# Cosolvent Effects of Ethanol and Dissolved Organic Matter on the Aqueous Solubility and Partitioning of Organochlorine Pesticides

by

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## ABSTRACT

In the effort to promote ethanol/gasoline blends as an alternative fuel, potential negative impacts on the environment have been overlooked. Ethanol is produced in the Midwest and transported to the coasts. With the increased usage and the long distances of transport, a spill is reported on the average of every two days. The Midwest is also a location of high pesticide usage. The coincidence of ethanol spills and high pesticide usage in agricultural watersheds raises the concern that ethanol might enhance the concentration of regulated organochlorine pesticides in surface waters. Thus, the objective of this research was to examine the aqueous solubility and partitioning behavior of organochlorine pesticides in the presence of ethanol.

The work reported here showed increases in the aqueous solubility of the organochlorine pesticides, dieldrin, lindane, and chlorpyrifos of about 7.46, 3.31, and 6.61 orders of magnitude, respectively, as the ethanol mass fraction increased from 0.0 to 1.0. A two-part log-linear model, with the breakpoint occurring at an ethanol mass fraction of approximately 0.35 was adequate to describe the relationship between the aqueous solubility of these compounds and the ethanol mass fraction, for all the pesticides examined. The breakpoint seems to be independent of the solute and dependent only on the ethanol-water interactions.

The increase in the aqueous solubility of pesticides in the presence of ethanol can affect the partitioning behavior of such compounds between an organic liquid phase (e.g. iso-octane and gasoline) and water. This research showed that, in a water/ethanol/organic liquid system, ethanol displays a high preference for the aqueous phase. The aqueous solubility of the organic

liquid also increased by orders of magnitude, but its concentration was still considerably lower than that of ethanol. The high concentration of ethanol resulted in an increased concentration of the organochlorine pesticides in the aqueous phase, causing a decrease in the partition coefficient by 4.83, 2.03, and 4.82 orders of magnitude for dieldrin, lindane, and chlorpyrifos, respectively. A log-log relationship between the partition coefficient versus the aqueous solubility of the pesticide was observed, with a slope of -1 and a y-intercept independent of the specific pesticide.

Additionally, river sediment contains organic matter that, if dissolved, can further increasing the aqueous solubility of the pesticides. This study showed that the presence of DOM can further increase the aqueous solubility of lindane by over one order of magnitude. The results suggest that both the composition and concentration of DOM are important factors in determining the extent of the impact on the aqueous solubility, with DOM extracted from contaminated river sediments, like that from the Anacostia River, having a greater effect relative to that extracted from natural soils dominated by humic materials. Moreover, the solute's polarity compatibility with the DOM was an important factor. In particular, a greater enhancement was noted for lindane, since its smaller size and more symmetric configuration made it more compatible with the bonding structure of the DOM.

# CHAPTER 1

# Introduction

## 1.1 Problem Statement

Negative environmental consequences of fossil fuel use and concerns about the adequacy and security of petroleum supplies have led the United States to implement policies to increase the use of renewable energy. To date, this requirement has been met primarily by blending conventional gasoline with ethanol in various proportions. Consequently, ethanol consumption (as a volume percentage of the total gasoline usage in the U.S.) increased from about 1% in 2001 (U.S. Energy Information Administration, 2012) to about 10% in 2015 (U.S. Energy Information Administration, 2016a), corresponding to 1.7 and 13.9 billions of gallons of ethanol, respectively (U.S. Energy Information Administration, 2016b).

Nearly all the ethanol for ethanol-blend fuels is produced in the Midwest (U.S. Energy Information Administration, 2012; Association of American Railroads, 2015). It is then transported by railroad cars, tanker trucks or barges to be mixed with gasoline near the point of use. Because of the long distances over which ethanol is hauled, the risk of accidents increases, resulting in the possible spillage of high amounts of ethanol into surface waters. In 2016, it was reported that an ethanol spill occurs, on average, every two days in the Midwest (Meers and Hettinger, 2016). For example, in January 2016, a barge carrying ethanol collided with a bridge, spilling nearly 300,000 gallons of ethanol into the Mississippi River (The Biomass Monitor, 2016).

Ethanol is mainly produced from corn, a crop with a heavy utilization rate of organochlorine pesticides. The estimated agricultural use for atrazine, one of the most commonly pesticides used for corn (Boyd, 2015), was over 11 kg/km$^2$ along the Mississippi River in 2014 (U.S. Geological Survey, 2016). While atrazine is in current use, other organochlorine pesticides like dieldrin, were banned in the mid-1970s (Agency for Toxic Substances and Disease Registry, 2015). However, because of their persistence in the environment, agricultural watersheds in the Midwest are still contaminated with such pesticides. The National Water Quality Assessment Program found that the majority of the streams and rivers sampled in both agricultural and urban areas contained legacy organochlorine pesticides (Gilliom et al., 2006). For example, a study done by McGee and others (2009) in the Anacostia River (Maryland) showed that the concentrations in the sediment of total DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane compounds), chlordane, lindane and dieldrin were as high as 152.9 ng/g, 169.9 ng/g, 5.81 ng/g, and 8.86 ng/g, respectively.

In the presence of ethanol/ethanol-blend fuel (biofuel) spills, the pesticides from these historically contaminated sediments may be desorbed as a consequence of the driving force created by the increase in solubilization potential in the aqueous phase. For example, Smith and others (2004) showed that as the volume fraction of different alcohols (methanol, ethanol, 1-propanol, and 2-propanol) in the aqueous phase increased, the amount of p, p'-DDT desorbed from the soil increased. In fact, up to 77% of the total p, p'-DDT present (975 ± 40 mg/kg) in the soil from a cattle-dip site was desorbed in the presence of a 50% volume fraction of 1-propanol, and up to 70% at a 30% volume fraction of 1-propanol. Given the low permissible quantities of organochlorine pesticides in water, even a relatively low amount of pesticide desorbed might be enough to violate regulatory standards, as the permissible levels of p, p'-DDT

and dieldrin in water are low, $3.0 \times 10^{-8}$ and $1.2 \times 10^{-9}$ μg/mL (U.S. Environmental Protection Agency, 2017), respectively. Consequently, the solubilization potential caused by ethanol spills could cause the desorption of a sufficient amount of pesticide that such standards may be violated.

Although gasoline and ethanol-based fuels are both used as automotive fuels, their behavior following a spill is different. Gasoline spills generally volatilize because of gasoline's low miscibility and high volatility (Okamoto et al., 2009). On the other hand, as Figure 1.1 shows, biofuels like E85 (85% ethanol and 15% gasoline by volume) are completely miscible in water (Toso and Higgins, 2011), thus presenting the possibility of mixing in rivers and lakes in high fractions. For blends within the two-phase region, ethanol will preferentially partition into the aqueous phase (Cline et al., 1991; Peschke and Sandler, 1995; Heermann and Powers, 1998). With most of the ethanol partitioning into the aqueous phase, ethanol can increase the solubility of hydrophobic organic compounds (HOCs), like BTEX (benzene, toluene, ethylbenzene, and xylene), in the aqueous phase (Heermann and Powers, 1998; Powers et al., 2001; Da Silva and Alvarez, 2002; Corseuil et al., 2004; Chen et al., 2008). Heermann and Powers (1998), for example, observed an increase of approximately two orders of magnitude in the aqueous phase concentration of the BTEX compounds, corresponding to a decrease of approximately two orders of magnitude in the fuel-water partition coefficient for a water/ethanol/gasoline system. Most of the literature on the partitioning behavior of HOCs between an organic liquid phase and water deal with the BTEX compounds and very few look at the behavior of organochlorine pesticides.

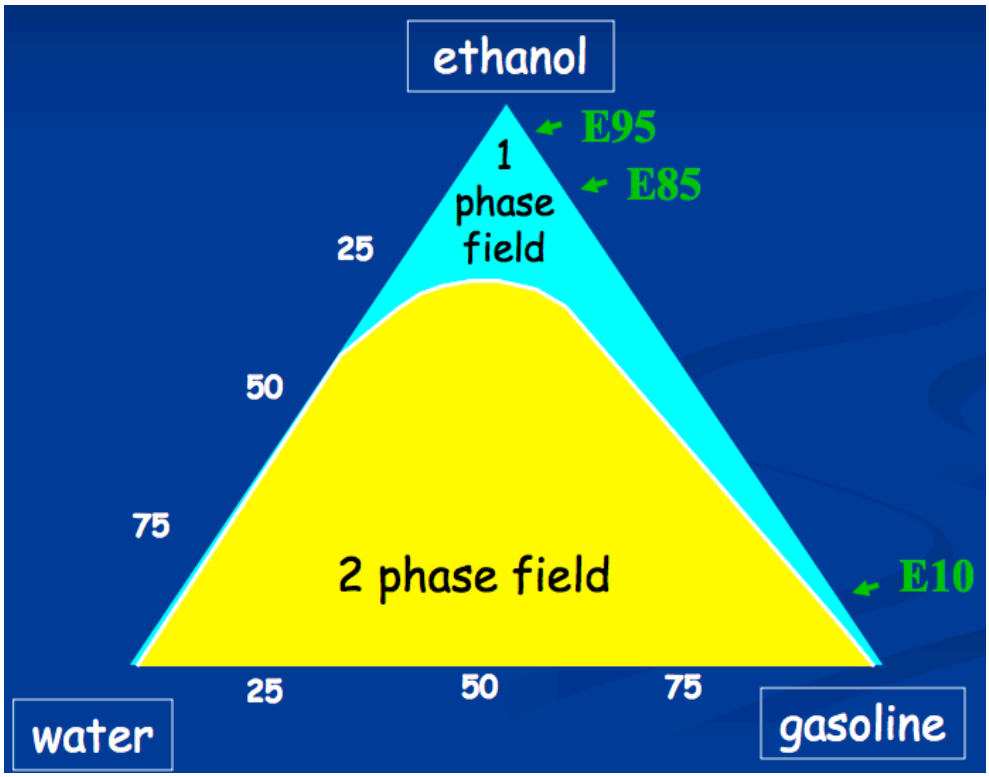


**Figure 1.1** Ternary phase diagram of the ethanol, water and gasoline system (as presented by Toso and Higgins, 2011).

When considering the impact of ethanol/ethanol-blended fuel spills, desorbed organic matter and other contaminants present in the sediment need to be considered as well. Interactions of dissolved organic matter (DOM) with HOCs, such as organochlorine pesticides, in surface waters may influence the transport and fate of such HOCs in natural waters (Chiou et al., 1986; Kile and Chiou, 1989; Ma, 2012). Typical concentrations of DOM in fresh waters can range from 0.05 to 50 mg/L (Hessen and Tranvik, 2013); however, the possibility exists that the concentrations may be higher in the presence of ethanol. The composition of DOM is very complex and can vary depending on the source material (Guerard et al., 2009). Both the concentration and composition of DOM have been observed to influence the extent of the impact

on HOCs (Stedmon et al., 2003). Therefore, an understanding is needed of the impact that DOM has on the behavior of organochlorine pesticides in natural waters in the presence of ethanol.

