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POLYCHLORINATED BIPHENYLS AND THEIR INTERACTION WITH THE ENVIRONMENT

K. S. Dickerson
N. E. Korte

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ACRONYMS AND ABBREVIATIONS

atm	--	atmosphere
BCF	--	bioaccumulation factor
C	--	centigrade
cm^2	--	square centimeters
d	--	day
DOC	--	dissolved organic carbon
ECD	--	electron capture detector
g	--	grams
GC	--	gas chromatography
h	--	hours
HECD	--	Hall electrolytic conductivity detector
L	--	liter
mg	--	milligram
min	--	minute
mol	--	mole
MS	--	mass spectroscopy
mV	--	millivolt
Pa	--	pascal
PCBs	--	polychlorinated biphenyls
ppm	--	parts per million
SS	--	suspended solids

EXECUTIVE SUMMARY

This document is a review of the existing technical literature regarding the physical and biological properties of polychlorinated biphenyls (PCBs) and their interaction with the environment. It is intended to be used when evaluating PCB-contaminated soil and the effects of specific environmental conditions on PCB degradation. PCBs are a class of chlorinated aromatic compounds with 209 possible structural arrangements (congeners). They are commonly referred to by the trade name Aroclor™ (Monsanto Corporation), followed by a four-digit number that identifies the congener.

The composition of PCBs in the environment changes over time due to various physicochemical and biological properties and processes: vapor pressure, solubility, octanol-water partitioning, adsorption, and biodegradation. As the number of chlorine atoms increases, both vapor pressure and water solubility decrease, while adsorption and the octanol-water partitioning coefficient increase. Dechlorination of PCBs occurs primarily through aerobic and anaerobic microbial degradation. Aerobic bacteria preferentially dechlorinate less-chlorinated PCBs, while anaerobic bacteria preferentially dechlorinate more highly chlorinated PCBs. The less-chlorinated PCB congeners are less persistent in the environment due to volatilization, solubility, and aerobic biodegradation, while the more-chlorinated PCBs are more persistent in the environment due to adsorption.

The composition of an original PCB mixture in the environment can be expected to change due to a combination of processes described above. Any attempt to determine the source of PCBs or Aroclors identified in an environmental sample must be approached with caution to avoid inaccurate conclusions.

1. INTRODUCTION

The purpose of this report is to review and interpret information from existing technical literature regarding the physical properties of polychlorinated biphenyls (PCBs) and their interaction with the environment. The document is designed for use by regulatory personnel, site managers, geologists, and other field personnel whose backgrounds in the environmental chemistry of PCBs are limited.

PCBs are a class of chlorinated, aromatic compounds that have found widespread application because of their general stability and inertness as well as their excellent dielectric properties (Hutzinger et al. 1974). A PCB is any of 209 compounds of the general formula $C_{12}H_xCl_y$, where $x = 0$ to 9 and $y = 10 - x$ (Fig. 1 and Table 1) (Alford-Stevens 1986). Each of the ten positions, shown as 2 to 6 and 2′ to 6′ on Fig. 1, can represent either a hydrogen or a chlorine atom. Different structural arrangements yield 209 possible homologs or isomers, collectively known as congeners (Alford-Stevens 1986). While homologs are PCBs differing in the number of chlorine atoms, isomers have the same number of chlorine atoms but differ in the positions of the chlorine atoms on the biphenyl group.

PCBs are described by various classification schemes, with the Aroclor™ nomenclature being the most popular (a registered trade name of the Monsanto Corporation). Aroclors are mixtures of PCBs that typically contain from less than 20 to 80 individual congeners (Waid 1986; Eganhouse, Gossett, and Cross 1990). Each Aroclor product is characterized by a four-digit number: the first two digits indicate the number of carbon atoms, and the last two digits represent the percent weight of chlorine (e.g., Aroclor 1242 is a mixture containing 12 carbon atoms, with a chlorine content of 42%).

Commercial PCBs were produced by collecting boiling-point fractions during distillation of chlorinated biphenyl mixtures. Not all PCBs are present in Aroclors because some biphenyl positions are more susceptible than others to chlorination (Griffin and Chian 1979). Although 125 PCBs have been found in the various Aroclors, the number of reported components varies depending on the type of analysis performed and the quantity analyzed (Alford-Stevens 1986).

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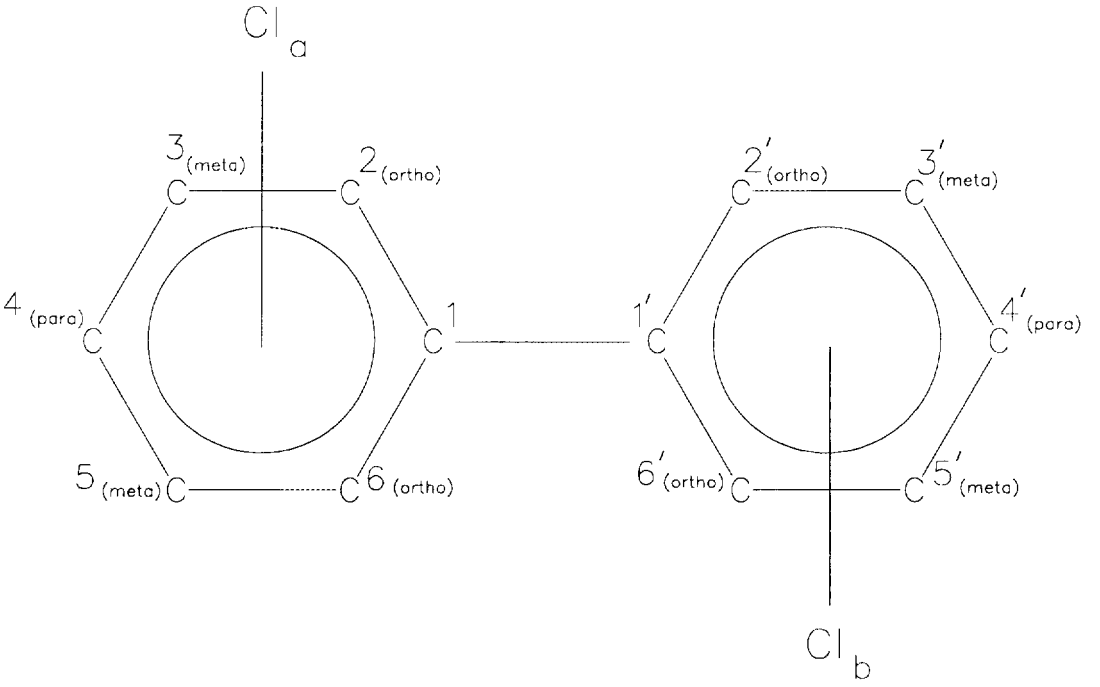

Fig. 1. General formula for PCB compounds where $a + b = 1$ to 10.

Table 1. PCB congeners

Isomer Group	Molecular Formula	No. of Congeners
Monochlorobiphenyls	$C_{12}H_9Cl$	3
Dichlorobiphenyls	$C_{12}H_8Cl_2$	12
Trichlorobiphenyls	$C_{12}H_7Cl_3$	24
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	42
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	46
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	42
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	24
Octachlorobiphenyls	$C_{12}H_2Cl_8$	12
Nonachlorobiphenyls	$C_{12}HCl_9$	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	1

Source: Alford-Stevens 1986.

While most PCB congeners are solids at room temperature, Aroclor formulations are viscous fluids that are resistant to acids, bases, and heat (Alford-Stevens 1986). The primary routes for introducing PCBs into the environment are through leaks from sealed and partially sealed transformers, heat exchangers, and hydraulic systems. Spills, vaporization, and direct disposal of PCBs to the environment have also occurred (Nisbet and Sarofim 1972). Transport of PCBs in the environment may occur by air, surface water, groundwater, dredging and dumping, and bioaccumulation (Nisbet and Sarofim 1972; Leis et al. 1978; Larsson 1983).

PCBs have low water solubilities, which decrease with increasing number of chlorine atoms, as does vapor pressure. The susceptibility of PCBs to degradation depends not only on the number of chlorine atoms but also on the structural arrangement of chlorine atoms among isomers. Sections 3 and 4.3 discuss these issues in more detail.

2. PCBs IN THE ENVIRONMENT

2.1 PERSISTENCE AND OCCURRENCE IN THE ENVIRONMENT

PCBs are among the most stable and, therefore, persistent organic compounds known. Indeed, the occurrence of PCBs in soils, sediments, and surface waters is well documented (NTIS 1990, 1991). The first indication of the worldwide dispersion of PCBs was found in Antarctic birds. Since then, PCBs have been detected in both the atmosphere and water of the open ocean and in marine organisms (Waid 1986). Higher concentrations of atmospheric PCBs are found in the northern regions over the Atlantic and Pacific Oceans; slightly lower concentrations are found over the northern Pacific than in the northern Atlantic. These observations are attributed to the fact that North America and Europe have used larger quantities of PCBs. Seasonal variations in atmospheric concentrations are attributed to higher

concentrations associated with higher precipitation and the seasonal use of specific chemicals. PCBs in ocean waters follow a similar trend to those detected in the ocean atmosphere. It is suspected that, once deposited in ocean waters, the less soluble, more highly chlorinated PCBs are rapidly transported to deeper layers of the water column as sinking particles (Waid 1986). The geographical distribution of PCBs in ocean fish and mammals correlates strongly with ocean-water and atmospheric concentrations (Waid 1986).

2.2 BIOACCUMULATION

The bioaccumulation of PCBs by an aquatic organism is quantified through use of a bioaccumulation factor: a ratio of PCB concentration in an organism to PCB concentration in water. As with PCB transport, the physicochemical properties of individual PCBs are the major controlling factors for bioaccumulation of PCBs (Waid 1986). Two principal factors are: 1) the equilibrium partitioning (as indicated by the octanol-water coefficient, K_{ow}) between an organism's lipids, where PCBs accumulate, and the ambient water; and 2) surface adsorption properties.

Three primary mechanisms govern the uptake of PCBs by biota: inhalation, direct contact, and, most importantly, ingestion of food. The most important uptake mechanism for aquatic organisms is absorption of PCBs through the gills (Waid 1986). Lloyd et al. (1976) observed that bioaccumulation, especially in tissue and organs, appears to be higher for the more chlorinated PCBs.

In addition to bioaccumulation, biomagnification occurs as a series of bioaccumulation steps that transfer PCB concentrations up the food chain, producing higher PCB concentrations in predators at the top of the food chain (Waid 1986).

A more comprehensive discussion of bioaccumulation is presented in *PCBs and the Environment, Volume II* (Waid 1986).

