organic liquid (e.g., n-octanol) and water. This partitioning is equivalent to partitioning an organic chemical between itself and water.

It has been linearly related to fish bioconcentration factors, to soil organic carbon partition coefficients, and to toxicities to a wide variety of aquatic and mammalian species.

The literature K_{ow} Values, however, are often not experimental, but rather calculated. Lyman et al [45], have summarised the methods that are commonly used for the estimation of K_{ow}.

In this study, reported experimental and calculated K_{ow} values are used. When more than one octanol-water partition coefficient value was available, one of them was selected, if they were close to each other. (Table 3.1)

3.2.4 Soil Sorption Coefficient

The soil sorption coefficient (K_{oc}), defined as the ratio between concentrations of a given chemical sorbed by the soil and dissolved in the soil water normalized to the total organic carbon content of the soil, is currently used as a quantitative measure of soil sorption [46].

$$K_{oc} = \frac{100\ K_D}{\%\ \text{organic carbon}} \qquad (3.8)$$

K_D = Soil Adsorption.

As the experimental determination of K_{oc} values is often a costly and time consuming process, the correlation between K_{ow} and K_{oc} has been examined in numerous studies involving a wide variety of chemicals.

In this thesis in order to find good correlation for soil sorption coefficients of phosphate esters (triaryl phosphates, triaryl alkyl phosphates , trialkyl phosphates and trihaloalkyl phosphates), an analogous regression analysis with K_{ow} values was carried out, resulting in the linear regression equation [41,43];

$$\text{Log } K_{oc} = 1.377 + 0.544 \log K_{ow} \qquad (3.9)$$

This equation has been applied for 45 chemicals, with a wide variety of chemicals and also for pesticides, and the correlation coefficient was 0.74.

On the other hand the following regression equation (Briggs) was used to calculate the K_{oc} values for chlorinated hydrocarbons (60). This equation has been applied for 106 compounds including chlorinated hydrocarbons.

$$\text{Log } K_{oc} = 0.53 \log K_{ow} + 0.64 \qquad (3.10)$$

3.2.5 Henry's Law Constant

The air-water partition coefficient is the ratio of concentrations in air and in water.

$$H = C_a / C_w \qquad (3.11)$$

Where C_a represents concentration in air, C_w represents concentration in water and H Henry's Law Constant.

The air-water partition coefficient can be expressed in various forms, the most convenient being Henry's Law Constant, H, in [Pa. m^3]/mol, which is the ratio of partial pressure in the atmosphere, P, in Pa, to concentration in water, C, in mol/ m^3.

Henry's Law constant expresses the proportionality between the concentration of a gas dissolved in a solvent and its partial pressure. In equation form, Henry's Law is

$$P= HC \qquad (3.12)$$

where P is the partial pressure of the gas, C is the concentration of the dissolved gas, and H is Henry's Law Constant.

For prediction and modelling purposes a knowledge of Henry's Law Constant is essential.

In this study. Henry's Law constants of both groups of flame retardants were calculated using equation 3.11 and a computer program which was written in Basic and applicable to IBM personal computer, given in the Appendix II.

3.2.6 Bioconcentration Factor

The accumulation of certain chemicals in aquatic organisms, such as fish, has become of increasing concern as an environmental hazard [47]. The extent of such concentration is expressed as the bioconcentration factor (K_B), i.e., by the ratio of the steady state concentration of a chemical in the organism to that in water. It has been generally assumed that the mechanism leading to the uptake of organic pollutants by organisms is analogous to the partitioning between an organic phase and water.

Log K_B values of organic compounds from both laboratory bioconcentration testing and natural water systems have been correlated either with the corresponding octanol-water partition coefficients or with their water solubilities [Melecter 93,94].

Because of the, lack of experimental bioaccumulation data for flame retardant chemicals bioconcentration factors for chlorinated alkanes were obtained from Mackay's correlation [57] which is

$$\log K_B = \log K_{ow} - 1.32 \qquad (3.13)$$

This equation was applied to 71 chemicals which includes clorinated hydrocarbons and has a high correlation coefficient (r = 0.95)

On the other hand bioconcentration factors of phosphate esters were predicted from the following equation [41],

$$\log K_{B} = 0.851 \log K_{ow} -0.7 \qquad (3.14)$$

which was applied to 55 chemicals with a high corelation coefficient (r = 0.98).

IV. MACKAY'S LEVEL I FUGACITY MODEL

4.1. APPROACHES TO ENVIRONMENTAL EXPOSURE ANALYSIS

The chemical industry has been concerned with the hazardous environmental properties of the product that are being manufactured and distributed. There have been many cases in which the health of humans and other organisms has been affected by the emission or formation of chemicals that are biologically active. In order to determine the environmental hazard associated with these chemicals, information on the environmental fate, production quantity, use, environmental release and toxicity are important.

The use of compartmental analysis provides substantial information for this type of environmental exposure prediction. The OECD Exposure Analysis Group initially considered four models [48], which are listed in Table 4.1.

Author	Basic Properties	Model
Klöpffer [49,50] (1979)	Water Solubility, Vapour Pressure	equilibria between media
Mackay [51,52] (1979)	Molecular Mass, Water Solubility, Adsorption, Vapour Pressure	fugacity capacities are used to explain various compartment relationships
Ncely [53,54] 1980	Molecular Mass, Water Solubility, Vapour Pressure	use laboratory and monitoring data in a pond environment
Wood [50] 1980		is independent of the compartment volume

Table 4.1. The Models were considered by the OECD Exposure Analysis Group.
(The numbers written in brakets [ ] show the reference numbers)

The Klöpffer, Mackay, and Wood models make slightly different assumptions regarding compartment sizes but if no degradation processes are considered and the chemical distribution accross the environmental media is considered to be at equilibrium, they reduce to essentially the same set of equations.

The Klöpffer Model and Neely Model were decided not to be considered in the context of the OECD hazard assessment, because the former did not make provision for degradation or non-equilibrium processes, the latter being applied to only a specific experimental environment.

As a result, the model developed by Mackay and adopted by Wood is considered to be applicable at several levels of sophistication depending on the chemical and environmental data available.

These two models are based on the concept of fugacity, i.e. the tendency for a substance to escape from a phase, and assume equilibrium or steady-state conditions among a set of environmental compartments. Both models are identical in predicting environmental distribution. They assume that

1. The environment is a closed system consisting of air (a), water (w), sediment (sd), soil (s), suspended solids (ss) and biota (b) compartments.

2. The chemical has reached thermodynamic equilibrium in the environment both with respect to interphase transfer and interphase transport.

3. No degradation processes occur during the distribution.

4.2. FUGACITY AND FUGACITY CAPACITY CONCEPTS

If it is assumed that each compartment is well mixed, that is homogenous and sufficient time has elapsed so that all compartments are in equilibrium then thermodynamics provides information about the nature of the partition.

Usually at considerably different concentrations equilibrium is achieved between phases. It is more illuminating to express these equilibrium partitioning situations in terms of a fundamental quantity that controls the differing concentrations.

Fugacity is a thermodynamic quantity related to chemical potential or activity and characterizes the tendency for a substance to escape from a phase. It has units of pressure. A chemical will diffuse from high to low fugacity. When equilibrium is achieved between two phases, the escaping tendencies from these phases are equal.

Fugacity can be directly related to concentration within different compartments (i) at low concentrations which are relevant to environmental contamination levels where the proportionality constant is the fugacity capacity Z_i mol/m^{3}Pa

$$C_i = f_i \cdot Z_i \tag{4.1}$$

where C_i is concentration in units of mol/m^3, f_i is fugacity in units of Pa and Z_i is "fugacity capacity" in units of mol/[m^{3}Pa].

The fugacity capacity Z, which quantifies the capacity of the phase for fugacity, depends on temperature, pressure, the nature of the substance and the medium in which it is present.

If there are two phases, then equilibrium of a substance will be reached when the fugacities are equal, that is

$$f_1 = f_2 \tag{4.2}$$

thus

$$C_1 / Z_1 = C_2 / Z_2 \tag{4.3}$$

or

$$C_1 / C_2 = Z_1 / Z_2 = K \tag{4.4}$$

The concentration ratio which is the partition coefficient controlling the distribution of the substance between two phases is simply the ratio of the fugacity capacities.

If Z for a substance can be found for each environmental phase then we can easily calculate how the substance will partition.

4.3. FUGACITY CAPACITY CALCULATIONS

The Mackay model consists of 1 km square with 20 km high atmosphere; 30 % of the area is covered by soil whose depth is 3 cm and 70 % is water covering an average depth of 10 m, with 3 cm of sediment, 5 ppm by volume of suspended solids and 0.5 ppm of biota.

The organic carbon contents are 2% for soil and 4% for sediment and suspended solids. A temperature of 25 °C is assumed and the total amount of solute is arbitrarily taken as 100 moles. It results in the general equation:

$$P_i = \frac{Z_i \times V_i}{V_i \times Z_i} \qquad (i = A, W, S)$$

with the fugacity capaties:

$$Z_{Air} = \frac{1}{RT}$$

$$Z_{Water} = \frac{1}{H}$$

$$Z_{soil}/\text{sediment} = \frac{K_D \rho_S}{H}$$

$$Z_{Biota} = \frac{K_{OW} B}{H}$$

where

$R\ (\mathrm{J/mol\,^{\circ}K})$ = Universal Gas Constant

$T\ (^{\circ}\mathrm{K})$ = Absolute Temperature

$H\ (\mathrm{Pa\ m^3/mol})$ = Henry's Law Constant

$K_D\ \dfrac{m^3\ \text{water}}{10^6\ \text{sorbernt}}$ = Sorption Coefficient

$$= \frac{K_{oc}\ \times\ \%\ \text{organic carbon content}}{100}$$

$\rho_s\ (\mathrm{g/cm^3})$ = Sorbent Density

B = Mass Fraction of Biota Times Total Biota or Lipid Part

K_{oc} = Soil Sorption Coefficient

K_{ow} = Partition Coefficient

The volumes V_A, V_W, V_S of the environmental compartments air, water and soil/sediment are listed in Table 4.2

Properties of the Unit World		
Compartment	Volume (m^3)	Media Densities (kg/m^3)
Air	$6x10^9$ (1 km^2 area x 6km height)	1.9
Soil	$4.5x10^4$ (30% area x 15cm depth)	1500
Water	$7x10^6$ (70% area x 10m depth)	1000
Biota	7 (Water Volume x 1 ppm)	1000
Suspended Solids	35 (Water Volume x 5 ppm)	1500
Sediment	$2.1x10^4$ (70% area x 3cm depth)	1500

Table 4.2. The volumes V_A V_W, V_S of the environmental compartments air, water and soil / sediment.

The model chosen needs the following physicochemical data.

1 - Molar Mass
2 - Water Solubility
3 - Vapour Pressure
4 - Soil Sorption Constant
5 - Partition Coefficient

It is generally accepted that such models should be validated by comparison with real environmental data. However, since models of this type do not describe any particular real environment, results can only be validated by, general comparison of the observed environmental concentrations and of predicted values based on direct calculation by using the observed data.

In this study, physicochemical property data taken from the literature and derived equations such as equation 3.1, 3.7. were used to compute the distribution of selected Flame Retardant Chemicals in various compartments on the basis of Mackay's Level I Fugacity Model.

In order to compute the environmental compartmentalization of selected flame retardants a BASIC program was written which is suitable for use in personal computers (such as IBM PS/2 model 30-H21)

4.4 Specimen Calculations of Dichloromethane

4.4.1 Calculation of Fugacity Capacity for Air

$Z_A = 1/RT$

$T = 298\ ^{o}K$

$R = 8.314\ Pa.m^3/mol.\ ^{o}K$

$$Z_A \quad \frac{1}{8.314x298} = 4.04\ x\ 10^{-4}\ mol/m^3\ Pa.$$

4.4.2 Calculation of Fugacity Capacity for Soil

$Z_s = Kp_s \quad s/H$

$_s = 1.5x10^6\ \ g/m^3$

$H = P/S$

$\log P = 2.641$ from Table (3.1)

$P = 437.522$

$$P = 437.522\ mm\ Hg \ \frac{1}{7.5x10^{-3}Pa} = 58336Pa$$

$\log S = -1.136$ from Table (3.1)

$S = 0.074$ mole/l

$S = 74.131$ mole/m^3

$$H = \frac{58336}{74.131} = 786.93 \quad \text{Pa m}^3\text{/mol}$$

$K_{ps} = \%\ OC\ \ K_{oc}$

% OC = 0.02 for soil

$$\log K_{oc} = 0.53 \log K_{ow} + 0.64 \qquad (3.10)$$

$= 0.53\ (1.25) + 0.64$

$\log K_{oc} = 1.3025$

$K_{oc} = 20.06$

$K_{ps} = 0.02 \times 20.06$

$K_{ps} = 0.4012$ m^3 of water / 10^6 g. sorbent

$$Z_s = \frac{0.4012 \times 1.5}{786.93} = 7.65 \times 10^{-4} \text{ mole/m}^3 \text{ Pa}$$

4.4.3 Calculation of Fugacity Capacity for Water

$Z_w = 1/H$

$H = 786.93$ Pa m^3/mole

$Z_w = 1.27 \times 10^{-3}$ mole/m^3 Pa

4.4.4 Calculation of Fugacity Capacity for Biota

$$Z_B = K_B \rho_B / H$$

$$\rho_B = 1\text{x}10^6 \text{ g/m}^3$$

$$\log K_B = \log K_{ow} - 1.32 \qquad (3.13)$$

$$= 1.25 - 1.32$$

$$= 0.07$$

$$K_B = 0.851 \text{ m}^3 \text{ of water / } 10^6 \text{ g biota}$$

$$Z_B = \frac{0.851\text{x}1}{786.93} = 1.081\text{x}10^{-3} \text{ mole/m}^3 \text{ Pa}$$

4.4.5 Calculation of Fugacity Capacity for Suspended Solids and Sediments

$$Z_{ss} = K_{pss} \rho_{ss} / H$$

$$Z_{sed} = K_{psd} \rho_{sd} / H$$

$$\rho_{ss} = 1.5\text{x}10^6 \text{ g/m}^3$$

$$\rho_{sd} = 1.5\text{x}10^6 \text{ g/m}^3$$

$$K_{pss} = \% \text{ OC x } K_{oc}$$

$$K_{psd} = \% \text{ OC x } K_{oc}$$

% OC = 0.04 for suspended solids and sediment

$$K_{pss} = 0.04\text{x}20.06$$

so,

K_{pss} = 0.8024 m^3 of water /10^6 g sorbent

$$Z_{ss} = \frac{0.8024x1.5}{786.93} = 1.53x10^{-3} \text{ mole/m}^3 \text{ Pa}$$

so the Z_{sd} has the same fugacity capacity constant

Z_{sd} = $1.53x10^{-3}$ mole/m^3 Pa

4.4.6 Calculation of Common Fugacity

$f = M_T / \Sigma Z;\ V;$

M_T = 100 mole

1) Z_a = $4.04x10^{-4}$ mole/m^3 Pa

V_a = 6.10^9 m^3

$Z_a V_a$ = $(4.04x10^{-4})$ $(6x10^9)$

$Z_a V_a$ = $24.23x10^5$ mole/Pa

2) Z_s = $7.65x10^{-4}$ mole/m^3 Pa

V_s = $4.5x10^4$ m^3

$Z_s V_s$ = $(7.65x10^{-4})$ $(4.5x10^4)$

$Z_s V_s$ = 34.425 mole/Pa

3) Z_w = $1.27x10^{-3}$ mole/m^3 Pa

V_w = $7x10^6$ m^3

$Z_w V_w = (1.27\text{x}10^{-3})(7\text{x}10^{6})$

$Z_w V_w = 8890$ mole/Pa

4) $Z_b = 1.081\text{x}10^{-3}$ mole/m^3 Pa

$V_b = 7$ m^3

$Z_b V_b = (1.081\text{x}10^{-3})(7)$

$Z_b V_b = 7.567\text{x}10^{-3}$

5) $Z_{ss} = 1.53\text{x}10^{-3}$ mole/m^3 Pa

$V_{ss} = 35$ m^3

$Z_{ss} V_{ss} = (1.53\text{x}10^{-3})(35)$

$Z_{ss} V_{ss} = 0.0535$ mole/Pa

6) $Z_{sd} = 1.53\text{x}10^{-3}$ mole/m^3 Pa

$V_{sd} = 2.1\text{x}10^{4}$ m^3

$Z_{sd} V_{sd} = (1.53\text{x}10^{-3})(2.1\text{x}10^{4})$

$Z_{sd} V_{sd} = 32.13$ mole/Pa

$\Sigma Z_i V_i = 2.43\text{x}10^{6}$ mole/Pa

$f = 100/2.43\text{x}10^{6}$

$f = 4.11\text{x}10^{-5}$ Pa.