In the effort to promote ethanol/gasoline blends as an alternative fuel, potentially major negative impacts on the environment post-production have not been examined. If a biofuel is spilled, the greater miscibility of ethanol in water leads to the possibility of the HOCs dissolving in the lake or river water in higher concentrations. Moreover, due to the coincidence of spills of ethanol and high pesticide usage in agricultural watersheds, the concern exists that ethanol might enhance the concentration of organochlorine pesticides in surface waters, resulting in the violation of regulatory standards and potential harm to riverine ecosystems.

## 1.2 Objectives

This dissertation aims to assess the equilibrium behavior of organochlorine pesticides in surface waters impacted by spills of ethanol and ethanol-blended fuels. When considering ethanol spills in surface water, the water/ethanol system will be present as one liquid phase. However, when ethanol-blended fuels are considered, the water/ethanol/gasoline system may be present as two phases due to gasoline's low miscibility in water. Moreover, natural surface waters are not pure; organic matter and other contaminants desorbed from the sediments may be present as well. Thus, the research reported in this dissertation has, as its goals, to:

1. Quantify the enhancement of the aqueous solubility of organochlorine pesticides due to the presence of ethanol,
2. Evaluate the partitioning of organochlorine pesticides between an organic liquid phase and an aqueous phase as a function of the ethanol content of the system,

3. Assess the relationship between dissolved organic matter, its concentration and composition, on the aqueous solubility of organochlorine pesticides as a function of the ethanol content of the system.

Each of the subsequent chapters of this dissertation addresses one of the specific research goals.

# CHAPTER 2

## Enhancement of the aqueous solubility of organochlorine pesticides by ethanol

### 2.1 Background

The coincidence of spills of ethanol and high pesticide usage in agricultural watersheds raises the concern that ethanol might enhance the concentration of regulated organochlorine pesticides in surface waters. Previous studies have demonstrated that water-miscible organic solvents, such as short-chain alcohols used in oxygenated fuels such as M85 (85% methanol and 15% gasoline) or E85 (85% ethanol and 15% gasoline), have the ability to substantially increase the aqueous solubility of a variety of hydrophobic organic compounds (HOCs), including polynuclear aromatic hydrocarbons (PAHs) (Morris et al., 1988; Pinal et al., 1990; Rao et al., 1990; Wood et al., 1990; Chen and Delfino, 1997; Fan and Jafvert, 1997; Schwarzenbach et al., 2003; Corseuil et al., 2004; Chen et al,. 2005), polychlorinated biphenyls (PCBs) (Schwarzenbach et al., 2003) and the BTEX compounds (Pinal et al., 1990; Cline et al., 1991; Heermann and Powers, 1998; Powers et al., 2001; Reckhorn et al., 2001; Da Silva and Alvarez, 2002; Corseuil et al., 2004; Lee and Peters, 2004; Chen et al., 2008; Lee, 2008). This increase is generally referred to as the "cosolvent effect," the magnitude of which is related to the amount of the cosolvent, and the type and extent of the interaction between the cosolvent and the organic solute (Li and Yalkowsky, 1998; Schwarzenbach et al., 2003). A measure of the "cosolvent effect" is the cosolvency power of a cosolvent for a given solute, $\sigma$, which may be calculated as

(Pinal et al., 1990; Rao et al., 1991; Li and Yalkowsky, 1994; Li and Yalkowsky, 1998; Chen et al., 2005):

$$\sigma = \log\left(\frac{S_c}{S_w}\right) \tag{2.1}$$

where $S_c$ and $S_w$ are the solubility of the solute in the pure cosolvent and in water, respectively. The larger the value of $\sigma$, the larger is the increase in the aqueous solubility of the solute by that cosolvent (Rao et al., 1991). The increase in solubility may be on the order of several orders of magnitude, as Fan and Jafvert (1997) found values of $\sigma$ of 3.3 - 5.5 for several PAHs, with the greatest increase corresponding to the most hydrophobic compound.

To describe the increase in solubility, a log-linear model has been proposed (Yalkowsky and Roseman, 1981; Rubino and Yalkowsky, 1987; Morris et al., 1988; Pinal et al., 1990; Rao et al., 1990; Cline et al., 1991; Li and Yalkowsky, 1994; Chen and Delfino, 1997; Li and Yalkowsky, 1998; Powers et al., 2001; Millard et al., 2002; Corseuil et al., 2004; Chen et al., 2005; Chen et al., 2008; Miyako et al., 2010):

$$\log S_m = \log S_w + \sigma\ f_c \tag{2.2}$$

where $S_m$ is the solubility of the solute in the mixed solvent and $f_c$ is the volume fraction of the cosolvent in the aqueous phase. Based on Eqn. 2.1, the cosolvency power describes the number of orders of magnitude increase over the cosolvent volume fraction range of 0.0 to 1.0. If the solubility of the solute in the mixed solvent is determined experimentally, then, the slope of the relationship of log $S_m$ versus $f_c$ (Eqn. 2.2) is, theoretically, equal to the cosolvency power, $\sigma$.

Deviations from Eqn. 2.2 have been reported in situations where the interactions between the water and the cosolvent are significant (Rubino and Yalkowsky, 1987; Rao et al., 1991; Chen and Delfino, 1997). These deviations depend on the cosolvent and may be positive or negative (Rubino and Yalkowsky, 1987; Miyako et al., 2010). Thus, an empirical coefficient, $\beta$, is sometimes introduced to account for water-cosolvent interactions (Rao et al., 1990 and 1991; Chen and Delfino, 1997; Chen et al., 2008):

$$\log S_m = \log S_w + \beta \, \sigma \, f_c \qquad (2.3)$$

Others have proposed that the relationship between $S_m$ and $f_c$ be split into two parts. Banerjee and Yalkowsky (1988) suggested that, at values of $f_c > 0.1$, the relationship between $S_m$ and $f_c$ is log-linear, and is described by Eqn. 2.3. But at low cosolvent concentrations, they reasoned that the solute would be influenced by only a single cosolvent molecule, as each cosolvent molecule would be hydrated in the aqueous solution. Thus the mechanism of solvation would differ depending on the cosolvent fraction, and at low cosolvent fractions, it would be linear and related to the amount of water in the hydration shell:

$$S_m = f_c V_H S_c^{\infty} + (1 - f_c V_H) S_w \qquad f_c V_H < 1 \quad (2.4)$$

where $S_c^{\infty}$ is the average solubility within the hydration shell or within the volume of water disrupted by the cosolvent, and $V_H$ is the ratio of the volume of the hydration shell to the volume of the cosolvent. Based on solubility enhancement measurements for toluene by methanol, they determined that $S_c^{\infty}$ was about 1.4 $S_w$ and $V_H$ was about 6.7 for methanol, suggesting that the cosolvent disruption of the water structure is appreciable at low volume fractions.

Powers and co-workers (Heermann and Powers, 1998; Powers et al., 2001) adapted the model by Banerjee and Yalkowsky (1988) for BTEX systems, proposing a two-part model with a linear relationship at low values of $f_c$:

$$S_m = \left(1 - \frac{f_c}{\eta}\right) S_w + \frac{f_c}{\eta} S_\eta \qquad \text{for } f_c < \eta \quad (2.5)$$

where $\eta$ is the volume fraction of ethanol in the aqueous phase at the division between the two parts or the "breakpoint," and $S_\eta$ is the solubility of the solute in the mixed solvent at $\eta$, and a log-linear relationship at higher values:

$$\log S_m = \left(1 - \frac{f_c - \eta}{1 - \eta}\right) \log S_\eta + \left(\frac{f_c - \eta}{1 - \eta}\right) \log S_c \qquad \text{for } f_c \geq \eta \quad (2.6)$$

The value of $\eta$ was about 0.23 for all the BTEX compounds studied. Since the breakpoint was at a relatively low value of $f_c$ and the increase in the aqueous solubility up to the breakpoint was relatively small, the researchers noted that a log-linear model could conceivably also be used for the lower cosolvent fractions.