2.3 MIGRATION OF PCBs

Physicochemical properties such as solubility, vapor pressure, and sorption, are important factors for determining the transport of PCBs. Because PCBs have very low water solubilities, low vapor pressures, and high sorption coefficients, they do not dissolve readily in water or vaporize easily and are strongly sorbed onto soils (see Sect. 3). These characteristics indicate that PCBs are not easily transported in an aqueous solution. Indeed, the primary transportation of PCBs in the groundwater environment is by transport of particles with adsorbed PCBs. Likewise, the transport of PCBs in rivers may occur primarily because of adsorption onto particles, readsorption in the sediments, and by sediment transport. Some dissolution will also occur. A less significant transport mechanism, similar to dredging, is bioturbation, the transport of subsurface sediments to the surface by marine organisms (Larsson 1983). This process makes PCB-contaminated sediments available at the water-sediment interface where biota can introduce PCBs into the food chain. PCB transport via bioaccumulation is a small, although important, transport process (Nisbet and Sarofim 1972; Waid 1986). As in the aqueous environment, airborne transport occurs primarily by adsorption of PCBs onto particles that are then distributed by wind and precipitation.

3. PHYSICOCHEMICAL PROPERTIES OF PCBs THAT GOVERN ENVIRONMENTAL TRANSPORT

3.1 VAPOR PRESSURE

The tendency of a compound to transfer to and from the gaseous phase is determined largely by its vapor pressure. Vapor pressure is defined as "the pressure of the vapor of a compound at equilibrium with its pure condensed phase, be it liquid or solid" (Schwarzenbach, Gschwend, and Imboden 1993). PCBs have

very low vapor pressures that decrease with increasing chlorine content (Table 2). For example, Waid (1986) reports Aroclor vaporization rates of 1.74×10^{-3} g/cm^2/h for 1221 decreasing to 9×10^{-6} g/cm^2/h for 1260. Although vaporization of PCBs in soils is low, due to high soil adsorption, vaporization from aqueous solution is anomalously high despite the low vapor pressure and high molecular weight (Waid 1986). For example, based on the escaping tendency (fugacity) of PCBs from a solution, the half-life of PCBs in a fast-flowing river is estimated to be 10 h. Thus, vaporization from an aqueous solution may be an important environmental-transport process.

Henry's Law constant, K_H, is the air to water distribution ratio and is frequently used to describe the air-water partitioning of a compound. Estimated values for K_H have been reported to range from 10 atm L mol^{-1} for less chlorinated congeners to approximately 10^{-2} atm L mol^{-1} for more highly chlorinated congeners (Schwarzenbach, Gschwend, and Imboden 1993). As K_H decreases, the air to water ratio decreases; thus, PCBs with smaller K_H values are less volatile. In other words, the higher chlorine content reduces the partitioning between the air-water phase (Burkhard, Armstrong, and Andren 1985). Burkhard, Armstrong, and Andren (1985) also note that within isomers, K_H increases with decreasing number of *ortho*-chlorine substitutions (or increasing number of *meta*- and/or *para*-chlorine substitutions, Fig. 1). It is important to note that when looking at three-phase PCB partitioning (air-water-soil), adsorption becomes the dominant process in reducing volatilization of the congener.

Several studies have focused on various aspects of vapor pressure and partitioning of PCBs. A study of six different soils reported by Haque, Schmedding, and Freed (1974) showed that isomers of higher chlorine content had the least vapor loss, that increased temperature increased vapor loss, and that adsorption to soils decreased vapor loss (see Sect. 3.4). The lower vapor loss of more highly chlorinated PCBs was attributed to the decrease in vapor pressure with increasing chlorine content. Swackhamer, McVeety, and Hites (1988) found similar results when looking at the partitioning between air, surface water, and lake sediments;

Table 2. Physicochemical properties of PCBs

Compound	Solubility, mg/L	log K_{ow}	log K_{oc}	Vapor Pressure, Pa @ 25°C	K_H	Source
Monochlorobiphenyls	1.19 to 5.90 0.06 to 7.2	4.17 to 4.90 4.3 to 4.73	3.47 to 3.90 ----	---- 0.271 to 2.3	---- 42.56 to 79.3	Waid[a] Mackay[b]
Dichlorobiphenyls	0.08 to 1.50 0.06 to 2.26	4.60 to 5.54 4.9 to 5.3	3.84 to 4.63 ----	---- 0.0018 to 0.6	---- 17.0 to 153.6	Waid Mackay
Trichlorobiphenyls	0.078 to 0.08 0.015 to 1.09	5.51 to 5.54 5.5 to 5.9	4.61 to 4.64 3.34 to 3.5[c]	---- 0.003 to 0.2	---- 24.3 to 102	Waid Mackay
Tetrachlorobiphenyls	0.034 to 0.18 8×10^{-5} to 0.38	5.20 to 5.81 5.6 to 6.5	4.41 to 4.86 3.43 to 5.11	---- 5.9×10^{-5} to 0.0653	---- 1.72 to 94	Waid Mackay
Pentachlorobiphenyls	0.022 to 0.031 0.004 to 0.11	5.84 to 5.94 6.2 to 6.85	4.89 to 4.98 4.15 to 4.51[c]	---- 0.0003 to 0.057	---- 12.2 to 151.4	Waid Mackay
Hexachlorobiphenyls	0.00095 0.0004 to 0.38	6.72 6.7 to 7.3	6.08 4.78 to 6.87	---- 2×10^{-5} to 0.005	---- 6.7 to 86	Waid Mackay
Heptachlorobiphenyls	0.00045 to 0.02	6.7 to 7.1	----	2.73×10^{-5} to 0.0015	5.4 to 100	Mackay
Octachlorobiphenyls	0.0002 to 0.02	7.1 to 8.55	----	2.66×10^{-5} to 0.006	38.8 to 100	Mackay
Nonachlorobiphenyls	1.8×10^{-5} to 0.002	7.2 to 9.14	----	6.3×10^{-6} to 0.00015	100	Mackay
Aroclor 1016	0.332 0.049 to 0.91	5.31 4.3 to 5.88	4.25 4.25 to 5.26	---- 0.053 to 0.2	---- ----	Waid Mackay
Aroclor 1221	3.5 0.59 to 40	4.09 2.8 to 4.7	3.62 3.62 to 3.76	---- 0.893 to 2.0	---- 0.75 to 60	Waid Mackay

Table 2. (cont.)

Compound	Solubility, mg/L	log K_{ow}	log K_{oc}	Vapor Pressure, Pa @ 25°C	K_H	Source
Aroclor 1232	1.45 1.45	4.62 3.18 to 4.54	3.85 2.89 to 3.85	---- 0.53 to 0.54	---- 1.14 to 60	Waid Mackay
Aroclor 1242	0.288 0.045 to 0.703	5.29 3.54 to 5.8	4.09 3.36 to 4.09	---- 0.0133 to 0.12	---- 20.32 to 768	Waid Mackay
Aroclor 1248	0.054 0.043 to 0.32	5.75 5.6 to 6.11	4.74 4.74 to 5.44	---- 0.004 to 0.11	---- 44.58 to 372	Waid Mackay
Aroclor 1254	0.42 0.01 to 0.14	6.11 4.08 to 6.72	4.81 4.81 to 6.65	---- 0.00263 to 0.0103	---- 0.007 to 284	Waid Mackay
Aroclor 1260	0.0027 0.003 to 0.08	6.61 4.34 to 7.5	5.54 5.54 to 6.83	---- 0.0003 to 0.012	---- 17.23 to 722.4	Waid Mackay

[a] *Source:* Waid 1986.
[b] *Source:* Mackay, Shiu, and Ma 1992.
[c] Value is the partitioning coefficient, K_d.

Note: Many values reported in this table are estimated or were determined under various conditions; consult the reference for specific information applicable to the values.

--- = no data available.

Burkhard, Armstrong, and Andren (1985) noted similar temperature effects. Haque, Schmedding, and Freed (1974) also noted that vapor loss under wet conditions was similar to and comparable in magnitude to vapor loss under dry conditions. Fries and Marrow (1984) conducted a laboratory experiment on PCBs in one type of soil only. Although limited in scope, the study showed that less-chlorinated PCBs were preferentially volatilized and also suggested that volatilization was a more significant removal mechanism than microbial degradation.

Although poorly understood, characteristics of the medium, such as surface area, organic content, and pH, also affect vaporization rates in environmental samples (Waid 1986). One recent case study by Anderson and Parker (1990) found that the diffusion of PCBs within soils was dominated by vapor-phase diffusion and that the organic-carbon fraction in the soil tended to limit the diffusion of the PCBs to the surface. These authors also noted that water evaporation had essentially no effect on volatilization of PCBs in subsurface soils.

PCBs also exist in the atmosphere associated with atmospheric aerosols (Swackhamer, McVeety, and Hites 1988). Manchester and Andren (1988) found that PCB concentrations in both the vapor phase and the aerosol phase increased with increasing temperature. Vapor concentrations increased exponentially above 0°C. Higher aerosol concentrations were reported at both the highest and lowest temperatures, with the minimum concentration reported at 0°C. This was attributed to the competition of PCBs and water for aerosol surface area. These results are not surprising because vapor pressure increases with temperature, which would result in a greater loss of less-chlorinated PCB congeners.

Duinker and Bouchertall (1989) also studied the vapor-aerosol partitioning and found that the vapor phase was enriched with a range of PCB congeners (trichlorobiphenyls to heptachlorobiphenyls) while the aerosol phase was enriched with more highly chlorinated PCBs (tetrachlorobiphenyls to hexachlorobiphenyls). They also found that the aerosol-vapor concentration ratio was inversely proportional to vapor pressure. Thus, the higher the aerosol concentration, the lower the volatility of the PCB. Although the concentrations of PCBs in each phase varied significantly, the percent distribution of individual congeners remained constant.

The authors identified two important differences between PCBs in the vapor phase and the aerosols. First, higher vapor-phase concentrations were attributed to particle variability (e.g., total surface area and organic content); and second, vapor-particulate partitioning differs with individual PCB congeners (e.g., lower volatility of more highly chlorinated congeners).

In summary, the composition of PCBs in the environment can be expected to gradually change through time as the less-chlorinated PCB congeners volatilize, leaving the more stable, more highly chlorinated PCB congeners behind.

3.2 SOLUBILITY

The mobility of a PCB in soils and sediments is directly proportional to its solubility in leaching solvents (including water). PCBs are soluble in most common organic solvents and lipids, but are only slightly soluble in water, glycerol, and glycol (Lloyd et al. 1976). Thus, PCBs are not mobile in soils unless very high concentrations of organic solvents are present to carry them (Griffin and Chou 1981).

