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PHOTODEGRADATION OF PCBS IN NATURAL WATERS

by

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Adriana R. Nicolaescu

PHOTODEGRADATION OF PCBS IN NATURAL WATERS

Adriana R. Nicolaescu, M.A.

Western Michigan University, 2000

PCBs are widely distributed in the environment and they are biologically refractory and toxic compounds. There is great interest in understanding their fate in the environment, and also for finding safe and effective degradation methods.

This study is concerned with the photodegradation of four PCB congeners: PCB 5, PCB 18, PCB 77, PCB 128 in natural waters. Natural waters contain humic substances which can greatly influence the environmental fate of the PCBs. The different degradation of the four congeners was studied in standardized systems and in humic acid or nitrate solutions, under environmental conditions. DMDE and Methoxyclor (whose environmental half-lifetimes were reported in the literature) were used to estimate the environmental half-lifetimes of the four PCB congeners.

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CHAPTER I

INTRODUCTION

Background

Polychlorinated biphenyls (PCBs) are a class of 209 discrete chemical compounds, called congeners, in which one to ten chlorine atoms are attached to biphenyl (Figure1).

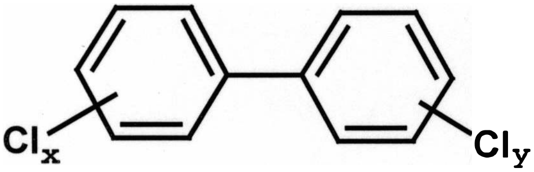


Figure 1. The Structure of the PCBs; x + y = 1 to 10.

The term “PCB” is used to refer to the entire class or any subset of one or more compounds and are listed in Chemical Abstracts under “1,1-biphenyl, chloroderivates” with a generic CAS registry number of 1336363. When PCBs are subdivided by degree of chlorination, the term homolog is used: e.g., the tetrachlorobiphenyl homolog. PCBs of a given homolog with different chlorine substitution position are called isomers. For example, 2,2’-dichlorobiphenyl and 2,3-dichlorobiphenyl are two of the twelve dichlorobiphenyl isomers. Many researchers have found the full chemical names unwieldy and have adopted various shorthand nomenclatures. For instance, 3,3’,4,4’,5,5’-hexachlorobiphenyl has been referred to as 3,3’,4,4’,5,5’-hexaCB, 3,3’,4,4’,5,5’-hexa, or simply 3,3’,4,4’,5,5’. Ballschmiter and Zell arranged the 209 congeners in ascendic numeric order and assigned BZ numbers from 1 to 209 [1]. For example, 2,3-dichlorobiphenyl is PCB 5, 2,2’,5-trichlorobiphenyl is PCB 18, 3,3’,4,4’-tetrachlorobiphenyl is PCB 77 and 2,2’,3,3’,4,4’-hexachlorobiphenyl is PCB 128.

PCBs are not known to occur naturally; instead, they were commercially manufactured and sold as mixtures of multiple isomers with different degrees of chlorination. The major USA producer, Monsanto Corporation (St. Louis, MO), marketed PCBs under the trade name of Aroclor$^{(R)}$ from 1930 to 1977. Other trade names of PCB products and mixtures containing PCBs are Aceclor, Clophen, Clorphen, Delor, Asbestol, Diaclor, Chlorinol, etc. [2]. Durfee et al. [3] estimated worldwide PCB production through 1976 at about 1.3 billion pounds, of which 1.25 billion pounds was produced by Monsanto in the U.S. The total production of PCBs through 1980 has been estimated to be more than 1.1 million metric tons (2.4 billion pounds), although the former USSR production of Sovol (composition fairly close to Aroclor 1254) is not included in that estimate [4, 5]. PCBs have been used in capacitors, as transformer coolants, as hydraulic fluids, as heat transfer fluids and as additives in pesticides, paints, copying paper, carbonless copy ("NRC") paper, adhesives, sealants and plastics. Of the total amount of PCBs used in the US in industrial products over the period 1929-1975, approximately 50% was used in capacitors (630 million pounds), 27% in transformers (335 million pounds) and 9% in plasticizers (115 million pounds); the remaining 14% was used in hydraulic systems, lubricants and heat transfer fluids [6]. None of these items are currently manufactured using PCBs; however electrical equipment and many other products that were manufactured prior to 1977 remain in service. The fate of PCBs as of 1977 was as following: 150,000 tons had been landfilled; 75,000 tons had entered the air, water and soil; 25,000 tons had been incinerated; and 375,000 tons remained in electrical equipment [7]. The most current inventory of PCBs remaining in use was conducted in 1988 [8]. Of the 167 million pounds of PCBs remaining in use in transformers and large capacitors in 1988, approximately 121 million pounds were in transformers and 46 million pounds were in capacitors. Approximately 54.9 million pounds of PCBs wastes were in storage in the U.S. at the end of 1994 [7, 9].

PCBs as Contaminants

Anectodal information suggests that PCBs were first detected in environmental samples when a Swedish chemist measuring chlorinated pesticides accidentally left the strip chart recorder on one night and discovered many late-eluting peaks which he identified as PCBs [10].

In the late 1960s, Jensen [11, 12, 13] reported the presence of PCBs in eagles, herring, and other Swedish environmental samples. In 1979, Wasserman et al. reported the occurrence of PCBs in organisms that included seals, whales, dolphins, freshwater and marine fish, birds and humans; PCB concentrations in the organisms were found to be as high as g/kg [14]. Since then, the environmental occurrence of PCBs has been addressed in numerous articles and monographs [15, 16]. PCBs also are reported to be present in flora such as trees, lichen and pasture grass [17, 18].

PCBs are very stable compounds, and consequently are persistent in the environment. PCBs are also lipophilic and tend to bioaccumulate [16, 19, 20, 21]. The toxicology of PCBs has been extensively studied, and while there is still much debate on the nature of the effects on man and other organisms, EPA considers PCBs a probable human carcinogen [25]. In 1976, after their widespread environmental occurrence was discovered, the PCBs were regulated by the Toxic Substances Control Act (TSCA), PL 94-469. In 979, he manufacture, processing, distribution in commerce, and non-enclosed use of PCBs was banned, and the minimum regulated PCB concentration was reduced from 500 to 50 μg/g. In spite of the ban in the US and in spite of restrictions on PCB use in numerous countries, PCBs are ubiquitous contaminants, being detected at the bottom of the ocean as well as in Arctic snow, in most samples of air, soil and sediments, and in most human and animal adipose tissues samples [20-25]. Some of the PCB mass in the environment was introduced during PCB production; PCB loading to the environment continues from storage and disposal sites. Seltzer (C & EN, Sept 5, 1994, pg. 20), for example, reported that 3600 accidents releasing PCBs into the environment occurred from 1988 to 1992.

Laboratory animal studies of PCBs indicate that PCBs are oncogenic (tumor causing) [25]. Aroclor 1016, 1242, 1254 and 1260, which contain the range of congeners most often found in environmental mixtures, have been found to induce liver tumors in female rats and increase the incidence of thyroid tumors in male rats [26]. Neurotoxicity also has been observed in several animal species exposed to PCBs in laboratory studies. For example, Rice observed neurobehavioral deficits in monkey dosed with a PCB-congener mixture representative of the PCBs found in breast milk of Canadian women [27]. PCBs also appear to have the ability to alter reproductive processes in mammals, and have been found to be toxic to fish at very low exposure levels, adversely affecting both their survival rate and reproductive success [15, 27, 28]. Chronic exposure of animals to PCBs appears to be linked to disrupted hormone balances, reproductive failure or carcinomas [15, 27-31].

Human exposure to PCBs is thought to occur primarily through food contamination because PCB levels increase through the food chain and humans are consumers near the top of the food chain. However, exposures from food, occupation, environment varies markedly between individuals and populations. Once in the body, many PCBs persist and retain biologic activity long after exposure ceases. Wolff et al., for example, have reported elimination half-lives on the order of 1-6 years for the less chlorinated PCB congeners and half-lives for the more highly chlorinated PCBs of 8-24 years [32]. Safe et al. have reported that it is the more highly chlorinated PCB congeners, as well as those that lack unsubstituted meta-para positions, that are resistant to metabolism and tend to accumulate in tissues [30, 31]. Elimination rates nevertheless vary according to complex metabolic factors such as weight, diet, activity level and maybe sex and race. As a consequence, not all humans have the same PCB body burden. In general, however, total human body burden is expected to increase with age if there is steady exposure.

Recent studies complement and add to the scientific data gathered over the last two decades documenting the health consequences associated with exposures to PCBs [33, 34]. The findings of elevated PCB levels in human populations, together with findings of developmental deficits and neurologic problems in children whose mothers ate PCB-contaminated fish have compelling implications. The reported average level of PCBs in breast milk in the US is 89 μg/Kg [35]. Dewailly reported in 1989 that the breast milk of Inuit women of Arctic Quebec contained very high levels of PCBs and also suggested a link between these levels and the immune system effects in their children [36]. Duarte-Davidson et al. reported in 1991 that PCB 138, PCB 153 and PCB 180 were found in >10% of all human breast milk [37].

Although PCBs are declining in the environment, health concerns are still warranted [38]. For example, while the concentration of PCBs in Great Lakes decreased from 0.8-31 ng/L in late 1970s to 0.4-0.7 ng/L in late 1980s (NRC, 1979) [39], the body burden levels in people who eat fish from Great Lakes are higher than in the general US population. In 1986, Gartrell et al suggested a background human daily PCB intake of 1.4×10^{-5} mg/kg [40].

Chemodynamic Modeling of PCBs

"A model is an imitation of reality which stresses those aspects that are assumed to be important and omits all properties considered to be nonessential" [41].

There is great interest in developing methods of predicting, or modeling, the environmental fate of PCBs. However, the environmental transport of PCBs is complex and global. PCBs are transported, for example, by air, water, fish and birds [42] (as shown in Figure 2). Even so, many models were proposed in the last decade or so in an attempt to predict or to describe concentrations of PCBs and other organic pollutants in specified regions of the environment (environmental compartments) such as water, air, soil, sediments and biota [43-46].

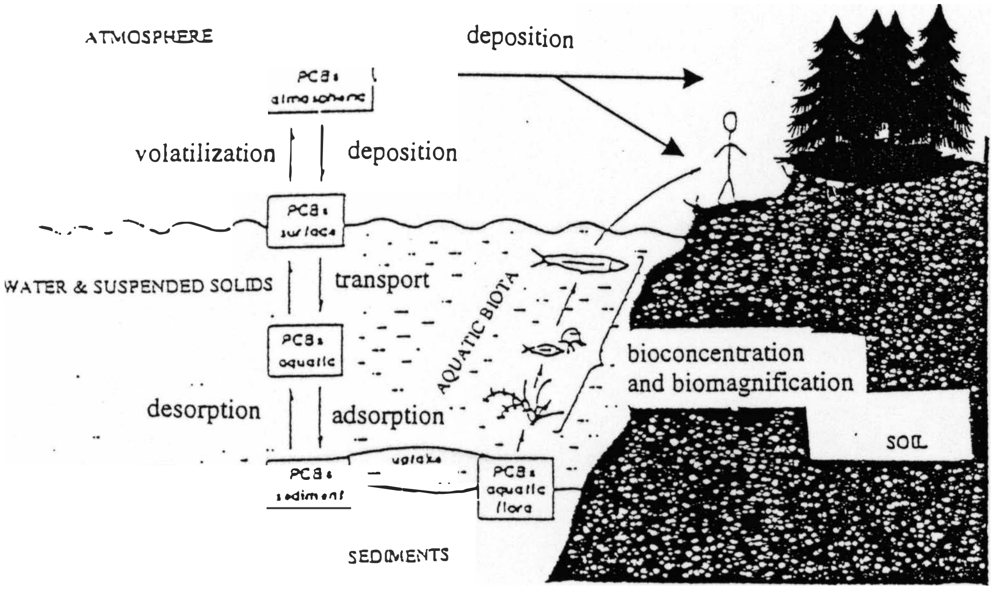


Figure 2. Environmental Compartments (adapted from [42]).

Fugacity

MacKay proposed "the fugacity approach"; that is, using fugacity to assess the likely environmental behavior of pollutants [46]. Fugacity can be regarded as the "escaping tendency" of a chemical substance from a phase. Fugacity has units of pressure and can describe the partitioning, or the equilibrium distribution, of a chemical between two phases, depending on the relative compatibility of the chemical with each phase. A pure substance (solid or liquid) has a fugacity usually approximately equal to its vapor pressure. In the vapor phase or atmosphere, fugacity is usually equal to partial pressure. In liquid phase fugacity is related to concentration, and in sorbed phases (e.g. soils, sediments), fugacity is related to the water concentration as well as the sorbed concentration.

Fugacity (f) in a phase is related to concentration (C, in mol/m^3) by the expression:

$$C = f \times Z \tag{1}$$

where Z is "fugacity capacity" in the phase expressed in Pa mol/m^3. Fugacity capacities describe the level at which a phase is saturated with a compound. As a consequence, the fugacity capacity of water is related to water solubility and the fugacity capacity of the atmosphere is related to vapor pressure. In general, toxic substances tend to accumulate in phases where either Z is high or high concentrations can be reached without creating high fugacities.

