Spring 2013

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Recommended Citation

Cicilio, Phylicia, "Octanol/Water Partitioning Coefficients of PCB Mixtures for Environmental Fate and Transport" (2013). *Honors Theses and Capstones*. 131.
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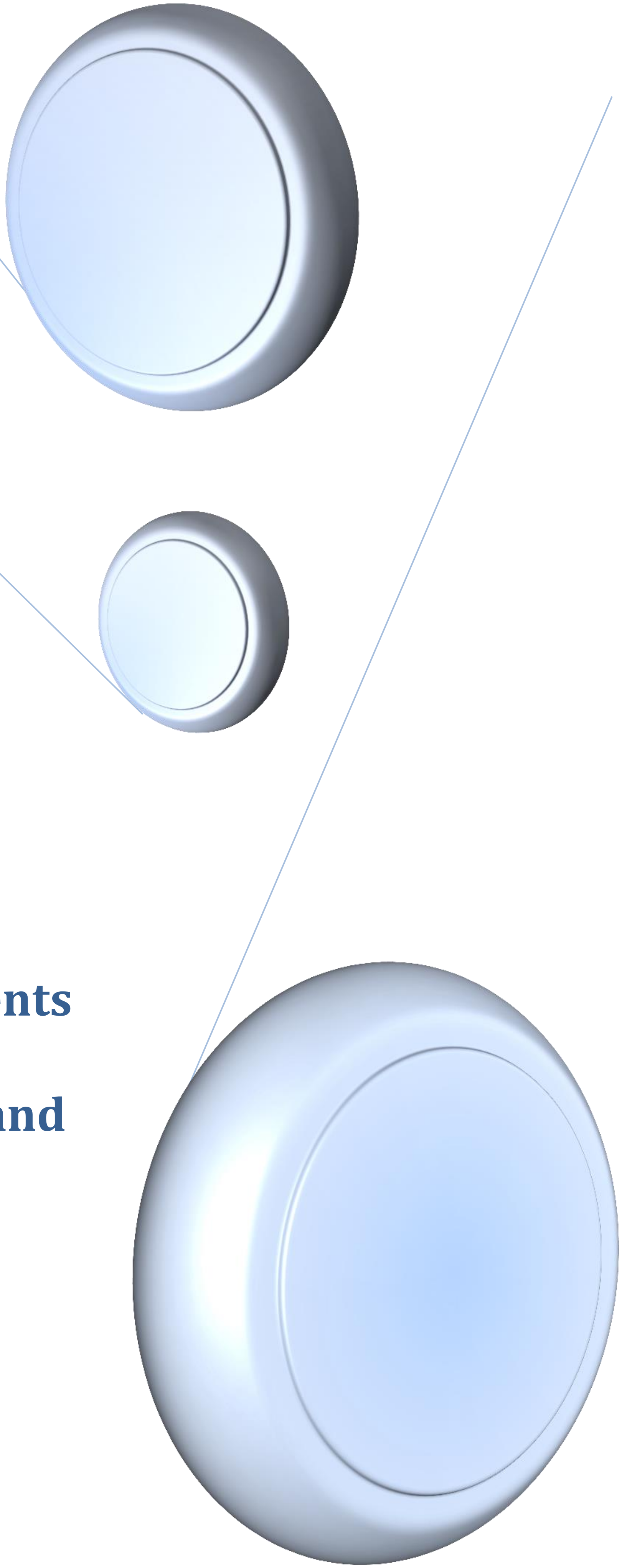

Octanol/Water Partitioning Coefficients of PCB Mixtures for Environmental Fate and Transport

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University of New Hampshire
Senior Honors Thesis

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Spring 2013

Contents

Introduction

PCBS

Polychlorinated biphenyls (PCBs) are a group of synthetic chemicals, totaling 209 congeners. The standard chemical formula for PCBs is $C_{12}H_{10-X}Cl_X$. The standard chemical structure for a PCB is seen in Figure 1.

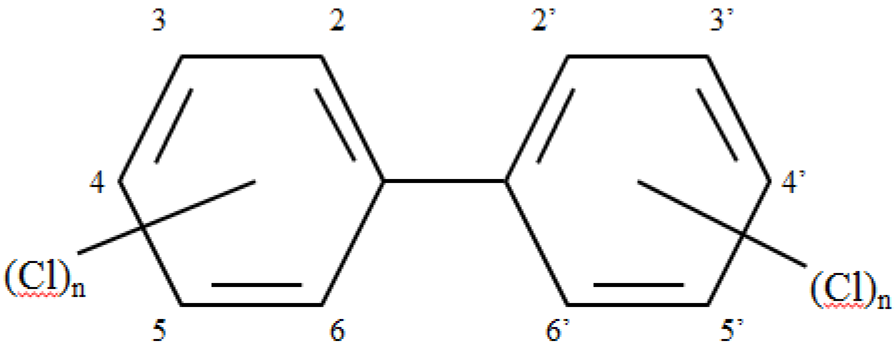

Figure 1: Standard PCB Chemical Structure

Due to the chemical structure of PCBs, these compounds are hydrophobic and highly resistive to chemical reaction [1]. The hydrophobicity of PCBs results in low water solubility and high octanol-water partitioning coefficients [1].