Previous studies have emphasized the increase in solubility of classes of compounds such as PCBs, PAHs and BTEX, and comparatively few studies have looked at pesticides, despite their environmental significance. Table 2.1 summarizes previous studies examining the impact of alcohols on the aqueous solubility of pesticides. Similar to the impact noted for other classes of compounds, the addition of alcohol increased the aqueous solubility of pesticides over orders of magnitude. For example, Cheng (1989) found that, with the addition of 8% (by weight) of methanol, the aqueous solubility of diuron increased by 190%. However, only three studies have reported cosolvency powers for a pesticide: Morris and others (1988), Cheng (1989), and Wood

and others (1990) reported a cosolvency power for diuron in a methanol-water system of 2.27, 2.99, and 2.83, respectively. Morris and others (1988) and Cheng (1989) obtained the cosolvency power from the slope of the relationship between log $S_m$ and $f_c$ (Eqn. 2.2) and Wood and others (1990) based it on Eqn. 2.1. For other pesticides, the increase in solubility may be even greater, as Kumbar and others (2002) observed an increase of almost five orders of magnitude in the aqueous solubility of fenvalerate as the methanol mass fraction increased up to 100%. A preliminary analysis of the data of Morris and others (1988) and Corseuil and others (2004) suggests that the volume fraction range of the cosolvent may affect the value of the slope of the relationship of log $S_m$ versus $f_c$. Furthermore, a two-part log-linear relationship, with the inclusion of a parameter such as $\beta$, may be warranted. But, it is difficult to make generalizations about the behavior of the aqueous solubility of pesticides as a function of alcohol content as there are data available for only two pesticides that cover the entire cosolvent range of 0 to 100% (Kulkarni et al., 2000; Kumbar et al., 2002).

Most of the work on the cosolvency effect has focused on the increased solubility of compounds such as PAHs, PCBs, and BTEX. Far fewer studies have addressed the enhanced aqueous solubility of pesticides in the presence of alcohols. While sufficient data are available to evaluate models for the relationship between $S_m$ and $f_c$ for PAHs, PCBs, and BTEX, this is not so in the case of pesticides. Because of possible concerns about the mobilization of pesticides in agricultural watersheds resulting from ethanol spills, this study seeks to evaluate the applicability of different models developed for other classes of compounds to describe the enhanced aqueous solubility of pesticides in the presence of ethanol.

**Table 2.1** Summary of literature data of the enhancement of the aqueous solubility of pesticides in the presence of an alcohol.

| Pesticide | Molecular formula | log $S_w$ (µg/mL) | Cosolvent | Cosolvent mass fraction range | Log increase in aqueous solubility over cosolvent range | Reference |
|---|---|---|---|---|---|---|
| Diuron | $C_9H_{10}Cl_2N_2O$ | 1.56 | Methanol | 0 - 0.44 | 1.59 | Cheng (1989) |
| | | 1.62 | Methanol | 0 - 0.50 | 1.50 | Pinal et al. (1990) |
| | | 2.05 | Methanol | 0 - 0.44 | 1.40 | Hardway and Yalkowsky (1991) |
| | | 2.05 | Ethanol | 0 - 0.44 | 2.00 | Hardway and Yalkowsky (1991) |
| Atrazine | $C_8H_{14}ClN_5$ | N/A | Ethanol | 0.08 - 0.42 | 1.86 | Curren and King (2001) |
| | | N/A | Ethanol | 0.01 - 0.60 | 3.49 | Jia et al. (2013) |
| Chlorpyrifos | $C_9H_{11}Cl_3NO_3PS$ | 0.80 | Methanol | 0 – 1.0 | 4.26 | Kulkarni et al. (2000) |
| Cypermethrin | $C_{22}H_{19}Cl_2NO_3$ | 1.88 | Methanol | 0 - 0.90 | 2.76 | Kumbar et al. (2002) |
| Fenvalerate | $C_{25}H_{22}ClNO_3$ | 0.41 | Methanol | 0 – 1.0 | 4.89 | Kumbar et al. (2002) |

## 2.2 Materials and Methods

To investigate the enhancement of aqueous solubility of organochlorine pesticides in the presence of ethanol, the aqueous solubility of three representative organochlorine pesticides was determined at different water-ethanol ratios, at room temperature and relative humidity (temperature = 21.7 ± 0.8 ºC and relative humidity = 32 ± 8%). Dieldrin ($C_{12}H_8Cl_6O$) (Cerilliant, 99% analytical standard grade), lindane ($C_6H_6Cl_6$) (ChemService, 99.5% analytical standard grade), and chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) (ChemService, 99.5% analytical standard grade) are nonionic chlorinated pesticides (Gevao et al., 2000) that have been identified in surveys of contamination in river sediment (U.S. Geological Survey, 2000). Lindane has a more symmetric configuration (Figure 2.1) and the highest aqueous solubility in the absence of ethanol (Table 2.2) among the three pesticides. The water used to create the aqueous solutions was created by passing deionized, distilled water through a series of four Milli-Q filters (Millipore), to give a resistivity of 18.3 MΩ-cm. Ethanol of HPLC (high performance liquid chromatography) spectrophotometric grade (99.8% pure) was obtained from Sigma Aldrich. Eqns. 2.2 – 2.6 include the parameter $f_c$, the volume fraction of ethanol. However, when water and ethanol are mixed together, the volume is not conserved. The volume of the mixture is less than the sum of the volumes of the individual liquids, with the greatest difference occurring around an ethanol molar fraction of 0.4 (Dortmund Data Bank, 2015). Hence, confusion may occur in reporting volume fractions. For this reason, the mixtures in this study are reported in terms of mass fractions of ethanol, $\omega_c$, rather than volume fractions.

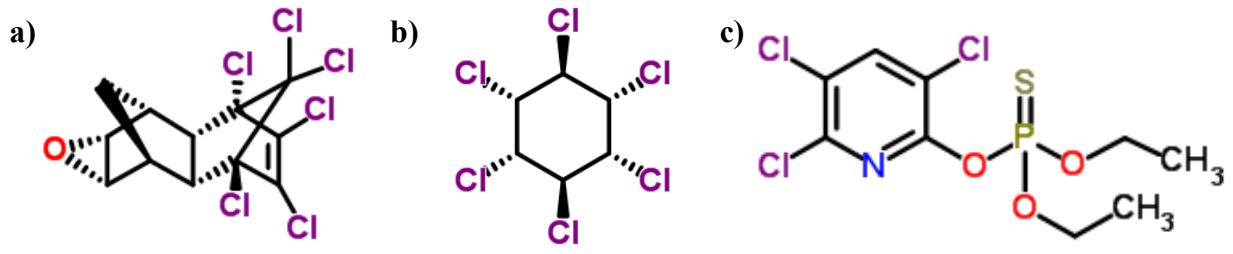


**Figure 2.1** Chemical structure of a) dieldrin, b) lindane, and c) chlorpyrifos as given by ChemSpider (2017).

Figure 2.2 shows a schematic of the experimental procedure used to determine the effect of ethanol on the enhancement of the aqueous solubility of the organochlorine pesticides. The methodology used in this study to determine the enhanced aqueous solubility of pesticides in the presence of ethanol was based on that presented by Millard and others (2002), with some modifications. Water and ethanol were mixed in 30 mL polytetrafluoroethylene (PTFE) centrifuge tubes for $\omega_c < 0.6$, and in 10 mL PTFE centrifuge tubes for $\omega_c \geq 0.6$, on a rotator overnight. After mixing, small increments of pesticide were added to the solution until an excess of pesticide was observed visually. After another 24 hours of rotation, the solution was checked to see if an excess of the pesticide was still present; if it appeared that all the pesticide was in solution, more was added until an excess was evident. If a solid phase appeared to be still present after 24 hours, the system was left to rotate for another 72 hours. After a total of 96 hours, three sets of samples were withdrawn, each set approximately one day apart, in order to confirm that the system had reach equilibrium. Each sample was passed through a 0.20 µm PTFE filter to remove undissolved pesticide, after which 2 µL of methanol were added to maintain the pesticide in solution during analysis. The samples were analyzed using a gas chromatograph (Hewlett Packard 6890) equipped with an electron capture detector (ECD). A DB-5ms 0.25 µm column (Agilent Technologies) was used with nitrogen as the carrier gas. At

higher ethanol fractions, the samples were diluted prior to analysis to reduce the potential of saturating the gas chromatograph column. The limit of detection for the measurements in this study were 6 ppb, 3 ppb, and 1 ppb for dieldrin, lindane, and chlorpyrifos, respectively.

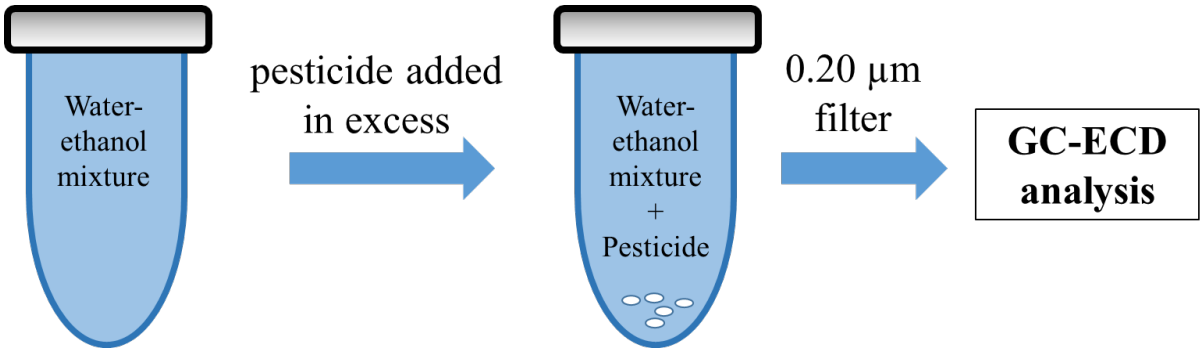


**Figure 2.2** Overall experimental procedure to determine the effect of ethanol on the aqueous solubility of organochlorine pesticides.