4.4.7 Calculation of Amounts

$$M_i = f.\ Z_i\ V_i$$

(1) $M_a = f.\ V_a\ V_a$

$M_a = (4.11\text{x}10^{-5})(24.73\text{x}10^{5})$

$= 99.63$ mole

(2) $M_s = f.\ Z_s\ V_s$

$M_s = (4.11\text{x}10^{-5})(34.425)$

$M_s = 1.41\text{x}10^{-3}$ mole

(3) $M_w = f.\ Z_w\ V_w$

$M_w = (4.11\text{x}10^{-5})(8890)$

$= 0.365$ mole

(4) $M_b = f.\ Z_b\ V_b$

$= (4.11\text{x}10^{-5})(7.567\text{x}10^{-3})$

$= 3.11\text{x}10^{-7}$ mole

(5) $M_{ss} = f.\ Z_{ss}\ V_{ss}$

$= (4.11\text{x}10^{-5})(0.0535)$

$= 2.19\text{x}10^{6}$ mole

(6) $M_{sd} = f.\ Z_{sd.}\ V_{sd}$

$= (4.11\text{x}10^{-5})\ (32.13)$

$= 1.32\text{x}10^{-3}$ mole

4.4.8. Calculation of concentration

$C_i = f.Z_i$

(1) $C_a = f.Z_a$

$= (4.11\text{x}10^{-5}\ \text{Pa})\ (4.04\text{x}10^{-4}\ \text{mole/m}^3\text{Pa})$

$= 1.66\text{x}10^{-8}\ \text{mole/m}^3$

$C_a = (1.66\text{x}10^{-8}\ \text{mole/m}^3\ (85\ \text{g/mole})\ (1\mu\text{g}/10^{-6}\text{g})$

$\text{x}\ (1\text{m}^3\ \text{air}/1.19\text{x}10^3\ \text{g})$

$C_a = 1.18\text{x}10^{-3}\mu\text{g/g}$ or ppm.

(2) $C_w = f.\ Z_w.$

$= (4.11\text{x}10^{-5}\text{Pa})\ (1.27\text{x}10^{-3}\ \text{mole/m}^3\text{Pa})$

$= 5.22\text{x}10^{-8}\ \text{mole/m}^3$

$C_w = (5.22\text{x}10^{-8}\ \text{mole/m}^3)\ (85\ \text{g/mole})\ (1\mu\text{g}/10^{-6}\ \text{g})$

$\text{x}\ (1\ \text{m}^3\ \text{water}/1\text{x}10^6\ \text{g})$

$= 4.44\text{x}10^{-6}\mu\text{g/g}$ or ppm.

(3) $C_B = f. Z_B$

$= (4.11\times10^{-5}\ \text{Pa})\ (1.081\times10^{-3}\ \text{mole/Pa.m}^3)$

$= 4.44\times10^{-8}\ \text{mole/m}^3$

$= (4.44\times10^{-8}\ \text{mole/m}^3)\ (85\ \text{g/mole})\ (1\mu\text{g}/10^{-6}\ \text{g})$

$\quad \times\ (1\ \text{m}^3\ \text{biota}\ /\ 1\times10^6\ \text{g})$

$C_B = 3.78\times10^{-6}\ \mu\text{g/g}$ or ppm

(4) $C_S = f. Z_S$

$= (4.11\times10^{-5}\ \text{Pa})\ (7.65\times10^{-4}\ \text{mole/m}^3\text{Pa})$

$= 3.14\times10^{-8}\ \text{mole/m}^3$

$C_S = (3.14\times10^{-8}\ \text{mole/m}^3)\ (85\ \text{g/mole})\ (1\mu\text{g}/1\times10^{-6}\ \text{g})$

$\quad \times\ (1\text{m}^3\ \text{soil}\ /\ 1.5\times10^6\ \text{g})$

$= 1.78\times10^{-6}\ \mu\text{g/g}$ or ppm.

$C_{SS} = f. Z_{SS}$

$= (4.11\times10^{-5}\ \text{Pa})\ (1.53\times10^{-3}\ \text{mole/m}^3\text{Pa})$

$= 6.29\times10^{-8}\ \text{mole/m}^3$

$= (6.29\times10^{-8}\ \text{mole/m}^3)\ (85\ \text{g/mole})\ (1\mu\text{g}/1\times10^{-6}\ \text{g})$

$\quad \times\ (1\text{m}^3\ \text{suspended solids}\ /\ 1.5\times10^6\ \text{g})$

$= 3.56\times10^{-6}\ \mu\text{g/g}$ or ppm

5. EVALUATION OF MODEL RESULTS

5.1. RESULTS AND DISCUSSION

The outputs are arranged into two families: chlorinated alkanes and phosphate esters and their partitioning behaviour between the environmental compartments are discussed here.

Chlorinated alkanes partition into the air compartment as shown in Table 5.1. in the Appendix I. Since their mass percentages in that compartment are greater than 95 percent, they are significant for the air compartment [61]. 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,3-dichloropropane as can be seen from Table 5.2 are important for the water compartment because their mass percentages in the water compartment are greather than two percent [61].

Looking closer at the chlorinated alkanes in smaller groups like mono, di, tri, tetra and polychlorinated alkanes the following conclusions may be made.

Figure 5.1.1 shows that monochlorinated alkanes partition into the air compartment by a ratio of 98 percent, and also it can be seen that the mass percentage of these monochlorinated alkanes in the water compartment is less than 0.2 % percent.

Very similar results were obtained with dichlorinated alkanes. As it can be seen in Figure 5.1.2 they also mostly partition into the air compartment, with mass percentages between 96.94 to 99.76. On the other hand,

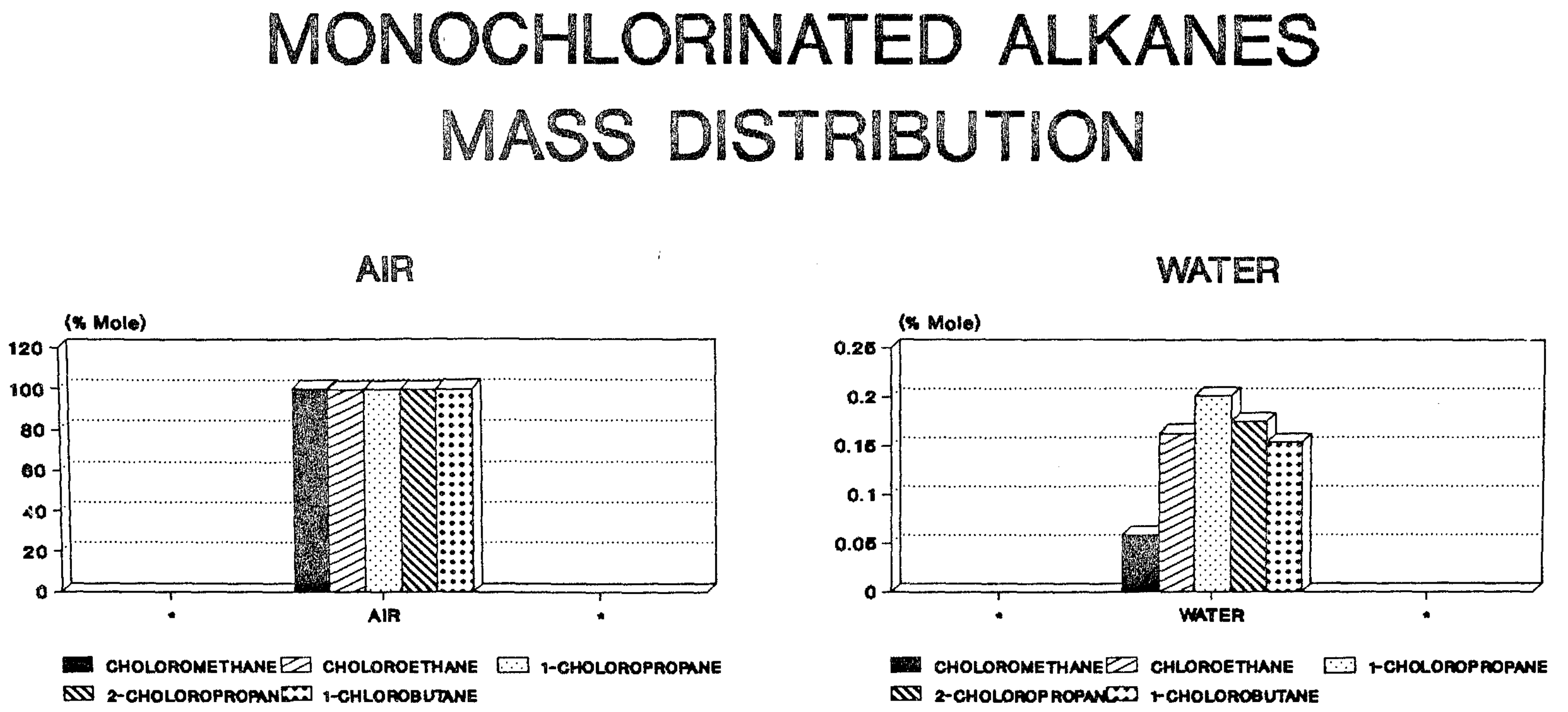


Figure 5.1.1. Mass Distribution of Monochlorinated Alkanes in Air and Water Compartments.

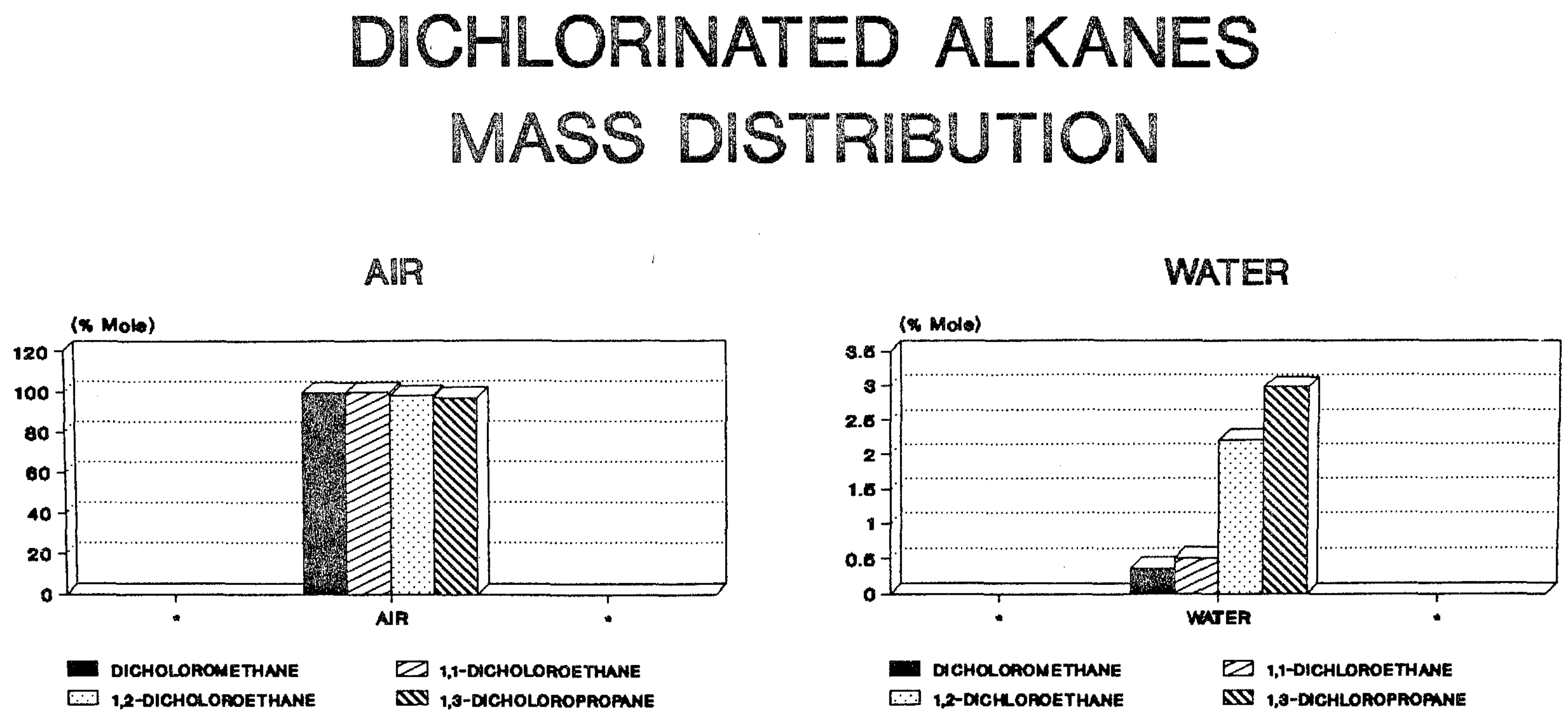


Figure 5.1.2. Mass Distribution of Dichlorinated Alkanes in Air and Water Compartments.

1,2-dichloroethane and 1,3-dichloroethane's mass partition inot the water compartment are more than 2.0 % percent.

It can be seen in Figure 5.1.3 that trichlorinated alkanes have almost the same mass distribution values in the air compartment, and their Mass partitions in the water compartment are less than 1 %.

Almost the same results can be seen for polychlorinated alkanes in Figure 5.1.4. On the other hand 1122-tetrachloroethane has the highest value of mass distribution in water which is 5.5 %.

These results can be explained by the physicochemical properties of these chemicals. The chemical having a vapor pressure of 10^{6} mm Hg partitions (Table 3.1) ultimately in the air compartment. When the vapor pressure decreases, the amount partitioning into the water compartment increases with increasing solubility. When the chemical has a low vapor pressure and low water solubility it becomes an important contaminant for the soil, sediment and biota compartments.

As it can be seen in Figure 5.2.1 monochlorinated alkanes have less than 20×10^{-4} percent mass partition into the soil and sediment compartments and less than 20×10^{-7} in biota and less than 40×10^{-7} in suspended solids compartments. The amounts partitioning in these compartments are very little.

It is possible to say that dichlorinated Alkanes also show a negligible mass distribution in Biota, Suspended Solids, Soil and Sediment compartments which can be seen in Figure 5.2.2.

TRICHLORINATED ALKANES
MASS DISTRIBUTION

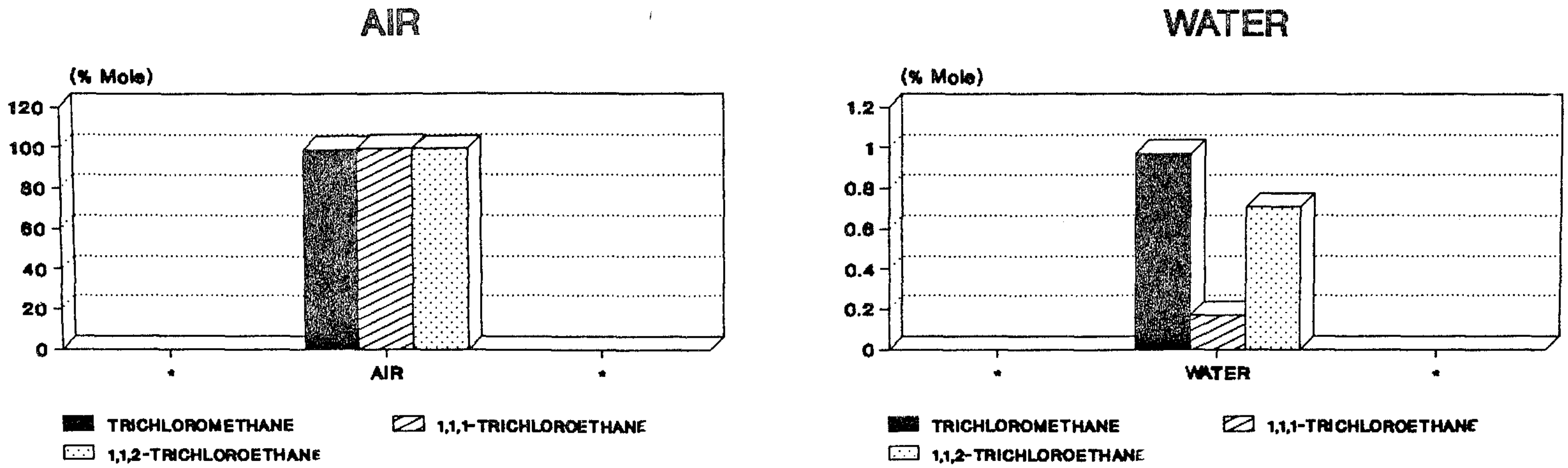


Figure 5.1.3. Mass Distribution of Trichlorinated Alkanes in Air and Water Compartments.