PCBs were used in many items from transformers to hydraulic fluids to carbonless copy paper from the 1920s to 1970s [2]. A list of all the common uses of PCBs, when used in manufacturing, is presented in Appendix Table 1.

PCBs were manufactured in groups of congeners by several brand names all over the world. Aroclor was the brand name for PCBs manufactured in the United States [3]. Different types of Aroclors were identified by the name Aroclor followed a 4 digit code, where the first two digits corresponded to the parent molecule (Biphenyl: 1200), and the second two digits corresponded to chlorine content by weight [3].

Human and Environmental Threats

In 1976 PCBs were discovered to be an environmental contaminant and a threat to human health [4]. The discovery of PCBs as a contaminant was made due to the increased ability of analytical equipment to detect the presence of PCBs [4]. PCBs were detected in air, water, and soils, and are still detected in these places today [4]. Studies by the EPA determined PCBs to be a probable carcinogen due to links between PCB exposure and liver cancer [3]. In 1979 the EPA placed a restrictive ban on the manufacturing and processing of PCBs in all items produced in the United States [3]. At the UN Stockholm Convention in 2001, PCBs were designated as a persistent organic pollutant (POPs) and an international agreement was made to reduce and eliminate POPs, including PCBs.

Despite PCBs no longer being produced in the United States, and in limited quantities across the world, they are still detected in the environment today. PCBs’ stability is the cause of their bioaccumulation in the environment. Their low water solubility and resistance to chemical reaction allows PCBs to travel easily in the environment through water, the atmosphere, and soils [3]. For example, when PCBs were used in manufacturing, they were released into the wastewater streams where they bound to soil and sediments where now they are released into water slowly [3]. Bioaccumulation occurs when organisms uptake PCBs from the water and atmosphere and the PCBs are accumulated in these organisms [5]. PCBs accumulate in the organisms because PCBs do not decompose easily in the environment due to their stability, and therefore persist in the environment for continuous uptake [3]. It is the effect of bioaccumulation, environmental persistence, and threat to human and environmental health that makes PCBs a serious pollutant [3].

Purpose

Individual congener octanol-water partitioning coefficient data currently exists for all PCB congeners. This study focuses on octanol-water partitioning coefficients for congeners in solution with a group other congeners. The octanol-water partitioning coefficients for the PCB congeners in mixtures are compared to individual data to see if the congeners partition differently as a group versus individually. Congener group data is necessary for understanding how PCBs will travel through the environment as PCBs are introduced to the environmental in commercial groups, not individually.

The octanol-water partitioning coefficient is the parameter used for creating environmental fate and transport models. Incorrectly calculated K_{ow} values could have implications including:

- Underestimating or overestimating partitioning to water phase which may lead to higher PCB levels in water than expected
- Unexpected pockets of PCB congeners collected in soil resulting in:
    - Pockets of PCBs volatilizing and potentially invade homes and businesses
    - Greater concentrations of PCBs in agriculture
    - Greater potential contact for humans and animals

Therefore, it is necessary to have the K_{ow} correctly calculated. Since PCBs are introduced to the environment as a mixture, such as an Aroclor, it is necessary to know if the congeners will partition differently as a mixture than as individuals which is already known.

Theory

The octanol-water partition coefficient is a quantitative means of measuring how PCB’s will travel in the environment. The octanol-water partition coefficient is a measure of how a PCB will partition in a solution of a polar and non-polar solvent.

PCB is put into contact of a solution containing octanol and water. The octanol represents an organic environment and the water represents an aqueous environment. The concentration of the PCB in the octanol phase is measured by a Shimadzu GCMS. The water PCB concentration is calculated from a series of mass balance equations using the known amount of total initial PCB in solution, and the concentration of PCB in the octanol phase determined by the GCMS. The mass balance equations are represented in Equations 1-3 below.

$$m_{ow} = c_{ow} V_{ow} \tag{1}$$

$$m_{wo} = m_{ow} + m_{total} \tag{2}$$

$$c_{wo} = \frac{m_{wo}}{V_{wo}} \tag{3}$$

The octanol-water partitioning coefficient is determined by using the concentrations of PCB in the octanol and water, shown by Equation 4.

$$\mathrm{K_{ow}} = \frac{\mathrm{c_{ow}}}{\mathrm{c_{wo}}} \tag{4}$$

Where K_{ow} is the octanol-water partitioning coefficient, c_{ow} is the concentration of solute in the octanol phase, and c_{wo} is the concentration of solute in the water phase.