A linear model was fit to the solubility data for dieldrin, lindane, and chlorpyrifos using linear regression. In order to evaluate the applicability of the different models, the parameter $\sigma$ was calculated using Eqn. 2.1 based on the experimental data. From this value and the slope obtained from linear regression, the empirical coefficient, $\beta$ (Eqn. 2.3), was calculated. To determine the suitability of Heermann and Powers model (Eqns. 2.5 and 2.6), the value of $S_\eta$ was obtained from the experimental data. For comparison, the same analysis was applied to the data from Kulkarni and others (2000) for chlorpyrifos, with methanol as the cosolvent, and from Kumbar and others (2002) for fenvalerate, with methanol as the cosolvent, as these two data sets present the solubility of pesticides over the complete range of alcohol volume fractions of 0.0 - 1.0.

## 2.3 Results and Discussion

Figure 2.3 shows the measured aqueous solubility of dieldrin, lindane, and chlorpyrifos as a function of alcohol mass fraction. An increase was observed in the solubility of dieldrin, lindane, and chlorpyrifos of about 7.46, 3.31, and 6.61 orders of magnitude, respectively, as the ethanol mass fraction, $\omega_c$, increased from 0.0 to 1.0 (Table 2.2). A linear regression analysis suggested that the data were best fit when divided into two parts, with a breakpoint at $\omega_c = 0.35$ for dieldrin, 0.45 for lindane, and 0.35 for chlorpyrifos. This figure also shows linear regression fits to the data for chlorpyrifos in methanol from Kulkarni and others (2000) and for fenvalerate from Kumbar and others (2002). This figure suggests that a breakpoint in the range of $\omega_c \approx 0.30$ - 0.45 is also appropriate for these pesticides. The aqueous solubility data from this study for dieldrin, lindane, and chlorypyrifos showed larger per unit increases at lower fractions of ethanol than at higher fractions, with the slope of the fitted lines dropping from 12.66 to 5.09 for dieldrin, from 5.22 to 1.95 for lindane, and from 10.38 to 4.32 for chlorpyrifos (Table 2.2). Moreover, this figure shows that the cosolvency power, $\sigma$ (Eqn. 2.1), was greater for the more hydrophobic pesticides, dieldrin and chlorpyrifos, and less for the most initially soluble compound, lindane (Table 2.2).

A different trend is observed in the data presented in Kulkarni and others (2000) and Kumbar and others (2002). The slopes increased from 1.78 to 5.24 for chlorpyrifos and from 1.39 to 6.23 for fenvalerate. These data for chlorpyrifos stand in contrast to the measurements made in this study, where the slope at low alcohol mass fractions was 10.38 and decreased to 4.32 after the breakpoint. In both of the literature studies, the increase in solubility of chlorpyrifos and fenvalerate did not have a log-linear relationship at low alcohol mass fractions. The fact that the solubility at $\omega_c = 0.0$ is similar to that at $\omega_c = 0.3$ suggests that the data reported

in these two studies may have been limited by the limit of detection of the instrument. Consequently, the fact that the slopes increased after the breakpoint may be an artifact of the measurement accuracy.

A comparison of the slopes obtained from the experimental data by linear regression and the calculated values of $\sigma$ (Table 2.2) show that they are not equal for any of the pesticides, suggesting that an additional parameter, such as $\beta$ (Eqn. 2.3), needs to be included to describe the data adequately. Using the slopes generated by linear regression and the values of $\sigma$ determined based on Eqn. 2.1, $\beta$ was determined to be equal to 1.71 and 0.69 for dieldrin, 1.58 and 0.59 for lindane, and 1.57 and 0.65 for chlorpyrifos at low and high values of $\omega_c$, respectively (Table 2.2). The variation in the values of $\sigma$ for the various pesticides suggests that $\sigma$ describes solute-cosolvent interactions, whereas the similarity in the values in $\beta$ suggests that $\beta$ describes solvent-cosolvent pairs. This observation corroborates the original conceptualizations of these parameters.

The models presented in Eqns. 2.2 and 2.3 suggest that the y-intercept of the relationship between log $S_m$ and the alcohol mass fraction is log $S_w$. A comparison of the y-intercept values obtained by linear regression and the measured aqueous solubilities in the absence of a cosolvent suggests that this is so at low ethanol fractions; however at high fractions, the y-intercept for the line fit through these data is considerably larger than log $S_w$ (Table 2.2). Consequently, Eqn. 2.3 can describe the aqueous solubility only at low ethanol fractions; it fails at higher mass fractions because the y-intercept is not log $S_w$, supporting the concept that a two-part model is necessary.

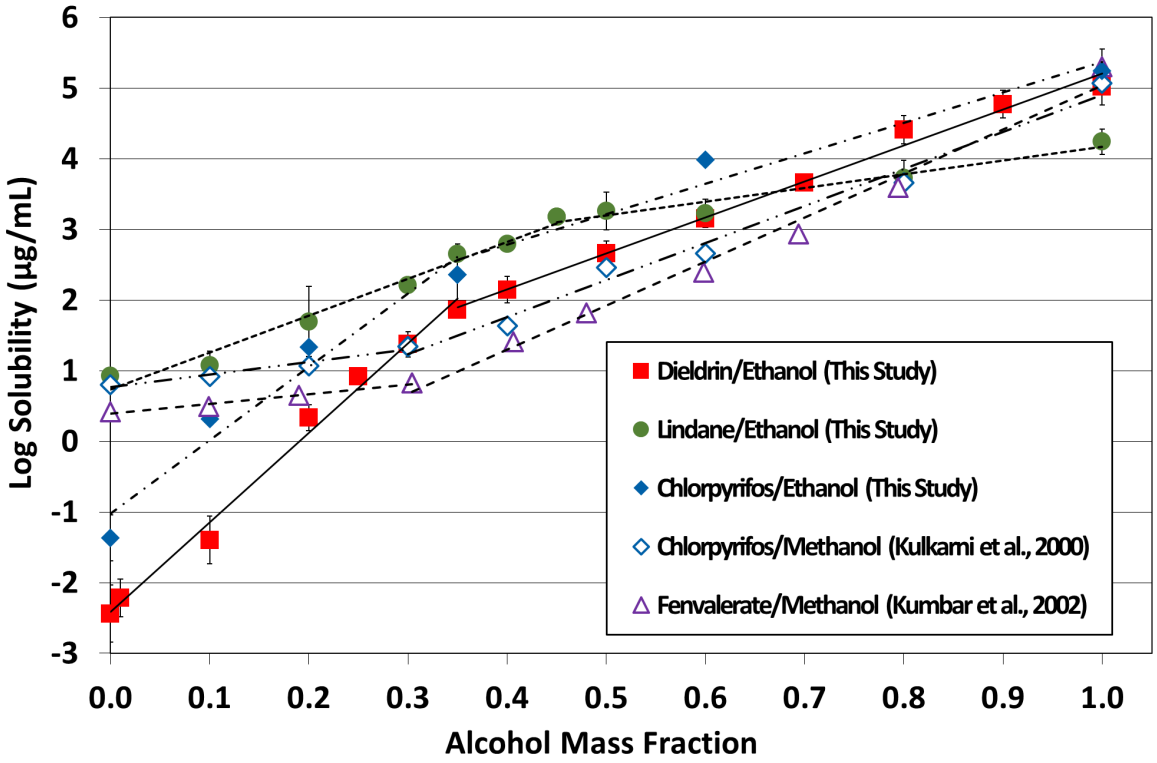


**Figure 2.3** Log of the aqueous solubility of several organochlorine pesticides as a function of alcohol mass fraction. The data for dieldrin, lindane, and chlorpyrifos in ethanol were measured in this study. The data for chlorpyrifos and fenvalerate in methanol are from Kulkarni and others (2000) and Kumbar and others (2002), respectively. The lines shown are best fit linear regressions for the various systems, with the values for the parameters for this study given in Table 2.2.

**Table 2.2** Properties and model parameter values for the aqueous solubility for several pesticides as a function of ethanol mass fraction at room temperature (21.7 ± 0.8 ºC) and relative humidity (32 ± 8%).

| Pesticide | Dieldrin ($C_{12}H_8Cl_6O$) | Lindane ($C_6H_6Cl_6$) | Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) |
|---|---|---|---|
| log $S_w$ (μg/mL) | -2.44 | 0.93 | -1.37 |
| Cosolvent | Ethanol | Ethanol | Ethanol |
| $\sigma$ [Eqn. 2.1] | 7.46 | 3.31 | 6.61 |
| Breakpoint, η (cosolvent mass fraction) | 0.35 | 0.45 | 0.35 |
| log $S_\eta$ (μg/mL) [Eqns. 2.5 and 2.6] | 1.86 | 3.18 | 2.36 |
| log $\delta$ (μg/mL) [Eqn. 2.7] | -2.56 | -1.29 | -2.42 |
| | | Below breakpoint | |
| Slope from linear regression | 12.66 | 5.22 | 10.38 |
| y-intercept | -2.41 | 0.73 | -1.03 |
| $R^2$ | 0.99 | 0.98 | 0.95 |
| $\beta$ [Eqn. 2.3] | 1.71 | 1.58 | 1.57 |
| | | Above breakpoint | |
| Slope from linear regression | 5.09 | 1.95 | 4.32 |
| y-intercept | 0.12 | 2.22 | 1.06 |
| $R^2$ | 0.91 | 0.95 | 0.96 |
| $\beta$ [Eqn. 2.3] | 0.69 | 0.59 | 0.65 |

Figure 2.4 shows the description of the aqueous solubility as a function of alcohol mass fraction using the linear/log-linear model proposed by Heermann and Powers (1998) (Eqns. 2.5 and 2.6). For dieldrin, lindane, and chlorpyrifos, the model adequately predicts the aqueous solubility at high cosolvent mass fractions. However, at low fractions, there are deviations between the data and the model due to the rapid increase in the aqueous solubility in this range that is not reflected in a linear relationship. Similarly, the model suggested by Banerjee and Yalkowsky (1988) (Eqn. 2.4), using the parameters provided for a toluene-methanol system, is not capable of adequately describing the solubility at low values of $\omega_c$ for dieldrin, lindane and chlorpyrifos. At $\omega_c = 0.1$, the difference between the measured solubility and the estimate calculated using the Banerjee and Yalkowsky (1988) model is about one order of magnitude for dieldrin, 15% for lindane, and over one order of magnitude for chlorpyrifos; at $\omega_c = 0.2$, the difference is over two orders of magnitude for dieldrin and chlorpyrifos, and about an order of magnitude for lindane. Consequently, for organochlorine pesticides like dieldrin, lindane, and chlorpyrifos, linear models do not perform satisfactorily, even at low values of $\omega_c$.