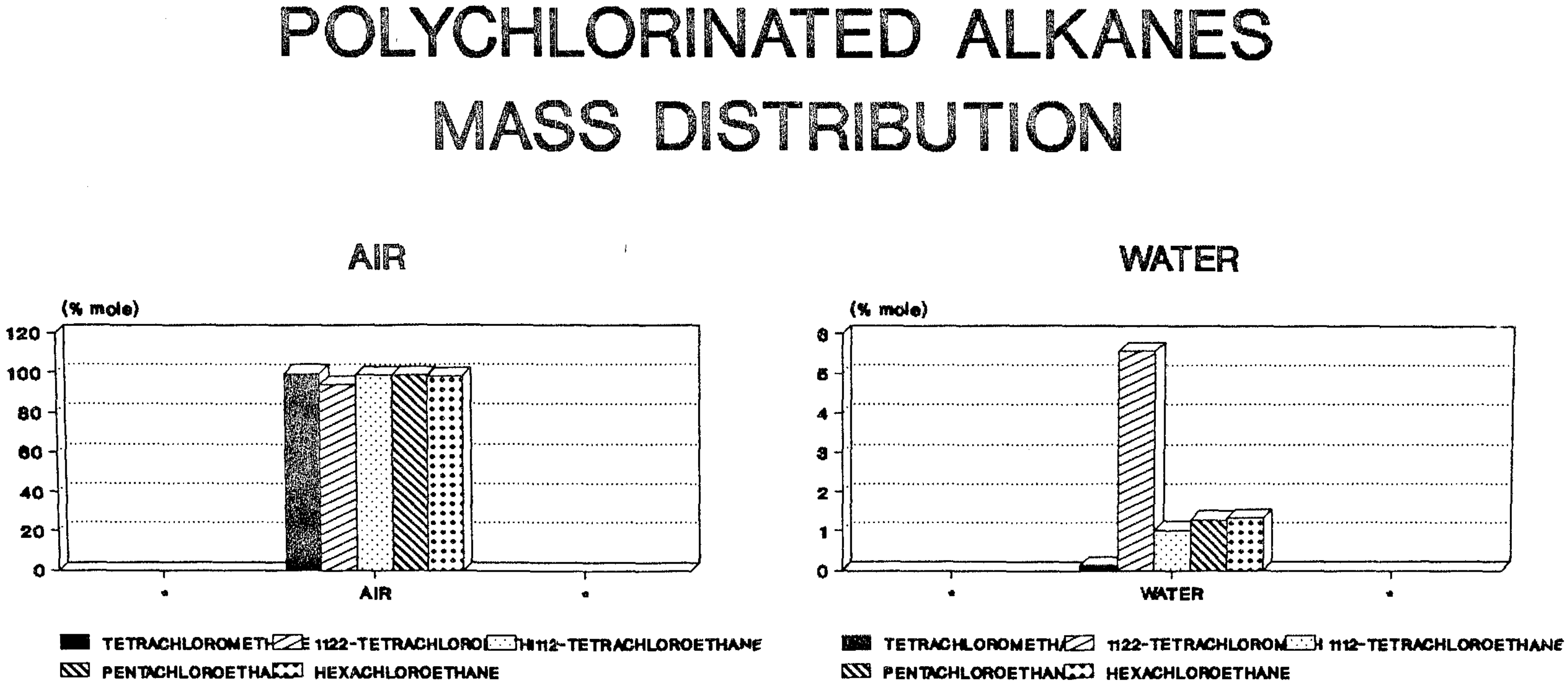


Figure 5.1.4. Mass Distribution of Polychlorinated Alkanes in Air and Water Compartments.

MONOCHLORINATED ALKANES
MASS DISTRIBUTION

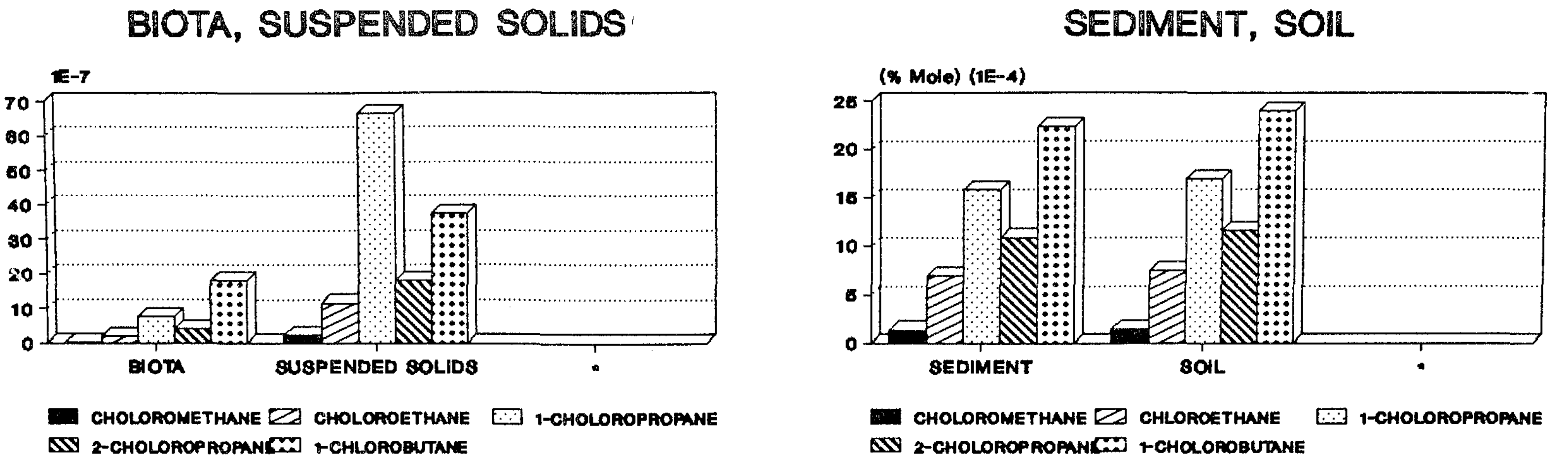


Figure 5.2.1. Mass Distribution of Monochlorinated Alkanes in Biota, Suspended Solids, Sediment and Soil compartments.

DICHLORINATED ALKANES
MASS DISTRIBUTION

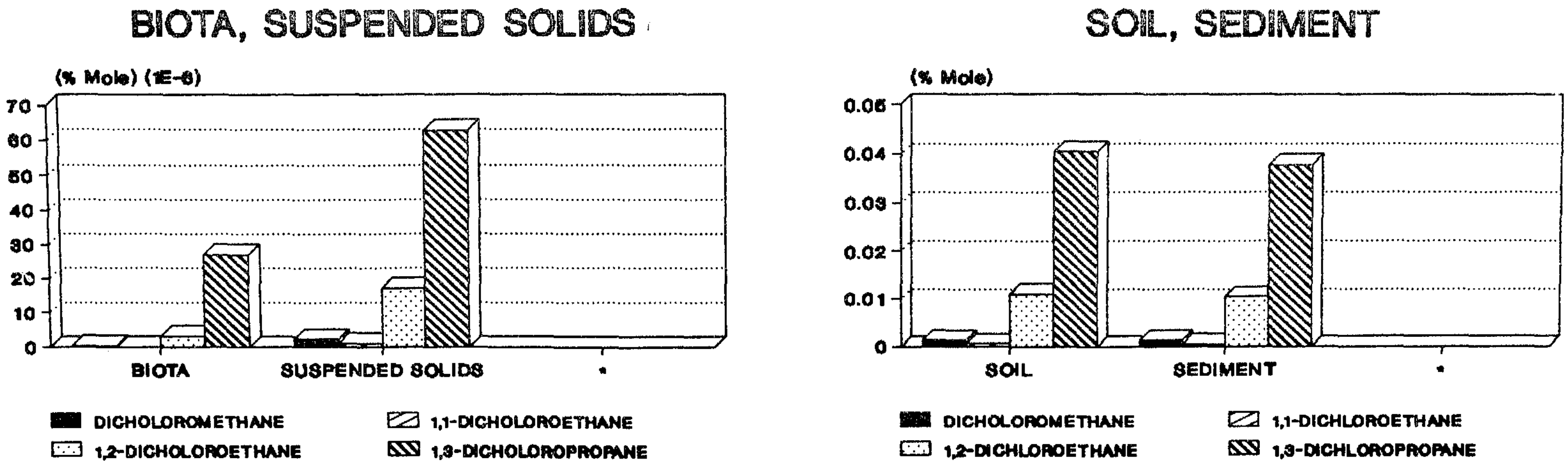


Figure 5.2.2. Mass Distribution of Dichlorinated Alkanes in Biota, Suspended Solids, Soil and Sediment Compartments.

The results of Compartmental Distribution of these compounds are also shown in Table 5.3 for Biota, in Table 5.4 for Soil, in Table 5.5 for Suspended Solids and finally in Table 5.6 for Sediment (given in the Appendix I).

Similar results have been obtained with trichlorinated alkanes which can be seen in Figure 5.2.3.

In figure 5.2.4. the results can be seen for polychlorinated alkanes which are not different from the other chlorinated alkanes.

For further studies equilibrium distribution of these alkanes should be taken into consideration. The equilibrium distribution at steady-state conditions among the environmental compartments are also shown in Tables 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6. given in the Appendix I.

It can be seen from Figure 5.3.1 that the eguilibrium distribution of 1-chlorobutane is about 45.88 % in Biota (Table 5.3).

This result shows that not only mass distribution but also equilibrium distribution in various compartments should be taken into account for a better understanding of distribution.

Figure 5.3.2 shows that 1,1 dichloroethane has an equilibrium distribution of 45.72 % (Table 5.2) in the water compartment and 1,3-dichloropropane has 43.97 % (Table 5.3) in the biota compartment.

It is obvious from these results that the chemical's distribution across the environmental compartments at equilibrium gives more information about its likely behaviour after the steady-state conditions.

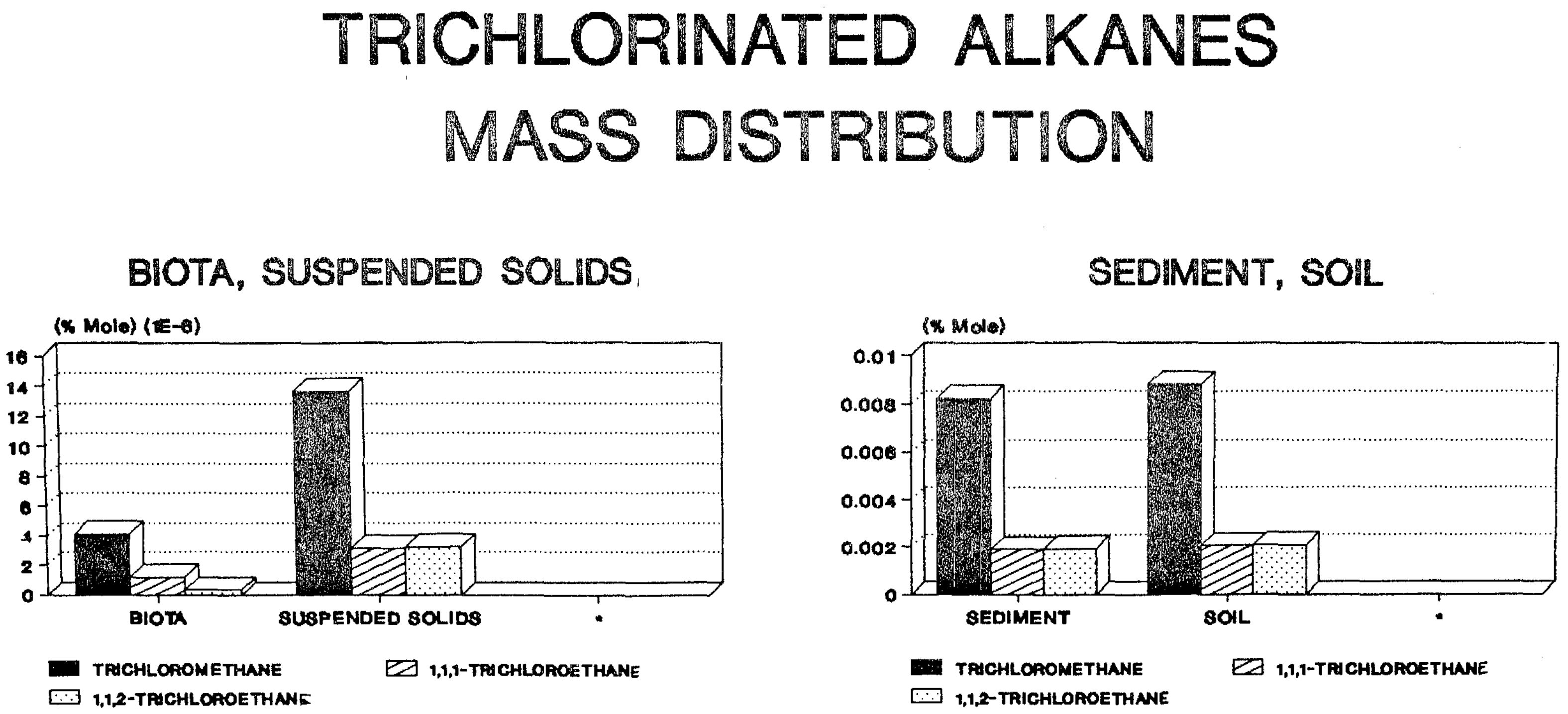


Figure 5.2.3. Mass Distribution of Trichlorinated Alkanes in Biota, Suspended Solids, Sediment, Soil compartments.

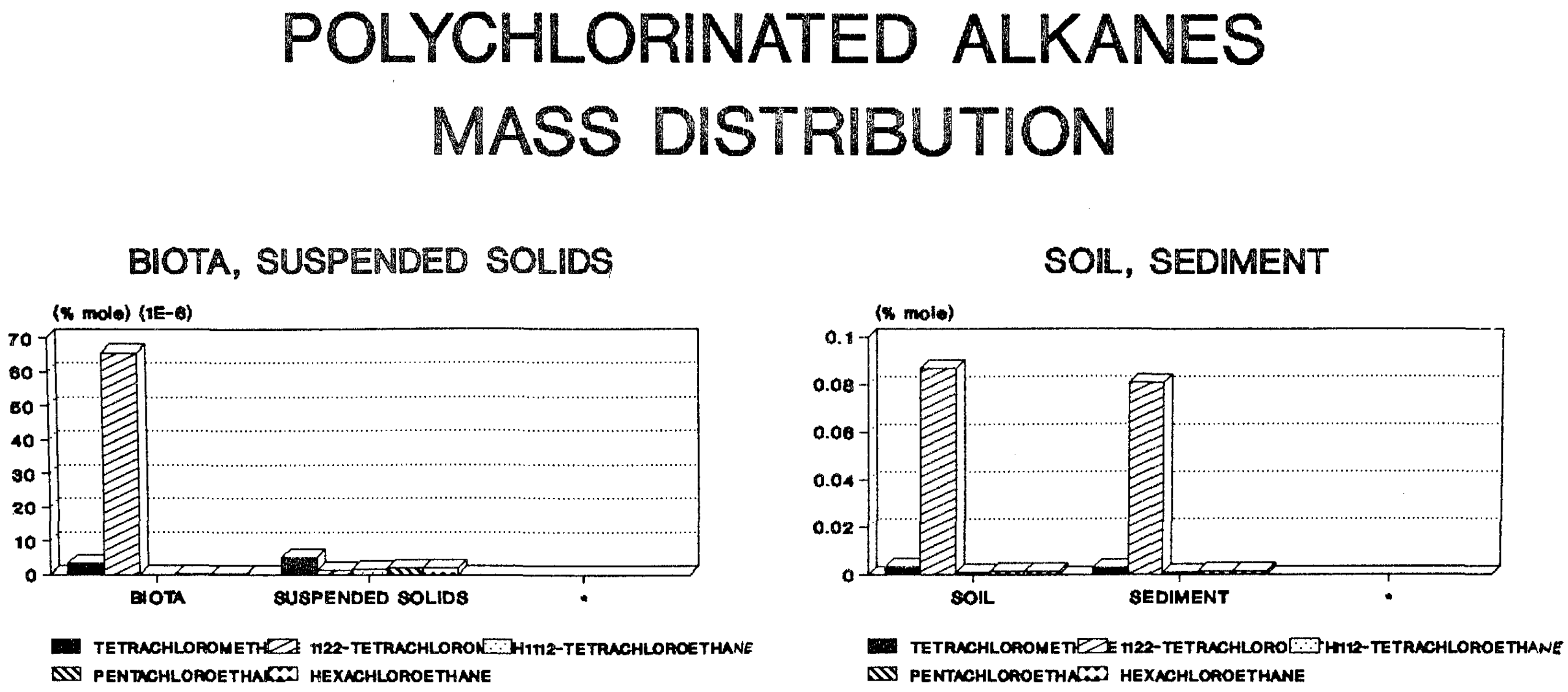


Figure 5.2.4. Mass Distribution of Polychlorinated Alkanes in Biota, Suspended Solids, Soil and Sediment compartments.