Different solubilities have been reported in the literature for various Aroclors and individual PCB congeners (Table 2). For example, the National Institute for Occupational Safety and Health (1985) reports that PCB water solubilities range from 0.007 to 5.9 mg/L, while Waid (1986) reports PCB water solubilities ranging from 0.00095 to 5.9 parts per million (ppm) and Aroclor water solubilities ranging from 0.0027 to 3.5 ppm. Haque, Schmedding, and Freed (1974) investigated the water solubility of the PCB isomers in Aroclor 1254 based on gas chromatograph (GC) peak intensities and observed that solubilities decreased with increasing chlorine atoms. The total solubility of Aroclor 1254 was reported to be 0.056 ppm (Haque, Schmedding, and Freed 1974). Equilibrium solubility in water was achieved in about 2 months (the concentration at this point was roughly equal to the concentration at 6 months), with a major portion of the equilibrium achieved rapidly, in

about 1 week (Haque, Schemedding, and Freed 1974). The variance in reported PCB solubilities may be the result of non-equilibrium conditions in the experiments.

It is not surprising that Aroclor solubility decreases with increasing chlorine content because the lower Aroclors, such as 1221, are enriched with less-chlorinated PCB isomers (mono- and dichlorobiphenyls with some trichlorobiphenyls) while the higher Aroclors, such as 1254, are enriched with more highly chlorinated isomers (tetrachlorobiphenyls and higher). Sawhney reports in Waid (1986) that solubility also varies within isomers because of differences in chlorine substitution positions.

Solubility has been correlated to a number of parameters, with the correlations subsequently used for estimating the solubility of individual PCB congeners in the absence of experimental data. For example, Abramowitz and Yalkowsky (1990) estimated PCB congener solubilities based on total surface area and melting point estimates from the number of chlorine atoms and molecular geometry. Although the estimated solubilities compared adequately (within 0 to 0.4 log units) with reported values in the literature for the less-chlorinated congeners, there was a greater variance (0.1 to 1 log units) of solubilities for more highly chlorinated congeners. Patil (1991) correlated solubility to molecular structure with relatively accurate predictions when compared to reported values (within an average of 0.45 log units). While these techniques may give adequate relative data, caution should be exercised when using these estimates to predict soluble concentrations. For example, a 0.45 log unit difference is equivalent to a 64% error, which may not be acceptable for more specific applications of the solubility data. Most importantly, although solubilities vary, the general trend of increasing solubility with decreasing number of chlorine atoms has been consistently reported.

The solubility of PCBs also affects the leaching of PCB-contaminated soil. In a study of the leaching effects of Aroclor 1016 transported by percolating water, the water, after percolating through the contaminated soils, contained PCB concentrations below the solubility range (approximately 0.225 to 0.250 ppm) of Aroclor 1016 in all cases (Tucker, Litschgi, and Mees 1975). Although leaching does not appear to be a major transport mechanism for PCBs, the less-chlorinated

PCBs are, in a relative sense, more readily leached from the soil. Griffin and Chou (1981) found that highly chlorinated PCBs were not leached in soil by water to any significant extent nor were they taken up by plants. However, they found that PCBs that were immobile in soil when leached with water or landfill leachate became highly mobile when leached with high concentrations of organic solvents.

As discussed in this section, solubility is an important mechanism for environmental transport. The solubility of a compound can be significantly influenced depending on the mixture of organic compounds introduced into the environment (Li, Doucette, and Andren 1992). This phenomenon is referred to as cosolvency.

The cosolvency mechanism for water-miscible cosolvents is based on the fact that the added solvent has a significant dipole moment. For example, methanol, because of the —OH group, has sufficient polarity to interfere with the hydrogen bonds in water. Indeed, the methanol molecule is sufficiently polar to be soluble in water in all proportions. The net effect is that a mixture of water and methanol contains fewer hydrogen bonds (less of an "ionic" character) than water alone. Similarly, because of the introduction of the $—CH_3$ group, a mixture of water and methanol has less polarity (more "organic" character) than water alone. Thus, a mixture of water and methanol can enhance the solubility of hydrophobic compounds such as PCBs. This has been demonstrated both in theoretical and laboratory studies (Nkedl-Kizza, Rao, and Hornsby 1985; Rao et al. 1985; Means, Zoeller, and Ma 1989; Rao, Lee, and Pinal 1990; Brusseau, Wood, and Rao 1991; Dickhut, Armstrong, and Andren 1991; and Li, Doucette, and Andren 1992). It is important to note that in order to obtain measurable effects with a polar, miscible cosolvent, these studies found that the cosolvent must be present in concentrations of several percent or greater. Indeed, Staples and Geiselmann (1988) stated "...cosolvents showed significant reproducible sorption/attenuation reductions but probably are ultimately not important to overall solution fate."

Only a few investigators have evaluated the cosolvency effect of partially-miscible or relatively-immiscible compounds. One of these studies compared a number of miscible and partially miscible cosolvents of varying polarity (Pinal et al. 1990). Their results for miscible cosolvents were consistent with other published

studies. They found that a partially miscible solvent can alter the solubility of a hydrophobic organic chemical provided that the concentration of the partially miscible organic solvent "is 1% by volume or higher". The study further concludes that partially polar cosolvents with strong functional groups (e.g., —OH and —NO_2) are more likely to have significant cosolvency than those with weak functional groups (e.g., chlorine).

Li, Doucette, and Andren (1992) examined the solubility of PCBs in several cosolvent systems. Consistent with the studies discussed above, they found an increase in solubility of PCBs with methanol as the cosolvent. Again, significant effects were observed only with relatively high concentrations (>1 mol/L). On the other hand, in aqueous systems saturated with increasingly non-polar cosolvents, the solubility of PCBs actually decreased. The solubility of PCBs decreased even with a solvent such as octanol, which has a strong functional group (—OH). This result is probably due to competition for the water's small capacity to dissolve hydrophobic compounds.

In summary, the composition of PCBs in the environment can be expected to change since the less-chlorinated PCBs are more soluble. For example, Aroclors that have been subjected to leaching with water would show greater proportions of more highly chlorinated PCB congeners than the original mixture. Polar miscible cosolvents are required in concentrations of several percent or higher to show a significant increase in the cosolvency effect for PCBs.

3.3 OCTANOL-WATER PARTITIONING

The octanol-water coefficient, K_{ow}, is a measure of the tendency of a compound to partition between an organic solvent (octanol) and water. PCBs have high octanol-water coefficients, which increase with increasing number of chlorine atoms. K_{ow} values for PCBs have been reported to range from $10^{4.17}$ to $10^{9.14}$ and for Aroclor mixtures to range from $10^{4.09}$ for 1221 to $10^{6.61}$ for 1260 (Table 2).

By definition, water solubility and K_{ow} are inversely related. Therefore, K_{ow} can be used as a measure of the hydrophobic nature of PCBs: a higher K_{ow} indicates a more hydrophobic compound. Opperhulzen et al. (1988) related hydrophobicity of PCBs to the ratio of molecular volume and total surface area. They found a similar trend: as the ratio increased (e.g., more highly chlorinated congeners), the hydrophobicity also increased. Hawker and Connell (1988) also reported a linear relationship between log K_{ow} and the total surface area of the PCB congener and determined estimates of K_{ow} based on this correlation for all PCB congeners. The correlation of K_{ow} and surface area suggests that the larger the surface area, as in more highly chlorinated congeners, the lower the solubility. Thus, the octanol-water partitioning concept further explains the fact that PCBs are readily adsorbed onto soils.

3.4 ADSORPTION

Because the hydrophobic nature of PCBs implies that they have a strong affinity for soils, adsorption is an important factor for determining PCB partitioning in the environment. Moreover, water molecules compete poorly with PCBs for hydrophobic surfaces in soil organic matter, further increasing the likelihood for PCBs to adsorb onto soil surfaces. A laboratory study conducted by Gresshoff, Mahanty, and Gortner (1977) indicated that when stirring an aqueous sample, "a major amount" of Aroclor 1242 adsorbed onto the glass flask from the biological sample. They extended this finding to the field by suggesting that PCBs in the environment would be likely to adsorb to environmental surfaces such as rocks, sand, etc. These early observations have been verified by later, more rigorous studies, resulting in the determination of organic carbon partitioning coefficients (K_{oc}) for various PCBs and Aroclors (Table 2).

Griffin and Chou (1981) found that, in general, more highly chlorinated isomers were adsorbed more readily than less-chlorinated isomers. It should also be noted that the more highly chlorinated isomers are also more tightly adsorbed (Waid 1986). This preferred adsorption is dependent on the positions of the chlorine atoms. The adsorption of Aroclor 1254 was found to be described by a Freundlich isotherm, and equilibrium was established within a few (2 to 4) hours (Wildish et al. 1980). The adsorption-desorption process is typically assumed to be reversible, but Wildish et al. (1980) observed the process to be relatively non-reversible for Aroclor 1254 based on higher desorption concentration factors than adsorption concentration factors. Harkness et al. (1993) observed similar processes in Hudson River sediments. They found that a fraction of the PCB readily desorbed with the remaining fraction desorbing at a rate orders of magnitude slower. This more resistant fraction was assumed to consist of PCBs that were dissolved into the natural organic-matter matrix of the sediment. Thus, desorption was controlled by diffusion through the natural organic matter.

If the adsorption-desorption reaction is non-reversible, the dominant process for contaminant migration becomes diffusion in interstitial water. For example, Di Toro, Jeris, and Clarcia (1985) stated, "The distribution of an adsorbing chemical in a sediment is determined by the diffusive migration in the interstitial water and its adsorption-desorption behavior." They reported the apparent sediment diffusion coefficient to be approximately 3.95×10^{-6} cm^2/d. When compared to bioturbation rates, which range from 10^{-1} to 10^{-2} cm^2/d in near-shore sediments to 10^{-5} to 10^{-6} cm^2/d in deep-sea sediments, the low sediment diffusion coefficient suggests that "in almost all cases transport by biological mixing will dominate the motion of highly sorbed chemicals in the bulk sediment" (Di Toro, Jeris, and Clarcia 1985).

The non-reversible nature of the adsorption-desorption process of PCBs is further supported by the effect of salinity. It was observed that adsorption increased with increasing salinity for silt-clay sediments, and although the results were inconclusive, desorption appears to decrease with increasing salinity (Wildish et al. 1980). pH and redox potential are reported to have no effect on the adsorption of Aroclor 1254 (Gambrell et al. 1984).