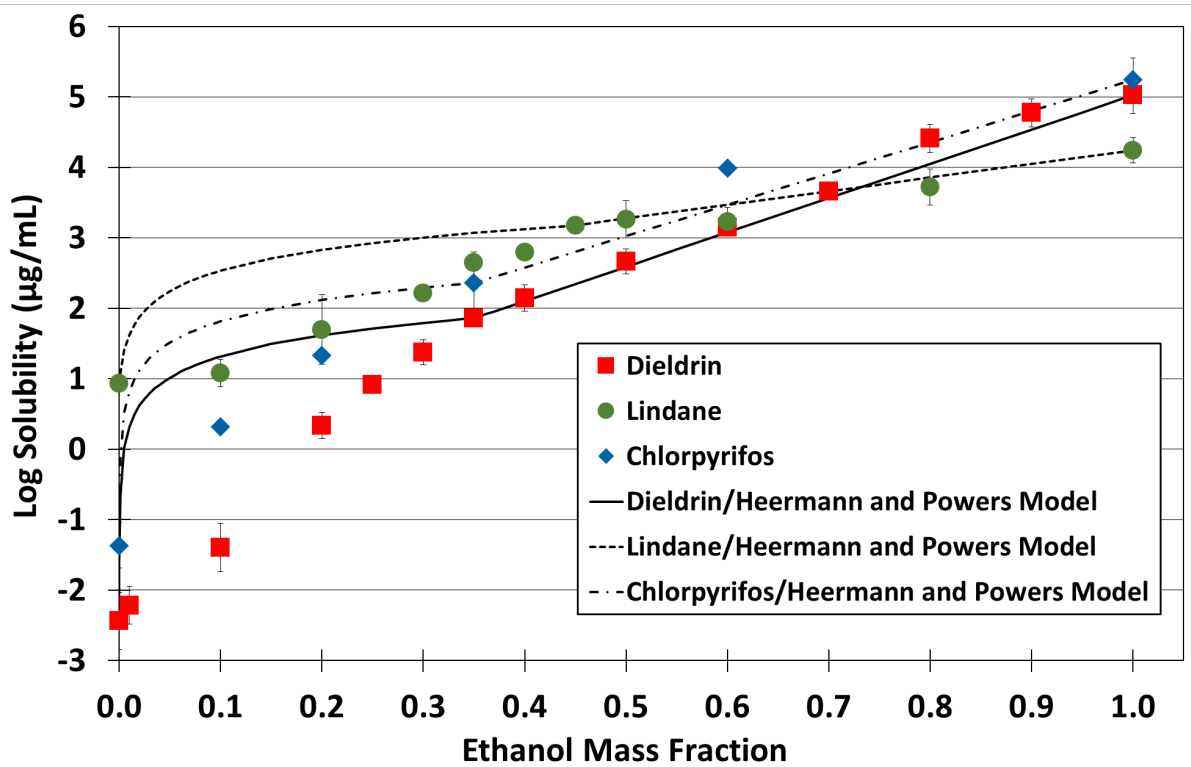


**Figure 2.4** Log of the aqueous solubility of several organochlorine pesticides as a function of ethanol mass fraction. The lines show the Heermann and Powers (1998) model (Eqns. 2.5 and 2.6) for the various systems, with the values for the parameters given in Table 2.2.

The data presented in Table 2.2 show that Eqn. 2.3 can adequately describe the enhanced solubility of the pesticides below the breakpoint. Above the breakpoint, the model fails due to the fact that the y-intercept at high values of $\omega_c$ is not equal to log $S_w$. To correct this shortcoming, an additional empirical coefficient, $\delta$, can be introduced into Eqn. 2.3 to describe the data for values of $\omega_c$ above the breakpoint:

$$\log S_m = \log\left(\frac{S_W}{\delta}\right) + \beta\,\sigma\,f_c \qquad \text{for } f_c \geq \eta \qquad (2.7)$$

This new empirical coefficient, $\delta$, is given by the difference between log $S_w$ and the y-intercept of the log-linear relationship above the breakpoint (Table 2.2). The value of log $\delta$ is related to

the difference in slopes below and above the breakpoint. All three pesticides examined in this study have negative values of log $\delta$ since the slope decreases after the breakpoint.

Alternatively, Eqn. 2.3 may be utilized below the breakpoint and Eqn. 2.6 above the breakpoint. As Figure 2.5 shows, the combination of these two equations has the ability to fit the entire relationship between the aqueous solubility and the mass fraction of ethanol for the three pesticides. With the modifications proposed, there exists two options to describe the relationship between the log of the aqueous solubility and the ethanol mass fractions: Eqn. 2.3, below the breakpoint, and either Eqn. 2.6 or Eqn. 2.7 above the breakpoint. Both options require a prior knowledge of the solute's solubility in pure water and in the pure cosolvent, the value of $\eta$ (which may be taken as equal to 0.35, as the $R^2$ values for the linear regressions to the various pesticide data sets do not change appreciably by setting $\eta = 0.35$) and the value of $\beta$ below the breakpoint. Utilizing Eqn. 2.7 to describe the relationship at higher values of $\omega_c$ would require, in addition, the values of $\beta$ above the breakpoint and the additional empirical coefficient, $\delta$.

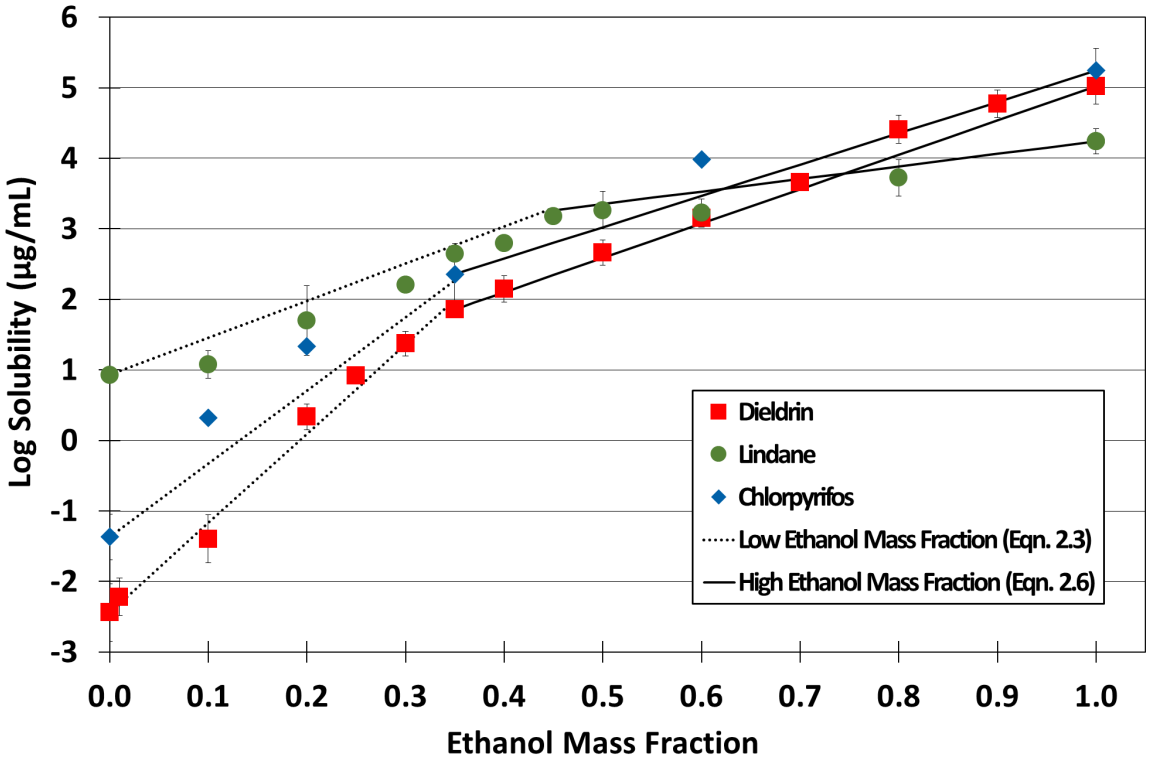


**Figure 2.5** Log of the aqueous solubility of several organochlorine pesticides as a function of ethanol mass fraction. The lines show the mathematical model given in Eqn. 2.3 for ethanol mass fractions below the breakpoint, and in Eqn. 2.6 above the breakpoint for the various systems. Values for the parameters are given in Table 2.2.

All of the ethanol-water-pesticide systems examined here show a breakpoint at a mass fraction of about 0.35, independent of the pesticide. The similarity of the values for the breakpoint among the various pesticides suggests that the change is related to the interactions between the alcohol and water and is independent of the solute. Preliminary calculations performed in this study of water-ethanol interactions performed in Gaussian 09 using the B3LYP/3-21g* function indicate that the clustering of water molecules is disrupted by the formation of ethanol structures as the ethanol fraction increases. The behavior observed in these simulations is supported by calculations of the excess partial molar activation free energy, enthalpy and entropy for ethanol from dielectric relaxation measurements presented by Sato and

others (1999) which show two distinct regimes. At $\omega_c < 0.36$, these excess partial molar quantities vary considerably with the mass fraction; however at $\omega_c > 0.36$, they are essentially equal to zero (Sato et al., 1999). It is postulated that at low mass fractions, the presence of ethanol enhances the structure of water, with the formation of clathrate cages around the ethanol. As the ethanol concentration increases, the rigidity of the cages relaxes to the point where water molecules are just orientationally ordered about the ethanol. Above $\omega_c = 0.36$, the excess partial molar quantities for ethanol are zero, suggesting that the ethanol molecules are experiencing an environment similar to pure ethanol. It is thought that the ethanol molecules form polymer-like chains stabilized by water, resulting in microheterogeneity at the molecular level in the system (Wakisaka and Matsuura, 2006).