Water Solubilities and Vapor Pressures

For predicting and interpreting the environmental behavior of PCBs, it is important to have reliable data for their physical properties. For PCBs, the physical and chemical properties vary widely across the class, and measurements and estimates of PCB physical properties, while plentiful, often differ by orders of magnitude [47, 48, 49]. For example, the vapor pressure of 2,2',5,5'-tetrachlorobiphenyl is reported to be ~0.007 Pa based on determination from gas chromatography retention time and ~0.005 Pa as estimated from melting point [47, 48 and references therein, 49]. Similarly, water solubilities reported for decachlorobiphenyl ranged from 5.5×10^{-6} to 1.2×10^{-12}, in g/g. PCBs appear to have low water solubilities (from 7 mg/L in the case of biphenyl to 0.0004mg/L for hexachlorinated biphenyls) and low vapor pressures (4.66×10^{-5} Pa at 25^{0} C for hexaCB). The interactions of the various physical properties and their relevance to specific applications can be extremely complex and are not well defined.

Mackay and Shiu published an extensive review of some physical properties of 85 congeners [47]. Their vapor pressures ranged from 2.3 Pa (or 2.3×10^{-5} atm) for monoCB to 0.005 Pa (or 4.9×10^{-8} atm) for hexaCB.

Shiu and Mackay reviewed aqueous solubilities for 44 congeners; standard deviation for the values tended to be around 10% although some were as high as 50% [48]. Solutions of very hydrophobic compounds, with solubilities less than 1 mg/L, are difficult to prepare, to handle and to analyze, so reported data often contain appreciable errors.

Henry's Constant

Henry's Law Constant is a measure of the equilibrium distribution coefficient between air and water (or other gas and liquid).

$K_H = P_I/C_W$ (expressed in atmL/mol) (2)

K_H quantifies the relative fugacity of a compound existing as vapor molecules as opposed to being dissolved in water. If K_H has a relatively large value for a particular compound, it means that it has a large tendency to escape from the water phase and enter the atmosphere. To get a large value for K_H either a high pressure P or a low concentration C (or both) is (are) required.

K_H is quite challenging to measure for PCBs, since they are hydrophobic and have low volatility. In the same review mentioned above Mackay et al. calculated K_H; the values ranged from 60 Pa m^3/mol (or 5.92 x 10^{-4} atm) for monoCB to 86 Pa m^3/mol (or 8.5 x 10^{-4} atm) for hexaCB.

The Octanol-Water Partition Coefficient

The distribution of nonpolar organic compounds between water and natural solids (soils, sediments, suspended particles) or organisms can be viewed as a partitioning process between the aqueous phase and the bulk organic matter present in natural solids or biota. The partitioning between an organic phase and the aqueous phase is determined by the relative fugacity of the compound in each phase, and may be described by a dimensionless equilibrium constant:

$K_{OW} = C_O/C_W$ (3)

In Shiu and Mackay's review the average of the reported log K_{ow} values ranged from 4.3 (for 2-monoCB) to 8.26 (for decaCB) [47]. Thus partition ratios from about 10,000 to over 100 million can be anticipated; this partitioning plays a key role in environmental fate and transport and also is critical to the design of extraction and cleanup techniques. A group-contribution model (UNIFAC) predicts the K_{OW} as well as other physical properties [50].

In 1991, Paya-Perez et al. showed that the distribution constants for PCBs in soil are proportional to the soil organic carbon content [51]. Cortes et al. showed that sorption is favored by high total organic carbon, high total aluminum and iron oxides, and smaller particle sizes [52]. Co-planar PCB sorb to soil stronger than nonplanar congeners with the same degree of chlorination.

Other Partition Coefficients

The octanol-air partition coefficient K_{OA} was proposed by Harner and Mackay to describe the air-vegetation and air-soil equilibria [53].

Karickhoff proposed a carbon-water partition coefficient [54]:

$$K_{OC} = 0.41\ K_{OW} \tag{4}$$

Mackay proposed a fish-water partition coefficient [55]

$$K_{B} = 0.05\ K_{OW} \tag{5}$$

Modeling Shortcomings

The inability of models to predict or describe pollutant fate and transport has numerous sources, including the inherent complexity of the natural world. Decisions about the level of detail needed for accurate representations of pollutant fate and transport are consequently difficult. One example of this can be found in the reported results of the application of a multimedia fugacity model developed by Mackay and Paterson to the distribution of hexachlorobiphenyl (HexaCB) in southern Ontario, which includes Lake Ontario [56]. Four bulk compartments were included in the model: the atmosphere, soil, lake water, and sediments at the lake bottom. Within each compartment were multiple subcompartments, such as particulate matter in the atmosphere and biota in the lake. Forty environment-specific parameters (volumes, velocities, diffusivities, sediment deposition and resuspension rates, etc.) were included in the model and were assumed to apply to all chemicals. According to the model, most hexaCB introduced into the air is advected from the region, but there is appreciable wet and dry deposition, which in case of water is offset by volatilization. hexaCB present in water is subject to deposition (sediment burial) and advective loss. The persistence of hexaCB was estimated at 7.8 years. They estimated that 0.07% of the hexaCB will end up in air, 2.16% in water, 87.10% in soil, 10.67% in the sediments. Since 98% of PCB mass is expected to be found in soil and sediments, one might not expect PCBs to be a multimedia problem.

In 1985, Murphy estimated that 900 tons of PCBs cycle through the U.S. atmosphere in a year [57]. Atmospheric transport is recognized as a primary mode of global distribution of PCBs. Panshin and Hites reported in 1994 that general atmospheric concentrations have not decreased appreciably from the 1970's to the

1990's [58, 59]. Eisenreich et al estimated that Lake Superior receives more than 78 % of its PCB burden from the atmosphere [60]. PCBs are lost to the atmosphere from the water via evaporation [61] and from aerosolization from bursting water bubbles [62]. Jeremiason et al reported in 1994 that volatilization and not sedimentation is the dominant loss process from Lake Superior [63].

Relatively recent evidence indicates that dissolved organic matter in natural waters can, like the organic carbon found in soil and sediments, "sorb" or bind nonpolar compounds [64, 65]. Some of this organic material is in the form of truly dissolved (soluble compounds), while other fractions consist of colloidal or particulate organic matter. The study of aqueous subsurface chemical transport has only recently considered the significance of transport within or on colloidal particles. Facilitated transport of otherwise immobilized chemicals can greatly enhance mobility. All natural waters contain some carbonaceous material. About 50% of the dissolved organic carbon in surface waters consists of humic substances.

Humic Substances

Humic substances are natural macromolecules found in lakes, rivers, soils and other locations where plant and animal material has undergone partial decomposition [66]. In spite of the widespread occurrence of humic material in natural waters and terrestrial systems, knowledge of the exact nature and formation mechanism of humic matter is still incomplete. The formation of humic substances probably involves a combination of degradation and condensation of plant and animal residual material.

The resulting materials are polyelectrolytes with various functional groups (carboxyl, phenolic, and methoxyl) attached to a hydrocarbon skeleton [67,68]. Humic substances soluble in both acidic and basic solution are classified as fulvic acids. Humic substances soluble at neutral and high pH are classified as humic acids. Humic substances not soluble at any pH are classified as humin.

Since humic substances consist of an extraordinarily complex mixture of compounds, when dealing with them in solution, researchers express the concentration of material either in terms of the mass of dissolved organic matter per volume solution, or in terms of the mass of dissolved organic carbon (DOC) per volume of solution. Although the DOC of colored surface waters is extremely variable, it typically is less than 5 mg/L DOC, but it can range to more than 50 mg/L DOC. The organic carbon content of humic materials is fairly constant at 50% by weight [67, 68, 69].

Dissolved organic carbon in natural waters must be considered as a separate environmental compartment in a model representing pollutant behavior. Interactions of PCBs with dissolved natural humic substances can significantly influence their transport and fate in aquatic systems. The role of humic substances in affecting pollutant fate and transport has been succinctly summarized by Caron and Suffet [70]: association with H.S. can: (a) increase the solubility, and thus the mobility of organic pollutants, (b) decrease pollutant's sorption to sediments and suspended sediments, (c) decrease pollutant's bioavailability to aquatic organisms, (d) decrease the volatility of pollutants, and (e) influence pollutant's photochemistry in surface waters.

The mechanisms of interaction between humic substances and organic pollutants are not yet fully elucidated. However, the tendency to associate with, and thus be affected by, humic materials does seem to be predictable based on K_{ow} values. Since these vary across the PCBs as a class, humic-mediated transport mechanisms would not be expected to act on all congeners equally. Consequently the composition of an Aroclor in the environment can become distorted over time, a phenomenon commonly referred to as "weathering". A weathered PCB pattern may be enriched in the higher congeners as the more volatile components selectively evaporate from a surface.

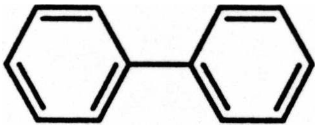
Loss Due to Reactions

Organic chemicals in the environment can undergo chemical and biologically mediated transformation. Chemical transformation can be either thermal or photochemical, with the photochemical transformation resulting from either direct photolysis or by reaction with some chemical species (e.g., free radicals) that is formed as a result of the incidence of sunlight on natural waters (indirect or sensitized photolysis).

PCBs are very stable compounds and do not degrade easily. It is generally accepted that environmental and metabolic degradation proceeds quite slowly relative to many other compounds [71, 1]. However, PCB photolysis has been hypothesized to be a degradation process [72].

The energy of solar ultraviolet (UV) and visible light is of the same order of magnitude as that of covalent bonds. Thus, in principle such bonds could be cleaved as a consequence of light absorption. Whether or not reactions take place depends on the probability with which a given compound absorbs light of a given wavelength, and on the probability that the excited species undergoes a particular reaction. Only if the radiation is absorbed by the molecule, as a result of this interaction, can the radiation be effective in producing chemical changes.

All PCBs are weak absorbers at $\lambda > 290$ nm (the solar region), compared to the biphenyl which absorbs around 250 nm, ε_{max} around 20,000 (ε_{max} represents the molar absorptivity of the chemical, at a specific wavelength, in the units $M^{-1}cm^{-1}$). Bunce reviewed PCBs' photochemistry [73]. The two phenyl moieties of the PCB structure can rotate about the connecting single bond in the ground state (1), while this is difficult in excited state (2):



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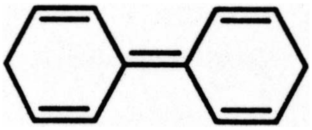


(1) (2)

In the case of PCBs, the low energy preferred conformation in the ground state depends on the degree of chlorine substitution, since chlorine is larger than hydrogen and creates more steric hindrance. Jakus and Miertus calculated the torsion angles for different PCBs: 48^0 for biphenyl and PCBs without ortho-chlorines, 68^0

for congeners with one ortho-chlorine and 79^0 for congeners with two ortho-chlorines [74].

Ortho substitution causes a blue shift and a reduction in intensity, and the compounds with ortho-chlorines absorb more weakly than those without. For PCBs having all ortho positions substituted by chlorine, twisting of the ground state becomes extreme, and the absorption is observed around 270-280 nm.

Thus at wavelengths of environmental interest, the more heavily chlorinated PCBs absorb most strongly and many studies suggested that highly chlorinated PCBs are the most photolabile, at least in organic solvents [73, 75, 76], PCBs lacking ortho substitution are intermediate and PCBs having one or two ortho chlorines are the least absorbing.

Direct Photolysis

The majority of direct photolysis studies for PCBs were done in organic solvents, due to the low molar absorptivities of PCBs at $\lambda > 300$ nm, and because of the solubility problems. PCBs react mainly by stepwise dechlorination (replacement of Cl by H), with ortho-chlorines being lost preferentially [73 and the references therein]. This means that if direct photolysis is proven environmentally significant, highly chlorinated PCBs that are the most persistent would be transformed into less chlorinated ones, which are thought to be more reactive metabolically, and more toxic. Bunce et al showed that the fraction of light absorbed by one PCB at environmental concentrations does not depend upon the number or concentrations of other PCBs present [75].

The average rate of disappearance of the chemical undergoing direct photoreaction, at a fixed wavelength λ is given by:

$$\text{Average rate} = -(d[C]/dt)_{\lambda} = \phi_{d\lambda} \times I^{d}_{a\lambda,} \qquad (6)$$

where [C] is the concentration of the pollutant, $\phi_{d\lambda}$ is the reaction quantum yield (the ratio of the number of molecules that photodegrade to the number of photons absorbed) and $I^{d}_{a\lambda}$ is the average rate of light absorption by the pollutant. The subscript and superscript d is used to denote that the pollutant is undergoing direct photolysis.

For most organic molecules in aqueous solution, the reaction quantum yield is independent of λ [77]. Integrating under the boundary conditions (t = 0, $[C_0]$) and (t, $[C_t]$) yields

$$\ln([C_0]/[C_t]) = k_d \times t \qquad (7)$$

where the first-order direct photolysis rate constant k_d is in the units of reciprocal time.

The half-life, $t_{1/2}$, is defined as the time required for the chemical to reach one-half of its initial concentration:

$$t_{1/2} = \ln 2/k_d = 0.693/\ k_d \qquad (8)$$

Direct photoreaction in sunlight represents an important mode of chemical transformation in the environment.

Environmental Studies of Photolysis

A number of problems arise when laboratory modeling of the effect of light on a natural system is attempted. For example, since typical pollutant concentrations are so low, very little light is absorbed by the pollutant. This makes it difficult to measure directly either the light absorbed or the concentration change at environmental concentrations. Also, the rates of photoreaction can be affected by dissolved and suspended matter in aqueous media (e.g. by the absorption or scattering of light in natural water bodies via physical processes or by photochemical processes involving sensitization or quenching of excited states).

Natural waters contain humic substances formed from decayed organisms, which can attenuate sunlight penetrating these water bodies. The rate of direct photoreaction of a chemical in natural water may be decreased because most of the sunlight is absorbed by the humics and only a fraction of the sunlight is available for the direct photolysis of the chemical. The absorption spectrum of the humics is presented in Figure 3.