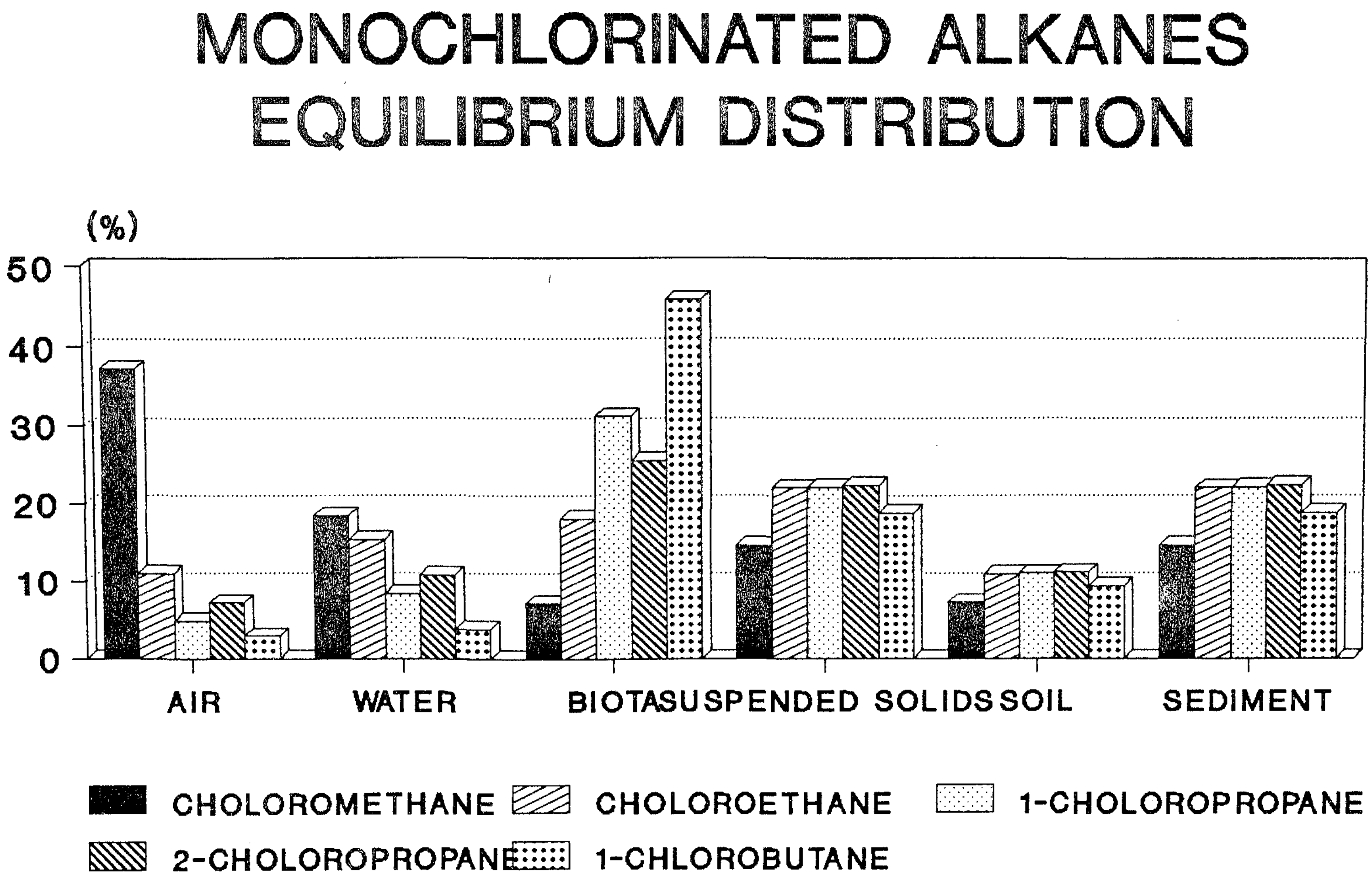


Figure 5.3.1. Equilibrium Distribution of Monochlorinated Alkanes in Air, Water, Biota, Suspended Solids, Soil and Sediment compartments.

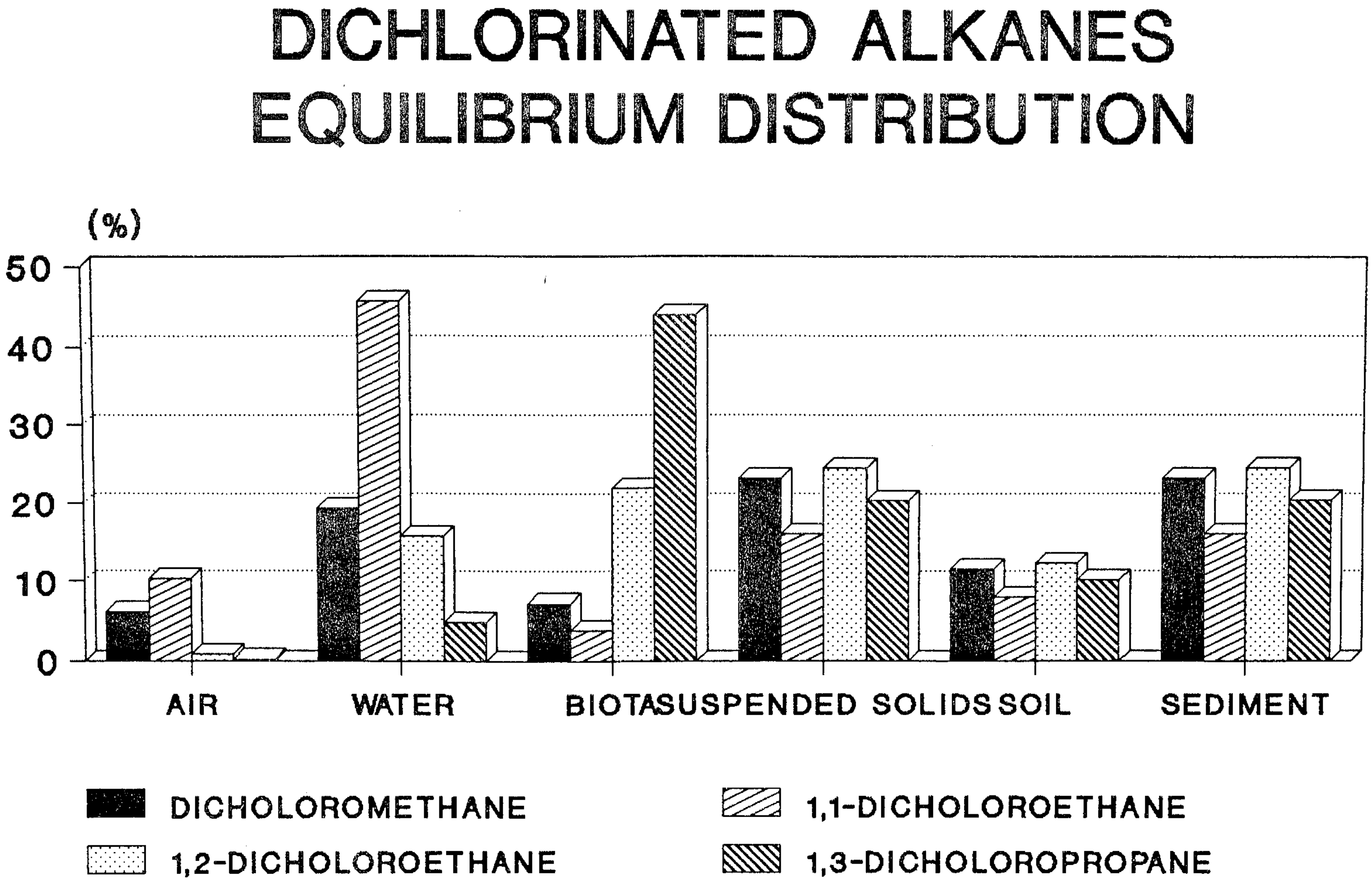


Figure 5.3.2. Equilibrium Distribution of Dichlorinated Alkanes in Air, Water, Biota, Suspended Solids, Soil and Sediment compartments.

Like in figure 5.3.3, 1,1,1-trichloroethane's equilibrium distribution in the Biota compartment is 39.32 % (Table 5.3) and in figure 5.3.4, Hexachloroethane's equilibrium distribution in water is 54.52 % (Table 5.2) but 2.93 % (Table 5.3) in the biota compartment.

The last parameter is the concentration values of these chemicals in the compartments. The concentration values (ppm) are given in Table 5.7, 5.8, and 5.9 for all compartments, in the Appendix I.

Mono chlorinated alkanes have concentrations which are parallel to their mass distributions. The concentration of monochlorinated alkanes can be seen in in Figure 5.4.1 and 5.4.1.1.

Almost the same results can be obtained for the concentration of dichlorinated alkanes, which can be seen in Figure 5.4.2.

On the other hand in Figure 5.4.3 the concentration of polychlorinated alkanes can be seen.

The second group of flame retardant chemicals which are computed in this thesis is phosphate esters. The physicochemical properties of these chemicals are given in Table 3.1 and their distribution between the environmental compartments are given in Tables 5.1 for Air, 5.2 for Water, 5.3 for Biota, 5.4 for Soil, 5.5 for Suspended Solids and finally 5.6 for Sediment compartments, in the Appendix I.

Phosphate esters have more complex structure than chlorinated alkanes and because of their rather different physicochemical properties they show different compartmental distribution.

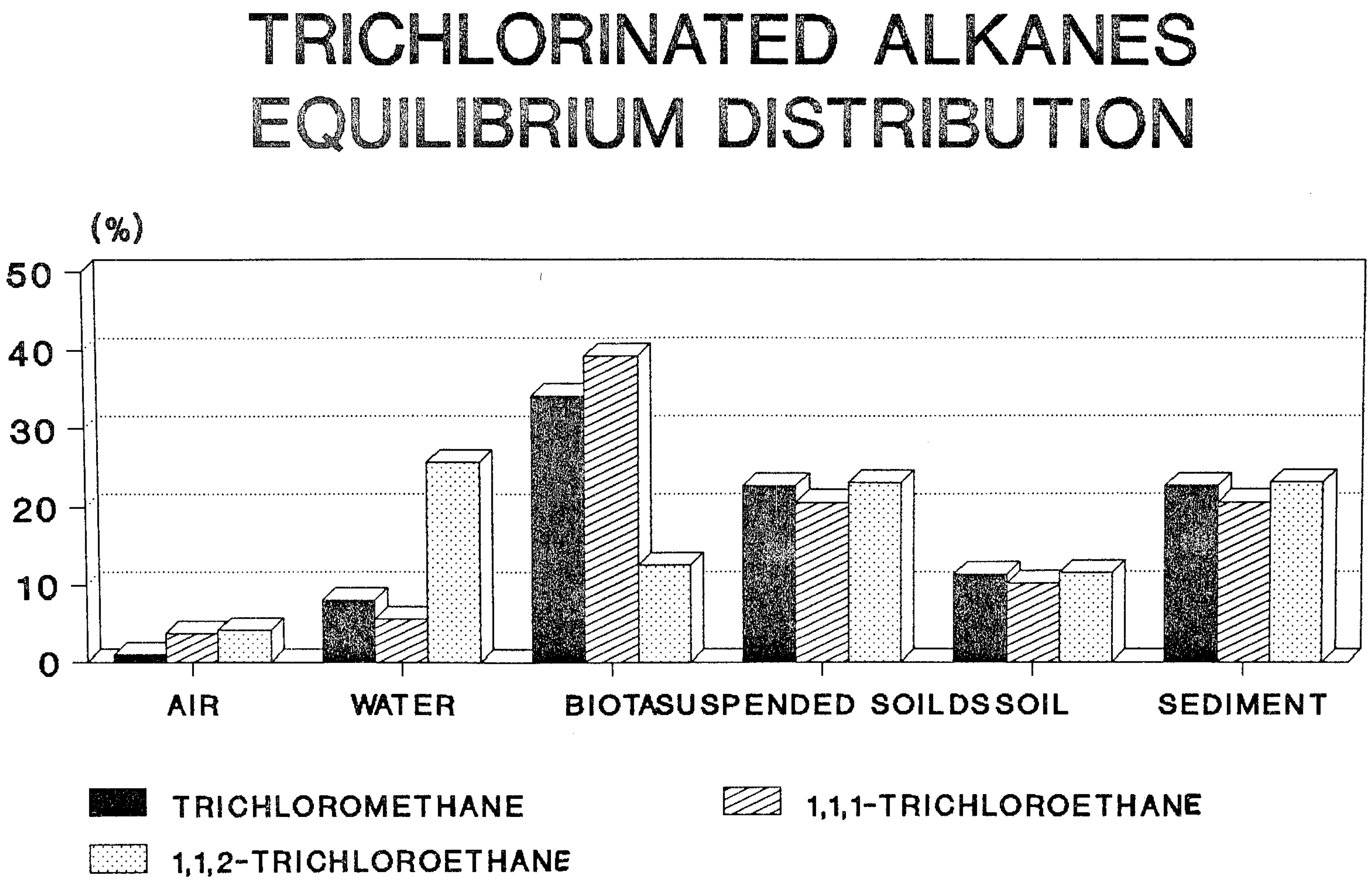


Figure 5.3.3. Equilibrium Distribution of Trichlorinated Alkanes in Air, Water, Biota, Suspended Solids, Soil and Sediment compartments.

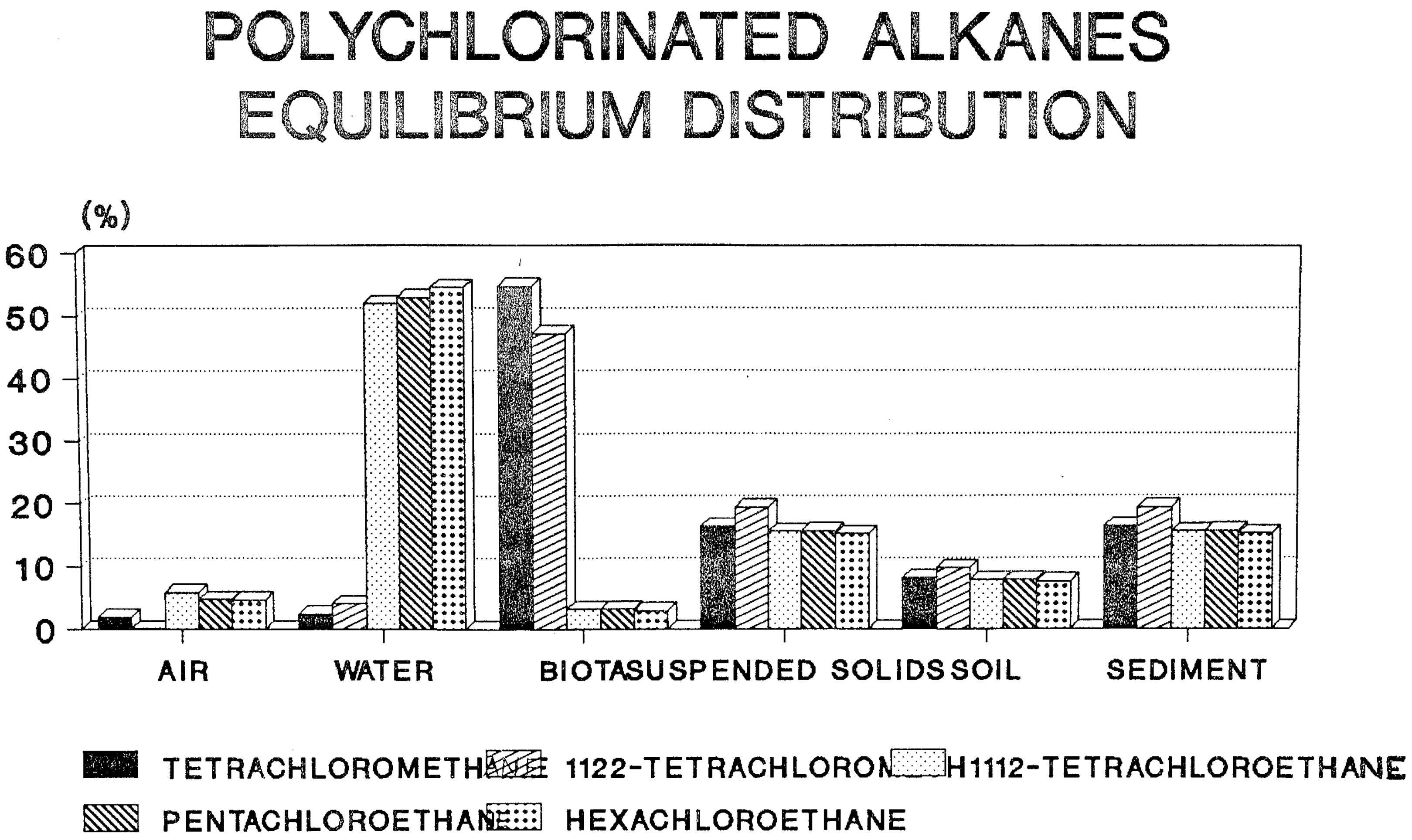
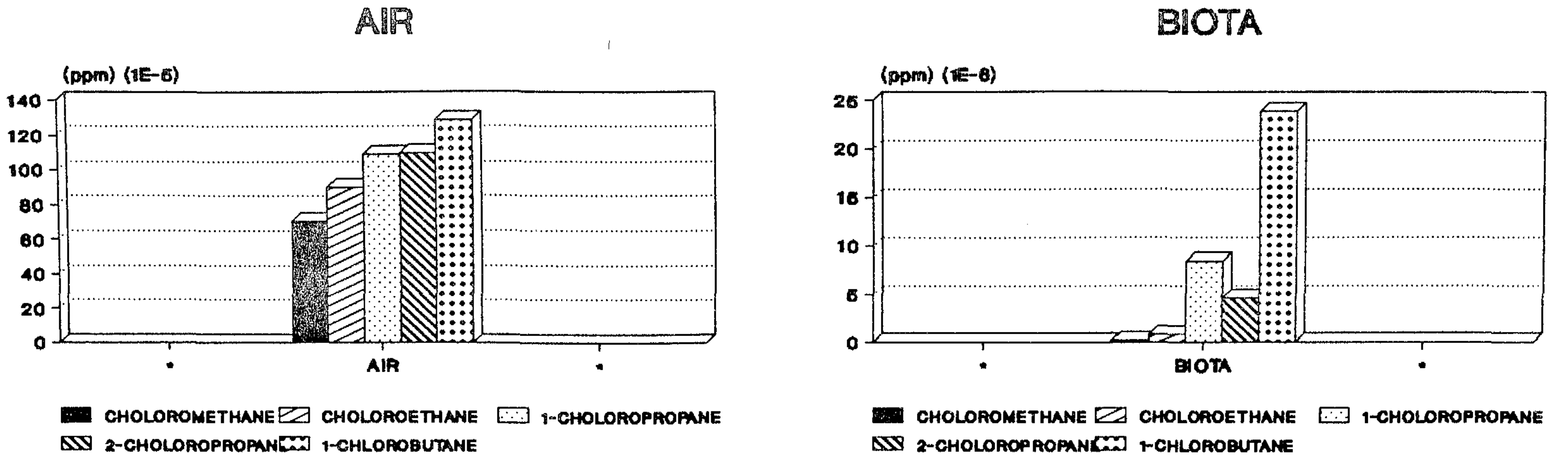


Figure 5.3.4. Equilibrium Distribution of Polychlorinated Alkanes in Air, Water, Biota, Suspended Solids, Soil and Sediment compartments.