In addition to chlorine content and hydrophobicity of individual isomers, organic matter and clay particles play an important role in the adsorption of PCBs. Organic carbon can be divided into two groups: soil organic carbon and dissolved organic carbon (DOC). Higher organic-carbon content in soil increases the amount of PCBs likely to adsorb onto the soils (Waid 1986). Increased adsorption with increasing clay or organic matter content is due to the high cation exchange capacity and high specific surface area of the clay and organic materials (O'Conner and Connolly 1980). For example, Haque, Schmedding, and Freed (1974) conducted a study on the adsorption of PCBs (specifically Aroclor 1254) onto soils with differing organic matter. They reported that soils with low organic matter (silica gel and sand) showed low adsorption, soils with moderate organic matter (kaolinite and montmorillonite clays) showed higher adsorption, and soils with high organic matter (illite clays) showed the highest adsorption.

A more recent study by Hassett and Anderson (1982) studied the adsorption of 2,2′,5,5′-tetrachlorobiphenyl on particles of sewage sludge origin and natural river origin. The PCB congener's greater affinity for the sewage particles was attributed to the higher organic content. 2-Chlorobiphenyl has been reported to be strongly adsorbed to inactive biomass (Bell and Tsezos 1987), which further supports the affinity between PCBs and organic matter. However, because there was considerable scatter in the data, a strong correlation was not identified.

The effect of DOC on adsorption of PCBs is somewhat more complex. An inverse relationship between suspended solids (SS) concentration and the solid-water partition coefficient, K_d, was first observed by O'Conner and Connolly (1980). As the SS concentration increased, K_d decreased. Furthermore, the inverse relationship was more pronounced for compounds characterized by higher K_ds (i.e., more highly chlorinated PCBs). O'Conner and Connolly (1980) also inferred that the SS concentration-dependent partitioning was a function of the solids as opposed to the organic compound. This has practical applications in determining the residence time of PCBs in aquatic systems. For example, because of the lower K_d, it will take longer to flush PCBs from a system if the SS concentration is high.

Hassett and Anderson (1982) also noted this inverse relationship and attributed it to binding of the congener with DOC, which resulted in stabilization of the compound in aqueous solution (i.e., soluble complex formation). It is interesting to note that the authors also identified the possibility of competition for adsorption sites by the congener and DOC. Although this process is possible in theory, it was assumed unlikely by the authors.

The effect of DOC, such as a humic acid, on PCB partitioning was studied in greater detail by Hassett and Milicic (1985). They reported the average equilibrium partitioning coefficient of DOC, K_{DOC} (determined in the laboratory using volatilization measurements) for 2,2′,5,5′-tetrachlorobiphenyl to be 7.1×10^{-4} and independent of DOC. They also reported the rate constants to be 1.7×10^{-4} L $mg^{-1}min^{-1}$ for adsorption and 3.5×10^{-3} min^{-1} for desorption (Hassett and Milicic 1985). These results indicate that equilibrium between the congener and DOC is approached in a matter of hours. Although this study was limited to one congener and one humic acid and may not represent all hydrophobic compounds and DOC in water, it is probable that hydrophobic solutes are at equilibrium with DOC in most aquatic systems. Evans (1988) noted DOC has a sorptive capacity of only 0.2 to 4% of that of octanol.

A field study by Baker, Capel, and Eisenreich (1986) considered the possibility of PCB sorption onto colloids. The K_ds for 28 PCB congeners from Lake Superior field samples were determined to vary by 1 to 3 orders of magnitude as follows: trichlorobiphenyls, $10^{4.5}$ to $10^{7.2}$; tetrachlorobiphenyls, $10^{4.5}$ to $10^{6.2}$; pentachlorobiphenyls, $10^{5.1}$ to $10^{5.7}$; and hexachlorobiphenyls, $10^{5.1}$ to $10^{5.8}$. This variation was attributed to the binding of PCBs to colloids. However, when K_d was plotted verses the fraction of organic carbon, f_{oc}, there was considerable scatter in the data, and a good correlation was not found. The authors noted that the Lake Superior field samples had organic carbon contents 5 to 10 times higher than sediments used in laboratory tests and, therefore, the relationship of K_d to f_{oc} may be weaker than those empirically derived from laboratory studies. More importantly, a strong inverse relationship between K_d and SS was observed. Similar to the observations of

O'Conner and Connolly (1980), they reported that partitioning of more hydrophobic compounds (i.e., high K_ds) was less dependent on the compounds' characteristics than on SS concentration.

Lara and Ernst (1989) considered only the humic substance fraction of DOC on partitioning of 26 PCB congeners, all of high chlorine content. They reported that partitioning to humic substances in the dissolved phase, as described by K_{HS}, increased with increasing number of chlorine atoms, decreased with increasing humic concentration, and decreased within an isomer group with the number of *ortho*-substituted chlorine atoms. When K_{HS} was correlated to other properties of the compound at a given humic substance concentration, they found an inverse correlation with solubility and a direct correlation with both K_{ow} and total surface area. Again, the relative solubility enhancement, indicated by K_{HS}, increased with increasing numbers of chlorine atoms (i.e., more hydrophobic congeners).

The importance of the effect of DOC on PCB partitioning indicates that PCBs may not be described adequately by simple two-phase (soil-water) equilibrium models. Baker, Capel, and Eisenreich (1986) developed a three-phase (dissolved-colloidal-particulate) equilibrium model based on their observations from Lake Superior field samples. The model indicated that in lakes with typically low SS concentrations, a significant portion of the PCB may be associated with colloids. The model also predicted that in water with moderately high DOC (>3.5 mg/L), the colloid phase is likely to be the dominant fraction. Because contaminants associated with colloids are not subject to either sedimentation or volatilization, they may have longer residence times in the water column.

Caron (1989) further illustrated the importance of DOC partitioning by observing model predictions for percent fraction of PCBs partitioned using an equilibrium partitioning model. When DOC was not taken into account, the model predicted that 94% of the PCB congener 2,2′,4,4′-tetrachlorobiphenyl was bound to the organic content of the sediment and most of the remaining 6% was in the water column. But when DOC was taken into account, the model predicted

only 64% of the PCB bound to the sediment, 22% bound to DOC in interstitial water, less than 5% bound to the DOC in the water column, and most of the remaining 9% in the water column.

These studies indicate that the effect of DOC on PCB partitioning cannot be ignored, but that the controlling processes are still poorly understood. For example, Baker, Eisenreich, and Swackhamer (1991) found a poor correlation between K_d and the organic-carbon content of surface-water particulates, which was attributed to the spatial and temporal variation of the particulate organic matter. They suggested that if the colloid concentrations are high relative to filterable SS, overestimation of dissolved PCBs is likely (with increasing estimation errors with increasing K_d). The poor correlation was also attributed to slow partitioning kinetics, with the more soluble PCBs reaching equilibrium faster than the less soluble PCBs. The authors suggest that further research is needed before hydrophobic organic compounds can be modeled accurately for partitioning in the environment.

In summary, the extent and rate of adsorption varies with the number of chlorine atoms on the biphenyl group, the organic carbon content, and the SS concentration. The more highly chlorinated PCBs will be more readily adsorbed onto soils and held to the soils more tightly. Soils with more organic matter will adsorb more PCBs than similar soils with less organic matter. Similarly, within the aqueous phase, more highly chlorinated PCBs will be more readily adsorbed to DOC. Adsorption decreases with increasing SS concentration in aquatic systems and is attributed to sorption by colloids and the formation of soluble complexes with DOC. The combination of adsorption of the more highly chlorinated PCBs and the greater water solubility of less-chlorinated PCBs indicates that the composition of PCBs in the environment can be expected to change with time, with the more highly chlorinated PCBs being less mobile in the environment.

3.5 OTHER PROCESSES

Other physicochemical processes include hydrolysis and oxidation. (See Sects. 4.1 and 4.2 for discussion on photochemical and thermal dechlorination.) Although these reactions are known to occur in the environment, they are of limited importance. Additionally, because of the complex nature of the reactions, most of the available information is based on laboratory studies.

Hydrolysis is defined as "a reaction where a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule" (Schwarzenbach, Gschwend, and Imboden 1993). A study by Roach presented by Waid (1986) states that in the environment, PCB hydrolysis is unlikely because of the vigorous conditions required.

Oxidation reactions are those where the compound donates electrons. Sedlak and Andren (1991) studied the aqueous oxidation of PCBs by hydroxyl radicals (—OH). They found that oxidation rates decreased with increasing number of chlorine atoms and that *meta*- and *para*-chlorine substitutions resulted in lower oxidation rates than *ortho*-chlorine substitutions. They concluded that oxidation of PCBs by hydroxyl radicals in freshwater is probably minor due to the low concentration of PCBs in water but that oxidation by hydroxyl radicals is a possible removal mechanism.

4. DECHLORINATION OF PCBs

Dechlorination is the removal of a chlorine atom from the biphenyl structure, converting more highly chlorinated PCB congeners into less-chlorinated congeners. However, complete destruction of the PCB molecule is not usually the case (Brown et al. 1987a). Dechlorination results from photochemical degradation, thermal degradation, and biodegradation, both aerobic and anaerobic. In general, less-chlorinated congeners are more susceptible to biodegradation, which is the principal dechlorination mechanism in the environment.

4.1 PHOTOCHEMICAL DECHLORINATION

Laboratory experiments have studied photolysis of PCBs in the gaseous, solution (primarily with solvents because of the low water solubility), and solid phases and indicate that photolysis occurs primarily at the high-energy end of the solar spectrum (Waid 1986). Photolysis causes dechlorination of more highly chlorinated PCBs to less-chlorinated PCBs, with photolysis rates faster in the more highly chlorinated PCBs (Brown et al. 1987a). In addition, preferential dechlorination of *ortho*-substituted molecules has been observed. Therefore, photochemical degradation is influenced by both the extent of chlorination and the position of the chlorine substitution.

As in laboratory studies, the more highly chlorinated commercial PCBs also photolyze preferentially in environmental samples (Brown et al. 1987a; Waid 1986). Although photolysis is assumed to be a minor process, Waid (1986) presents a study by Bunce, Kumar, and Brownlee that suggests that photolysis may play a significant role in PCB chemistry in the environment. They estimated that for shallow surface water, at least one chlorine was removed by photolysis from a highly chlorinated PCB annually.

4.2 THERMAL DECHLORINATION

Numerous laboratory experiments show that pyrolysis below 700°C produces various hazardous compounds and that higher temperatures decompose PCBs completely (Waid 1986). However, the vigorous conditions required for this reaction make its occurrence in the environment unlikely. Further discussion on thermal degradation of PCBs may be found in Korte, Muhr, and Greene (1992).