Under these conditions, a "light screening factor (S_λ)" can be defined as the ratio of the first-order rate constant in the natural water ($k_{d,HA)}$ to the first-order rate constant in pure water ($k_{d,w}$):

$$S_\lambda = k_{d,HA} / k_{d,w} \tag{9}$$

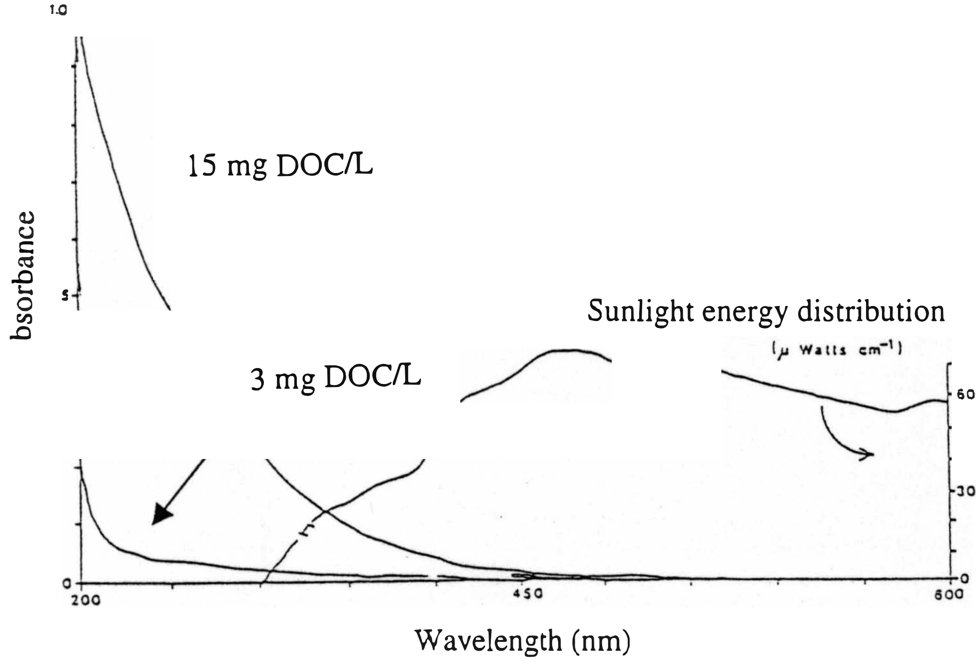


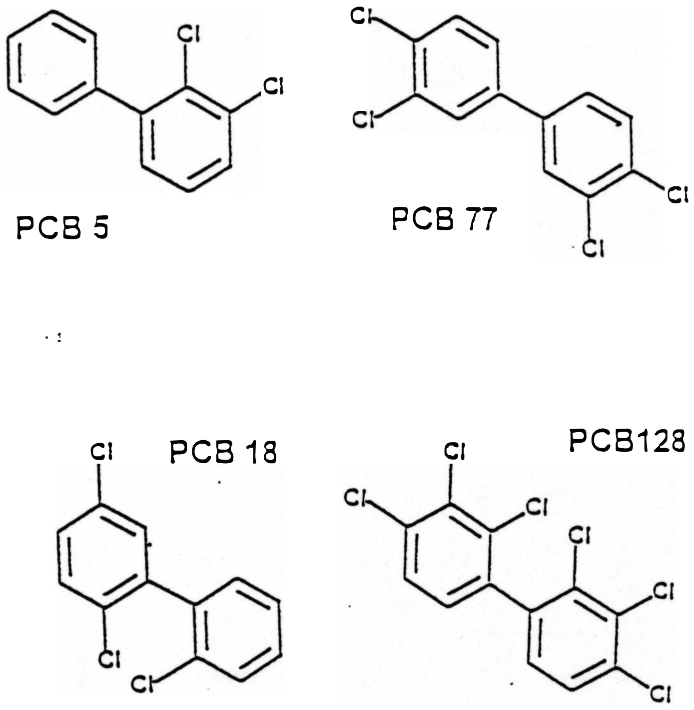
Figure 3. The Absorption Spectrum of the Humics.

Another difficulty is the extent to which non-polar pollutants, such as PCBs, are actually free in aqueous solution in natural waters, as opposed to present as associations of pollutant molecules, or adsorbed on to particles and humics, or dissolved in non-polar surface films. These factors can influence greatly the photochemistry of the PCBs. Besides being shielded from the light, the UV/Vis absorption spectrum of a compound may be significantly different in the sorbed state as compared to the dissolved state and because of the different molecular environments, sorbed species may exhibit very different reaction quantum yields and photoreaction distributions [78].

It is possible for suspended particulates and humics to enhance the rate of organic photolysis. Natural water bodies, which contain a wide range of chromophoric substances (substances that undergo chemical change as a consequence of absorbing photons), both natural and anthropogenic, are large photochemical reactor systems. As sunlight enters these waters, the chromophores absorb light, a number of reactive species are generated and a diverse number of chemical reactions occur. These chemical changes involve primary and secondary reactions, including homolytic and heterolytic cleavages, redox reactions, energy transfer reactions, reactions with water and isomerizations and play a role in a number of secondary reactions. Recent studies showed that pollutants sorbed to humic materials in water can undergo reactions nor readily available to freely dissolved molecules [79].

Present Work

This study is concerned with the photodegradation of four PCB congeners: PCB 5, PCB 18, PCB 77 and PCB 128 (Figure 4). The question is what is the significance of two potential degradation routes (direct photolysis and degradation by $HO^{\cdot}$ in natural waters) to the fate of PCBs in the aquatic environment.



PCB 5

PCB 77

PCB 18

PCB128

Figure 4. The Structures of PCB 5, PCB 18, PCB 77, PCB 128.

CHAPTER II

EXPERIMENTAL SECTION

Materials

PCB 5 (2,3-dichlorobihenyl), PCB 18 (2,2',5-trichlorobiphenyl), PCB 77 (3,3',4,4'-tetrachlorobiphenyl), PCB 128 (2,2',3,3',4,4'-hexachlorobiphenyl), and lindane were purchased from Ultra Scientific; they were 99% in purity and used without further purification. Methoxyclor was purchased from Sigma. Its purity was 95%, and the initially orange crystals were recrystallized two times from 95% ethanol to yield colorless crystals with the melting range at 86-88 ^{0}C (literature melting point is reported as 87-88 ^{0}C). 1,1-Bis (p-methoxyphenyl)-2,2-dichloroethylene (DMDE) was prepared from Methoxychlor according to the method of Zepp et al. [80]; the melting range was 108-109 ^{0}C (literature melting point is reported as 109 ^{0}C). Humic acid (sodium salt), and hexachlorobenzene (99%) were purchased from Aldrich Chemical Company. Hexane (Optima grade), acetone (Optima grade), methanol (HPLC grade), sodium chloride (ACS certified) were purchased from Fisher Scientific. Chromic acid (10% w/v) was purchased from Lab Chem Inc. All solutions were prepared with ELGA water (Elgastat Maxima-HPLC water, Elga Ltd).

Humic Acid Solutions

Humic acid (HA) stock solution was prepared using a variation on the method of Zepp et al. [81]. Around 1 g of Aldrich HA was dissolved in 1 L of 0.1 N sodium hydroxide and then filtered under pressure (2-4 psig) through a 0.20 μm capsule filter (Gelman Sciences no. 12117). The filtrate was adjusted to pH 6 using HCl and filtered again. HA working solutions (pH ~ 6) were made by diluting small volumes of very concentrated stock solution with ELGA water. Concentrations of HA solutions were determined spectroscopically using the method of Zepp [81]. HA stock solution was kept in amber bottles at 4 ^{0}C.

Experimental Procedures

The reaction vessels used in most experiments, were 50 ml-Kimax borosilicate tubes with Teflon lined caps or the 2L-borosilicate roll bottle with the wavelength cutoff ~ 295 nm. Tubes were filled with 40 ml of solution. Known volumes (25-35 μl) of PCBs and other internal standards (DMDE, methoxychlor, lindane) dissolved in hexane or methanol were added to the solutions. The roll bottles, used as reaction vessels for a few experiments, were filled with ~ 400-500 ml of solution and the added amounts of PCBs and the internal standards were scaled to be comparable to the concentrations in the tubes. Time-series samples (5-10 samples) were taken during irradiation in the roll bottle using a through-port in the bottle cap using a glass syringe. The final concentrations of PCBs were 5-50 μg/L, below the solubility limits reported in the literature. All solutions were allowed to equilibrate overnight. In the experiments dealing with degradation of the PCBs by hydroxyl radicals, potassium nitrate was added the day prior to irradiation and the solutions were kept at 4 ^{0}C in the dark, while in other experiments potassium nitrate was added immediately prior to irradiation. The competition kinetic experiments were done the same day or the following day. Dark controls were included. The Fenton Reaction experiments were done in triplicates in the dark. The controls included solutions of PCBs in ELGA water, solutions of PCBs and H_2O_2 and solutions of PCBs and $FeSO_4 7H_2O$.

Time-series samples (5-10 samples, 40 ml each) were taken during irradiation in the roll bottle using a through-port in the bottle cap using a glass syringe and transferred to the culture tubes with Teflon-lined caps. In all the photolysis experiments, In all the photolysis experiments, immediately following irradiation a liquid-liquid extraction was performed in the culture tubes. In case of water solutions, the extraction was done using only 2 ml of hexane containing hexachlorobenzene or pentachlorobenzene as an internal standard for each 40-ml sample. In the case of HA solutions, an additional chromic acid digestion extraction technique was used [79]. The concentration loss for each PCB congener was quantified relative to the internal standard.

Apparatus

All analyses for PCB conversion were performed on a Hewlett Packard 5890 II Plus gas chromatograph equipped with flame and ^{63}Ni electron capture detectors. A

30m x 0.32mm (i.d.) capillary column coated with 5% polydiphenyldimethylsiloxane (0.25 μm film thickness) was used for separations. Product studies were performed on a 5970 Hewlett Packard MS interfaced to a 5890 GC. The irradiation of the samples in tubes was done in a "merry-go-round" apparatus placed at a fixed distance (47 cm) from the Cermax 300 W xenon arc lamp; the irradiation in roll bottles was done on a magnetic plate with constant stirring, at the same distance (47 cm) from the lamp. Spectroscopic measurements were made using a Beckman DU 7400.

Curve Fitting and Calculations

In the time-series experiments, Scientist V 2.0 (Micromath Scientific) was used for curve-fitting and calculation of the rates constants (at 95% C.I.). In 2- or 3-point experiments (one averaged relative concentration value for dark controls and one or two averaged relative concentration values for irradiated samples), the calculation of the rate constants was performed using Maple V (Waterloo Maple Inc). Statistics was calculated using either Scientist or Microsoft Excel.

CHAPTER III

PCB PHOTODEGRADATION: RESULTS AND DISCUSSION

PCB Direct Photolysis

PCBs are known to undergo direct photolysis at sunlight wavelengths ($\lambda \geq 290$nm). Ruzo et al., for example, investigated the direct photolysis of six tetrachlorinated PCBs in cyclohexane at 300 nm [82]. PCB loss, accompanied by the formation of lesser chlorinated congeners, was observed for all four PCBs. Based on these results, Ruzo et al. concluded that dechlorination is the major reaction. Similar results were observed by Lepine et al. who also used cyclohexane and a 300 nm light source to study the direct photolysis of more heavily chlorinated PCBs [76, 83]. In their work, as in that of Ruzzo et al., parent compound loss was observed simultaneously with the formation of lesser-chlorinated congeners.

In the current work, the direct photoreactions of PCB 5, PCB 18, PCB 77, PCB 128 were studied in aqueous solutions contained in borosilicate reaction vessels and exposed to light from a 300 W Xe arc lamp. The spectral output of a Xe lamp closely approximates that of the sunlight, with the exception that lamp output typically extends further into the UV than sunlight. As a consequence, reaction vessels made of borosilicate glass are commonly used in environmental work involving broad-spectrum light sources, since borosilicate glass has an effective wavelength cutoff ~295 nm.

Direct photolysis of congeners was estimated in the current work by concentration decreases of the congeners over time series versus dark controls. A representative photolysis time series for the congeners appears in Figure 5.