MONOCHLORINATED ALKANES CONCENTRATION



AIR

BIOTA

Figure 5.4.1. Concentration values of Monochlorinated Alkanes in Air, and Biota compartments.

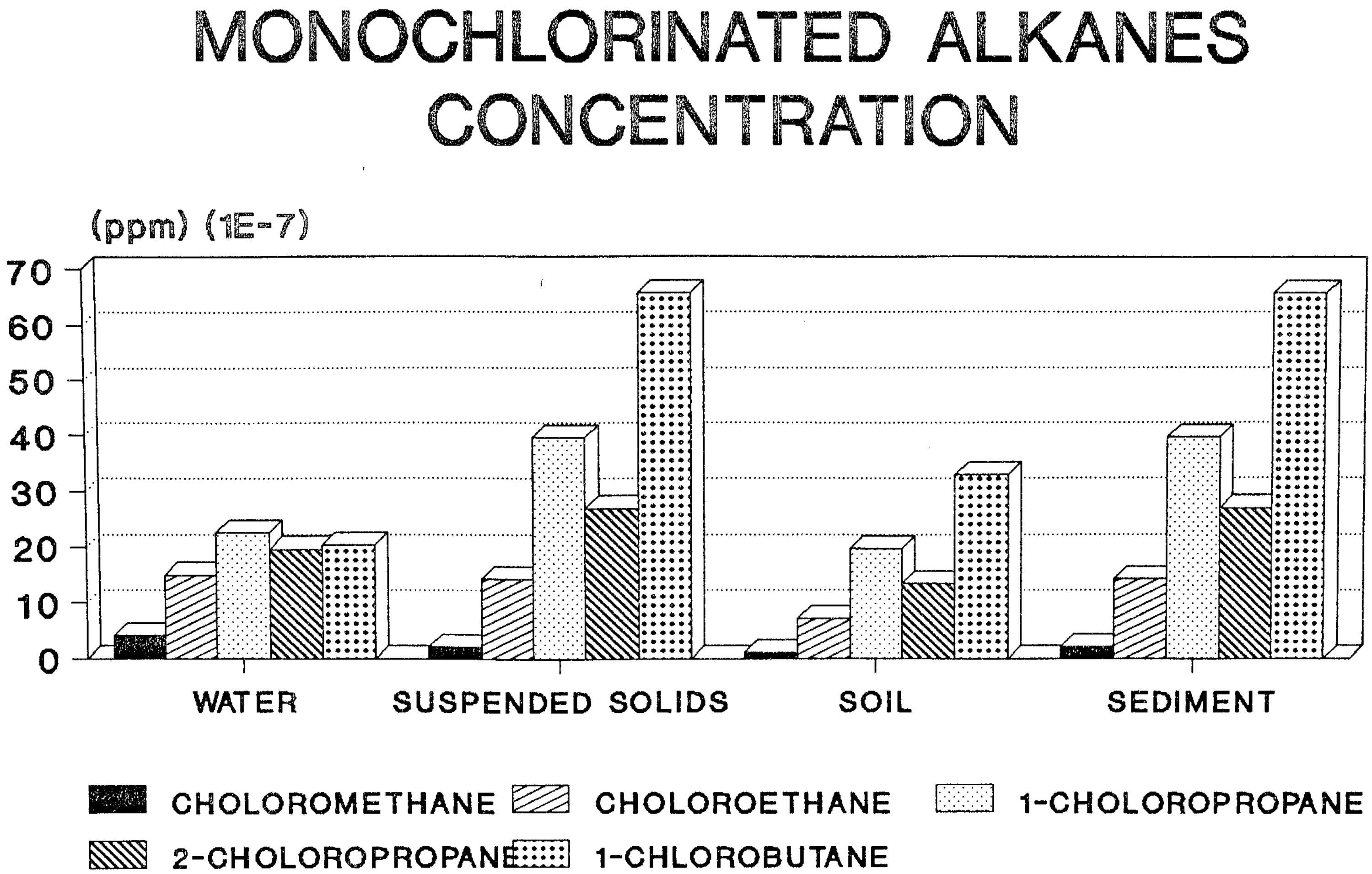


Figure 5.4.1.1. Concentration values of Monochlorinated Alkanes in Water, Suspended Solids, Soil and Sediment compartments.

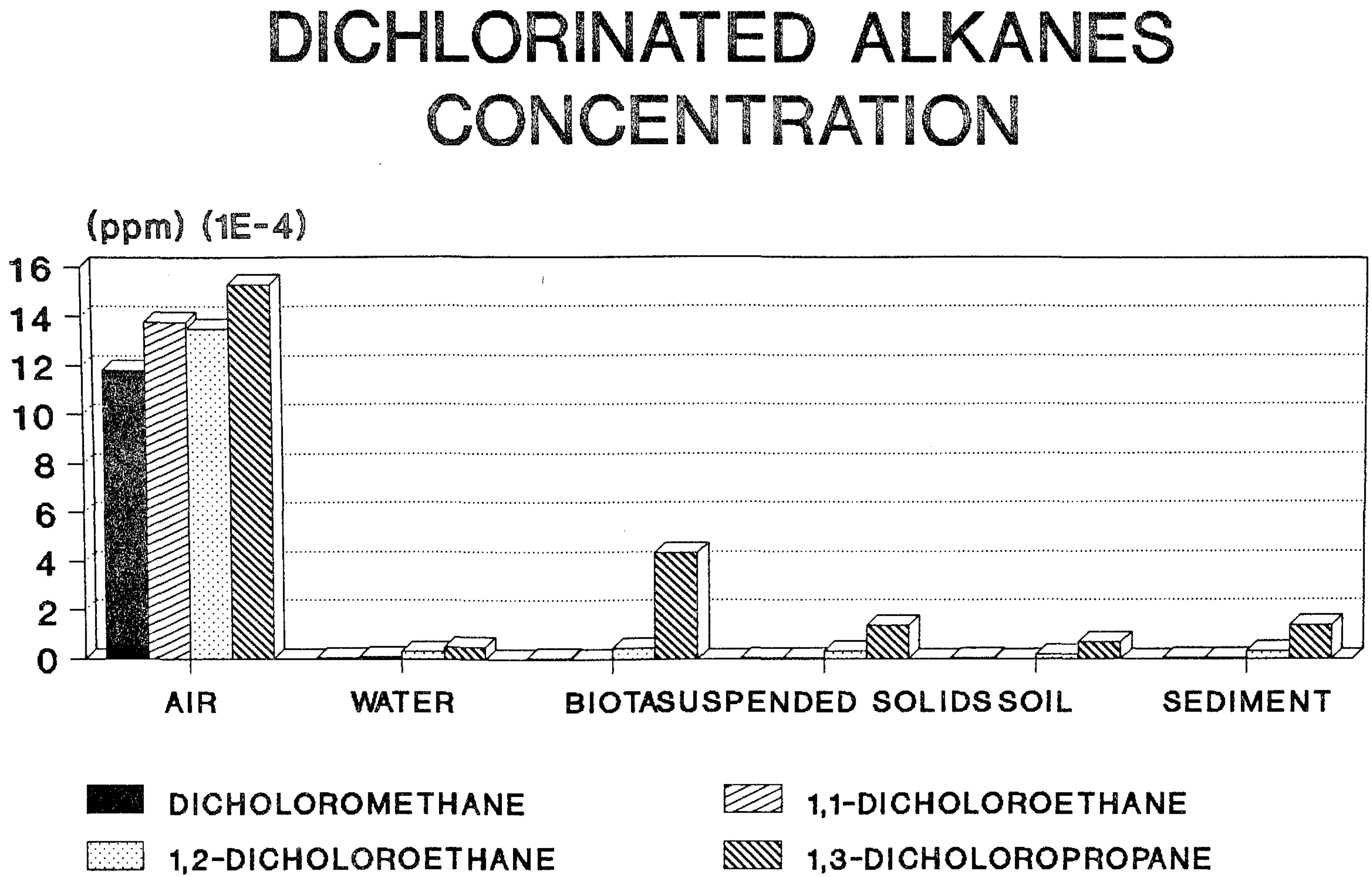


Figure 5.4.2. Concentration values of Dichlorinated Alkanes in Water, Suspended Solids, Soil and Sediment compartments.

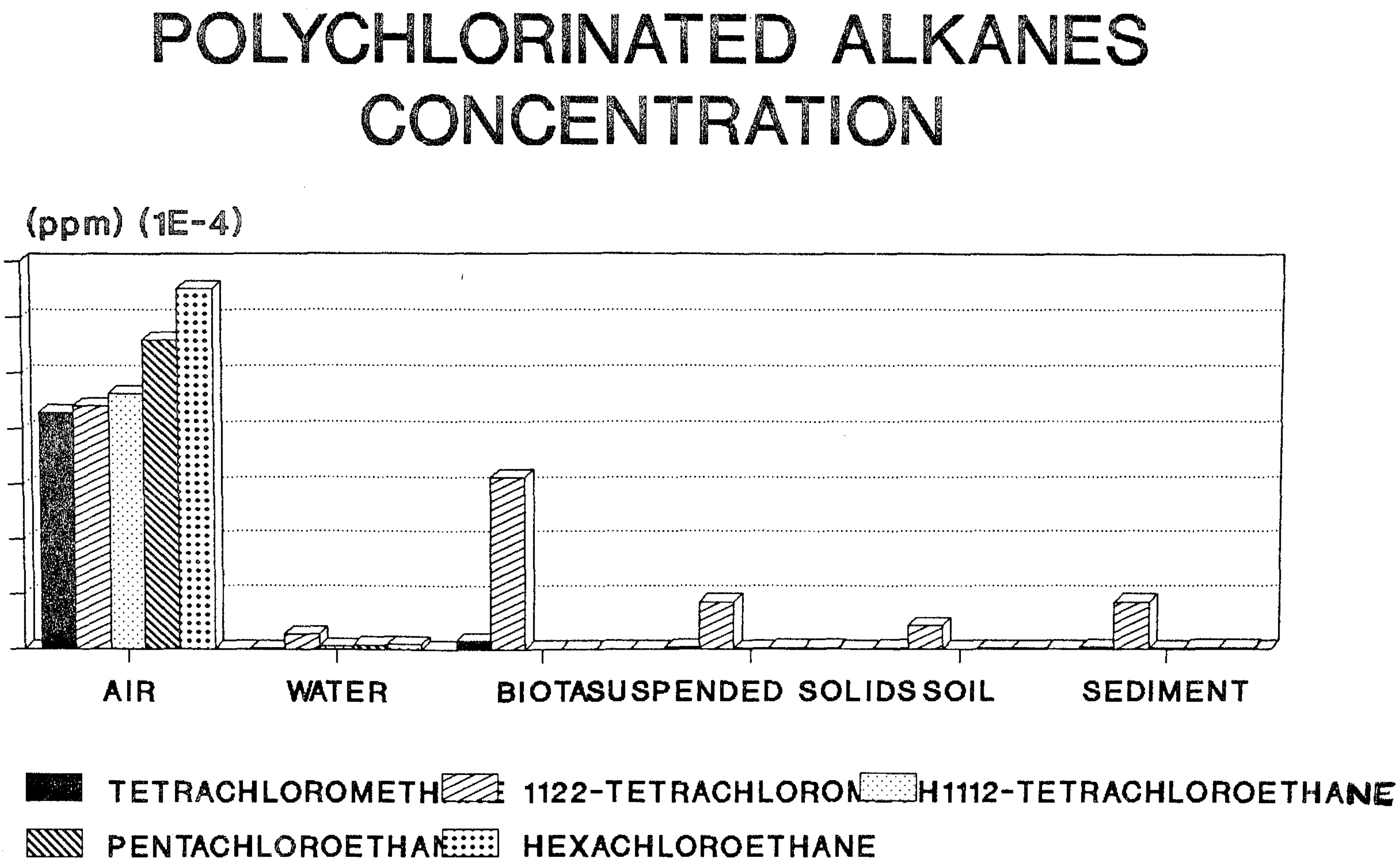


Figure 5.4.3. Concentration values of Polychlorinated Alkanes in Water, Suspended Solids, Soil and Sediment compartments.

If we have a closer look at mass distribution of phosphorus flame retardants in air it can be seen that all except TDBP [Tris (2,3-dibromopropyl) phosphate] which has a mass distribution value of 53.62 % in the Air Compartment (Table 5.1.), have very small values. This can be explained by its rather high molecular weight. TDBP has the highest molecular weight which is 697.7 (Table 3.3). Its partitioning between the other compartments can be seen in Figure 5.5.1.

In Figure 5.5.2. the concentration in different compartments for TDBP can be seen. The concentration in biota shows higher importance. As biota is a very small amount even this concentration of TDBP may cause serious effects for it.

According to the studies Tris (2,3-dibromopropyl) phosphate was detected in childrens urine [27,28] before it was banned from use in chieldrens clothing in 1977.

BPDP T-butyldiphenyl phosphate has quite a small value of mass partition in the air compartment which is 7.49E-20 ppm (Table 5.1) and a rather high value for Water: 15.54 ppm (Table 5.2).

It can be seen in Figure 5.5.3 that sediment and soil are the most important compartments. When concentration values are taken into consideration it can be seen that biota has the highest value of concentration of 3.89 ppm (Figure 5.5.2).

From all these compartmental analyses, it can be said that phosphate esters mostly partition in water, soil and sediment compartments have totally different behaviors compared to Chlorinated Alkanes.

TDBP
TRIS(2,3-DIBROMOPROPYL) PHOSPHATE

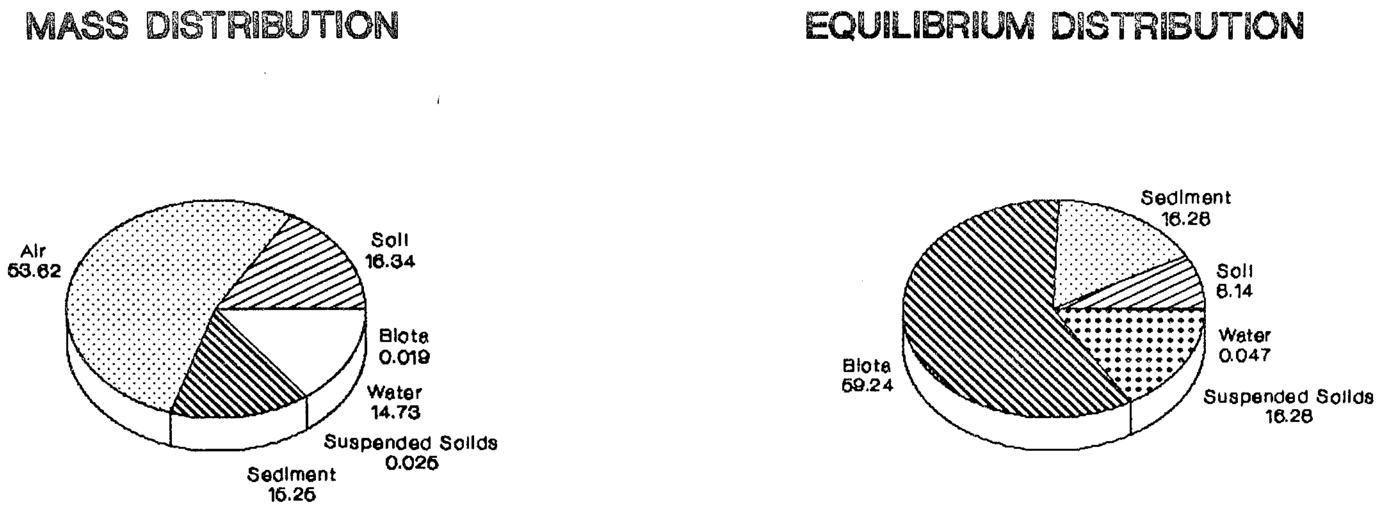


Figure 5.5.1. Mass and Equilibrium Distribution of TDBP in all compartments.

As the air figure is extremely low, the computer is unable to show this figure on the graph.

CONCENTRATION
(ppm)

TDBP
TRIS(2,3-DIBROMOPROPYL) PHOSPHATE

BPDP
T-BUTYLPHENYLDIPHENYL PHOSPHATE

Figure 5.5.2. Concentration Values of BPDP and TDBP in all compartments.
As the air figure is extremely low, the computer is unable to show this figure on the graph.