4.3 MICROBIAL DECHLORINATION

Biodegradation of PCBs is of interest not only for an improved understanding of their environmental fate but also for their treatability (Hill et al. 1989; Donaldson et al. 1988). Several studies have investigated the biodegradation of PCBs by specific bacterial strains to help understand possibilities for bioremediation (Bedard et al. 1987a, 1987b; Bedard and Haberl 1990; Morris et al. 1992; May et al. 1992). Although microbial degradation of PCBs could be both practical and economically possible for remediation, it has not yet been successfully demonstrated on a large scale (Hill et al. 1989). While low concentrations of PCBs can stimulate bacterial growth, large concentrations are clearly toxic to microorganisms (Waid 1986). Thus, bioremediation of PCBs must be evaluated on an individual basis.

Iwata, Westlake, and Gunther (1973) observed the degradation of Aroclor 1254 in six soil types varying in organic content, pH, and composition (sand, silt, and clay). Degradation of the PCBs occurred in the soils in 4 to 12 months. Although no attempt was made to correlate soil characteristics to degradation, it was observed that the various soil types preferentially degraded the less-chlorinated PCBs at different rates. Thus, the composition of PCBs in soil was changed with time from less-chlorinated congeners to more-chlorinated congeners. Degradation of PCBs in aquatic systems varies with salinity (U.S.EPA 1983). PCBs readily biodegrade in fresh waters while the process is considerably slower is saltwater.

Both aerobic and anaerobic biodegradation have been demonstrated to result in dechlorination of PCB congeners. Furukawa, Tonomura, and Kamibayashi (1978) investigated aerobic biodegradation of pure PCB congeners. They found that biodegradation decreased with increasing number of chlorine atoms. In particular, PCB congeners with more than four chlorine atoms were less susceptible to aerobic biodegradation. Additionally, preferential biodegradation was observed based on the chlorine substitution pattern. Congeners with *ortho*-chlorine substitutions were poorly degraded after 20 h, and congeners with all of the chlorine atoms substituted on one ring degraded more readily than when the same number of chlorine atoms were substituted on both rings.

Fries and Marrow (1984) studied the degradation of seven PCB congeners in soil. They also reported that aerobic biodegradation occurred faster for less-chlorinated PCBs than for more highly chlorinated PCBs. The maximum rate (measured as respired CO_2 without separating volatilization from degradation) was reached at about six weeks after incubation. While aerobic degradation of Aroclors has been demonstrated, it may require additional growth substrate that is not present in the environment to maintain the microbial population (Brunner, Sutherland, and Focht 1985; U.S.EPA 1983).

Larsson and Lemkemeier (1989) reported that aerobic degradation of Aroclor 1254 in lake waters and sediments with either a high or low content of humic substances was very low, <0.23%. Because up to 90% of the PCBs were found sorbed onto soil, the low amount of degradation was attributed to lower microbial availability.

Biological dechlorination rates vary due to individual PCB congeners. Berthouex and Gan (1991) estimated aerobic biodegradation half lives of di-, tri-, and tetrachlorobiphenyls (i.e., the more readily biodegradable PCB congeners) to be six, seven, and 38 months respectively. These half lives were determined in surface soils (0 to 12 in.) with rich cultures of both aerobic and facultative anaerobic bacteria present. Because no attempt was made to quantify PCB losses by specific mechanisms such as biodegradation or volatilization, these rates should be considered as overall disappearance rates.

Harkness et al. (1993) looked at the aerobic biodegradation of PCBs in Hudson River sediments. They found that both aerobic and anaerobic degradation occurred but that field biodegradation rates were 2 to 3 times slower than those determined in the laboratory. In addition, no more than 60% of the PCBs in the sediments were degraded in both field and laboratory studies. This finding was attributed to the "pseudo-non-reversible" adsorption-desorption process (Sect. 3.4). In other words, some of the adsorbed PCBs desorb so slowly that they are essentially not available for biodegradation. Nies and Vogel (1990) also indicated that desorption may control biodegradation. They also reported that the addition of

various substrates (acetate, acetone, glucose, and methanol) increased the dechlorination rate of Aroclor 1242. Thus, the combination of environmental conditions and the number of chlorine atoms affects the rate at which a congener is aerobically biodegraded. The U. S. National Research Council's Committee on the Assessment of Polychlorinated Biphenyls in the Environment (1979) stated that "attempts to extrapolate the [biodegradation] results to environmental conditions introduce considerable uncertainty," which is indicated by the above, more recent studies.

It has been noted that in some cases, individual PCBs do not degrade as easily as PCB mixtures. Baxter et al. (1975) found that some less-chlorinated congeners appeared to be slowly degraded when alone but degraded readily when present in a PCB mixture. For example, they observed that 4,4′-dichlorobiphenyl degraded to 50% in 2 days when present in Aroclor 1242 but was essentially unaffected when degraded alone after 12 days. This "enhanced" degradation was attributed to possible cometabolism. Cometabolism requires a secondary source of energy that is not available from the compound (primary source of energy) undergoing microbial degradation (Roberts 1987). Most importantly, these results indicate that behavior of individual PCB congeners may not enable predictions to be made on the biodegradability of PCB mixtures (Baxter et al. 1975).

Several studies have demonstrated that anaerobic reductive dechlorination occurs in PCB contaminated sediments (Brown et al. 1984, 1985, 1987a, 1987b; Quensen, Tiedje, and Boyd 1988; Nies and Vogel 1990; Ye et al. 1992; Harkness et al. 1993). Aroclors 1242, 1248, 1254 and 1260 have also been shown to undergo anaerobic degradation in sediments (Quensen, Boyd, and Tiedje 1990). Unlike aerobic degradation, anaerobic degradation occurs more readily in the more highly chlorinated PCB congeners. Thus, anaerobic dechlorination converts highly chlorinated PCB congeners to less-chlorinated congeners that are biodegradable by environmental aerobes.

Brown et al. (1984, 1985, 1987a, 1987b) found that several different dechlorination patterns (determined by chromatogram congener peak distributions) existed in Hudson River sediments. These results suggested that various microbial populations selectively dechlorinate PCBs. This preferential dechlorination occurred in

two main categories based on the chlorine substitution patterns on the biphenyl group (Brown et al. 1987a). In the first category, chlorine atoms were selectively removed from only the *meta*- and *para*-substituted positions while in the second category, chlorine atoms were removed from the *ortho*-substituted positions as well as the *meta*- and *para*-substituted positions. While anaerobic dechlorination has been shown in laboratory experiments, total dechlorination of PCBs to biphenyl has not been observed (Van Dort and Bedard 1991). Preferential dechlorination of *meta*- and *para*-chlorine substitutions and the subsequent accumulation of less-chlorinated, *ortho*-substituted congeners has also been demonstrated by Nies and Vogel (1990); Abramowicz et al. 1993; Ye et al. 1992; and Williams 1991, 1994). Preferred *meta*- and *para*-dechlorinations convert a large variety of highly chlorinated PCB congeners into predominately mono- and dichlorobiphenyls with *ortho*-substitutions. This is important because oxidation, which breaks the rings, occurs at the *meta* position.

Anaerobic dechlorination rates were found to correlate linearly with PCB concentration at sediment concentrations <250 ppm, while dechlorination rates were independent of concentration at higher PCB sediment concentrations (Abramowicz et al. 1993). Dechlorination was observed after 4 weeks and degradation rates (measured as direct chlorine removal) were higher at higher sediment concentrations. The rates were attributed to partitioning of PCBs between the aqueous phase and the solid organic phase of the sediments (i.e., organic matter). Sediment concentrations of nearly 300 ppm (using typical partitioning coefficients) would be required to saturate the sediment pore water. Thus, rates are directly proportional to the aqueous phase PCB concentration, with saturated aqueous concentrations at sediment concentrations >300 ppm. As indicated by the anaerobic dechlorination rates, anaerobic degradation of more highly chlorinated congeners in sediments is possible and is achieved because the microbes typically have a sufficient energy source (organic matter).

Both pH and redox potential have also been shown to influence dechlorination of PCBs in contaminated sediments. Pardue, Delaune, and Patrick (1988) found that biodegradation was higher under moderately aerobic conditions

(maximum influence at +250 mV) than either aerobic conditions (+500 mV) or anaerobic conditions (-200 mV). Indeed, degradation rates (measured as respired CO_2 with volatilization accounted for) were 30 to 40 times higher in moderately aerobic sediments than in anaerobic sediments. This indicates that oxygen availability to the microbial population is the limiting factor for PCB biodegradation (Pardue, Delaune, and Patrick 1988). The highest degradation rates were observed at pH 6.5. However, because the sediment sample pH was 6.7, the maximum degradation rates at pH 6.5 were not surprising and are probably due to the adaptation of the microbial population near this pH. This indicates that the effects of pH on biodegradation will vary based on individual site conditions.

In summary, both aerobic and anaerobic microbial dechlorination are known to occur and are controlled by adsorption-desorption, oxygen availability, and type of microbe present. While aerobic dechlorination occurs more readily in less-chlorinated PCBs, anaerobic dechlorination preferentially reduces more-chlorinated PCBs. Thus, alternate anaerobic/aerobic degradation is necessary for complete PCB destruction. Both aerobic and anaerobic dechlorination occurs preferentially based on the chlorine substitution pattern, with *ortho*-substitutions less readily biodegradable.

5. ANALYSIS OF PCBs AND AROCLORS

Three problems are frequently encountered when analyzing for PCBs: composition, analytical sensitivity, and incurred or environmental residues (Waid 1986). Analyzing Aroclor mixtures that typically include from less than 20 to 80 congeners means having to detect and measure a group of compounds differing in chemical and physical properties and varying significantly in molecular weight. Analytical sensitivity may also present a problem because different analytical methods have different sensitivities. For example, halogen-sensitive chromatographic detectors can identify PCBs in soils at concentrations below 1 ppm (Waid

1986). Mass spectrometric methods are typically not so sensitive but instead, permit more accurate identification.

Environmental residues cause the most serious problem because analytical results often cannot be correlated to known standards. For example, preferential removal or alteration of a PCB congener will result in a residue that does not resemble the parent mixture and will not have the same chemical properties (Waid 1986). From an analytical viewpoint, the environmental residue will not extract from the sample or elute during analysis in the same manner as the parent mixture. A primary focus of this report, therefore, is to describe the mechanisms that alter environmental samples of PCBs in order to understand the precautions that must be taken when drawing conclusions from PCB analyses.

5.1 METHODS

PCB analysis requires the separation of extracted components from a sample and the subsequent identification and measurement of these compounds. The sample components are separated by gas chromatography (GC), where the detectors most widely used for PCBs are the electron capture detector (ECD) and the Hall electrolytic conductivity detector (HECD). Both the ECD and HECD are sensitive to chlorine and are suitable for detecting very low (sub-picogram) levels of PCBs (Holms and Carmichael 1991). However, the analysis of PCBs containing impurities (e.g., coal-tar residue) can result in large background interference, making confirmation of target compounds difficult (Holmes and Carmichael 1991). Furthermore, because the ECD is sensitive to the amount and position of chlorination, the detector response may vary as much as two to four orders of magnitude between mono- and polychlorinated species (Waid 1986). For most samples, however, both the ECD and HECD offer high sensitivity and provide reliable results (Waid 1986).