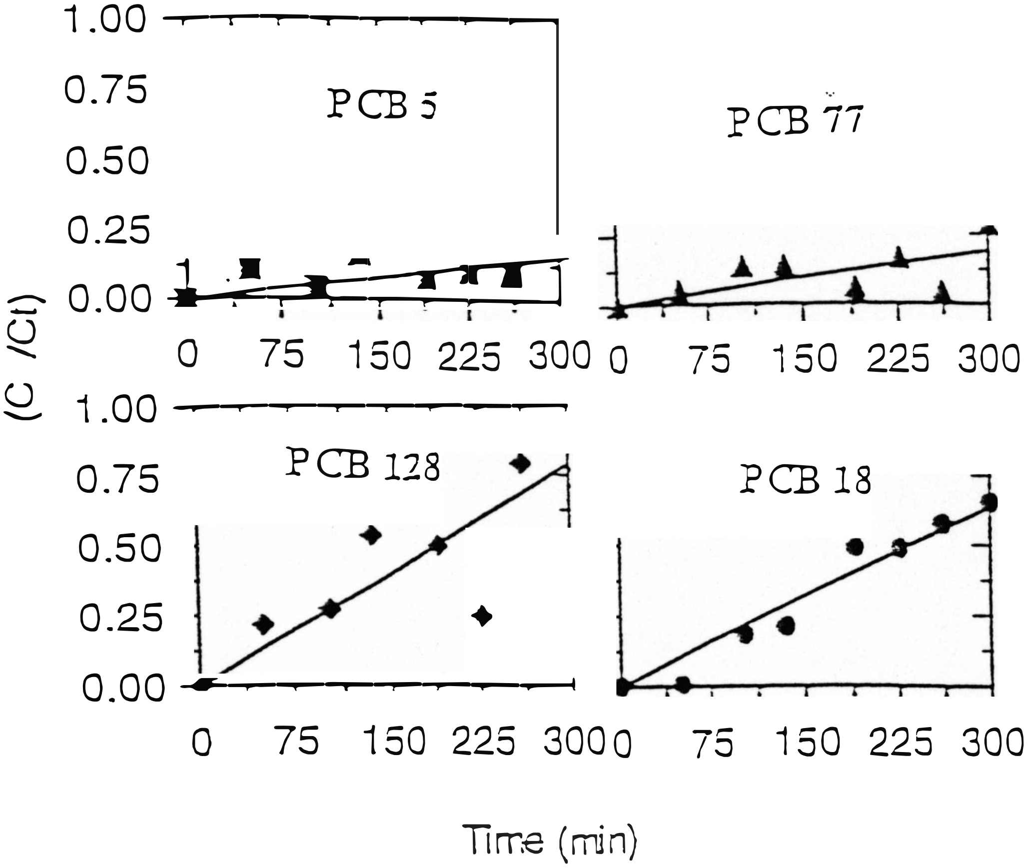


Figure 5. Direct Photolysis of PCB Congeners in a 0.3 M Methanol Solution.

Initial PCB concentrations in the time series were 8-33 µg/L (22-126 nM). PCB loss during irradiation was followed as a function of exposure time and data were evaluated using equation (7).

All four PCB congeners were observed to undergo loss during irradiation, but no loss was observed in identical solutions maintained in the dark for equal exposure times (controls). This suggests that all four congeners are capable of being transformed by direct photolysis in aqueous solution at sunlight wavelengths. This result is in agreement with previous work indicating that PCBs absorb light at wavelengths λ ≥290nm and may be transformed as a result of that light absorption [75, 82, 83].

Rate Constants for Direct Photolysis

Rate constants for PCB direct photolysis varied widely between congeners. The results in Figure 6, for example, show no detectable loss for PCB 77 but 38% loss for PCB 5 during the same exposure time (270 minutes).

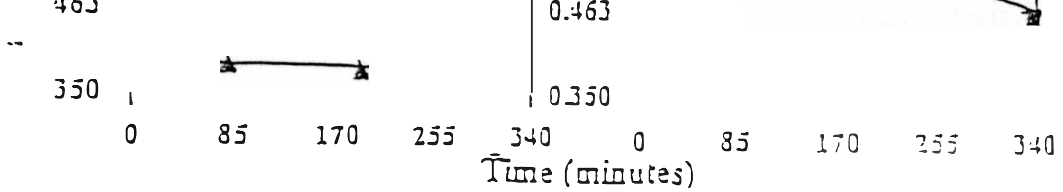


Figure 6. Change in Relative Concentration of PCB 5 and PCB 77 Due to Direct Photolysis in Water.

Although the four congeners are not at identical concentrations in the solution, their low concentrations (22-126 nM) and the observed low molar absorptivities of PCBs ($\varepsilon \approx 10\text{-}10^3\,M^{-1}cm^{-1}$, [82]) mean that competitive absorption between congeners in the solution is unlikely.

Lepine et al. also found that rate constants for direct photolysis varied widely between congeners, and noted in particular the slow photoreaction of PCB 77 [76, 83].

In the current work, a preliminary assessment of the environmental rate constants for the four congeners was accomplished using DMDE (1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene) as a standard in relative rate experiments. DMDE was used because its direct photolysis action spectra ($\lambda \geq 290$nm) in aqueous solutions has been determined previously [84]. This action spectrum also has been combined with solar irradiance data to estimate an environmental rate constant for the direct photolysis of DMDE in surface waters. Comparison between the computed rate constants and the rate constants obtained from rooftop exposures of dilute DMDE solutions did show they were in reasonable agreement, within 30%. The resulting DMDE direct photolysis environmental half-lifetime during summer, at 34° N latitude, is ~ 60 minutes^{-1}.

Relative rate experiments were performed using combined aqueous solutions of DMDE and PCBs. DMDE concentrations were 17 ppb (parts per billion). PCBs concentrations in relative rate experiments using DMDE were 0.022-0.126 μM.

A sample relative rate plot appears in Figure 7, and relative rate constants, environmental rate constants and half-lives for the congeners are tabulated in Table 1.

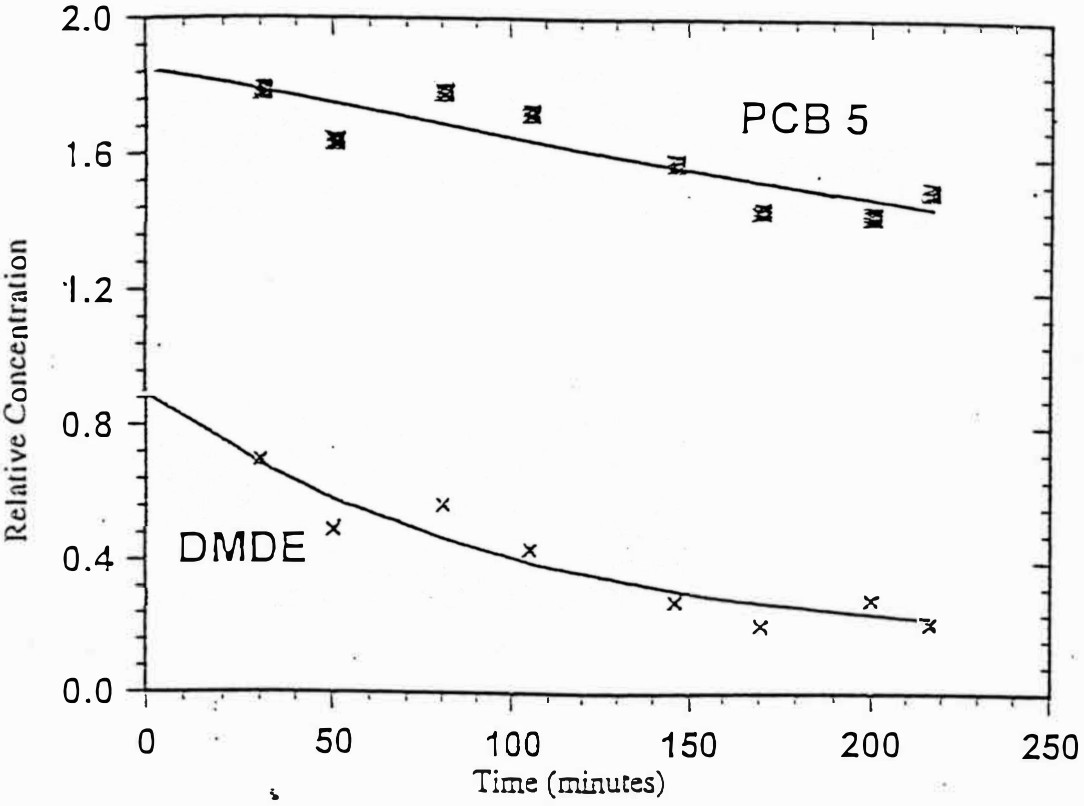


Figure 7. Direct Photolysis of DMDE and PCB 5 in Distilled Water.

Table 1

Rate Constants and Environmental Half-Lifetimes for PCB Congeners in Direct Photolysis Experiments, Relative to DMDE

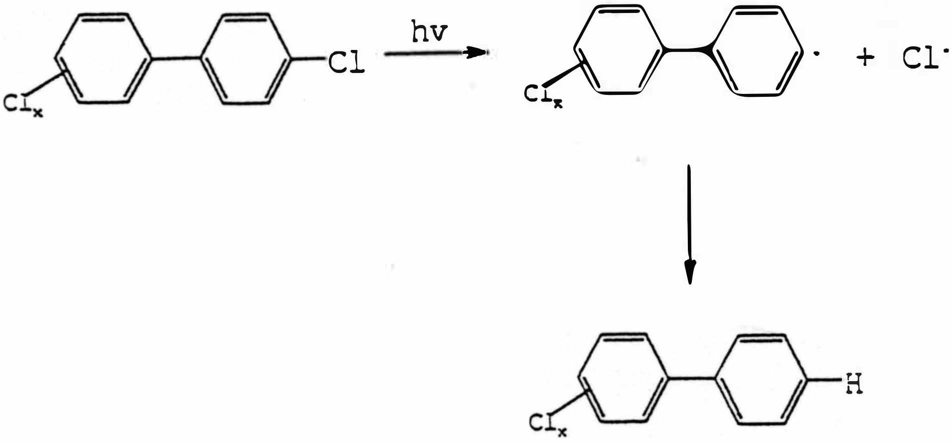
	No. of Exp.	Average	Std. Dev	$t_{1/2}$ env (h)
k_{DMDE}	12	0.041	0.018	1
k_5/k_{DMDE}	10	0.023	0.02	108.7
k_{18}/k_{DMDE}	12	0.052	0.036	48
k_{77}/k_{DMDE}	4	0.031	0.025	80.6
k_{125}/k_{DMDE}	4	0.0403	0.04	62

Product Studies

Products of PCB direct photolysis were not observed by GC-ECD in hexane extracts of any of the irradiated time-series samples, even when congener loss was around 50%. Previous studies, done mostly in organic solvents, have included observations about the products formed from the direct photodegradation of PCBs. Ruzo et al., for example, found that tetrachlorinated PCBs underwent stepwise dechlorination in cyclohexane at 300 nm [82]. All PCBs containing ortho-chlorines also were found to yield dechlorination products arising from the loss of these chlorines. In the absence of ortho-chlorines, meta-chlorines were found to be preferentially cleaved. Chlorines in the para position were not observed to undergo cleavage even after 20 hours irradiation.

Similar results have been reported by Lepine et al., and Zabick et al., both of whom studied the photodegradation patterns of PCBs in organic solvents [76, 83, 85]. Dechlorination in their work was found to occur almost exclusively on the more substituted ring of congeners having odd-numbers of chlorines. For congeners bearing two or fewer ortho-chlorines, ortho-dechlorination was found to be rapid. However for congeners bearing three ortho-chlorines, ortho-dechlorination occurred less readily.

When PCBs are irradiated in hydrocarbon solvents, homolysis of the C-Cl bond generates an aryl radical, which can rapidly abstract a hydrogen atom from a donor such as a solvent. This is not possible in aqueous solution.



The products of direct photoreactions in aqueous solutions are reported to include photonucleophilic replacement of the halogen by HO$^{\cdot}$, reductive dehalogenation, photooxidation and photoisomerisation. Dulin et al., for example, studied the direct photolysis of 2- and 4-chlorobiphenyl in a mixed solvent of acetonitrile and water [86]. In this system, replacement of Cl by $HO^{\cdot}$ was found to result in the production of phenols, which are capable of photoreacting further to form much more toxic compounds. Also in a mixed solvent system of acetonitrile and water, Orvis et al. found that 3-ClBP appears to undergo photoisomerisation along with C-Cl bond homolysis and heterolysis [87]. The isomerisation products, 4- and 2-ClBP, were found to photohydrolyze to give the corresponding phenols.

Although PCBs are soluble in alcohols, alkanes and mixed solvent systems of acetonitrile and water, these solvents are not necessarily good models for purely aqueous solutions. Water, in addition to its nucleophilic character and large dielectric constant, has a very large hydrogen-oxygen bond strength. This means that the abstraction of a hydrogen atom from the water by an aryl radical will be inefficient. Even so, some of the results obtained in acetonitrile/water systems appear to be reproduced in purely aqueous systems. For example, Moore and Pagni using deoxygenated and double distilled water, found that photodegradation of 4-ClBP produced equimolar amounts of 3- and 4- hydroxybiphenyl [88]. The same photoisomerisation followed by photohydrolysis apparently occurs in acetonitrile/water systems as well.

Direct Photolysis in Methanol

Direct photolysis of PCB 5, PCB 18, PCB 77 and PCB 128 in methanol was also conducted in the current work to determine if photolysis products could be detected at higher PCB concentration possible in methanol. Methanol was chosen because it is the preferred proxy solvent for water in environmental photochemistry work [84]. All PCB congeners used in this work degraded when irradiated in methanol (Figure 8).