BPDP
T-BUTYLPHENYLDIPHENYL PHOSPHATE

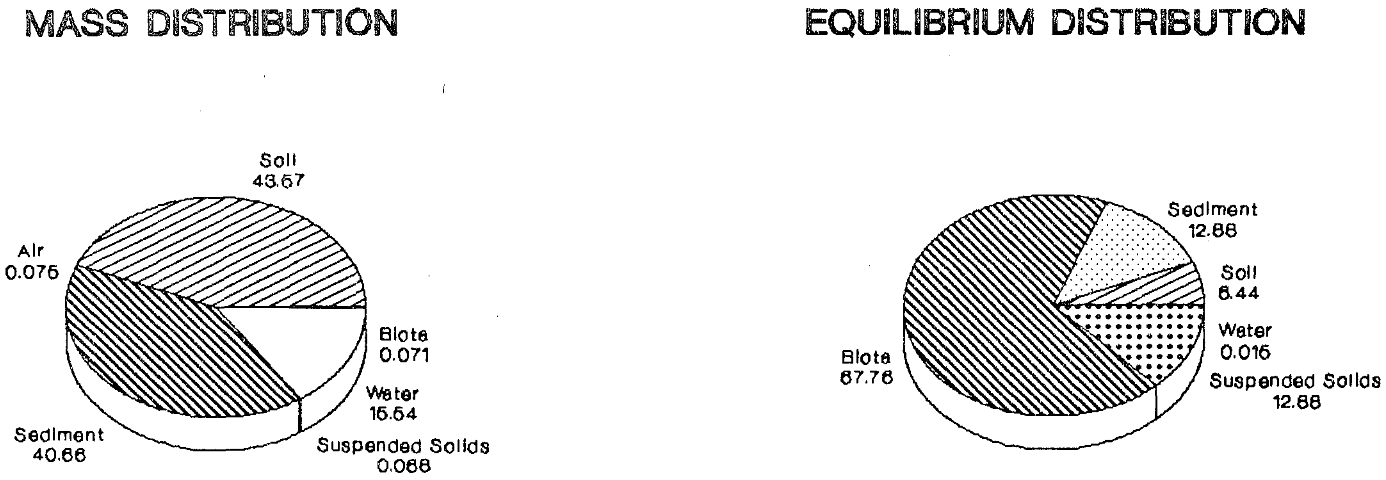


Figure 5.5.3. Mass and Equilibrium Distribution of BPDP in all compartments.
As the air figure is extremely low, the computer is unable to show this figure on the graph.

5.2 CONCLUSION

Mackay Fugacity Model Level I can be used to predict the potential enviromental hazard of chemicals even before the compounds are synthesized. The establishment of regression equations is a useful and convenient method for extending the existing data bases on the distribution of environmentally important pollutants. Depending on the data available, the simpliest verison of Mackay's Models is extended to provide an estimate of the potential enviromental distribution of selected flame retardands under equilibrium conditions.

However, the limitations of Mackay's Level Fugacity Model should be restated. The technique is only applicable to a set of well-defined organic structures. For example, it would be meaningless to attempt an analysis of chemicals such as inorganics, polymers or formulations. The other limitation is that the model is based on the equilibrium situation and says nothing about the kinetics involved in the transfer processes from one medium to another. It presents a picture of the ultimate distribution of a persistent substance in the environment in terms of both relative concentrations and relative masses.

Nevertheless, using the model, it is possible to set priorities and suggest new directions for continuing the investigation of potential problems associated with chemicals that have been or will be introduced into the environment.

Finally, in order to complete the environmental picture and make a hazard assessment, the exposure prediction should be combined with expected use patterns, toxicity and presistence characteristics, such as hydrolysis and photodegradability.

APPENDIX I

Table 3.1. PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL SELECTED FLAME RETARDANTS

COMPOUND	Log S (Mol/l)	Log Kow	Log P (mmHg)
Chloromethane	-0.974 [34] α	0.38 [34] 0.91 [41] α	3.634 σ
Dichloromethane	-0.809 [37] -1.136 [34] α	0.10 [34] 0.33 [34] 1.25 [41] α	2.641 σ
Trichloromethane	-1.179 [37] -1.187 [34] -2.748 [38] -1.163 [40] -1.190 αδ	0.16 [34] 0.03 [34] 1.89 [38] 1.95 [57] 1.95 [41] α	2.110 σ
Tetrachloromethane	-2.284 [38] -2.289 [37] -3.159 [38] -2.283 [36] -2.292 [40] α	1.20 [34] 0.04 [34] 2.73 [38] α 2.64 [57]	1.953 [36] α 1.819 [34] 2.053 [34]
Chloroethane	-1.052 [34, 37] α	0.46 [34] 1.39 [41] α	3.070 σ
1,1-Dichloroethane	-1.301 [40] -1.316 [37] -1.292 [34] -2.393 [40] -1.271 αδ	0.24 [34] α	2.352 [34] α
1,2-Dichloroethane	-1.068 [37, 40] α -1.055 [34] -2.719 [38]	1.45 [55, 56] α 1.42 [38] 0.05 [34]	1.914 [34] α
1,1,1-Trichloroethane	-1.949 [37] -2.268 [34,40] -2.005 αδ	2.47 [55,38] 1.20 [34] 2.17 [41] α	2.093 [34] α

Table 3.1. continued

PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL SELECTED FLAME RETARDANTS			
	Log S (Mol/l)	Log Kow	Log P (mmHg)
1,1,2-Trichloroethane	-1.483 [37] α -2.262 [34] -2.181 [34] -1.480 [34] -1.472 [40]	1.01 [34] α 0.36 [34] 0.04 [34]	1.995 [34] α 1.602 [34] 1.362 [34] 1.482 [58]
1,1,2,2-Tetrachloroethane	-1.749 [34,40] -1.754 [37] α -2.903 [38]	2.39 [55, 56] α 0.02 [34] 2.38 [38]	0.813 [34] α
1,1,1,2-Tetrachloroethane	-2.184 [34, 38] α	0.11 [34] α	1.143 [34] α
Pentachloroethane	-2.607 [37] -2.568 [34] α	0.10 [34] α 2.89 [41]	0.653 [34, 58] α
Hexachloroethane	-3.675 [37, 40] α -4.471 [34]	3.58 [59] 0.05 [34] α 4.14 [47] 3.93 [41]	-0.48 [34] α
1-Chloropropane	-1.494 [37] α	1.89 [41] α	2.537 σ
2-Chloropropane	-1.379 [37] α	1.69 [41] α	2.712 σ
1,3-Dichloropropane	-1.618 [37] -1.623 [40] α	2.28 [41] α	1.229 σ
1-Chorobutane	-2.140 [35] α -2.020 [39]	2.55 [47] 2.39 [35] α	2.007 σ

Table 3.1. continued

PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL SELECTED FLAME RETARDANTS			
	Log S (Mol/l)	**Log Kow**	**Log P (mmHg)**
BPDP 1-Butylphenyldiphenyl	-5.077 [41] α	5.12 [41] α	-6.058 σ
IPDP Isopropylphenyldiphenyl phosphate	-5.224 [41] α	5.30 [41] α	-6.254 σ
DBPP Dibutyl phenyl phosphate	-3.474 [41] α	4.27 [41] α	-3.124 σ
TBP Tributyl phosphate	-2.978 [41] α	4.04 [41] α	-2.610 σ
EHDP 2-Ethylhexyl diphenyl phosphate	-5.280 [41] α	5.72 [59] α	-6.776 σ
TEHP Tris(2-ethylhexyl) phosphate	-2.638 [41] α	4.22 [41] α	-4.674 σ
TBEP Tris(2-butoxyethyl) phosphate	-2.600 [41] α	3.65 [41] α	-5.185 σ
TCEP Tris(2-chloroethyl) phospate	-1.610 [41] α	1.47 [41] α	-3.363 σ
TDBP Tris(2,3-dibromopropyl) phosphate	-5.639 [41] α	4.38 [41] α	-3.742 σ
TDCP Tris(1,3-dichloropropyl) phosphate	-3.634 [41] α	3.74 [41] α	-5.345 σ
TXP Trixylyl phosphate	-5.664 [41] α	5.63 [41] α	-6.020 σ

α : the properties used for the calculations of compartmental distributions.
σ : calculated vapor pressure values
δ : mean values of concentration

Table 3.3. PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL SELECTED FLAME RETARDANTS

COMPOUND	Boiling Point °C/mmH	Molecular Weight
Chloromethane	24.2	50.5
Dichloromethane	40.0	85.0
Trichloromethane	61.7	119.5
Tetrachloromethane	76.5	154.0
Chloroethane	12.3	64.5
1,1-Dichloroethane	57.3	99.0
1,2-Dichloroethane	83.5	99.0
1,1,1-Trichloroethane	74.1	133.5
1,1,2-Trichloroethane	113.8	133.5
1,1,2,2-Tetrachloroethane	146.2	168.0
1,1,1,2-Tetrachloroethane	130.5	168.0
Pentachloroethane	162.0	5
Hexachloroethane	186.0 (777 Atm.)	237.0
1-Chloropropane	46.6	78.5
2-Chloropropane	35.7	78.5
1,3-Dichloropropane	120.4	113.0
1-Chorobutane	78.4	92.5

Ref. [64]

Table 3.3. continued

<table>
<tr><th colspan="3">PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL SELECTED FLAME RETARDANTS</th></tr>
<tr><th>COMPOUND</th><th>Boiling Point °C/mmH</th><th>Molecular Weight</th></tr>
<tr><td>BPDP
1-Butylphenyldiphenyl</td><td>261 / 6</td><td>382.4</td></tr>
<tr><td>IPDP
Isopropylphenyldiphenyl phosphate</td><td>225 / 1</td><td>368.4</td></tr>
<tr><td>DBPP
Dibutyl phenyl phosphate</td><td>200 / 20</td><td>286.3</td></tr>
<tr><td>TBP
Tributyl phosphate</td><td>292 /760</td><td>266.3</td></tr>
<tr><td>EHDP
2-Ethylhexyl diphenyl phosphate</td><td>239 / 1</td><td>362.4</td></tr>
<tr><td>TEHP
Tris(2-ethylhexyl) phosphate</td><td>216 / 5</td><td>434.6</td></tr>
<tr><td>TBEP
Tris(2-butoxyethyl) phosphate</td><td>226 / 4</td><td>398.5</td></tr>
<tr><td>TCEP
Tris(2-chloroethyl) phospate</td><td>214 / 25</td><td>285.5</td></tr>
<tr><td>TDBP
Tris(2,3-dibromopropyl) phosphate</td><td>65 /0.005</td><td>697.7</td></tr>
<tr><td>TDCP
Tris(1,3-dichloropropyl) phosphate</td><td>236 / 5</td><td>430.9</td></tr>
<tr><td>TXP
Trixylyl phosphate</td><td>260 / 4</td><td>410.5</td></tr>
</table>

Ref. [41]

Table 5.1 . Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	AIR	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
Chloromethane	99.94	37.29
Dichloromethane	99.63	6.13
Trichloromethane	99.01	0.95
Tetrachloromethane	99.85	1.90
Chloroethane	99.83	11.03
1,1-Dichloroethane	99.48	10.35
1,2-Dichloroethane	97.76	0.81
1,1,1-Trichloroethane	99.82	3.74
1,1,2-Trichloroethane	99.27	4.12
1,1,2,2-Tetrachloroethane	94.24	0.07
1,1,1,2-Tetrachloroethane	98.97	5.88
Pentachloroethane	98.71	4.73
Hexachloroethane	98.63	4.59
1-Chloropropane	99.79	4.87
2-Chloropropane	99.82	7.24
1,3-Dichloropropane	96.94	0.18
1-Chorobutane	99.84	2.94
Mirex	99.57	6.27E-04

Table 5.1. Continued

	AIR	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
BPDP t-Butylphenydiphenyl phoshate	7.49E-02	8.31E-08
IPDP Isopropylphenyldiphenyl phosphate	5.51E-02	5.57E-08
DBPP Dibutyl phenyl phosphate	34.72E-01	6.73E-06
TBP Tributyl phosphate	42.88E-01	9.99E-06
EHDP 2-Ethylhexyl diphenyl phospate	1.17E-02	9.69E-09
TEHP Tris(2-ethylhexyl) phosphate	1.53E-02	2.99E-08
TBEP Tris(2-butoxyethyl) phosphate	6.43E-03	1.99E-08
TCEP Tris(2-chloroethyl) phosphate	7.70E-02	3.01E-06
TDBP Tris(2,3-dibromopropyl) phosphate	53.62	2.00E-04
TDCP Tris(1,3-dichloropropyl) phosphate	4.56E-02	1.31E-07
TXP Trixylyl phosphate	1.79E-01	1.54E-07

Table 5.2. Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	WATER	
FLAME RETARDANT CHEMICALS	MASS DISTRIBUTION (%)	EQUILIBRIUM DISTRIBUTION (%)
Chloromethane	5.80E-02	18.56
Dichloromethane	3.66E-01	19.31
Trichloromethane	9.72E-01	8.03
Tetrachloromethane	1.44E-01	2.36
Chloroethane	1.63E-01	15.48
1,1-Dichloroethane	5.12E-01	45.72
1,2-Dichloroethane	22.09E-01	15.72
1,1,1-Trichloroethane	1.72E-01	5.55
1,1,2-Trichloroethane	7.21E-01	25.66
1,1,2,2-Tetrachloroethane	55.88E-01	4.02
1,1,1,2-Tetrachloroethane	10.20E-01	51.98
Pentachloroethane	12.88E-01	52.92
Hexachloroethane	13.36E-01	54.52
1-Chloropropane	2.01E-01	8.42
2-Chloropropane	1.75E-01	10.92
1,3-Dichloropropane	29.75E-01	4.82
1-Chorobutane	1.54E-01	3.90
Mirex	4.94E-02	2.67E-04

Table 5.2. Continued

	WATER	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
BPDP t-Butylphenydiphenyl phoshate	15.54	1.48E-02
IPDP Isopropylphenyldiphenyl phosphate	12.81	1.11E-02
DBPP Dibutyl phenyl phosphate	33.62	5.59E-02
TBP Tributyl phosphate	39.84	7.95E-02
EHDP 2-Ethylhexyl diphenyl phospate	7.99	5.64E-03
TEHP Tris(2-ethylhexyl) phosphate	36.26	6.04E-02
TBEP Tris(2-butoxyethyl) phosphate	53.65	1.43E-01
TCEP Tris(2-chloroethyl) phosphate	94.57	31.70E-01
TDBP Tris(2,3-dibromopropyl) phosphate	14.73	4.72E-02
TDCP Tris(1,3-dichloropropyl) phosphate	50.92	1.25E-01
TXP Trixylyl phosphate	8.85	6.53E-03

Table 5.3. Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

FLAME RETARDANT CHEMICALS	BIOTA	
	MASS DISTRIBUTION (%)	EQUILIBRIUM DISTRIBUTION (%)
Chloromethane	2.26E-08	7.22
Dichloromethane	3.11E-07	16.43
Trichloromethane	4.14E-06	34.24
Tetrachloromethane	3.34E-06	54.75
Chloroethane	1.92E-07	18.19
1,1-Dichloroethane	4.26E-08	3.80
1,2-Dichloroethane	3.08E-06	21.95
1,1,1-Trichloroethane	1.22E-06	39.32
1,1,2-Trichloroethane	3.53E-07	12.57
1,1,2,2-Tetrachloroethane	6.56E-05	47.24
1,1,1,2-Tetrachloroethane	6.29E-08	3.20
Pentachloroethane	7.76E-08	3.19
Hexachloroethane	7.33E-08	2.93
1-Chloropropane	7.48E-07	31.31
2-Chloropropane	4.11E-07	25.59
1,3-Dichloropropane	2.71E-05	43.97
1-Chorobutane	1.81E-06	45.88
Mirex	1.84E-02	99.21

Table 5.3. Continued

	BIOTA	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
BPDP t-Butylphenydiphenyl phosphate	7.12E-02	67.76
IPDP Isopropylphenyldiphenyl phosphate	8.05E-02	69.69
DBPP Dibutyl phenyl phosphate	3.48E-02	57.91
TBP Tributyl phosphate	2.76E-02	55.09
EHDP 2-Ethylhexyl diphenyl phospate	1.04E-01	73.91
TEHP Tris(2-ethylhexyl) phosphate	3.44E-02	57.30
TBEP Tris(2-butoxyethyl) phosphate	1.89E-02	50.27
TCEP Tris(2-chloroethyl) phosphate	7.38E-04	24.75
TDBP Tris(2,3-dibromopropyl) phosphate	1.85E-02	59.24
TDCP Tris(1,3-dichloropropyl) phosphate	2.08E-02	51.36
TXP Trixylyl phosphate	9.89E-02	73.04

Table 5.4. Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	SOIL	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
Chloromethane	1.48E-04	7.38
Dichloromethane	1.41E-03	11.62
Trichloromethane	8.84E-03	11.35
Tetrachloromethane	3.22E-03	8.19
Chloroethane	7.50E-04	11.05
1,1-Dichloroethane	5.78E-04	8.02
1,2-Dichloroethane	1.11E-02	12.30
1,1,1-Trichloroethane	2.05E-03	10.27
1,1,2-Trichloroethane	2.08E-03	11.53
1,1,2,2-Tetrachloroethane	8.69E-02	9.73
1,1,1,2-Tetrachloroethane	9.82E-04	7.78
Pentachloroethane	1.22E-03	7.83
Hexachloroethane	1.22E-03	7.58
1-Chloropropane	1.70E-03	11.08
2-Chloropropane	1.16E-03	11.24
1,3-Dichloropropane	4.04E-02	10.20
1-Chorobutane	2.24E-03	9.45
Mirex	1.86E-01	0.15