To analyze a sample for PCBs, a small amount of the extracted sample is injected into a GC column where the components are vaporized as they move through the column. As sample components exit the GC column, they are observed as peaks on a graph (called a chromatogram) of relative abundance verses time (Alford-Stevens 1986). The pattern of peaks is then examined and compared to the patterns of standard Aroclor samples. This technique is referred to as peak matching. Peaks having retention times corresponding to standard peak retention times are an indication of which Aroclor is present in the sample. Figures 2 and 3 are chromatograms of the standard Aroclors 1242 and 1248. A sample containing both Aroclor 1242 and 1248 is shown in Fig. 4. Finally, Fig. 5 is a chromatogram of a soil sample containing PCBs of unknown origin. As can be observed when attempting to match peaks from Figs. 4 and 5 with the standard peaks in Figs. 2 and 3, problems occur when mixtures of Aroclors are contained in the same sample. This is analogous to the situation when either degraded or weathered PCBs are contained in the sample. In these cases, it may be necessary to examine the samples by mass spectroscopy (MS) following separation by GC (GC/MS).

With GC/MS analysis, the unique mass of an ion is identified. GC/MS utilizes the entire isotopic distribution of chlorine in identifying the chlorination of PCBs. Thus, identification problems encountered with GC analysis can be resolved using MS. If unique ions known to result from PCBs are found, it can be possible to confirm the Aroclor identification determined with the GC. For example, Fig. 6 shows a sample in which the peaks for the ions 190 and 222 represent a close match to the Aroclor 1232 standard, confirming its presence in the sample.

5.2 PROBLEMS

Several researchers have studied the problems involved when determining PCBs congeners based on matching chromatograms of Aroclor standards. In one study, peaks from biological PCB samples (fish and turtle) analyzed by GC were compared to peaks of a known Aroclor (Schwartz, Stalling, and Rice 1987). PCB

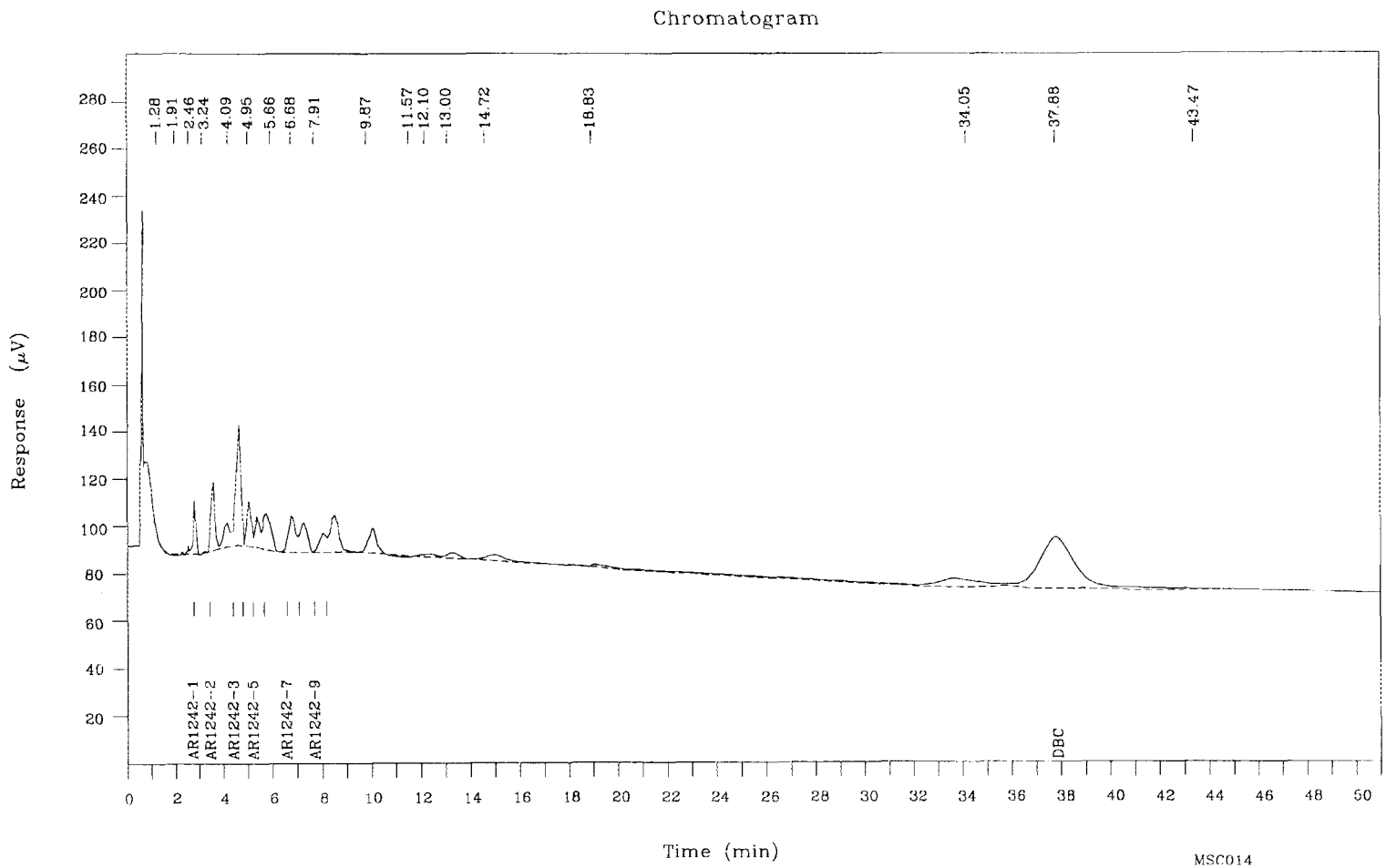

Fig. 2. Standard Aroclor 1242 chromatogram. *Source:* Pace Laboratories, Inc., 1990.

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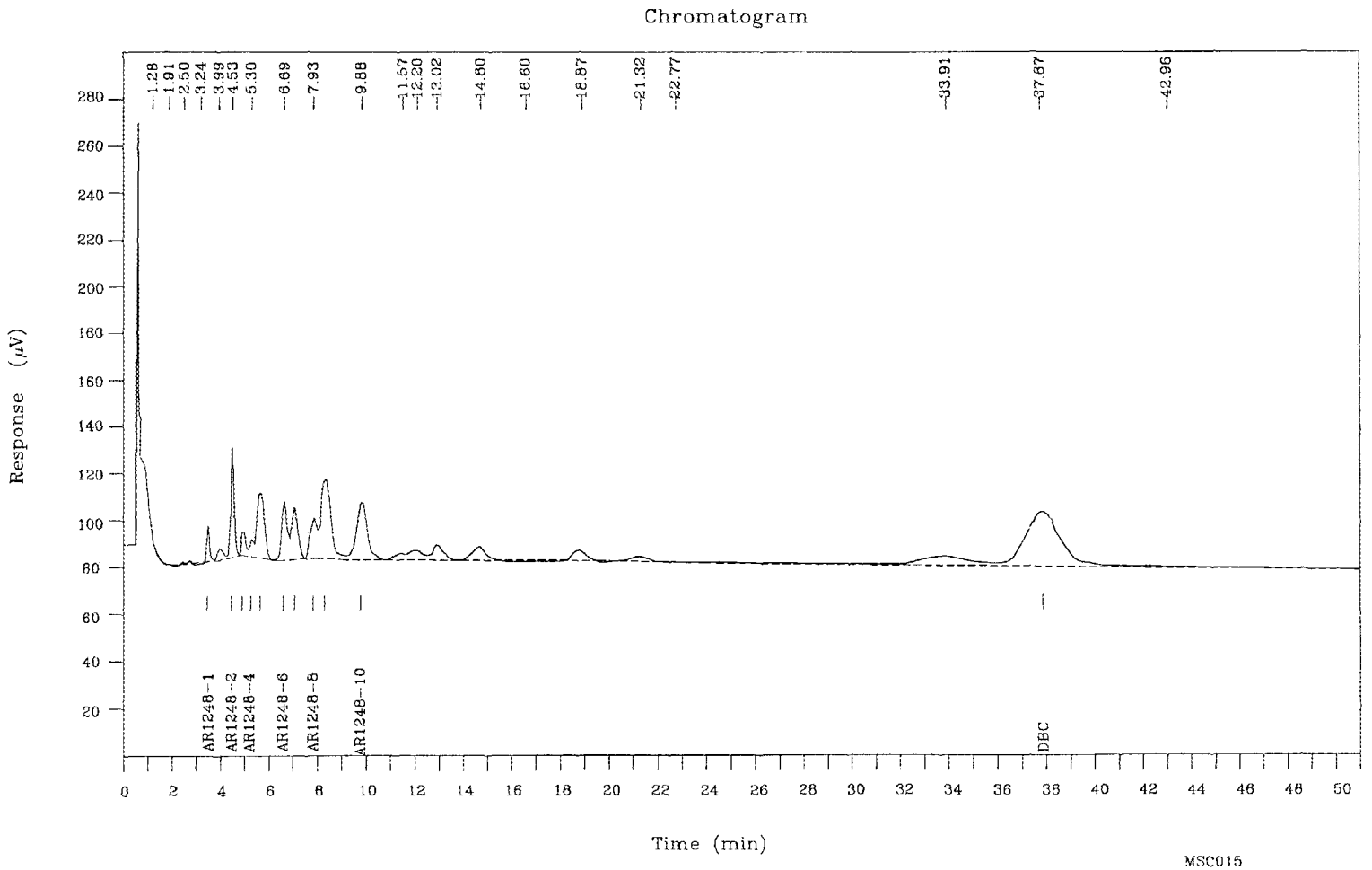

Fig. 3. Standard Aroclor 1248 chromatogram. *Source:* Pace Laboratories, Inc., 1990.