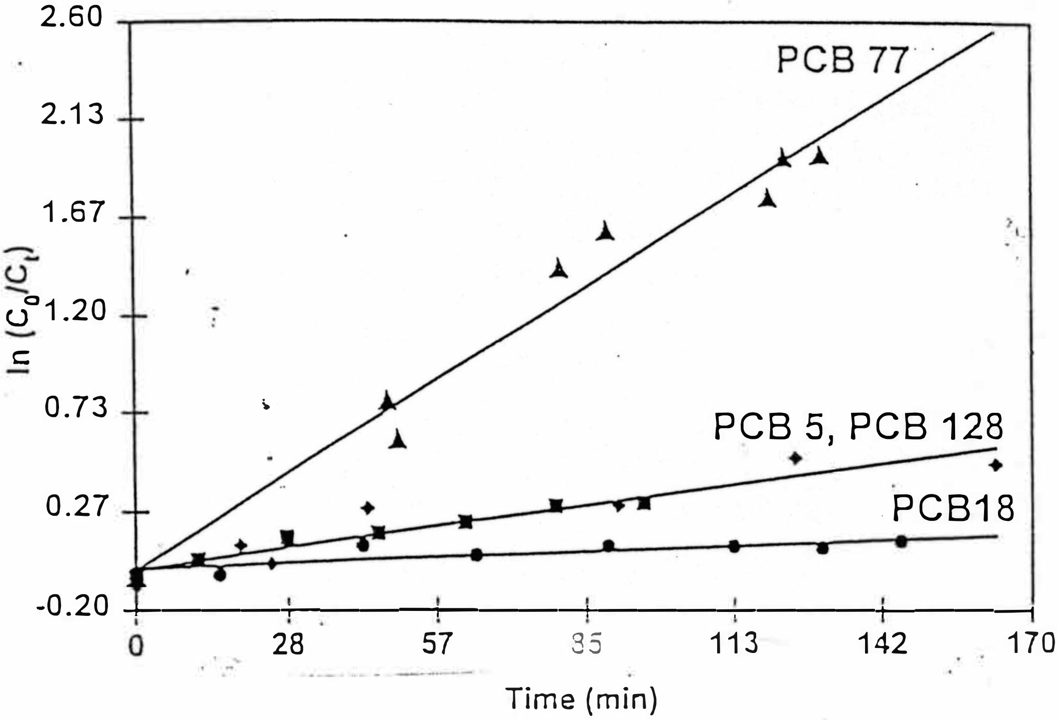


Figure 8. Photodegradation of PCB Congeners at High Concentrations in Methanol.

The direct photolysis of the four PCBs in methanol yielded detectable products in all cases. Products were identified by a combination of GC/MS and a comparison of the GC-FID chromatograms of the irradiated PCB solutions against the GC-FID chromatogram of a 50:50 mixture of Aroclor 1242 and Aroclor 1260. MS analysis permits identification of PCBs by degree of chlorination, but does not distinguish between chlorination patterns. Comparison of GC retention times against a standard containing most of the common congeners consequently was necessary in order to confirm chlorination pattern.

The four PCBs were found to react in methanol by sequential dechlorination. For example, a sample chromatogram of PCB 77 irradiated in methanol appears in Figure 9, and the GC/MS spectra of the irradiated PCB 77 sample in methanol are presented in Figure10.

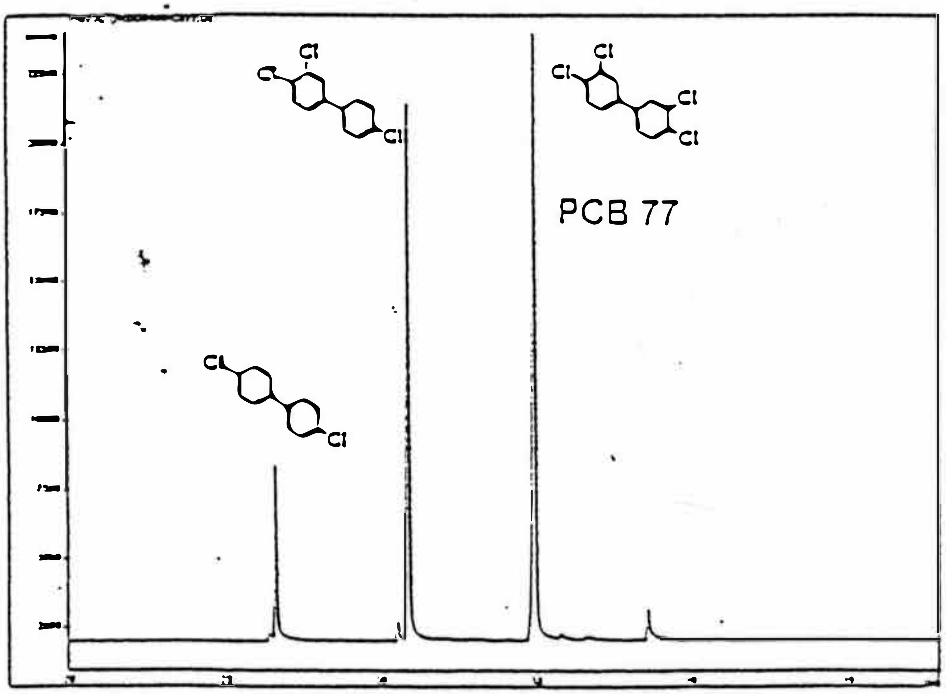


Figure 9. GC Chromatogram of a PCB 77 Sample Irradiated in Methanol.

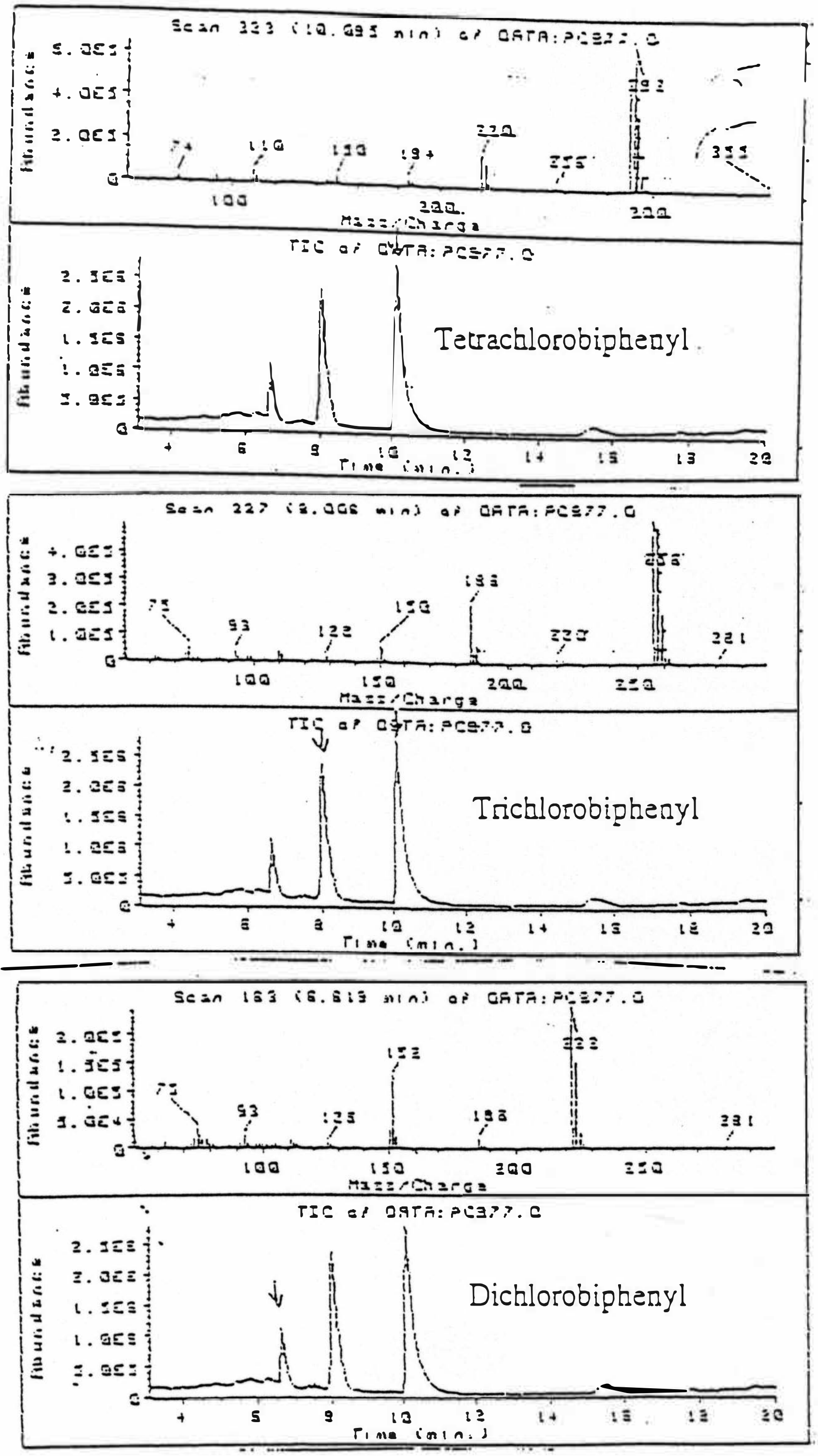


Figure 10. GC Chromatogram and GC/MS Spectra of an Irradiated PCB 77 Sample.

Two dechlorination products were observed: 3,4,4'-Trichlorobiphenyl and 4,4'-Dichloribiphenyl, the same as the dechlorination products reported by Ruzo et al. [80]. In a similar way, the products of direct photolysis of other congeners were identified. Ruzo et al. observed some methoxylated products as well, although in very small amounts (< 3 % of reacted PCB in all cases). No methoxylated products were identified in our work. The photodechlorination leads to preferential loss of ortho-chlorine, followed by meta chlorine. This is in good agreement with previous studies.

Degradation of PCBs by Hydroxyl Radical

Hydroxyl radicals are among the strongest environmental oxidants known in the environment, with second-order reaction rate constants for many organic pollutants of 10^9 to10^{10} $M^{-1}s^{-1}$ [89]. Many studies have demonstrated that $HO^{\cdot}$ can oxidize a wide variety of hydrophobic organic compounds (e.g., Pignatello, [90]), but the rates at which these processes occur in the environment, and the factors affecting reaction efficiencies are not fully understood. PCBs have been known to be degraded by hydroxyl radicals and therefore, provided that $HO^{\cdot}$ fluxes in the environment are enough, this could provide an important removal pathway. Studies of the photodegradation of PCB congeners by hydroxyl radical in the gas-phase concluded that $^{\cdot}OH$ reactions are the major removal pathway for PCBs in the atmosphere [91, 92]. However, there is some disagreement in the literature about the products and the mechanism of this reaction [91, 92, 93]

In contrast to most other oxidants, reactions of $HO^{\cdot}$ radicals with organics containing multiple bonds generally proceed with rate constants approaching the diffusion-controlled limit (10^{10} $M^{-1}s^{-1}$), and therefore oxidation rates are usually limited by the rates of $HO^{\cdot}$ generation and competition by other hydroxyl radical scavengers present in the solution. Haag and Yao measured rate constants for reaction of hydroxyl radicals with several drinking water contaminants and estimated others from structure-activity relationships [94]. They concluded that hydroxyl radicals are relatively nonselective toward C-H bonds and their estimated rate constants k_{HO} for a pentachlorinated biphenyl and a hexachlorobiphenyl were 5×10^9 $M^{-1}s^{-1}$ and 5×10^9 $M^{-1}s^{-1}$. Sedlak and Andren studied the oxidation of some PCBs with $HO^{\cdot}$ in aqueous solutions [95]. Using estimated rate constants and reported or predicted steady-state hydroxyl radical concentrations, they calculated the environmental half-lives in surface waters for PCBs with as many as eight chlorines as being on the order of days.

A variety of reaction pathways are available for the generation of hydroxyl radical in natural waters. The major sources appear to be the photolysis of nitrate, nitrite, hydrogen peroxide and dissolved organic carbon.

Fenton's Reagent Experiments

One nonphotolytic pathway of $HO^{\cdot}$ production is the Fenton system of iron, manganese or copper species in conjunction with hydrogen peroxide [96]:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\cdot} + OH^{-} \qquad (10)$$

This reaction was used in our study to assess the extent of the oxidation of the four congeners by the hydroxyl radicals. Figure 11 shows the decrease in the relative concentrations of PCB 5, PCB 18, PCB 77, PCB 128 due to degradation involving hydroxyl radicals. These results are in agreement with previous studies. For example, Sedlak and Andren found that lower chlorinated congeners are more reactive towards the hydroxyl radicals than the more chlorinated congeners [95]. In our study using Fenton reagent, PCB 5 and PCB 18 were degraded to levels below the detection limit of the GC-ECD while PCB 77 and PCB 128 showed some degree of degradation. PCB 77 appears to be the least degraded congener.

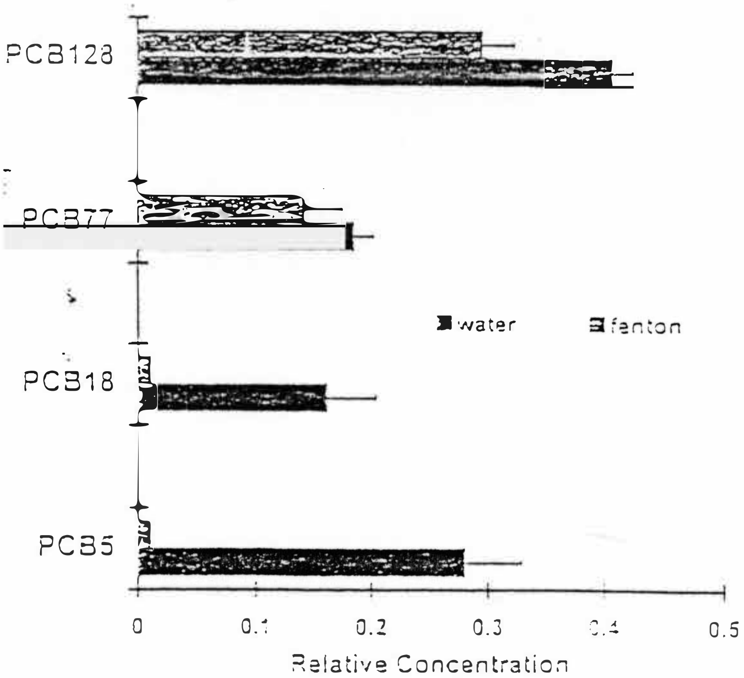


Figure 11. Degradation of PCB Congeners in the Fenton Experiment.