Table 5.4. Continued

	SOIL	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRUBITION (%)**
BPDP t-Butylphenydiphenyl phoshate	43.57	6.44
IPDP Isopropylphenyldiphenyl phosphate	44.99	6.06
DBPP Dibutyl phenyl phosphate	32.49	8.40
TBP Tributyl phosphate	28.86	8.96
EHDP 2-Ethylhexyl diphenyl phospate	47.49	5.21
TEHP Tris(2-ethylhexyl) phosphate	32.91	8.52
TBEP Tris(2-butoxyethyl) phosphate	23.93	9.92
TCEP Tris(2-chloroethyl) phosphate	2.76	14.41
TDBP Tris(2,3-dibromopropyl) phosphate	16.34	8.14
TDCP Tris(1,3-dichloropropyl) phosphate	25.33	9.70
TXP Trixylyl phosphate	46.96	5.39

Table 5.5. Results of Compartmental Distrubition Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	SUSPENDED SOLIDS	
FLAME RETARDANT CHEMICALS	MASS DISTRIBUTION (%)	EQUILIBRIUM DISTRUBITION (%)
Chloromethane	2.31E-07	14.76
Dichloromethane	2.20E-06	23.24
Trichloromethane	1.37E-05	22.71
Tetrachloromethane	5.00E-06	16.39
Chloroethane	1.16E-06	22.11
1,1-Dichloroethane	8.99E-07	16.05
1,2-Dichloroethane	1.73E-05	24.60
1,1,1-Trichloroethane	3.19E-06	20.55
1,1,2-Trichloroethane	3.24E-06	23.05
1,1,2,2-Tetrachloroethane	1.35E-06	19.46
1,1,1,2-Tetrachloroethane	1.53E-06	15.57
Pentachloroethane	1.90E-06	15.66
Hexachloroethane	1.89E-06	15.18
1-Chloropropane	2.65E-06	22.16
2-Chloropropane	1.81E-06	22.49
1,3-Dichloropropane	6.29E-05	20.40
1-Chorobutane	3.73E-06	18.90
Mirex	2.90E-04	0.31

Table 5.5. Continued

	SUSPENDED SOLIDS	
FLAME RETARDANT CHEMICALS	MASS DISTRIBUTION (%)	EQUILIBRIUM DISTRIBUTION (%)
BPDP t-Butylphenydiphenyl phoshate	6.78E-02	12.88
IPDP Isopropylphenyldiphenyl phosphate	6.99E-02	12.12
DBPP Dibutyl phenyl phosphate	5.05E-02	16.81
TBP Tributyl phosphate	4.48E-02	17.93
EHDP 2-Ethylhexyl diphenyl phospate	7.38E-02	10.43
TEHP Tris(2-ethylhexyl) phosphate	5.12E-02	17.05
TBEP Tris(2-butoxyethyl) phosphate	3.72E-02	19.83
TCEP Tris(2-chloroethyl) phosphate	4.29E-03	28.82
TDBP Tris(2,3-dibromopropyl) phosphate	2.54E-02	16.28
TDCP Tris(1,3-dichloropropyl) phosphate	3.94E-02	19.40
TXP Trixylyl phosphate	7.30E-02	10.78

Table 5.7. Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	AIR	WATER
FLAME RETARDANT CHEMICALS	CONCENTRATION (ppm)	CONCENTRATION (ppm)
Chloromethane	7.06E-04	4.18E-07
Dichloromethane	1.18E-03	4.44E-06
Trichloromethane	1.65E-03	1.66E-05
Tetrachloromethane	2.15E-03	3.17E-06
Chloroethane	9.02E-04	1.50E-06
1,1-Dichloroethane	1.38E-03	7.25E-06
1,2-Dichloroethane	1.35E-03	3.12E-05
1,1,1-Trichloroethane	1.86E-03	3.29E-06
1,1,2-Trichloroethane	1.85E-03	1.37E-05
1,1,2,2-Tetrachloroethane	2.21E-03	1.34E-04
1,1,1,2-Tetrachloroethane	2.32E-03	2.44E-05
Pentachloroethane	2.80E-03	3.72E-05
Hexachloroethane	3.26E-03	4.61E-05
1-Chloropropane	1.09E-03	2.26E-06
2-Chloropropane	1.10E-03	1.97E-06
1,3-Dichloropropane	1.53E-03	4.80E-05
1-Chorobutane	1.29E-03	2.04E-06
Mirex	7.13E-03	3.61E-06

Table 5.6. Continued

	SEDIMENT	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
BPDP t-Butylphenydiphenyl phoshate	40.66	12.88
IPDP Isopropylphenyldiphenyl phosphate	41.99	12.12
DBPP Dibutyl phenyl phosphate	30.32	16.81
TBP Tributyl phosphate	26.93	17.93
EHDP 2-Ethylhexyl diphenyl phosphate	44.32	10.43
TEHP Tris(2-ethylhexyl) phosphate	30.72	17.05
TBEP Tris(2-butoxyethyl) phosphate	22.34	19.83
TCEP Tris(2-chloroethyl) phosphate	2.57	28.82
TDBP Tris(2,3-dibromopropyl) phosphate	15.25	16.28
TDCP Tris(1,3-dichloropropyl) phosphate	23.64	19.40
TXP Trixylyl phosphate	43.83	10.78

Table 5.6. Results of Compartmental Distrubition Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	SEDIMENT	
FLAME RETARDANT CHEMICALS	**MASS DISTRIBUTION (%)**	**EQUILIBRIUM DISTRIBUTION (%)**
Chloromethane	1.38E-04	14.76
Dichloromethane	1.32E-03	23.24
Trichloromethane	8.25E-03	22.71
Tetrachloromethane	3.00E-03	16.39
Chloroethane	7.00E-04	22.11
1,1-Dichloroethane	5.39E-04	16.05
1,2-Dichloroethane	1.04E-02	24.60
1,1,1-Trichloroethane	1.92E-03	20.55
1,1,2-Trichloroethane	1.94E-03	23.05
1,1,2,2-Tetrachloroethane	8.11E-02	19.46
1,1,1,2-Tetrachloroethane	9.16E-04	15.57
Pentachloroethane	1.14E-03	15.66
Hexachloroethane	1.14E-03	15.18
1-Chloropropane	1.59E-03	22.16
2-Chloropropane	1.09E-03	22.49
1,3-Dichloropropane	3.78E-02	20.40
1-Chorobutane	2.24E-03	18.90
Mirex	1.74E-01	0.31

Table 5.7. Continued

	AIR	WATER
FLAME RETARDANT CHEMICALS	**CONCENTRATION (ppm)**	**CONCENTRATION (ppm)**
BPDP t-Butylphenyldiphenyl phosphate	4.01E-06	8.49E-04
IPDP Isopropylphenyldiphenyl phosphate	2.84E-06	6.74E-04
DBPP Dibutyl phenyl phosphate	1.39E-04	1.37E-03
TBP Tributyl phosphate	1.60E-04	1.51E-03
EHDP 2-Ethylhexyl diphenyl phosphate	5.97E-07	4.14E-04
TEHP Tris(2-ethylhexyl) phosphate	9.37E-07	2.25E-03
TBEP Tris(2-butoxyethyl) phosphate	3.59E-07	3.05E-03
TCEP Tris(2-chloroethyl) phosphate	3.08E-06	3.86E-03
TDBP Tris(2,3-dibromopropyl) phosphate	5.24E-03	1.47E-03
TDCP Tris(1,3-dichloropropyl) phosphate	2.76E-06	3.13E-03
TXP Trixylyl phosphate	1.03E-05	5.19E-04

Table 5.8. Results of Compartmental Distribution Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	BIOTA	**SOIL**
FLAME RETARDANT CHEMICALS	**CONCENTRATION (ppm)**	**CONCENTRATION (ppm)**
Chloromethane	1.63E-07	1.11E-07
Dichloromethane	3.78E-06	1.78E-06
Trichloromethane	7.07E-05	1.56E-05
Tetrachloromethane	7.34E-05	7.33E-06
Chloroethane	1.77E-06	7.17E-07
1,1-Dichloroethane	6.03E-07	8.48E-07
1,2-Dichloroethane	4.36E-05	1.63E-05
1,1,1-Trichloroethane	2.33E-05	4.06E-06
1,1,2-Trichloroethane	6.73E-06	4.11E-06
1,1,2,2-Tetrachloroethane	1.57E-03	2.16E-04
1,1,1,2-Tetrachloroethane	1.51E-06	2.44E-06
Pentachloroethane	2.24E-06	3.67E-06
Hexachloroethane	2.47E-06	4.28E-06
1-Chloropropane	8.39E-06	1.98E-06
2-Chloropropane	4.61E-06	1.35E-06
1,3-Dichloropropane	4.38E-04	6.77E-05
1-Chorobutane	2.39E-05	3.29E-06
Mirex	13.41E-01	1.41E-03

Table 5.8. Continued

	BIOTA	SOIL
FLAME RETARDANT CHEMICALS	**CONCENTRATION (ppm)**	**CONCENTRATION (ppm)**
BPDP t-Butylphenydiphenyl phopshate	3.89	0.24
IPDP Isopropylphenyldi-phenyl phosphate	4.23	0.24
DBPP Dibutyl phenyl phosphate	1.42	0.14
TBP Tributyl phosphate	1.05	0.11
EHDP 2-Ethylhexyl diphenyl phosphate	5.42	0.25
TEHP Tris(2-ethylhexyl) phosphate	2.14	0.21
TBEP Tris(2-butoxyethyl) phosphate	1.07	0.14
TCEP Tris(2-chloroethyl) phosphate	0.03	0.01
TDBP Tris(2,3-dibromopropyl) phosphate	1.84	0.17
TDCP Tris(1,3-dichloropropyl) phosphate	1.28	0.16
TXP Trixylyl phosphate	5.80	0.28

Table 5.9. Results of Compartmental Distrubition Values for Selected Flame Retardants Computed by Experimental Input Data, Using Mackay Fugacity Model I.

	SUSPENDED SOLIDS	SEDIMENT
FLAME RETARDANT CHEMICALS	CONCENTRATION (ppm)	CONCENTRATION (ppm)
Chloromethane	2.22E-07	2.22E-07
Dichloromethane	3.56E-06	3.56E-06
Trichloromethane	3.12E-05	3.12E-05
Tetrachloromethane	1.46E-05	1.46E-05
Chloroethane	1.43E-06	1.43E-06
1,1-Dichloroethane	1.69E-06	1.69E-06
1,2-Dichloroethane	3.26E-05	3.26E-05
1,1,1-Trichloroethane	8.11E-06	8.11E-06
1,1,2-Trichloroethane	8.22E-06	8.22E-06
1,1,2,2-Tetrachloroethane	4.32E-04	4.32E-04
1,1,1,2-Tetrachloroethane	4.88E-06	4.88E-06
Pentachloroethane	7.35E-06	7.35E-06
Hexachloroethane	8.55E-06	8.55E-06
1-Chloropropane	3.96E-06	3.96E-06
2-Chloropropane	2.70E-06	2.70E-06
1,3-Dichloropropane	1.35E-04	1.35E-04
1-Chorobutane	6.58E-06	6.58E-06
Mirex	2.83E-01	2.83E-01

Table 5.9. Continued

	SUSPENDED SOLIDS	SEDIMENT
FLAME RETARDANT CHEMICALS	**CONCENTRATION (ppm)**	**CONCENTRATION (ppm)**
BPDP t-Butylphenydiphenyl phoshate	0.49	0.49
IPDP Isopropylphenyldiphenyl phosphate	0.49	0.49
DBPP Dibutyl phenyl phosphate	0.27	0.27
TBP Tributyl phosphate	0.22	0.22
EHDP 2-Ethylhexyl diphenyl phospate	0.51	0.51
TEHP Tris(2-ethylhexyl) phosphate	0.42	0.42
TBEP Tris(2-butoxyethyl) phosphate	0.28	0.28
TCEP Tris(2-chloroethyl) phosphate	0.02	0.02
TDBP Tris(2,3-dibromopropyl) phosphate	0.33	0.33
TDCP Tris(1,3-dichloropropyl) phosphate	0.32	0.32
TXP Trixylyl phosphate	0.57	0.57

APPENDIX II

APPENDIX II

Computer Programs

```
12 REM
14 REM    MACKAY LEVEL 1 FUGACITY MODEL
15 REM
16 REM LOAD "CLORINATED ALKANES", 8
17 REM
140 DIM D(6)
180 DIM P(6)
190 DIM Z(6)
200 DIM M(6)
210 DIM E(6)
220 DIM A(6)
230 DIM C(6)
240 DIM T$(6)
250 T$(1) = "******AIR"
260 T$(2) = "*****SOIL"
270 T$(3) = "****WATER"
280 T$(4) = "****BIOTA"
290 T$ (5) = "S. SOLIDS"
300 T$(6) = "*SEDIMENT"
310 REM----PARAMETERS---------------
320 V(1) = 6E+09
330 V(2)= 45000!
340 V(3) = 7000000!
350 V(4) = 7
360 V(5) = 35
370 V(6) = 21000
380 D(1) = .00119
390 D(2) = 1.5
400 D(3) = 1
410 D(4) = 1
420 D(5) = 1.5
430 D(6) = 1.5
440 P(2) = 2
450 P(5) = 4
460 P(6) = 4
470 T = 298
480 R = 8.314
490 REM-----------------VARIABLES------------
540 INPUT "NAME OF CHEMICAL: ",C$
560 INPUT "MOLECULAR WEIGHT: ",M
580 INPUT "LOGP: ",P8
590 INPUT "LOGS:", C8
700 INPUT "LOGKOW: ", L7
701 REM------CONVERSION-------------
702 P5 = (10^P8)/.0075
703 C5 = (10^C8)*1000
704 H=P5/C5
705 LPRINT "NAME OF CHEMICAL:"C$
706 LPRINT
707 LPRINT "HENRY CONSTANT (Pa m3/mol) :"H
708 LPRINT
710 REM-----FUG CAP CONSTANT
```

```
711 LPRINT "MOLECULAR WEIGHT:"M
712 LPRINT
713 LPRINT "LOGP:"P8
714 LPRINT
715 LPRINT"LOGS:"C8
716 LPRINT
717 LPRINT "LOGKOW:"L7
718 LPRINT
721 Z(1) = 1/(R*T)
740 Z(3) = 1/H
750 K8 = 10^(L7-1.32)
760 Z(4) = K8*D(4)/H
770 K2 = 10^(L7+.64)
780 Z(5) = K2*D(5)*P(5)/H/100
790 K3 = 10^(.53*L7+.64)
800 Z(2) = K3*D(2)*P(2)/H/100
810 K9 = 10^(.53*L7+.64)
820 Z(6) = K9*D(6)*P(6)/H/100
821 LPRINT "Z1 = "Z(1)
822 LPRINT "Z2 = "Z(2)
823 LPRINT "Z3 = "Z(3)
824 LPRINT "Z4 = "Z(4)
825 LPRINT "Z5 = "Z(5)
826 LPRINT "Z6 = "Z(6)
830 REM---DIST VALUE-----------------
840 S8 = 0
850 S5 = 0
860 FOR I = 1 TO 6
870 S8 = S8+Z(I)
880 S5 = S5+Z(I)*V(I)
890 NEXT I
900 F = 100/S5
910 FOR I = 1 TO 6
920 M(I) = Z(I)*V(I)/S5
930 E(I) = Z(I)/S8
940 A(I) = F*Z(I)*V(I)
950 C(I) = A(I)/V(I)*M/D(I)
960 NEXT I
980 REM PRINT DIST VALUES------------
990 LPRINT
1000 LPRINT SPC(9)"MASS PART", "EQ PART", "AMOUNT","CONC"
1020 FOR I = 1 TO 6
1025 LPRINT T$ (I) M(I) E(I) A(I) C(I)
1026 LPRINT
1040 NEXT I
1050 REM REPEAT PROCEDURE FOR NEW CHEM
1110 INPUT AB
1120 IF AB = 1 THEN 490
1121 IF AB = 0 THEN 1130
1130 END
```

```
12 REM------------------------------------
14 REM---MACKAY LEVEL 1 FUGACITY MODEL
15 REM------------------------------------
16 REM---LOAD "ORGANO PHOSPHATES", 8
17 REM------------------------------------
140 DIM D(6)
180 DIM P(6)
190 DIM Z(6)
200 DIM M(6)
210 DIM E(6)
220 DIM A(6)
230 DIM C(6)
240 DIM T$(6)
250 T$(1) = "******AIR"
260 T$(2) = "*****SOIL"
270 T$(3) = "****WATER"
280 T$(4) = "****BIOTA"
290 T$(5) = "S. SOLIDS"
300 T$(6) = "*SEDIMENT"
310 REM---PARAMETERS-------------
320 V(1) = 6E+09
330 V(2) = 45000!
340 V(3) = 7000000!
350 V(4) = 7
360 V(5) = 35
370 V(6) = 21000
380 D(1) = .00119
390 D(2) = 1.5
400 D(3) = 1
410 D(4) = 1
420 D(5) = 1.5
430 D(6) = 1.5
440 P(2) = 2
450 P(5) = 4
460 P(6) = 4
470 T = 298
480 R = 8.314
490 REM-----------VARIABLES------------
540 INPUT "NAME OF CHEMICAL:", C$
560 INPUT "MOLECULAR WEIGHT:",M
580 INPUT "LOGP:", P8
590 INPUT "LOGS:", C8
700 INPUT "LOGKOW: ",L7
701 REM-----CONVERSION-----------------
702 P5= (10^P8)/.0075
703 C5 = (10^C8)*1000
704 H=P5/C5
705 LPRINT "NAME OF CHEMICAL :"C$
706 LPRINT
707 LPRINT "HENRY CONSTANT (Pa m3/mol):"H
708 LPRINT
```

```
710 REM----FUG CAP CONSTANT---------
711 LPRINT "MOLECULAR WEIGHT:"M
712 LPRINT
713 LPRINT "LOGP:"P8
714 LPRINT
715 LPRINT "LOGS:"C8
716 LPRINT
717 LPRINT "LOGKOW:"L7
718 LPRINT
720 Z(1)=1/(R*T)
740 Z(3) = 1/H
750 K8 = 10^((.76*L7)-.23)
760 Z(4) = K8*D(4)/H
770 K2 = 10^(1.377+(.544*L7))
780 Z(5) = K2* D(5)*P(5)/H/100
790 K3 = 10^(1.377 + (.544*L7))
800 Z(2) = K3*D(2)*P(2)/H/100
810 K9 = 10^(1.377 + (.544 *L7))
820 Z(6) = K9*D(6)*P(6)/H/100
821 LPRINT "Z1 = "Z(1)
822 LPRINT "Z2 ="Z(2)
823 LPRINT "Z3 ="Z(3)
824 LPRINT "Z4 = "Z(4)
825 LPRINT "Z5="Z(5)
826 LPRINT "Z6="Z(6)
830 REM---DIST VALUE------------
840 S8 = 0
850 S5 = 0
860 FOR I = 1 TO 6
870 S8 = S8+Z(I)
880 S5 = S5+Z(I)*V(I)
890 NEXT I
900 F = 100/S5
910 FOR I = 1 TO 6
920 M(I) = Z(I)*V(I)/S5
930 E(I) = Z(I)/S8
940 A(I) = F*Z(I)*V(I)
950 C(I) = A(I)/V(I)*M/D(I)
960 NEXT I
980 REM PRINT DIST VALUES
990 LPRINT
1000 LPRINT SPC(9) "MASS PART", "EQ PART", "AMOUNT", "CONC"
1020 FOR I = 1 TO 6
1025 LPRINT T$(I) E(I) A(I) C(I)
1026 LPRINT
1040 NEXT I
1050 REM REPEAT PROCEDURE FOR NEW CHEM
1110 INPUT AB
1120 IF AB=1 THEN 490
1121 IF AB=0 THEN 1130
1130 END
```