A greater K_{ow} represents a greater PCB presence in octanol than water, and a lower K_{ow} represents a greater PCB presence in water than octanol.

Environmental fate and transport behavior can be predicted from the octanol-water partitioning coefficient. Knowing how PCBs will partition in organic/aqueous solutions will suggest how PCBs will or will not migrate in or out of certain mediums in the environment [7].

Methods and Materials

Materials and Chemicals

For the partitioning of PCBs in octanol and water solution, Agros Organic 99% 1-octanol and deionized water was used. PCBs were obtained from Sigma Aldrich (PCB 18 and 153) and SPEX CertiPrep (PCB 29). PCB concentration was evaluated by Shimadzu GCMS with EI ion detection.

Slow Stirring Procedure

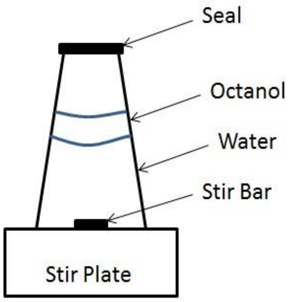

Figure 2: Equipment Diagram of Slow-Stirring Method

The octanol-water partition coefficients were determined using the slow-stirring method in a 250mL Erlenmeyer flask. A magnetic stir bar was placed in the 250mL Erlenmeyer flask. 120mL of deionized water was measured using a Fisherbrand Finnpipette II and pipetted into the Erlenmeyer flask. 10mL of 1-octanol was slowly pipetted along the side of the flask. The solution was set to stir at 70rpm for 1 hour on a magnetic stir plate, ensuring no emulsions were created. After 1 hour of stirring, another 29mL of 1-octanol was slowly pipetted into the Erlenmeyer flask along the side of the flask. The solution was set to stir at 70rpm again for 1-3 hours to allow for mutual presaturation of the octanol and water phases prior to introduction of the PCB [8].

For individual congener solutions 1mL of diluted PCB in 1-octanol solution was pipetted into solution as done previously. The solution was then left stirring at 70rpm for 1, 6, or 14 days.

For group congener solutions 1mL of each diluted PCB in 1-octanol solution was pipetted into solution as done previously. However the amount of 1-octanol in the Erlenmeyer flask was adjusted from 29mL to 30mL minus the volume of total diluted PCB. The solution was then left stirring at 70rpm for 1, 6, or 14 days.

The 1-octanol phase was extracted from solution using a glass pipette for testing on GCMS.

GCMS Procedure

A Shimadzu GCMS with EI detection was used for determining the concentration of PCB in the octanol phase. The method used for the GCMS included:

- Carrier Gas: He
- Column Oven Temp: 80°C
- Injection Temp: 225°C
- Injection Mode: Split
- Pressure: 29.8kPa
- Temperature Program: 80°C hold 1 min, 10°C/min to 210°C, 0.8°C/min to 250°C, 10°C/min to 290°C.
- Column: Restek Rxi-5

The GCMS method was based off previous studies' methods for PCB analysis [9][10].

A calibration curve was created by correlating 3 different samples of known concentration peak areas on the GCMS chromatograph to their corresponding known concentrations of PCB in octanol. From this correlation of peak area to concentration, unknown concentrations of PCBs in octanol from slow-stirring experiments could be determined.

The concentrations determined by the GCMS of PCBs in the octanol phase are then used to calculate the PCB concentration in the water phase as stated in Theory. With the concentration of PCB in octanol and in water the octanol-water partitioning coefficient can be calculated.

Expected Results

Due to the inoperability of the GCMS, no data was able to be collected to calculate K_{ow} for individuals or mixtures of PCBs. The potential expected results for this project for individuals and mixtures of PCBs' K_{ow} include:

- Individual PCB K_{ow} will be comparable to literature K_{ow} values:

Table 1: Literature values for properties of PCB congeners for this study [1][11]

PCB	Name	K_{ow}	Molecular Weight (g/mol)	Relative Retention Time
18	2,2',5-Trichlorobiphenyl	5.6 ± 0.1	257.542	0.2678
29	2,4,5-Trichlorobiphenyl	5.6 ± 0.2	257.540	0.2990
153	2,2',4,4',5,5'-Hexachlorobiphenyl	6.9 ± 0.2	360.876	0.5421