Nitrate Experiments

Many natural waters contain substantial concentrations of nitrate, which undergoes direct photolytic breakdown at wavelengths greater than 290 nm to form hydroxyl radicals according to the following processes:

$$\mathrm{NO_3^-} + \text{light} \rightarrow \mathrm{NO_3^{-*}} \rightarrow \mathrm{NO_2^-} + \mathrm{O} \tag{11}$$

$$\mathrm{NO_2} + {}^{\cdot}\mathrm{O}^- \tag{12}$$

followed by:

$${}^{\cdot}\mathrm{O}^- + \mathrm{H_2O} \rightarrow {}^{\cdot}\mathrm{OH} + \mathrm{OH}^- \tag{13}$$

${}^{\cdot}\mathrm{O}^-$ is rapidly protonated to its conjugated acid, the hydroxyl radical (equation 4), a potent oxidant that reacts much more rapidly with most organic chemicals than does atomic oxygen O. The major fate of the atomic oxygen produced in reaction (2) is likely to be the reaction with dioxygen to form ozone which then reacts with nitrite or decomposes to hydroxyl [97 and references therein].

In our study all four PCB congeners were degraded in irradiated solutions containing nitrate. A sample photolysis time series for the congeners in the presence of nitrate appears in Figure 12. In the experiment presented in Figure 12, at a nitrate concentration of 5.4 mM and after four hours of irradiation, the PCB 5 loss was around 20%, the PCB 18 loss was around 42%, the PCB 77 loss was around 23% and the PCB 128 loss was around 58%.

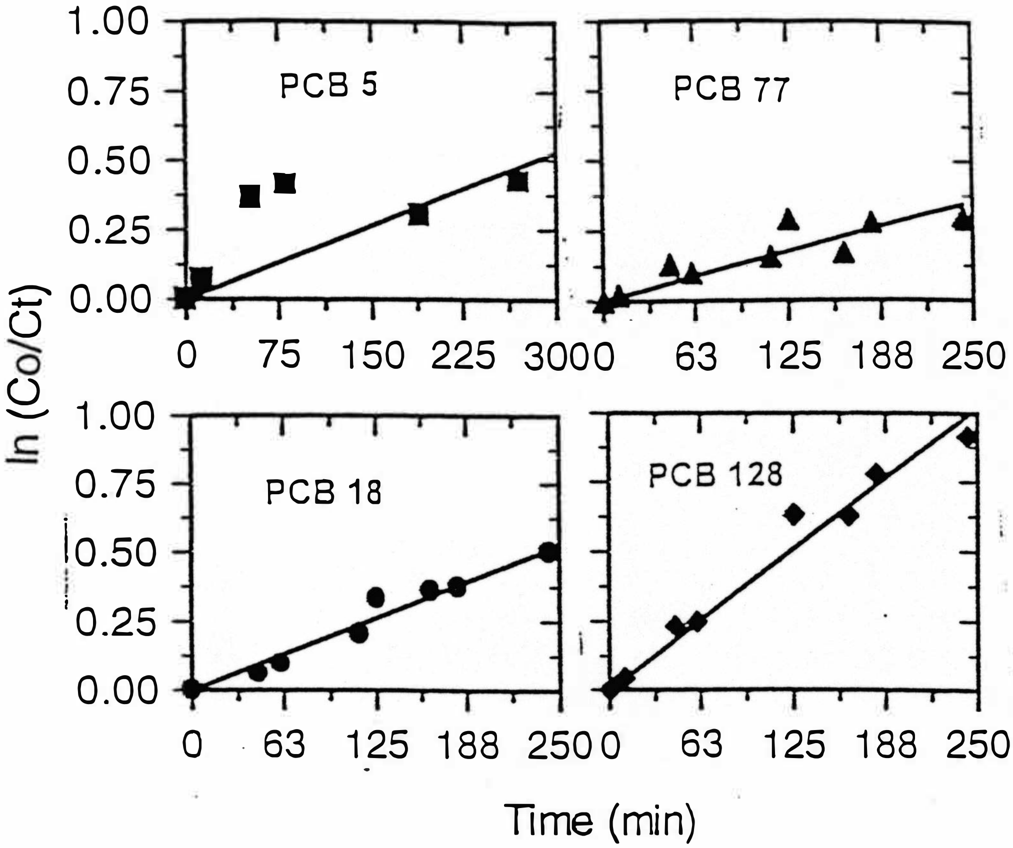


Figure 12. The Photodegradation of PCB Congeners in a 5.4 mM Nitrate Solution.

The addition of nitrate to the irradiated PCB solutions has the effect of increased loss for all congeners compared to the PCB loss due only to direct photolysis. This is illustrated in Figure 13.

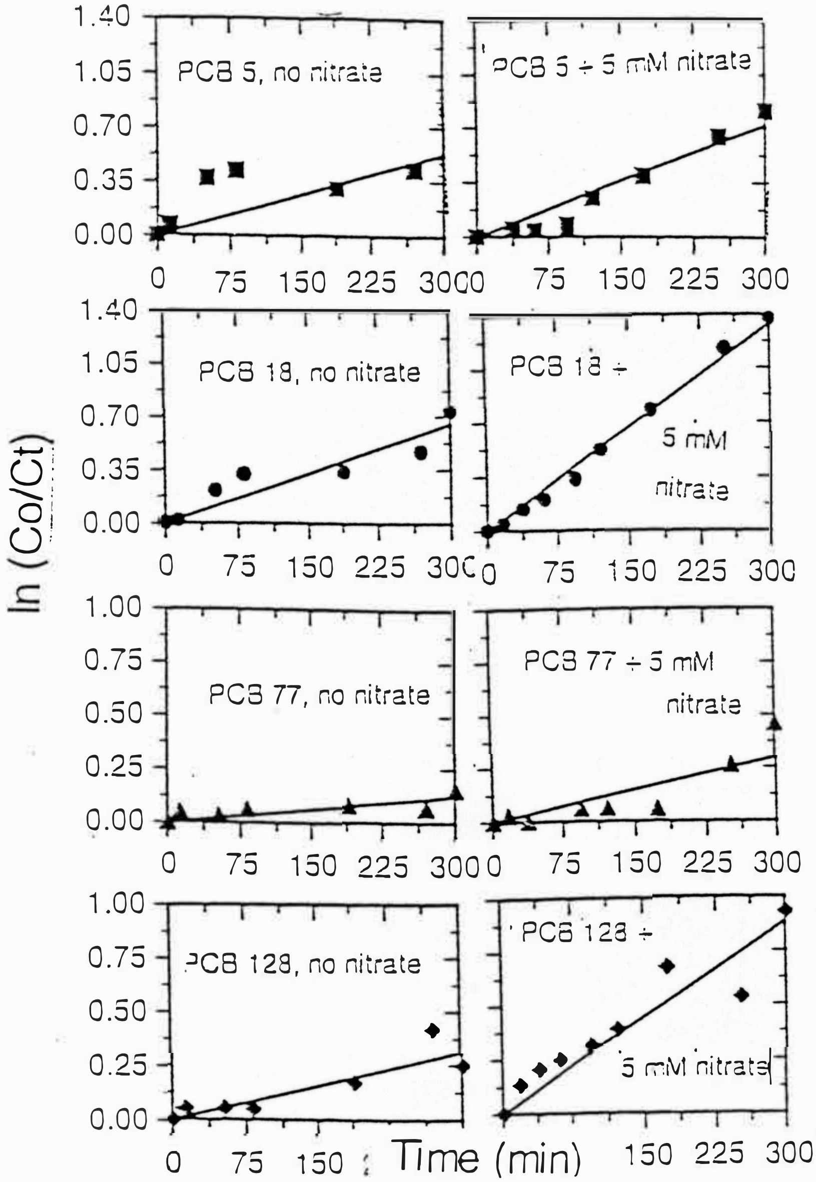


Figure 13. Comparison Between the Photodegradation of PCB Congeners in the Absence and in the Presence of Nitrate.

These results suggest that photodegradation in the presence of nitrate may be an important removal pathway even for the least photolabile congeners like PCB 77, provided that they are truly dissolved in the solution and that no other scavengers of hydroxyl radicals are present.

Photodegradation of PCBs in Natural Waters

Reactions attributable to hydroxyl radicals have been observed when humic substances were irradiated [98]. In the last two decades, many studies have provided unequivocal evidence that hydroxyl radicals are generated in natural water by the photolysis of nitrite and nitrate and photo-Fenton chemistry [99, 100, 101]. Zepp et al. described shallow water bodies with a high concentration of nitrate and low in natural scavengers as having the highest potential for degradation mediated by $HO^{\cdot}$ [97]. Mopper and Zhou reported in 1990 that another source of $HO^{\cdot}$ in marine waters may be due to the direct photolysis of the dissolved organic matter [102, 103]. Vaughan et al. found a pathway for hydroxyl radical production that is dioxygen-independent and which cannot be assigned to nitrate/nitrite photolysis or to Fenton-type chemistry [104].

Besides generating reactive intermediates that may degrade PCBs, humic acid may influence their reactivity in natural waters by screening the light reaching them, thus decreasing the direct photolysis rates and by binding the strongly hydrophobic PCBs and changing their access to the hydroxyl radicals produced in the solution. Using Scientist, the screening factor of humics with different DOC concentrations was calculated for wavelengths between 400 nm and 290 nm, as it is presented in Figure 14.

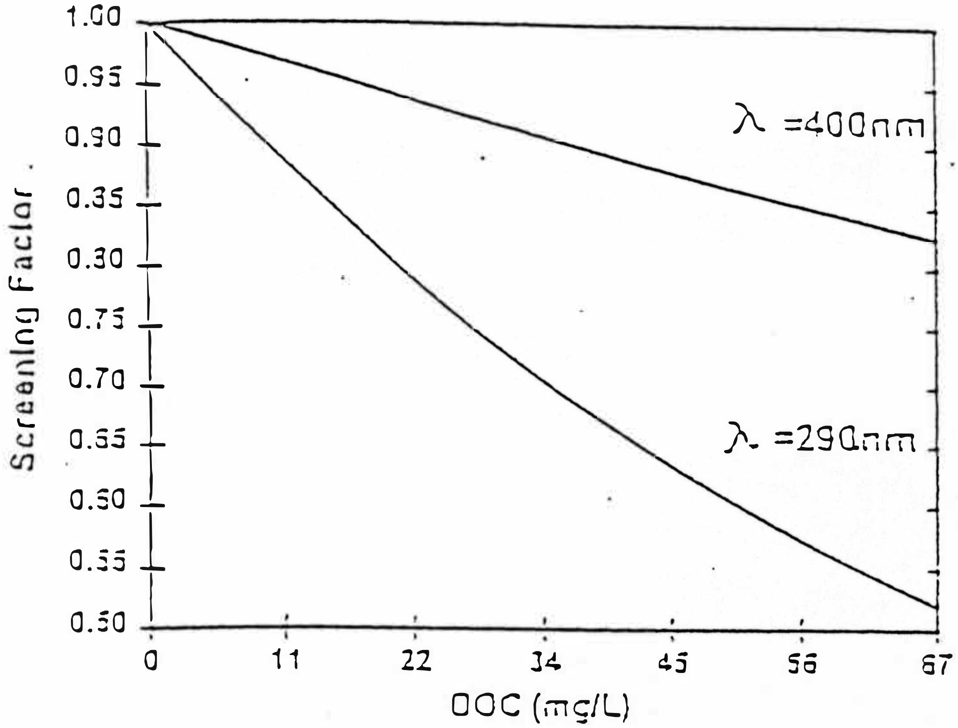


Figure 14. Screening Factor of Humic Acid.

Using Karichoff's method for estimation of K_{DOC} from K_{ow} (Equation 4), the fraction bound by humics for each PCB congener over a wide range of DOC concentrations, was calculated using the formula:

$$f_b = \frac{K_{DOC}[DOC]}{1 + K_{DOC}[DOC]} \qquad (14)$$

Log K_{ow} values for each congener were taken from reference [46]: 5 for PCB 5, 5.5 for PCB 18, 6.2 for PCB 77, 7 for PCB 128.

The binding of the four congeners by HA is presented in Figure 15.

The binding of the four congeners by HA is presented in Figure 15.

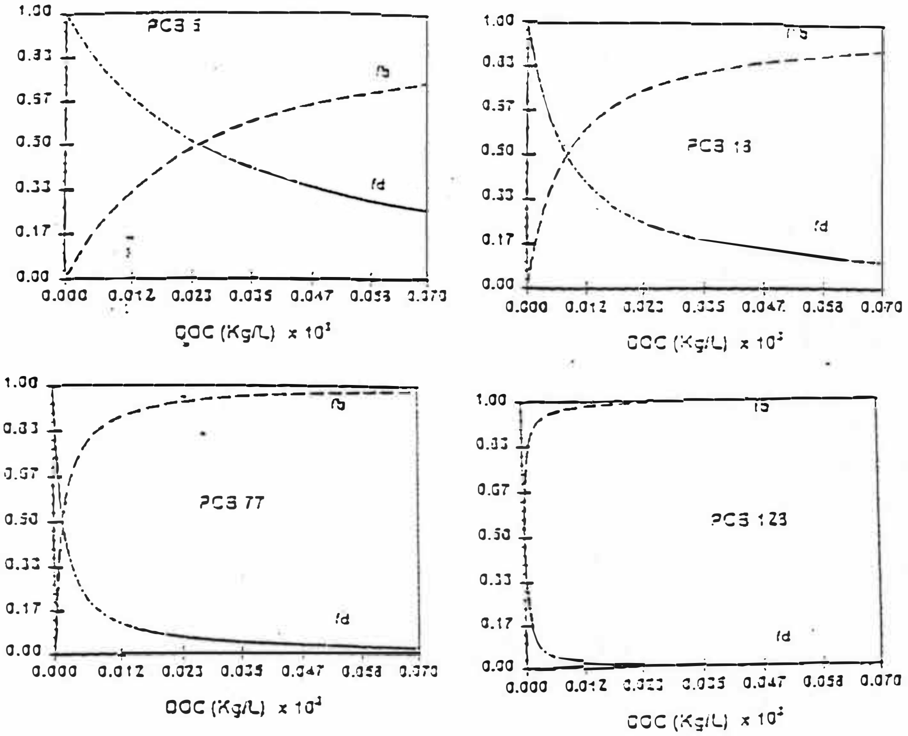


Figure 15. The Binding of the PCB Congeners by Humic Acid.