**2.4 Conclusions**

The work reported here showed increases in the solubility of dieldrin, lindane, and chlorpyrifos of about 7.5, 3.3, and 6.6 orders of magnitude, respectively, as the ethanol mass fraction, $\omega_c$, increased from 0.0 to 1.0. All the pesticides examined here displayed about the same breakpoint, at $\omega_c \approx 0.35$. The similarity of this value for all the systems suggests that the change in solubility regimes stems from interactions between the cosolvent and water. Simulations and literature data suggest that as the mass fraction of the cosolvent increased, the molecular-level organization moves from individual ethanol molecules surrounded by structured water, to a regime of ethanol polymer chains stabilized by orientated water. Models have been previously proposed in order to describe the enhanced aqueous solubility of HOCs as a function of the alcohol concentration. These models were evaluated in this study and the results indicated that two-part models are necessary to describe the enhancement of pesticide solubility in the presence of alcohol. The Heermann and Powers (1998) two-part model (Eqns. 2.5 and 2.6) was

not able to describe adequately the data for dieldrin, lindane, and chlorpyrifos below the breakpoint due to the fact that the relationship between the aqueous solubility and cosolvent mass fraction was not linear at low mass fractions. At low mass fractions ($\omega_c < \sim 0.35$), the log-linear model given in Eqn. 2.3 is satisfactory for all the pesticides examined here. The use of this equation requires a knowledge of the solute's solubility in pure water and in the pure cosolvent, the alchohol mass fraction at the breakpoint (which can be taken as 0.35), and the coefficient $\beta$ representing the cosolvent-water interactions at low fractions. At high fractions, two options are available: Eqn. 2.7 may be used, which requires a value for $\beta$ representing the cosolvent-water interactions at high cosolvent mass fractions and an additional empirical coefficient, $\delta$, which describes the change in slope above and below the breakpoint. Alternatively, the model given in Eqn. 2.6 can be utilized with no further parameters needed.

With the move towards ethanol-blended fuels, the impact of ethanol on the solubility of sparingly soluble organic compounds, such as organochlorine pesticides, needs to be considered. The enhancement in the aqueous solubility of organochlorine pesticides by the presence of ethanol can affect other properties that influence the mobilization of such pesticides in the water column. For example, in the presence of an organic liquid, like gasoline, the aqueous solubility enhancement may affect the partitioning behavior of the pesticides between the organic liquid and the aqueous phase. The following chapter examines how the partitioning behavior is influenced by the presence of ethanol.

# CHAPTER 3

## Partitioning of organochlorine pesticides between an organic liquid phase and an aqueous phase as a function of ethanol content

### 3.1 Background

With the increase in use of ethanol-blend fuels, ethanol and gasoline in various proportions may be introduced into the water column in the event of a spill. In the previous chapter, it was shown that ethanol, a water-miscible organic solvent, can act as a cosolvent, increasing the aqueous solubility of organochlorine pesticides of over three to seven orders of magnitude. Ethanol is completely miscible in water; consequently with ethanol spills, only a one-phase system needs to be considered. However, gasoline is sparingly miscible in water (Yüksel and Yüksel, 2004); thus spills of ethanol-blend fuels may result in a two-phase system. In the presence of an organic liquid like gasoline, the increase in the aqueous solubility due to ethanol can affect the partitioning behavior of the pesticides between gasoline and water. In such a case, the behavior of all the components of the system, water, ethanol, gasoline and pesticide, needs to be considered.

Partitioning is described by a partition coefficient, defined here as:

$$K = \frac{C_{org}}{C_{aq}} \tag{3.1}$$

where $C_{org}$ is the concentration of the species of interest in the organic liquid phase, and $C_{aq}$ is the concentration of the species of interest in the aqueous phase at equilibrium. Perhaps, the most frequently determined partition coefficient is the octanol-water partition coefficient, $K_{ow}$, as it is commonly used as a measure of a compound's hydrophobicity (McDuffie, 1981; Miller et al., 1985; De Bruijn et al., 1989; Kawamoto and Urano, 1989; Ruelle, 2000; Schwarzenbach et al., 2003) (Table 3.1). In the context of ethanol-blended fuels in the environment, the simplest representative system may consist of a single alkane and water. The studies done by Cline and others (1991) and Ruelle (2000) are some of the few that look at the partitioning of HOCs, such as PAHs, PCBs or BTEX, between an alkane and water. Based on these studies, it seems that the trend of the alkane-water partition coefficient, $K$, for various compounds is similar to that of their corresponding octanol-water partition coefficient, $K_{ow}$, as $K$ increased with $K_{ow}$ (Table 3.1).

**Table 3.1** Partition coefficients between octanol and water, $K_{ow}$, and between n-hexane and water, $K$, for several compounds (from Ruelle, 1991).

| Solute | log $S_w$[a] (µg/mL) | log $K_{ow}$ | log $K$ |
|---|---|---|---|
| Benzene | 3.25 | 2.13 | 2.06 |
| Toluene | 2.76 | 2.73 | 2.75 |
| Naphthalene | 1.49 | 3.30 | 2.82[b] |
| 2,4,5-PCB | -0.79 | 5.74 | 5.76 |
| 2,2',4,4'6,6'-PCB | -3.39 | 7.20 | 6.50 |
| Decachlorobiphenyl | -5.14 | 8.16 | 7.14 |

[a]The aqueous solubilities, $S_w$, were obtained from Miller and others (1985). [b]The n-hexane-water partition coefficient for napththalene was obtained from Cline and others (1991).

The partition coefficient of HOCs may vary depending on the composition of the organic phase. Gasoline is a complex mixture that contains hundreds of hydrocarbons, and its composition varies with the fuel source and refinery process (Dagaut and Togbé, 2008; Lemaire

et al., 2010; Zhong and Zheng, 2014). Gasoline generally contains linear, branched and cyclic paraffins, aromatics, olefins, naphthenes, and oxygenated components (Lemaire et al., 2010; Mehl et al., 2011; Zhong and Zheng, 2014). However, Figure 3.1 suggests that the partition coefficient for naphthalene and toluene is only slightly greater for actual fuels than for pure alkanes (approximately 59% difference for a parameter that can vary over orders of magnitude). Thus, in the case of gasoline, the partition coefficient may be only minimally affected by the complexity of the organic liquid phase. Because of the seeming lack of a dependence on composition, a general terminology, independent of the specific composition, is often adopted to describe the partition coefficient between an organic liquid phase, including gasoline or iso-octane, and water, referred to as the fuel-water partition coefficient.

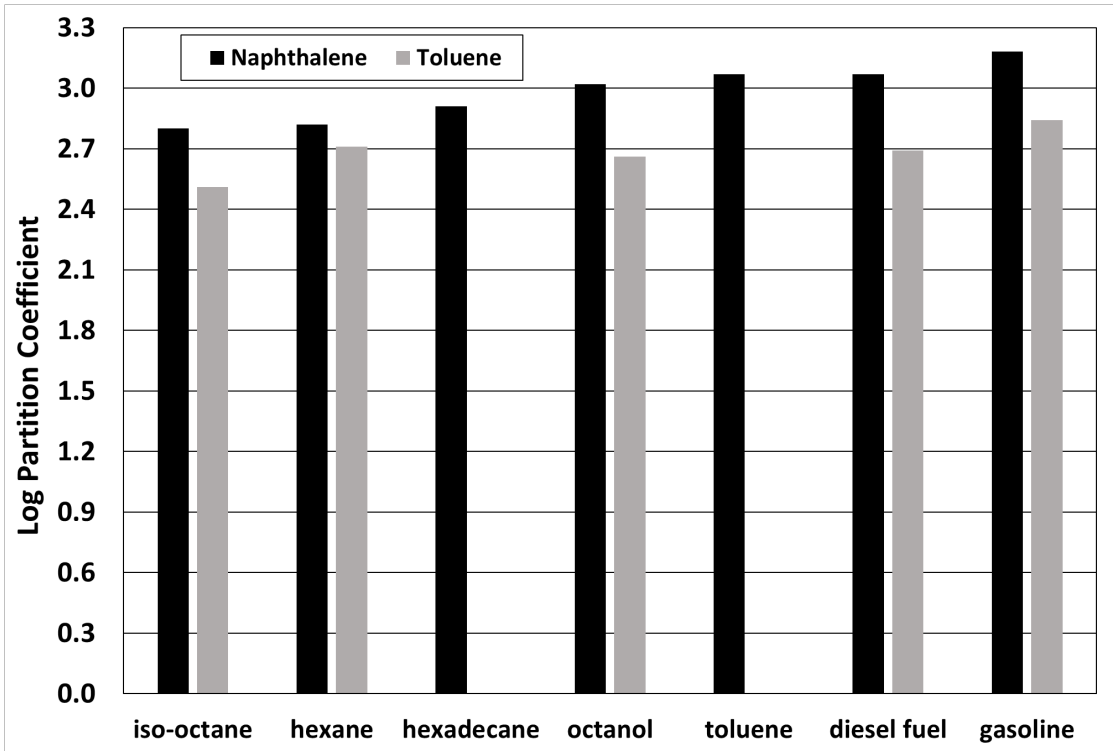


**Figure 3.1** Log of the partition coefficient for naphthalene and toluene between various organic liquids and water (data from Cline et al., 1991).