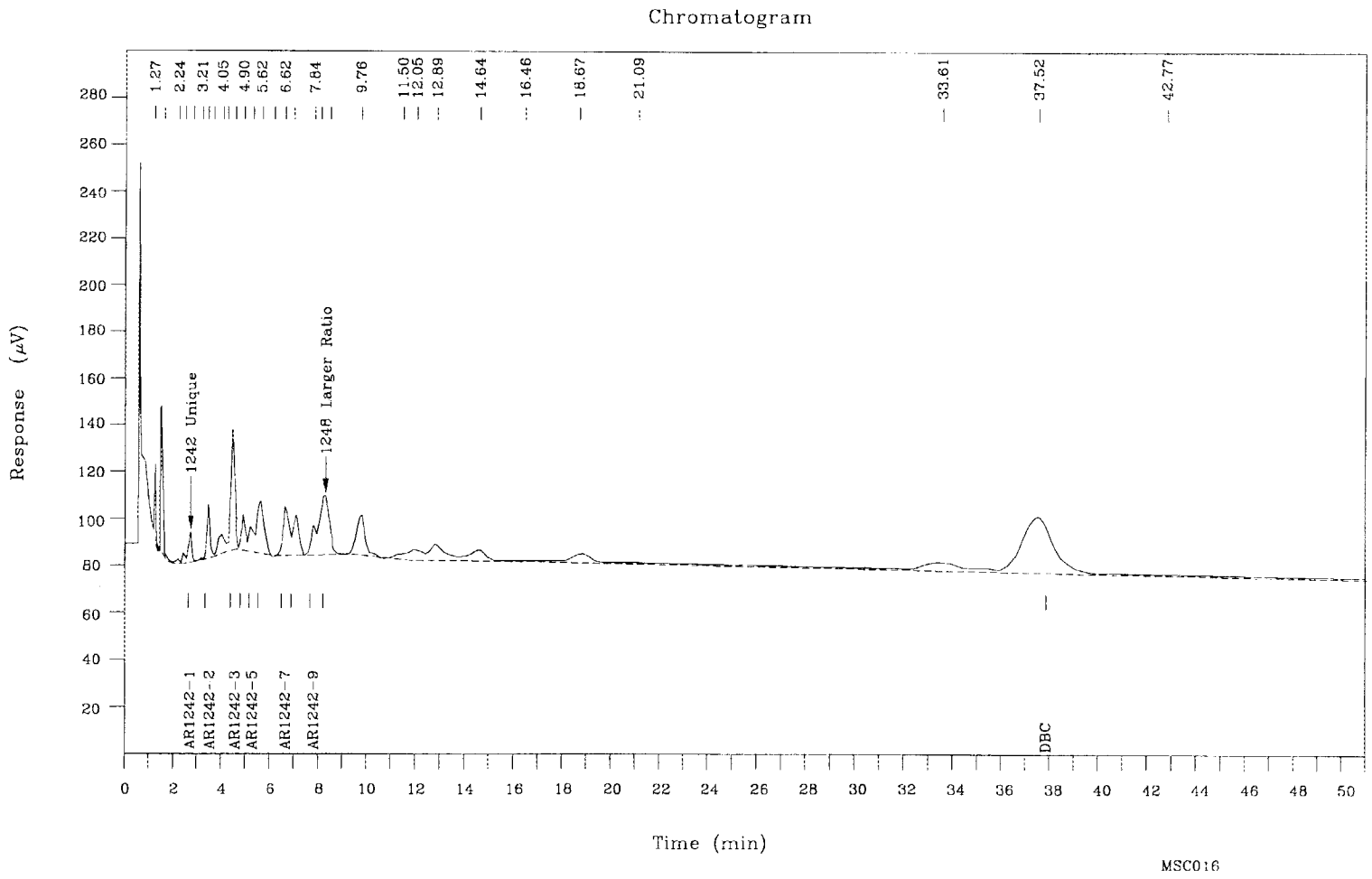

Fig. 4. Chromatogram of an Aroclor 1242 and 1248 sample. *Source:* Pace Laboratories, Inc., 1990.

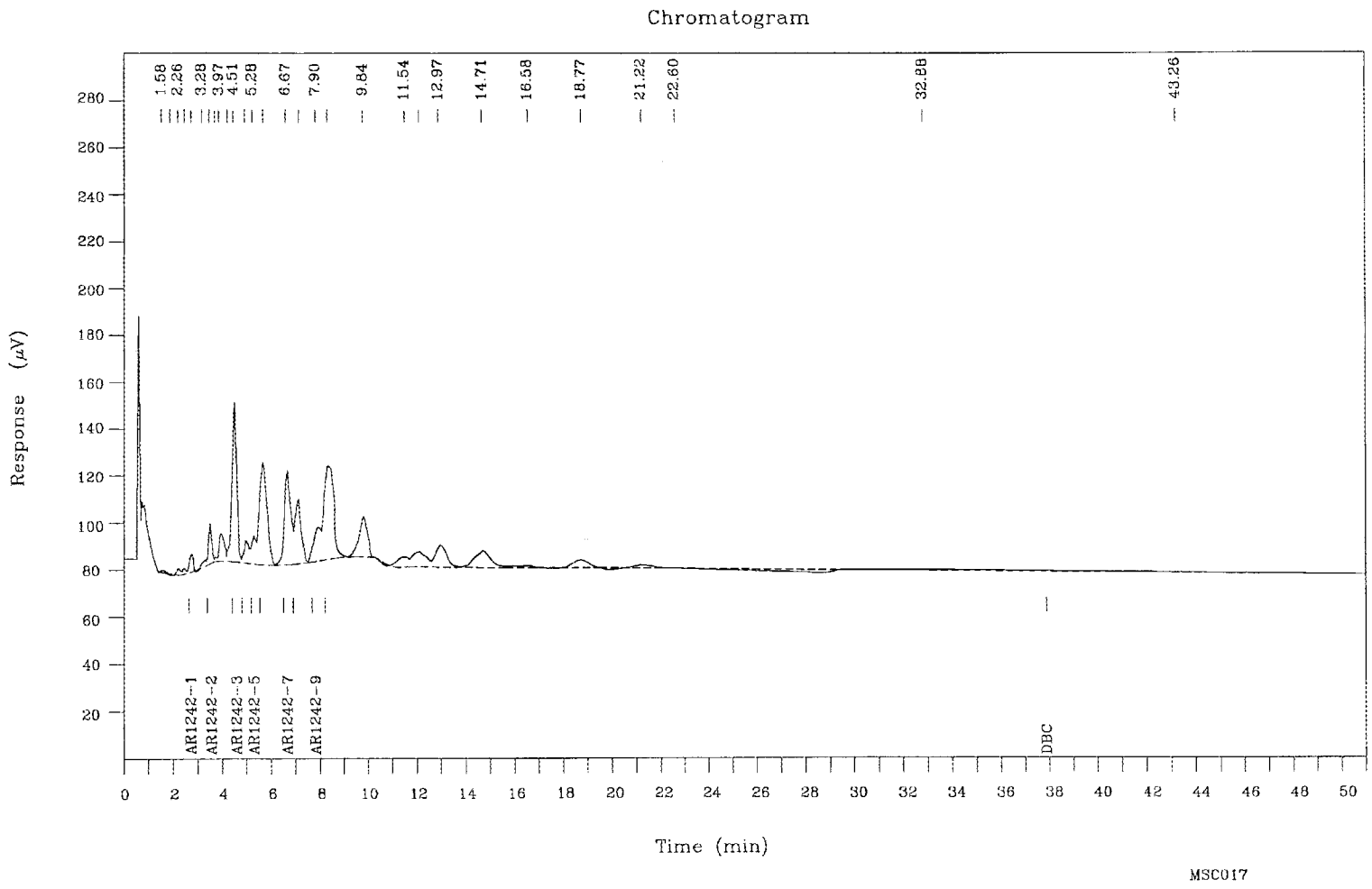

Fig. 5. Chromatogram of a PCB soil sample. *Source:* Pace Laboratories, Inc., 1990.

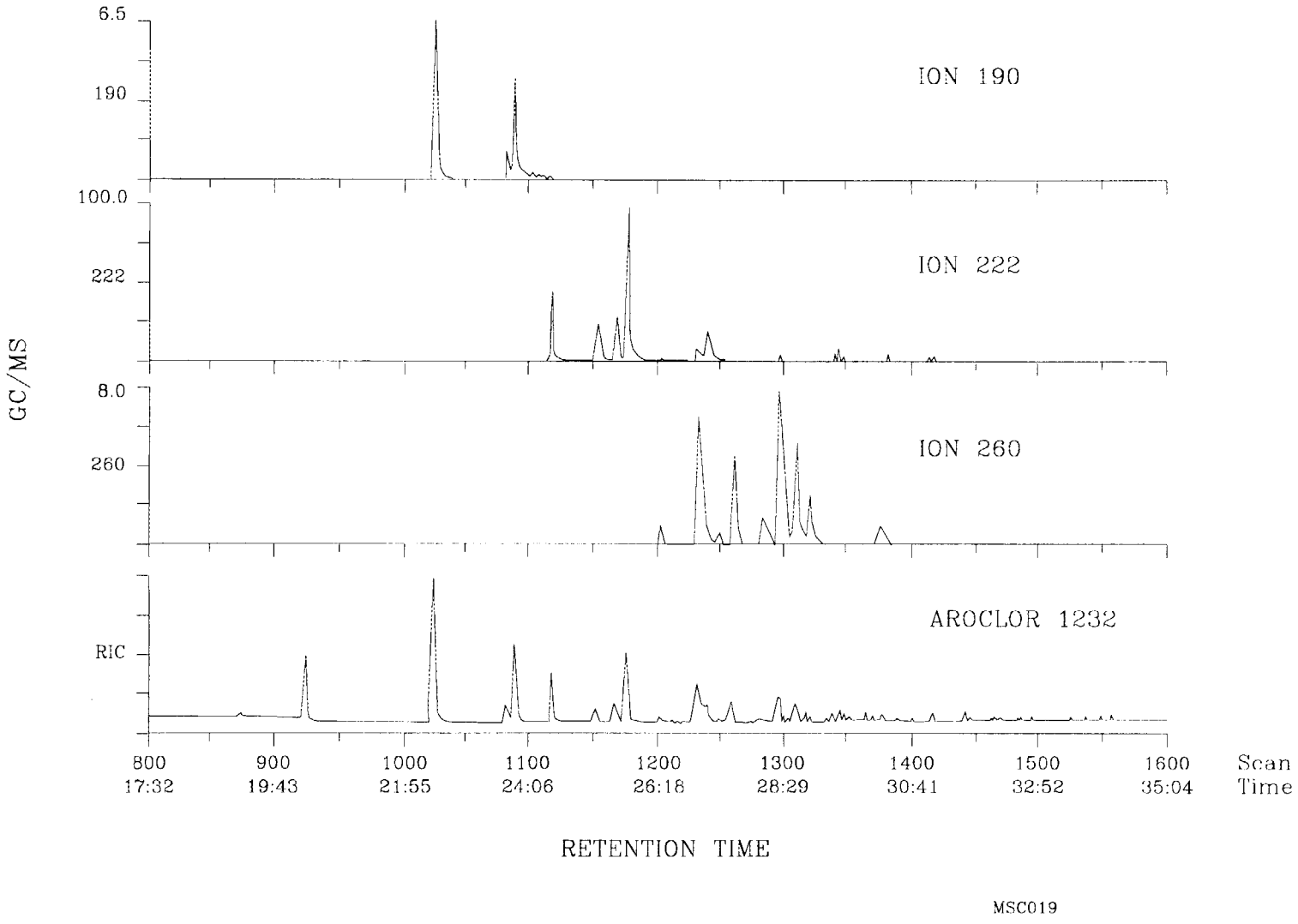

Fig. 6. MS peak pattern for Aroclor 1232 standard.