In our study, PCB 5, PCB 18 and PCB 128 did show photodegradation in the presence of humics. PCB 77 appeared not to be degraded in the presence of humics in our time-series experiments. Competition experiments with different HA concentrations and with /without nitrate were done usually during the same day or in consecutive days; each set of solutions were irradiated around 200 minutes. The PCB 5 and PCB 128 loss in water versus the loss in solutions of humics of different concentrations are presented in Figure 16 and Figure 17 respectively.

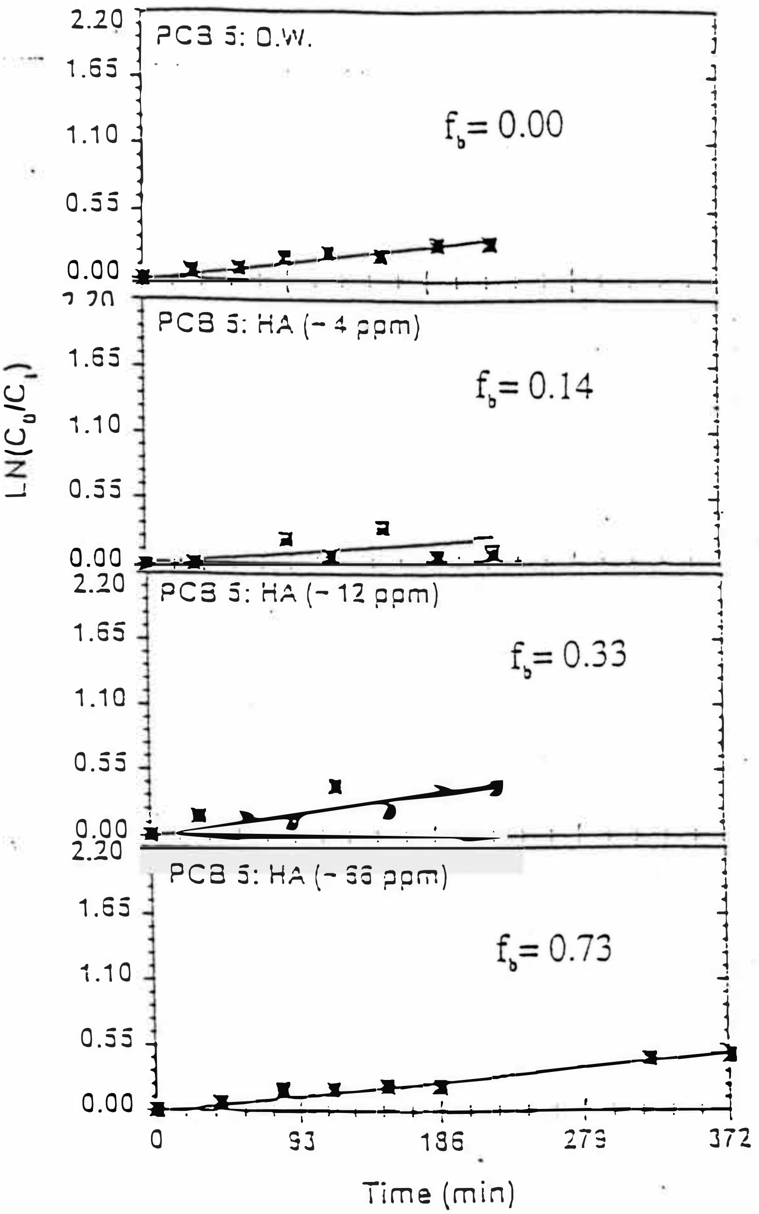


Figure 16. PCB 5 Photodegradation in Distilled Water Versus Varying Humic Solutions.

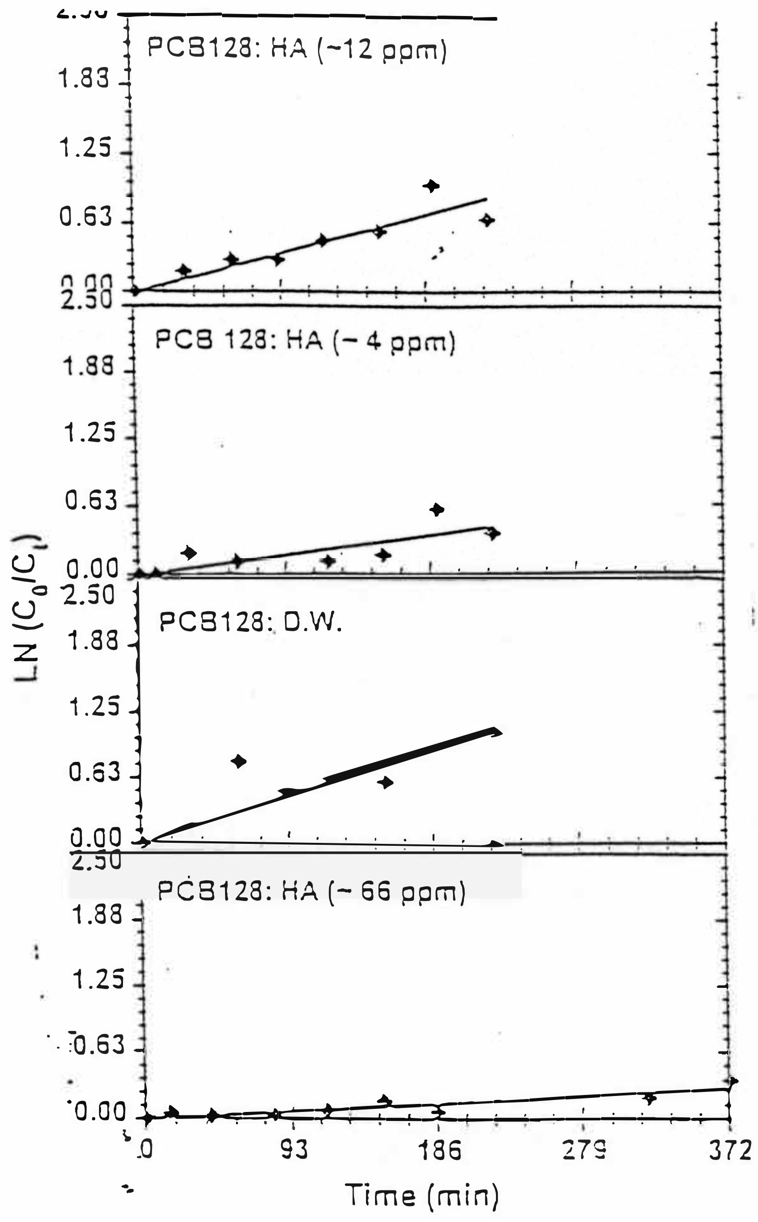


Figure 17. PCB 128 Photodegradation in Distilled Water Versus Humic Solutions of Varied Concentrations.

It appears from Figure 16 that there is no significant difference in the rates of photodegradation of PCB 5 when humic acid is present, even at very high concentrations. This may indicate acceleration in the photodegradation rates of PCB 5 due to the presence of humics. Due to screening, a decrease in the reaction rates of PCBs degraded by direct photolysis is expected as the concentration of DOC increases. For example, at a DOC concentration of 4 mg DOC/L, only 1-3% decrease in the direct photolysis rate is expected, while at 66 mg DOC/L between 20 and 50% decrease in the direct photolysis rate Also as the concentration of DOC increases, the amount of the PCB congener bound to the humics becomes significant. If the PCB congener is degraded by some reactant present in the solution, the binding to the humics is going to hinder the access to it and therefore lower rates of degradation (or less loss) are expected. If the PCB congener is degraded by some reactive species produced by humic acid, binding can improve the access and therefore higher rates of degradation would be expected. PCB 5 is the least-bound congeners in this work. For example, in a HA solution with 4 mg DOC/L, 14% of PCB 5 is in bound-form, at 12 mg DOC/L 33% is in bound-form, while at very high DOC concentrations like 66 mg DOC/L, 73% of the PCB 5 is bound by the humic acid. The influence of the humic acid on the relative photodegradation rates of PCB 5 is illustrated in Table 2.

As it can be observed in Table 2, the rate constants for the photodegradation of PCB 5 are very low and the fact that they are indistinguishable may be due to the experimental limitations.

The influence of the humic acid on the relative photodegradation rates of PCB 128 is illustrated in Table 3; a sample of typical rate constant values, standard deviation of the fit, and the 95% confidence intervals are presented for different DOC concentrations.

Table 2

A Sample of Typical Rate Constant Values for the Photodegradation of PCB 5 in Humic Solutions

DOC (mg/L)	$k_5(s^{-1})$	Std. Deviation	95% C.I.
0	15E-4	.8E-4	[13E-4, 17E-4]
4	9.3E-4	3.2E-4	[0, 15E-4]
12	19E-4	2.5E-4	[13E-4, 25E-4]
66	13E-4	.6E-4	[11E-4, 15E-4]

Analyzing the 95% C. I., it can be observed that the rate constants of the photodegradation of PCB 128 in distilled water and a solution of HA of 4 ppm can be distinguished (smaller k_{128} in HA vs distilled water), and the rate constants of the photodegradation of PCB 128 in a 4 ppm HA solution and a 12 ppm HA solution can be distinguished (bigger k_{128} in the more concentrated HA solution, which would suggest an increase in photodegradation). On the other hand, the rate constants of the photodegradation of PCB 128 in distilled water and in the 12 ppm HA solution cannot be distinguished. Comparing the photodegradation rates of PCB 128 in distilled water and a very concentrated solution of HA (66 ppm)in which most of the congener would be bound, it appears that there is a considerable decrease in reactivity for the HA solution. But in another experiment, the rate constants between water and a concentrated HA solution (47 ppm) in which the congener would also be mostly bound, cannot be distinguished. This is illustrated in Table 4.

Table 3

A Sample of Typical Rate Constant Values for the Photodegradation of PCB 128 in Humic Solutions

DOC (mg/L)	$k_{128}(s^{-1})$	Std. Deviation	95% C.I.
0	48E-4	4.8E-4	[37E-4, 60E-4]
4	3.3E-4	3.3E-4	[11E-4, 27E-4]
12	38E-4	3.5E-4	[30E-4, 46E-4]
66	82E-4	.8E-4	[5.7E-4, 9.6E-4]

Zepp et al. [80] determined the environmental half-lifetime of methoxychlor in a 20 ppm HA solution. In our study, methoxychlor was added to the PCB solutions in trying to assess the environmental halflifetimes of the four PCB congeners. The results are presented in Table 5.

Table 4

Comparison of Rate Constants for the Photodegradation of PCB 128 in Water Versus Very Concentrated HA Solutions

DOC (mg/L)	$k_{128}(s^{-1})$	Std. Deviation	95% C.I.
0	73E-4	.8E-4	[54E-4, 92E-4]
47	76.3E-4	9.3E-4	[54E-4, 98E-4]
0	19E-4	4.9E-4	[37E-4, 60E-4]
66	82E-4	.8E-4	[5.8E-4, 9.6E-4]

Table 5

Estimated Environmental Half-lifetimes of the PCB Congeners Relative to Methoxyclor, in HA 20 ppm

	kMxcl	k5/kMxcl	k18/kMxcl	k77/kMxcl	k128/kMxcl
No. exp.	10	6	9	6	9
Average	0.00114	0.35	0.29	0.37	0.3
Std. Deviation	0.0005	0.24	0.26	0.32	0.25
t1/2 (h)	7.3	20.86	24.91	19.36	24.01

The following applies when discussing the reactivity of all four PCB congeners. Due to the hydrophobicity of the PCBs very low concentration had to be used, as it was discussed earlier, and the volume of the reaction vessels was quite small (50 ml). This may have had an influence on the observed magnitude of the change during one experiment. Another factor that may represent a limitation in these experiments was the irradiation time. Since competition experiments had to be done in the same day, the usual irradiation time for each set of samples was around 200 minutes. Longer irradiation times may have given more conclusive results about the change in the photodegradation rates of the PCB congeners due to humic acids.

Previous work has shown that nitrate is the primary source of hydroxyl radical in natural water, but $HO^{\cdot}$ is also consumed rapidly by natural scavengers [104 and the references therein]. Zepp et al. described shallow water bodies high in nitrate and low in natural scavengers as having the highest potential for degradation mediated by hydroxyl radicals [97]. Availability of hydroxyl radicals for reaction with PCBs depends on the concentrations of naturally occuring scavengers of hydroxyl radicals as well as species that produce it photochemically. A major scavenger of hydroxyl radicals in natural waters is dissolved organic matter (DOC) [104].