Predictive models have been developed to describe the fuel-water partition coefficient of different HOCs like BTEX and PAHs (Cline et al. 1991; Lee et al. 1992; Chen et al. 1994; Chen et al. 2008). These studies suggested that an inverse relationship exists between the log of the fuel-water partition coefficient and the log of the aqueous solubility of the solute, with a slope equal to -1:

$$\log K = -\log S_w^* + a \tag{3.2}$$

where $S_w^*$ is the aqueous solubility of the HOCs (expressed in mol/L) and $a$ is the intercept determined by linear regression. It has been suggested that the y-intercept can be determined as the log of the ratio of the density of the organic liquid (expressed in g/L), $\rho_{org,}$ to the molecular weight of the organic liquid (expressed in g/mol), $MW_{org}$, (Lee et al. 1992; Chen et al. 1994; Chen et al. 2008):

$$\log\left(\frac{\rho_{org}}{MW_{org}}\right) \tag{3.3}$$

Consequently, the fuel-water partition coefficient of HOCs may be estimated if the aqueous solubility of the solute is available and basic properties of the organic liquid solvent are known. However, this model was developed to describe the partitioning of a solute between water and a variety of pure organic liquid phases. It does not incorporate the cosolvent effect on the aqueous solubility of an HOC and it is unknown whether the model can be extended to systems in which a cosolvent is present.

In understanding the partitioning behavior of HOCs in a water/ethanol/organic liquid system, the partitioning of ethanol between water and the organic liquid phase needs to be

considered. In a water/ethanol/organic liquid system, it has been noted that ethanol displays a high preference for the aqueous phase (Peschke and Sandler, 1995; Heermann and Powers, 1998), with the partition coefficient of ethanol constant up to a high ethanol mass fraction (Peschke and Sandler, 1995). For example, for a water/ethanol/iso-octane system, Peschke and Sandler (1995) observed a partition coefficient of ethanol (expressed as a log) ranging from –2.0 to –1.5 up to an ethanol mass fraction in the system of approximately 0.7 (above a mass fraction of 0.7, the system exists as a single liquid phase [Figure 1.1]). With most of the ethanol partitioning into the aqueous phase, an increase in the aqueous solubility of the organic liquid phase can occur. For example, Peschke and Sandler (1995) observed an increase of approximately three orders of magnitude in the aqueous solubility of iso-octane as the ethanol mass fraction in the system increased up to 0.7.

The partitioning of ethanol into the aqueous phase can also increase the aqueous solubility of HOCs, and in turn, affect the partitioning of HOCs between the organic liquid phase and the aqueous phase. For example, for a water/ethanol/gasoline system, Heermann and Powers (1998) observed an increase of approximately two orders of magnitude in the aqueous phase concentration of the BTEX compounds in the presence of ethanol, corresponding to a decrease of approximately two orders of magnitude in the fuel-water partition coefficient of the BTEX compounds as the ethanol mass fraction in the system increased up to approximately 0.7. Chen and others (2008) also reported a decrease in the fuel-water partition coefficient for the BTEX compounds as the presence of ethanol in the system increased. As the highest ethanol mass fraction in the system was only approximately 0.06, the orders of magnitude of difference recorded by Heermann and Powers (1998) were not observed. As Chen and others (2008) noted,

an ethanol mass fraction in the system of approximately 0.4 would be necessary in order for an appreciable decrease in the partition coefficient to occur.

There is a scarcity of studies that examine the impact of an alcohol, like ethanol, on the partitioning behavior of HOCs between an organic liquid phase and water. There are a few studies looking at the BTEX compounds, but no studies for PCBs and PAHs. For organochlorine pesticides, Kumbar and others (2002) examined the impact of methanol on the heptanol-water partition coefficient for two pesticides, fenvalerate and cypermethrin, up to a methanol mass fraction in the aqueous phase of approximately 0.3. Over this range, they observed a decrease in the partition coefficient of about 50% and one order of magnitude for fenvalerate and cypermethrin, respectively. However, it is difficult to make generalizations about the partitioning behavior as a function of alcohol content as there is limited data for a number of types of HOCs and no data for pesticides that cover the entire cosolvent range.

Little work is present in the literature examining the cosolvency effect of alcohols on the partitioning of HOCs between water and an organic liquid phase. Because of possible concerns about the behavior of organochlorine pesticides in agricultural watersheds in the presence of oxygenated fuel spills, this study seeks to evaluate the fuel-water partition coefficient of organochlorine pesticides in the presence of ethanol. Moreover, this study investigates the incorporation of cosolvency in the linear relationship presented in Eqn. 3.2 between the logarithm of the partition coefficient and the logarithm of the aqueous solubility of HOCs.

## 3.2Materials and Methods

To investigate the partitioning of organochlorine pesticides between an aqueous phase and an organic liquid in the presence of ethanol, the partition coefficient of the three representative organochlorine pesticides, dieldrin, lindane, and chlorpyrifos, described in Chapter 2, was determined at different system ethanol fractions, performed at room temperature (21.7 ± 0.8 ºC) and relative humidity (32 ± 8%). Milli-Q water was used to create the aqueous solutions. Iso-octane (Fisher Chemical, 99% HPLC grade) and 87 octane unleaded regular gasoline (BP gas station, Ann Arbor, MI, Summer 2016), which may contain up to 10% by volume of ethanol, were used as the organic liquid phases. Ethanol was used as the cosolvent. The mixtures in this chapter are reported both in terms of the mass fraction of ethanol in the system and in the aqueous phase; it will be specifically noted which unit of concentration is being used.

The systems were composed of three liquids: water, ethanol, and the organic liquid at different ratios. The partition coefficient between water and the organic liquid was determined for ethanol and the three representative organochlorine pesticides; additionally the solubility of iso-octane in the aqueous phase as a function of ethanol content was determined as well. In order to determine the partitioning of ethanol between iso-octane and water, 200 mL (total volume) mixtures of iso-octane (at a system mass fraction held constant at 0.15), ethanol, and water, at system ethanol mass fractions ranging from 0.10 to 0.50, were placed in a sealed glass container containing a magnetic stir bar. The glass container was placed on a magnetic stir plate and mixed for three days. After three days, the aqueous phase was separated from the mixture using a separatory funnel and the ethanol concentration in the aqueous phase was analyzed using a HI96816 Digital Wine Refractometer (Hanna Instruments). The refractometer was

independently calibrated using known ethanol concentrations to take into account possible interference from the presence of iso-octane. Based on a knowledge of the total amount of ethanol present in the system, the ethanol concentration in the organic liquid phase was determined by mass balance. Subsequently, the ethanol partition coefficient between iso-octane and the aqueous phase was calculated.

To determine the partition coefficient of dieldrin, lindane, and chlorpyrifos, a slow-stirring method developed for determining the octanol-water partition coefficient was used (Finizio et al., 1997; OECD, 2006). 400 mL glass vessels (height: 21 cm; inner diameter: 5 cm), with a sampling port for the organic liquid phase located at the top of the vessel and a sampling port for the aqueous phase located at a height of 10 cm from the base, were constructed (Figure 3.2). In each system, the system mass fraction of the organic liquid (iso-octane or gasoline) was held constant at 0.15, while the ethanol mass fraction in the system varied from 0.0 to 0.7 (above an ethanol mass fraction of 0.7, the system is present as one phase [Figure 1.1] [Letcher et al., 1986; Peschke and Sandler, 1995]). Water comprised the third liquid component of the system, bringing the total mass fraction to 1.0. First, the aqueous phase was prepared by stirring the appropriate amount of ethanol and water in a sealed glass container for an hour. Then the aqueous phase and the organic liquid were placed in the vessel to mutually saturate. The exchange between the liquid phases was accelerated by stirring the system with a magnetic stir bar. The stirring rate was controlled so that the vortex formed at the interface between the aqueous and organic liquid phases was no more than 0.5 cm in order to avoid the formation of microdroplets, which may cause the overestimation of the aqueous concentration of HOCs (OECD, 2006). After three days, some pesticide was dissolved in a small amount of the organic liquid phase and added gently to the organic phase. The amount of pesticide that was added was

equal to a concentration in the organic liquid phase in the vessel of 1 g/L. The completed system was allowed to equilibrate for seven days. After a total of ten days, four samples were taken from the aqueous phase and two samples from the organic liquid phase. A total of four sets of samples were taken, each a day apart. Two samples from each liquid phase were analyzed for the pesticide concentration using a gas chromatograph (Hewlett Packard 6890) equipped with an electron capture detector (ECD). A DB-5ms 0.25 µm column (Agilent Technologies) was used with nitrogen as the carrier gas. Two samples from the aqueous phase were analyzed for iso-octane content using a gas chromatograph (Hewlett Packard 5890) equipped with a flame ionization detector (FID). A fused silica capillary 0.25 µm column (Nukol™) was used with hydrogen as the carrier gas. For both the pesticide and iso-octane analyses at higher ethanol fractions, the samples were diluted with methanol prior to analysis to reduce the potential of saturating the gas chromatograph column.