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concentrations were determined based on an assumption that the PCB patterns of the samples were similar to the Aroclor standards. The test results plotted both Aroclor concentrations and total PCB concentrations for the fish and turtle samples. While the PCB patterns from the fish samples were similar to the Aroclor standards, the PCB patterns from the turtle samples were not. As this study indicates, it is incorrect to report the biological residue as an Aroclor mixture. Rather the total concentration of PCBs should be reported.

Lin and Hee (1987) studied the effects of volatilization on the identification of compounds when using peak matching of gas chromatograms. Typically, the vapor phase is enriched with less-chlorinated PCBs (higher vapor pressure), and the residue is enriched with more highly chlorinated PCBs (lower vapor pressure). This enrichment and depletion of PCBs caused errors in quantification of Aroclors when only major peaks were matched (Lin and Hee 1987). Furthermore, the longer PCBs are in the environment, the more likely it is that the pattern will be different from the original Aroclor (Sect. 5). Thus, visual matching of gas chromatograms of weathered samples with those of standard Aroclors may not be sufficient to identify a specific Aroclor (Lin and Hee 1987).

For example, observed PCB concentrations are reported in terms of whichever Aroclor has about the same average chlorine level (Brown et al. 1987a). Thus, "qualitative errors arise because the names of certain well-defined PCB congener mixtures, the commercial Aroclors, are used to describe other PCB congener mixtures, the environmental specimens, which need not have (in the worst instance) more than one component in common with them. A common consequence of such qualitative errors is misidentification of discharged compositions. On the upper Hudson, for example, it is common to refer to the observed PCBs as mixtures of Aroclors 1221, 1016, 1242, and 1254 and sometimes also 1232 and 1248 as well, despite the fact that the original discharge was almost solely Aroclor 1242" (Brown et al. 1984).

In summary, GC/ECD is most commonly used for PCB analysis because of its sensitivity. Because environmental samples frequently contain several Aroclors and undergo a variety of physical, biological, and chemical processes that can significantly alter the original composition, it is difficult to identify and apply a standard to a weathered sample during analysis. Moreover, it may be impossible to draw specific conclusions concerning the sample composition or parent composition based on reported Aroclor concentrations.

6. SUMMARY AND CONCLUSIONS

The composition of PCBs in the environment changes over time due to various physicochemical and biological properties and processes. These include vapor pressure, solubility, octanol-water partitioning, adsorption, and biodegradation. The effect of the physiochemical properties can be summarized as follows: as the number of chlorine atoms increases, both the vapor pressure and the water solubility decrease. Thus, less-chlorinated PCBs are more soluble in water and more likely to be volatilized to the atmosphere. As the number of chlorine atoms increases, both adsorption and the octanol-water coefficient increases. Thus, the more highly chlorinated PCBs are more likely to adsorb to soils.

Dechlorination of PCBs occurs primarily through aerobic and anaerobic microbial degradation. Aerobic bacteria preferentially dechlorinate less chlorinated PCBs while anaerobic bacteria preferentially dechlorinate more highly chlorinated PCBs. Thus, alternate anaerobic/aerobic degradation is necessary for complete PCB destruction. In addition, aerobic biodegradation is much faster (up to 30 to 40 times) than anaerobic biodegradation. Photolysis causes dechlorination of the more highly chlorinated PCBs to less-chlorinated PCBs but to a much lesser extent than microbial dechlorination.

Depending on the dominant process in the environment, a combination of processes can be expected to change the composition of the PCBs. In general, the less-chlorinated PCB congeners are less persistent in the environment due to volatilization, solubility, and aerobic biodegradation, while the more-chlorinated PCB congeners are more persistent in the environment due to adsorption. The more highly chlorinated PCBs are preferentially degraded by the slower processes of photolysis and anaerobic biodegradation. The overall effects of these processes have not been quantified. As stated by Brown et al. (1987a) "Every chemical, physical, or biological PCB transformation process has its own selectivity pattern (e.g., set of relative transformation rates) for attacking the various individual congeners present in an Aroclor. Thus, an environmentally altered Aroclor will show a new congener distribution (and GC pattern) characteristic of the alteration process." This is specific not only to Aroclors but also to other PCB mixtures.

Analysis of PCBs is typically accomplished through matching GC peak patterns to standard Aroclor mixtures. Because of the degradation process, the reported PCB or Aroclor concentrations must be interpreted with caution. Virginia Stout states in Waid (1986) that, "To compare residue levels over the years is, in a sense, like asking whether we now have as many Winesap apples as we previously had MacIntosh apples. Numbers can be compared, but what do the answers mean?" Finally, trying to identify the source of the PCBs or Aroclors identified in a environmental sample may lead to inaccurate conclusions because of the changes in composition of the sample due to the numerous physicochemical and biological processes.

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GLOSSARY

Aerobic: Requiring or living in the presence of molecular or free oxygen.

Anaerobic: Capable of living or growing in an environment devoid of free oxygen.

Bioaccumulation: The uptake and retention of a chemical, by any mechanism or pathway, by biota.

Biomagnification: A process by which the tissue concentrations of bioaccumulated chemical residues increase as passed up the food chain through two or more trophic levels. Biomagnification tends to produce high chemical concentrations in top predators.

Bioturbation: The mixing of sediments by biota.

Biphenyl group: The building block of the PCB molecule consisting of two benzyl groups ($-C_6H_5$ where the carbon atoms are arranged in a benzene ring) held in approximately perpendicular planes by the *ortho* substituents. See Fig. 1 in the text.

Boiling point fraction: The fraction of a complex mixture that contains the same boiling point during distillation. Distillation is a process in which a complex mixture is broken up into relatively pure or individual components by being heated until the components vaporize one by one and are made to condense one by one.

Colloids: Solid or liquid particles suspended in a liquid or gas. The particles do not settle out of suspension and generally range in size from 10 Å to 1 μm.

Cometabolism: Biodegradation of a hazardous chemical occurs when a microorganism can utilize the chemical as an energy source. In some cases a second compound may be required as the energy source, but in the process of metabolizing the secondary energy source, the chemical compound of concern is also degraded. This biochemical piggybacking is known as cometabolism (Roberts 1987).

Dielectric: A material having a relatively low electric conductivity; an insulator. PCBs were commonly used as heat-transfer fluids in transformers and hydraulic presses for molding and plastics fabrication because of their excellent dielectric properties.

Diffusion: The spontaneous mixing of substances under the influence of their kinetic activity in the absence of any bulk hydraulic movement of the solution.

Dipole moment: A measure of the total polarity of a molecule in terms of the product of the charge on the ends of the dipole (polar molecule) and the charge separation.

Elute: To remove an adsorbed material from an adsorbent by means of a solvent, as from a chromatographic column during analysis.

Freundlich isotherm: The relationship between the concentrations of a compound's total sorbed state and its dissolved state at a constant temperature (i.e., isotherm). Experimentally determined isotherms commonly fit the Freundlich isotherm, which is defined as $C_s = K (C_w)^n$, where C_s is the sorbed concentration, C_w is the dissolved concentration, and n and K are constants. In cases where $n<1$, compounds at higher concentrations have more difficulty sorbing to additional surfaces; where $n>1$, sorption is favored at higher concentrations; and where $n=1$ the relationship is linear.

Fugacity: The relative tendency of a substance to escape from the phase in which it exists.

Glycerol: $C_3H_8O_3$. A liquid obtained from fats and oils used as a solvent, antifreeze, a sweetener, and in making dynamite, liquid soaps, and lubricants.

Glycol: A compound containing two —OH groups; a di-alcohol.

Halogen: Any member of Group VII A elements in the periodic table: F, Cl, Br, I, and At.

Humic acid: The portion of humic substances that is soluble in dilute bases but is precipitated by dilute acids. Humic substances are a complex and diverse group of organic materials of poorly biodegraded decomposition products and by-products of natural organic matter produced by both plants and animals.

Hydrolysis: The chemical reaction of water and salt to form a solution that may be either acidic or basic. In general, the chemical reaction of anything with water.

Hydrophobic: Incapable of dissolving in water; water-hating; nonpolar.

Hydroxyl radical: A simple functional group consisting of —OH.

Interstitial water: Water within the void pore space of sediments or soils.

Isomer: One of two or more molecules all having the same atomic makeup, but with atoms arranged differently in the molecule.

Miscible: Capable of being mixed in all proportions.

Molecular weight: The weight (mass) of a molecule determined by the sum of the atomic weights of all the atoms in the molecule.

Octanol-water partitioning coefficient, K_{ow}: A measure of the tendency of a compound to partition between an organic solvent (octanol) and water. A high K_{ow} indicates the tendency of a compound to have an affinity for the organic-solvent phase, while a low K_{ow} indicates an affinity for the water phase. Because the magnitude of this coefficient is typically large, it is often expressed in log units as log K_{ow}.

Oxidation: The reaction of a substance with oxygen; also, an increase in the positive valence of an atom.

Partitioning: The distribution of a substance between two or more phases or solvents.

Photochemical degradation: Breakdown of substances due to interaction with radiant energy.

Photolysis: Chemical change caused by light.

Polarity: Electrostatic charge of a molecule where one end may be negative or positive with respect to the other end because of unequal sharing of the electrons.

Pyrolysis: Chemical change caused by heat.

Redox potential: The potential for the oxidation state of a compound to become more positive by donating electrons (oxidation) or more negative by accepting electrons (reduction).

Reductive dechlorination: Replacement of a chlorine atom in a molecule, usually with a hydrogen atom.

Solar spectrum: The range of radiant energy derived from the sun.

Solubility: The maximum amount of a substance that will dissolve in a given amount of another substance. For example, the solubility of NaCl in water (at 20°C) is 360 g per kg of H_2O.

Sorption: The process in which a substance is taken up or held by physical or chemical forces. *Ad*sorption is onto a two-dimensional surface, *ab*sorption is into a three dimensional matrix, and *de*sorption is disassociation with the solid phase.

Vapor pressure: The pressure exerted when a solid or liquid is in equilibrium with its own vapor.

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