In this work, we tried to assess the effect of nitrate-produced hydroxyl radical on the photodegradation of the four PCB congeners at high nitrate concentrations and different DOC concentrations. However we were unable to see a clear trend in the raectivity for all PCB congeners. In the case of PCB 18 an increase of reactivity was observed in the presence of nitrate, at different DOC concentrations. This is shown in

Table 6 and Figures 18-20.

Table 6

Photodegradation of PCB 18 in the Presence and the Absence of Nitrate, in Humic Acid Solutions of Different Concentration

DOC (mg/L)	$k_{18}(s^{-1})$	Std. Deviation	95% C.I.
0	56.8E-4	2.19E-4	[51.7E-4, 61.9E-4]
47	12.1E-4	2.2E-4	[7E-4, 17E-4]
47 + nitrate	23.9E-4	1.3E-4	[20.8E-4, 27E-4]
12	41E-4	1.6E-4	[37E-4, 44.6E-4]
12 + nitrate	89E-4	2.6E-4	[83E-4, 96E-4]
4	23.8E-4	2.1E-4	[18.8E-4, 28.8E-4]
4 + nitrate	44.9E-4	4.3E-4	[35E-4, 55E-4]
115.9	1.05E+11	4.57E+10	1.10E+11
123.7	1.02E+11	4.38E+10	1.05E+11
139.5	9.67E+11	4.33E+10	1.04E+11

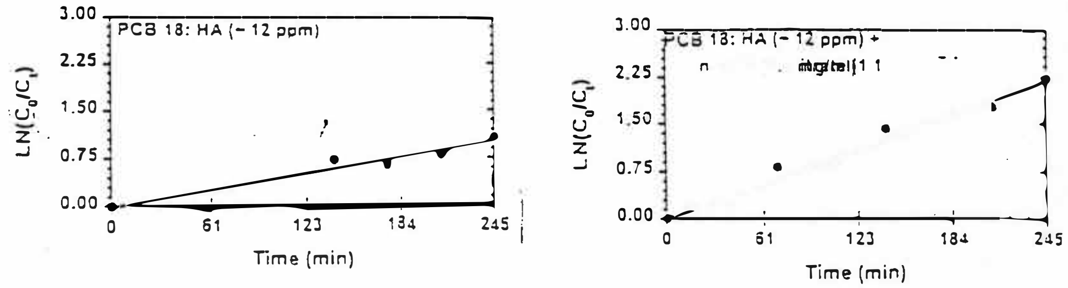


Figure 18. The Effect of Nitrate on the Reactivity of PCB 18 in a 12 ppm Humic Solution.

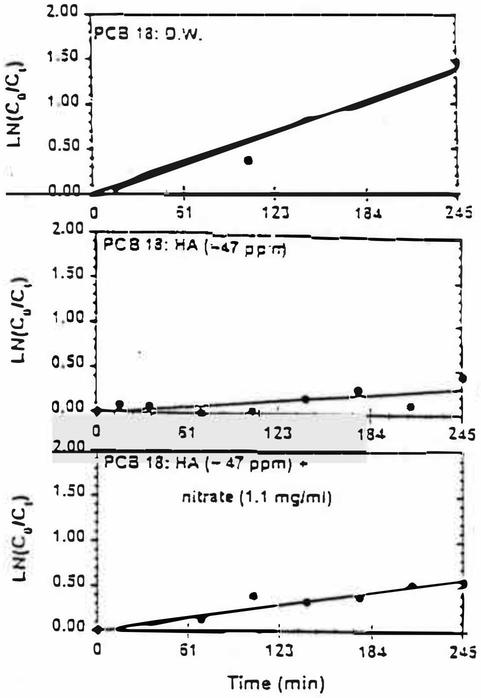


Figure 19. The Effect of Nitrate on the Reactivity of PCB 18 in a 47 ppm Humic Solution.

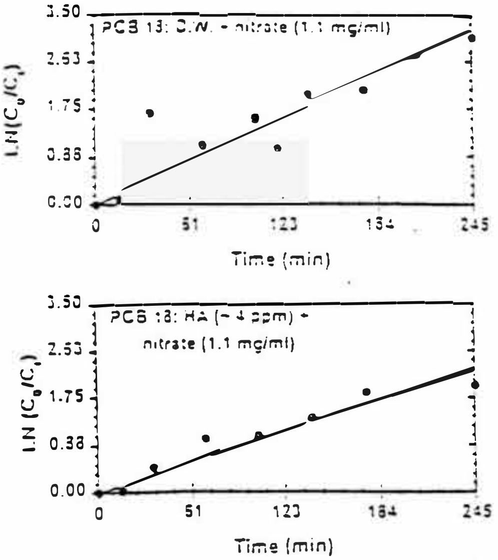


Figure 20. The Effect of Nitrate on the Reactivity of PCB 18 in a 4 ppm Humic Solution.

CHAPTER IV

CONCLUSIONS

PCBs are widely distributed in the environment and they are biologically refractory and toxic pollutants. There is a great interest in understanding their fate and transport in the environment, and also for finding safe and effective degradation methods. Although in the last 15 years the numbers of articles discussing PCBs increased dramatically, the move from the laboratory to the field has been very slow, as can be seen from the history attempts to translate research results into cleanup methods for PCB-contaminated sediments in the Hudson river.

This study was performed in order to understand the photodegradation of four PCB congeners with different degree of chlorination. It appears that all four congeners have the potential to degrade by direct photolysis at sunlight wavelenghts. In our competition experiments using DMDE, an approximate half-lifetime on the order of hours was found for each congener. However, the standard deviations were very large (up to 100%). PCB 5, which is the lowest chlorinated congener and with only one ortho-chlorine, appears to have the longest environmental half-lifetime due to direct photolysis, as expected. PCB 77 loss was very difficult to quantify in many of our experiments because of the scattering of the points and an almost flat slope. It's estimated environmental half-lifetime due to direct photolysis is shorter than that of

PCB 5. PCB 18 appeared to be the most photolabile congener, which was not what we expected. PCB 18 is tri-chlorinated and according to the literature, the more heavily chlorinated PCBs are the most photoreactive. Thus we expected PCB 128 to be the one congener with considerable loss in the direct photolysis experiments. Even with the very big standard deviations for the direct photolysis rate constants, our results suggest that loss due to direct photolysis deserves some more attention and investigation in the modeling of PCBs.

A definite increase in photodegradation rates was observed for all four congeners upon addition of nitrate to the distilled water solutions. This supports the idea that reaction with hydroxyl radicals produced in the environment may provide an important removal pathway for the PCBs. The effect of nitrate may prove to be important in the photodegradation of some less photolabile PCB congeners in the absence of other hydroxyl radical scavengers. For example, PCB 5 showed increased photodegradation in the presence of nitrate, which would translate into a much shorter half-lifetime.

Our experiments in the humic acid solutions were extremely challenging. Even when the standard deviations for the fitting slope were very low, we had a lot of trouble interpreting the results because of their irreproducibility, as it was presented in the previous chapters.

Some explanations for this were offered in the previous chapter. In our experiments, there were many variables which were not taken into consideration; e.g. intensity of the lamp was not determined, the temperature was not controlled, the intensity of the lamp was not determined, the temperature was not controlled, the quantum yields were not determined. An estimate on part of the experimental error could be obtained by extracting as many identical dark control samples and analyzing them. Other factors that may have contributed to the variations in our results were the very low concentrations and the relative short time of irradiation, making it very difficult to measure the light absorbed or the concentration change.

A source of hydroxyl radicals in natural waters is dissolved organic matter or more specifically, humic acid. Humic acid plays a complex role in the fate of pollutants in water: by screening the light it may slow down the photodegradation due to direct photolysis, by binding highly hydrophobic compounds it may affect their access to the reactive species found in the solution or photoproduced intrahumically. The UV/Vis absorption spectrum of the PCBs may be different in the bound phase compared to the dissolved state, which may also influence their photochemistry.

Our results showed that PCB 5, PCB 18, PCB 128 were somewhat degraded upon photoirradiation of humic acid solutions, although no trend could be established. PCB 77 was mostly inert. Also, the extent of photodegradation of the PCB congeners when nitrate was added to humic acid solutions is not very clear.

In our competitive experiments in humic acid solutions, a very large variation in the rate constants for the four PCB congeners was observed compared to that of the DMDE and Methoxyclor. This may give an indication on the variability involved in PCBs reactivity studies (Figure 21, Figure 22).

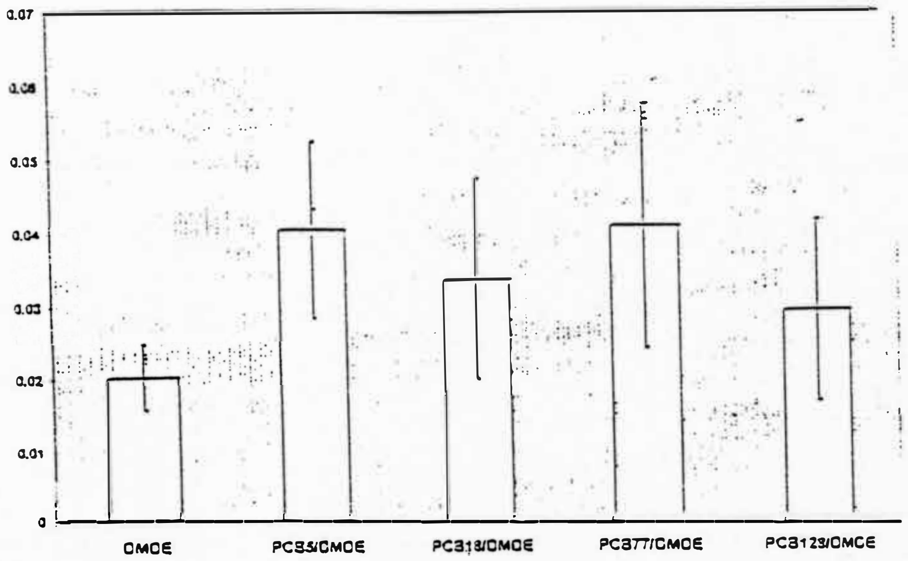


Figure 21. Variability in the Photodegradation Rates of the Four PCB Congeners Versus DMDE.

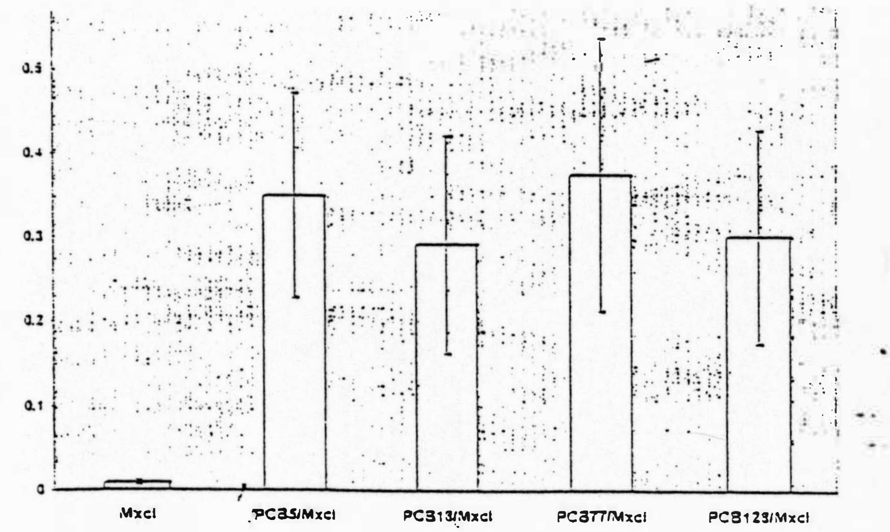


Figure 22. Variability in the Photodegradation Rates of the Four PCB Congeners Versus Methoxyclor.

No single reaction system can simulate what actually occurs in the environment, and more systematic and long studies would be needed to find out what really happens to the PCBs in the natural waters. As shown here, our experimental set-up and design may not be optimal for quantifying the photoconversion of PCBs in humic solutions, but it brings attention to possible relevant removal pathways of these pollutants from the shallow and transparent natural waters. Considering that we are so close to the polluted Lake Michigan, a very interesting experiment that could correlate the lab data with the environmental half-lifetime for the PCB congeners would be photodegradation of the PCB congeners under natural sunlight conditions.

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Appendix A

List of Symbols and Abbreviations

1.	PCBs	PolychlorinatedBiphenyls
2.	TSCA	Toxic Substances Control Act
3.	EPA	Environmental Protection Agency
4.	f	Fugacity
5.	C	Concentration
6.	Z	Fugacity Capacity
7.	K_H	Henry's Law Constant
8.	P	Pressure
9.	K_{OW}	Octanol Water Partition Coefficient
10.	K_{OC}	Carbon Water Partition Coefficient
11.	K_{OA}	Octanol Air Partition Coefficient
12.	K_B	Fish Water Partition Coefficient
13.	HA	Humic Acid
14.	HS	Humic Substances
15.	DOC	Dissolved Organic Carbon
16.	λ	Wavelength
17.	ε	The Molar Absorptivity Coefficient
18.	mM	Millimolar
19.	t	Time
20.	ϕ	The Reaction Quantum Yield
21.	I	The Average Rate of Light Absorption
22.	k_d	Direct Photolysis Rate Constant
23.	$t_{1/2}$	The Half-lifetime
24.	μg	Micrograms

25. S_λ	Light Screening Factor
26. C.I.	Confidence Intervals
27. T	Absolute Temperature
28. f_d	Dissolved Fraction
29. f_b	Bound Fraction
30. ppm	Parts per Million
31. nm	Nanometer
32. D.W	Distilled Water

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