REFERENCES

REFERENCES

1. Neely, W.B.; Blau, G.E; "Environmental Exposure From Chemicals".

2. Kirk-Othmer; Encyclopedia of Chemical Technology Vol.10, 348-444

3. Morita, Y.; Hagiwara, M.; "Synthesis of Brominated Acenaphthylenes and their Flame-Retardant Effects on Ethylene-Propylene-Diene Terpolymer", J. of Applied Polymer Science, Vol. 27, 3329-3339 (1982)

4. Bednas, M.E; Day, M.; Sander, R.; Wiles, D.M; "Combustion and Pyrolysis of Poly(ethylene Terephthalate). I. The Role of Flame Retardants on Products of Pyrolysis" , J. of Appied Polymer Science Vol. 26, 277-289 (1981)

5. Khanna, Y.P.; Pearce, E.M.; "Aromatic Polyamides. III.Mechanistic Studies on the Role of Substituent Chlorine in Flame Retarding Aromatic Polyamides", J. of Polymer Science: Polymer Chemistry Edition, Vol. 19, 2835-2840 (1981)

6. Jha, N.K.; Bajaj, P.; Mısra, A.C.; Maurya, P.L.; "Flame Retardation of Polypropylene: Effect of Organoantimony Compounds on the Flammability and Thermal Behavior", J. of Applied Polymer Science Vol. 32, 4393-4403 (1986)

7. Bajaj, P.; Jha, N.K.; Maurya, P.L.; Mısra, A.C.; "Flame Retardation of Polypropylene: Effect of Organoantimony Compounds on the Structural and Mechanical Properties.", J. of Applied Polymer Science Vol. 34, 1785-1801 (1987)

8. Kroenke, W.J.; "Melaminium Molybdate Smoke and Fire Retarders for Poly (vinyl chloride)" , J. of Applied Polymer Science, Vol. 32, 4155-4168 (1986).

9. Yang C.P.; Lee T.W.; "Synthesis and Properties of 4-Hydroxy-2,3,5,6-Tetrabromebenzyl Phosphonates and Effects of Their Flame Retardance on Impact Polystryrene." , J. of Applied Polymer Science Vol. 32, 30053025 (1986)

10. Ravey, M.; "The Examination of Bromine-Containing Fire Retardants in Unsaturated Polyester Resins by Means of Pyrolysis Residue Analysis.", J. of. Polymer Science, Poly. Chem. Edition, Vol. 21, 375-384 (1983)

11. Hutzinger, O.; Sundström G.; Chemosphere Vol. 1, 3 (1976).

12. Norström, A.; Anderson, K.; Rappe, C.; "Major Components of some Brominated Aromatics Used as Flame Retardants", Chemosphere N.4, 255-261, (1976).

13. Mattsson, P.E.; Norström, A.; Rappe,C.; "Identification of the Flame Retardant Pentabromotoluene in Sewage Sludge"; J. of Chromatography, No. 111 209-213, (1975).

14. Kubiczak, G.A.; Oesch, F.; Borlakoglu, J.T.; Kunz, H.; Robertson, L.W.; "A unique Approach to the Synthesis of 2,3,4,5-Substituted Polybrominated Biphenyls: Quantitation in Fire Master FF-1 and Fire Master BP-6" , J. of Agriculture and Food Chemistry., Vol. 37, 1160-1164 (1989)

15. "Feed Contaminant in Farmers' Blood", Feb. 24, 1975 C&EN P.7.

16. Robertson, L.W.; Parkinson, A.; Bandiera, S.; Lambert, I.; Merrill, J.; Safe, S. H., " PCB$_s$ and PBB$_s$: Biologic and Toxic Effects on C 57 BL/6j and DBA/2j Inbred Mice", Toxicology, Vol. 31, 191-206, (1984).

17. Höfler, F.; Melzer, H.; Möckel, H.J.; Robertson, L.W.; Anklam, E.," Relationship between Liquid and Gas Chromatographic Retention Behavior and Calculated Molecular Surface Area of Selected Polyhalogenated Biphenyls" , J. of Agriculture and Food Chemistry., Vol. 36, 961-965, (1988).

18. Robertson, L.W; Safe, S.H.; Parkinson, A.; Pellizzari, E.; Pochini, C.; Mulling, M.D.; "Synthesis and Identification of Highly Toxic Polybrominated Biphenyls in the Fire Retardant Fire Master BP-6" J. of Agriculture and Food Chemistry Vol. 32, 1107-1111, (1984)

19. Kohli, J.; Safe, S.; "The Metabolism of Brominated Aromatic Compounds", Chemosphere, No.6, 433-437, (1976).

20. Mey-Marom, A.; Rajbenbach, L.A.; "Flame Retardance in Polyester Fabric Radiolytically Grafted with Bromostyrene." , J. of Applied Polymer Science, Vol. 28, 2411-2424, (1983)

21. Laham, S.; Potvin, M.; " Microdetermination of Dichloromethane in Blood with a Syringeless Gas Chromatographic Injection System." , Chemosphere, No. 6, 403-411, (1976).

22. Zitko, V.; "The Uptake and Excretion of Mirex and Dechloranes by Juvenile Atlantic Salmon" , Chemosphere Vol. 9, 73-76, (1980).

23. Lawler, T.E.; Drews, M.J.; Barker, R.H.; "Pyrolysis and Combustion of Cellulose. VIII. Thermally Initiated Reactions of Phosphonomethyl Amide Flame Retardants." J. of Applied Polymer Science, Vol. 30,2263-2277, (1985).

24. Muir, D.C.G.; Yarechewski, A.L.; Grift, N.P.; "Biodegradation of Four Triaryl/alkyl Phosphate Esters in Sediment under Various Temperature and Redox Conditions", Toxicological and Environmental Chemistry, Vol. 18, 269-286, (1989).

25. Muir, D.C.G.; Grift, N.P.; Lockhart, W.L.; "Comparison of Laboratory and Field Results for Prediction of the Environmental Behavior of Phosphate Esters", Environmental Toxicology and Chemistry, Vol. 1, 113-119, (1982).

26. Bellet,E.M.; Casida,J.E.; "Bicyclic Phosphorus Esters: High Toxicity without Cholinesterase Inhibition", Science, Vol.182,1135-1136, 14 December 1973.

27. Gold,M.D.; Blum,A.; Ames,B.N., "Another Flame Retardant, Tris-(1,3-Dichloro-2-Propyl)- Phosphate, and Its Expected Metabolites are Mutagens", Science, Vol.200, 785-787, 19 May 1978.

28. McCoy, E.C.; Gutter,B.; Rosenkranz,H.S.; "Tris (2,3-Dibromopropyl) Phosphate: Mutagenicity of a widely used Flame Retardant", Science, Vol.195, 76-78, 7 January 1977.

29. Soderlund,E.J.; Dybing,E.; Holme,J.A.; Hongslo,J.K.; Rivedal.E.; Sanner.T.; Nelson,S.D., "Comparative Genotoxicity and Nephrotoxicity Studies of the Two Halogenated Flame Retardants Tris (1,3-Dichloro-2-Propyl) Phosphate and Tris (2,3-Dibromoproyl) phosphate", Acta Pharmacol, et toxicology Vol.56, 20-29, (1985)

30. Nakamura,A.; Tateno,N.; Kojima,S.; Kaniwa,M.; Kawamura,T., "The Mutagenicity of Halogenated Alkanols and Their Phosphoric Acid Esters for Salmonella typhimurium", Mutation Research, Vol.66, 373-380, (1979).

31. Nakamura,A.; Kojima,S.; Kaniwa M., "Quantitative Gas Chromatographic Determination of Tris(2,3-Dibromoproyl) Phosphate in the 10-ng Range by Using a 0.8-mm I.D. Column Packed with a High Liquid Loaded Support", J. of Chromatography Vol. 196, 133-141, (1980)

32. Nakamura,A.; Tateno,N.; Iwata,T.; Kojima,S.; Kaniwa,M.; Kawamura,T., "Mutagenicity of bis-and mono(2,3-dibromopropyl) phosphate, and their salts used as Flame Retardants, in the Salmonella / Microsome System", Mutation Research, Vol.117, 1-8, (1983).

33. Neely,W.B., "Organizing Data For Environmental Studies", Environmental Toxicology and Chemistry, Vol.1, 259-266, (1982).

34. Dilling,W.L., "Interphase Transfer Processes. II. Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and Propylene from Dilute Aqueous Solutions comparisons with Theoretical Predictions.", Environmental Science and Technology Vol.11, 405-409, (1977).

35. Tewari,Y.B.; Miller,M.M.; Wasik,S.P.; Martire,D.E., "Aqueous Solubility and Octanol/Water Partition Coefficient of Organic Compounds at 25.0C", J.Chem. Eng. Data, Vol.27, 451-454, (1982).

36. Mackay,D.; Veun,A.T.K.; "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water", Environmental Science and Technology Vol. 17, 211-217, (1983).

37. Nirmalakhandan, N.N..; Speece, R.E.; "Prediction of Aqueous Solubility of Organic Chemicals Based on molecular structrue", Environmental Science and Tehcnology Vol.22, 328-337, (1988)

38. Arbuckle,W.B., "Estimating Activity Coefficients for use in Calculating Environmental Parameters", Environmental Sciences Technology Vol.17, 537-542 (1983)

39. Miller,M.M.; Wasik,S.P.; "Relationships between Octanol-Water Partition Coefficient and Aqueous Solubility", Environmental Science Technology, Vol.19 No.6, 522-529, (1985).

40. Jeffers,P.M.; Ward,L.M.; Woytowitch,L.M.; Wolfe,N.L., "Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes, and Propanes", Environmental Science Technology Vol.23, 965-969, (1989)

41. Muir,D.C.G.; "Phosphate Estery", The Handbook of Environmental Chemistry, Vol.3/ Part C (1984).

42. Mallhot,H.; Peters,R.H., "Empirical Relationships between the 1- Octanol/Water Partition Coefficient and Nine Physicochemical Properties", Environmental Science Technology Vol.22, 1479-1488, (1988) and the Supplemantary Material.

43. Lyman,W.J.; Reehl,W.F., Rosenblatt,D.H.; Handbook of Chemical Property Estimation Methods", American Chemical Society, Washington D.C., (1990).

44. Chiou,C.T.; Schemedding,D.W.; Manes, M.; "Partitioning of Organic Compounds in Octanol-Water Systems", Environmental Science Technology, Vol.16, 4-10, (1982).

45. Kamlet,J.M.; Doherty,R.M.; Carr,P.W.; Mackay,D.; Abraham,H.M.; Taft,R.W.; "Linear Solvation Energy Relationships", Environmental Science Technology Vol.22, 503-509, (1988).

46. Sabljic,A.; "Predictions of the Nature and Strength of Soil Sorption of Organic Pollutants by Molecular Topology", J.Agriculture, Food. Chem., Vol.32, 243-246 (1984)

47. Chiou,C.T., "Partition Coefficients of Organic Compounds in Lipid-Water Systems and Correlations with Fish Bioconcentration Factors", Environmental Science Technology Vol.19, 57-62. (1985).

48. Hushon,J.M.; Klein,A.W.; Stratchan,W.J.M., Schmidt-Bleek,F.; "Use of OECD Premarket Data in Environmental Exposure Analysis for New Chemicals", Chemosphere, Vol.12, 887-911, (1983)

49. Frische,R.; Klöpffer,W., Schönborn,W., "Bewertung von Organish-Chemishen Stoffen und Produkten in bezug auf ihr Umwelt verhalten-chemische, biologische und wirt-schaffliche Aspekte. (1979) Battelle, Institut e.v. Frankfurt, Germany.

50. Schmidt.B.F.; Haberland,W.; Klein, A.W.; Caroli,S.; "Steps Towards Environmental Hazard Assessment of New Chemicals.", Chemosphere, Vol.11, 383-412, (1982).

51. Neely, W.B., "A preliminary Assessment of the Environmental Exposure to be Expected from the Addition of a Chemical to a Simulated Aquatic System", International Journal of Environmental Studies, Vol.13, 101-108, (1979).

52. Neely,W.B., "Estimating Rate Constants for the Uptake and Clearance of Chemicals by Fish", Environmental Science and Technology, Vol.13, 1506-1510, (1979).

53. Mackay,D., "Finding Fugacity Feasible", Environmental Science and Technology, Vol.13, 1218-1223, (1979).

54. Mackay,D., Paterson,S., "Fugacity Revisited", Environmental Science and Technology Vol.16 654A-660A, (1982).

55. Karickhoff, S.W.; "Semi-Empricial Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Solids", Chemosphere, Vol.10, 833-846 (1981).

56. Sabijic, A., "On the Prediction of Soil Sorption Coefficients of Organic Polluttants from Molecular Structure: Application of Molecular Topology Model", Environmental Science and Technology Vol. 21, 358-368 (1987).

57. Mackay, D.J "Correlation of Bioconcentration Factors", Environmental Science and Technology, Vol. 16, 274-278, (1982)

58. Mackay, D.J "Dobra, A.; Chan, D.W.; Shiu, W.Y.; "Vapor Pressure Correlations for Low Volatility Environmental Chemicals", Environmental Science and Technology, Vol. 16, 645-649 (1982).

59. Thomann, R.V., "Bioaccumulation Model of Organic Chemical Distribution in Aquatic Food Chains, Environmental Science and Technology Vol.23, 699-707, (1989)

60. Briggs, G.G.; "Theoretical and Experimental Relationships Between Soil Sorption, Octonol-Water Partition Coefficients, Water Solubilities, Bioconcentration Factors, and Parachor", J.Agric. Food. Chem. Vol. 29, 1050-1059, (1981).

61. Neely, W.B., "Chemicals in the Environment, Distribution, Transport, Fate Analysis" Marcel Dekker, New York, (1980)

62. Banarjee, S., Yalkawskey, S.H; Valvani, S.C.; "Water Solubility and Octanol Water Partition Coefficients of Organics", Enviromental Science and Technology Vol. 14, 1227-1229, (1980).

63. Yalkowsky, S.H.; Valvani, S.C.; "Solubilities and Partitioning Relationships between Aqueous Solubility, Partition Coefficients and Molecular Total Surface Area of Rigid Aromatic HC_s ", J. Chem. Eng. Data, Vol: 24, 127, (1979)

64. CRC Handbook 1990