  - PCB 18, 29, 153 were the congeners chosen for this study because two congeners (18, 29) had comparable physical and GCMS properties and two congeners (18/29, 153) had varied physical and GCMS properties. Having similar congeners and varied congeners would give a greater overall comparison of how PCBs in mixtures might partition for in a mixture there would be congeners on a range of similar to varied.
  - If the results of this study did not match the literature values the slow-stirring method would be reevaluated and adjusted so comparable experimental values could be obtained.
- For mixtures of PCBs there are two competing hypothesizes on the expected K_{ow}:
  - Solution of groups PCBs will partition as they partition individually, resulting in similar K_{ow} [1].
  - K_{ow} may be decreased because of overall increase in PCBs present, therefore less individual PCB will be able to partition to the octanol phase.

A potential complication for completing the study includes:

- Separation in GCMS for detection of individual PCB congeners in solution of mixture of PCBs during GCMS analysis of PCB concentration in octanol [11].

Acknowledgements

- Dr. Jillian Goldfarb, honors thesis advisor
- Ana Celaya

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Appendix

Table 1: Common Uses of PCBs [13]

PCB Uses	
Primary Applications	
Dielectric fluids and transformers	Used as insulating material, coolant, and for fire-resistant properties. Potential sources would be facilities which used, stored, and serviced electrical equipment and which used significant amounts of electricity. These facilities could include, but are not limited to: Electrical transmission and distribution facilities; electrical equipment maintenance facilities and salvage yards; rail yards; and manufacturing facilities (sawmills, pulp and paper mills, chemical manufacturing, shipyards, primary and secondary metals smelting and refining, etc.)
Capacitors	Present in industrial facilities, industrial machinery both fixed and mobile, and consumer products. Includes larger power-factor correction capacitors associated with transformers, manufacturing facilities, and commercial buildings (usually near high power-usage equipment such as computer rooms and heating and cooling units); and smaller electric motor-start capacitors used in industrial 4 PCB FACT SHEET.CP.8-6-03.DOC equipment and appliances such as hair dryers, air conditioners, refrigerators, power tools, and submersible well pumps. Also includes capacitors used in appliances and electronics such as televisions and microwave ovens.
Fluorescent light ballasts	PCB-containing capacitors were used in fluorescent light ballasts. PCB-containing asphaltic resin (potting material) was also utilized as insulating material for some ballasts.
Electromagnets	Oil-cooled electromagnets are constructed with coils immersed in transformer oil to prevent over-heating and shorting. Used in cranes for picking up metal and for metal separation in recycling operations (metal

	scrap yards, tire shredding, concrete crushing, slag operations, etc.).
Miscellaneous electrical equipment	Switches, voltage regulators, circuit breakers, reclosers, rectifiers, and some oilcooled electric motors.
Heat transfer systems	Where oil is circulated through a non-contact system as a heat transfer medium for heating, cooling, and maintaining uniform temperature throughout a system or manufacturing process. Wide variety of applications in manufacturing industries including high-tech, asphalt, pulp and paper, metal products such as steel tubing and die casting, adhesives, chemicals, food processing, paint & coatings, textiles, etc.
Hydraulic fluids	Any application of hydraulic oil such as industrial equipment and machinery, commercial equipment, automotive brake fluid, etc.
Plasticizers	Used in polyvinyl chloride plastic, neoprene, chlorinated rubbers, laminating adhesives, sealants and caulking, joint compounds (concrete), etc.
Lubricants	Cutting oils, compressors, electrical equipment, oil-impregnated gaskets and filters; also currently present in low concentrations in recycled oil. Also used in vacuum pumps at high tech and electronics manufacturing facilities, research labs, and wastewater treatment plants.
Other applications of PCBs	
Dust control (dedusting agents)	Present in dust control formulations, and used oil historically used for dust suppression.
Pesticides	As an extender to extend the life of pesticides.
Fire retardants	Coatings on ceiling tiles, and textiles including ironing boards and yarn.
Paints, coatings	As plasticizers in paint, corrosion resistant paints for various applications including military/navy ships, corrosion resistant epoxy resins on metal surfaces, film casting solutions for electrical coatings, varnish, lacquers, and waterproofing coatings for various applications.

Carbonless copy paper	Used as an ink pigment carrier (microencapsulation of dye); when the top sheet was pressed down, ink and PCB oil were transferred to the copy.
Printing inks	Ink for newsprint and as a dye carrier; also used as a solvent for deinking newsprint for recycling.
Investment casting waxes	Used as wax extenders.
Wood treatment	May be present as an impurity in pentachlorophenol (Warrington, 1996).
Sources: ATSDR (2000), DEQ (1997), EIP Associates (1997), UNEP Chemicals (1999)	