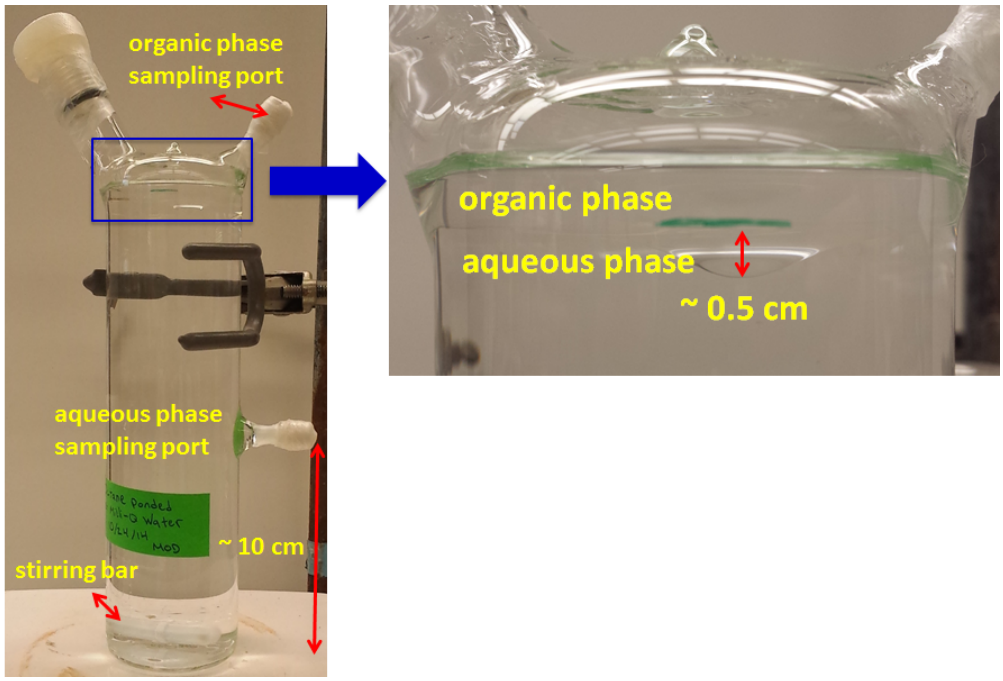


**Figure 3.2** Experimental set up for determination of the fuel-water partition coefficient of organochlorine pesticides.

A log-log model was fit to the partitioning data for dieldrin, lindane, and chlorpyrifos using linear regression, with the exception of the data points corresponding to 0% ethanol mass fraction. In the empirical model described by Eqns. 3.2 and 3.3, the solubility is expressed in mol/L; however, the solubilities reported in this study are expressed in µg/mL. Combining Eqns. 3.2 and 3.3 and converting units yields:

$$\log K = -\log S_w + \log\left( MW_{pesticide} \frac{\rho_{org}}{MW_{org}} \right) \qquad (3.4)$$

where $S_w$ is the aqueous solubility of the pesticide (expressed in µg/mL), $\rho_{org}$ is the density of the organic liquid phase (expressed in µg/mL), $MW_{org}$ and $MW_{pesticide}$ are the molecular weight (expressed in g/mol) of the organic liquid and pesticide, respectively. In order to evaluate the applicability of the empirical model described by Eqn. 3.2, the parameter $a$ was obtained from

the y-intercept of the linear regression and compared to the y-intercept given in Eqn. 3.4, equal to the log of the molecular weight of the pesticide times the ratio of the density to the molecular weight of the organic liquid.

### 3.3 Results and Discussion

Figure 3.3 shows the measured partition coefficient, defined in Eqn. 3.1, of ethanol between iso-octane and water as a function of ethanol mass fraction in the system. Similar to the observations reported by Peschke and Sandler (1995) and Heermann and Powers (1998), the partition coefficient seems to be constant over the range of ethanol mass fractions considered. The average value (expressed as log) was –3.54 ± 0.27, suggesting that ethanol displays a high preference for water in the presence of an organic liquid.

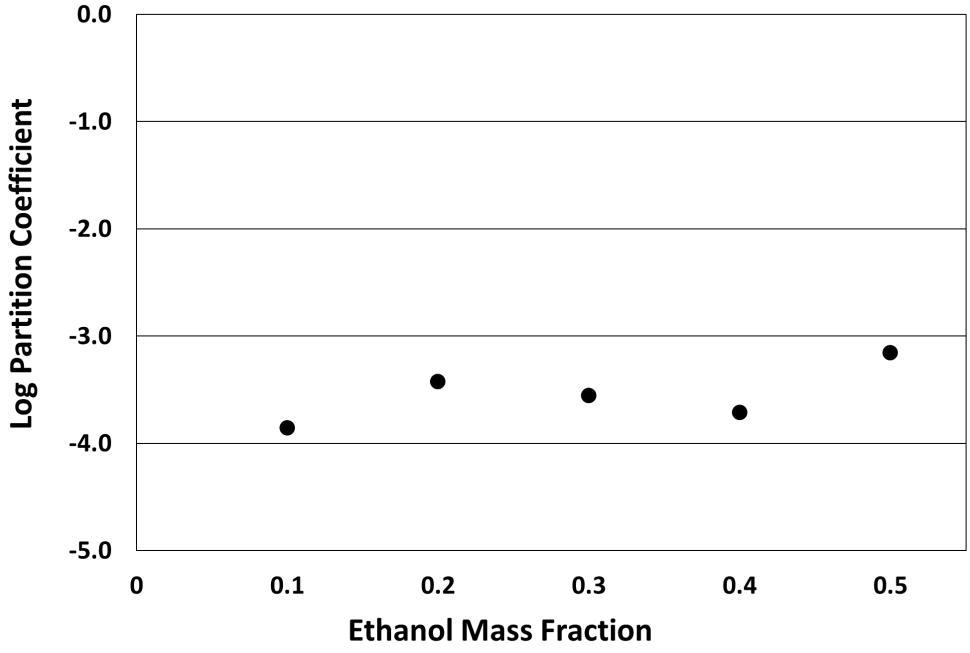


**Figure 3.3** Log of the partition coefficient (Eqn. 3.1) of ethanol between iso-octane and water as a function of ethanol mass fraction in the system. *The standard deviations from duplicate samples are reported in the figure, however due to their small magnitude they are obscured by the data point markers.

Figure 3.4 shows the measured aqueous solubility of iso-octane as a function of ethanol mass fraction in the system. The increase in the aqueous solubility of iso-octane was over four orders of magnitude. A linear regression analysis suggested that the data were best fit when divided into two parts, with a breakpoint at a system ethanol mass fraction of 0.3, corresponding to an ethanol mass fraction in the aqueous phase of approximately 0.35. This behavior is similar to that of the pesticides (Figure 2.1 and Table 2.2), thus corroborating the observation that the breakpoint reflects the interaction between the alcohol and water, and is independent of the solute.

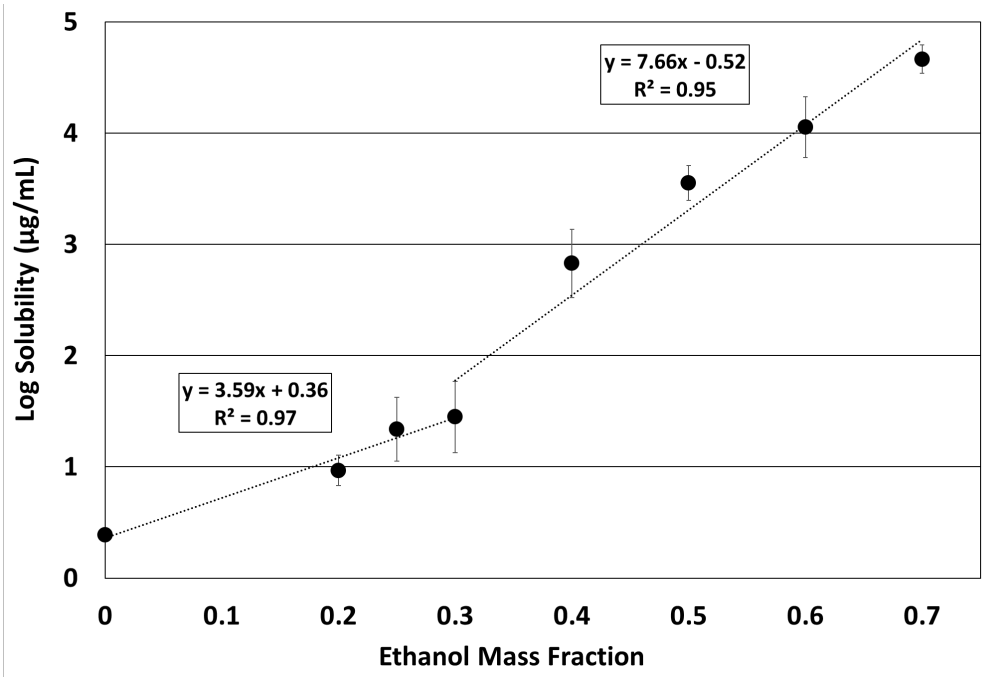


**Figure 3.4** Log of the solubility of iso-octane as a function of ethanol mass fraction in the system. The lines shown are best fit linear regressions.

Figure 3.5 shows the measured fuel-water partition coefficient (Eqn. 3.1) of dieldrin, lindane, and chlorpyrifos as a function of system ethanol mass fraction. At low system ethanol mass fractions, the pesticides are principally in the organic liquid phase. However, as the ethanol

content of the system increases, the pesticide concentration in the aqueous phase increases until it is almost equal to that in the organic liquid phase. With iso-octane as the organic liquid phase, the partition coefficient (expressed as a log) decreased from 5.10 to 0.27, 2.15 to 0.11, and 5.57 to 0.75, corresponding to total decreases of 4.84, 2.04, and 4.82, for dieldrin, lindane, and chlorpyrifos, respectively, as the system ethanol mass fraction increased from 0.0 to 0.7. With gasoline as the organic liquid, the decrease was of about 4.70 orders of magnitude for dieldrin as the system ethanol mass fraction increased from 0.0 to 0.6. Moreover, the partition coefficient for dieldrin was only slightly greater for gasoline than for iso-octane (approximately a 27 to 79% difference), corroborating similar observations such as those by Cline and others (1991) for naphthalene and toluene. The differences might be somewhat greater if the ethanol present in the gasoline originally was taken into account. However, it appears that iso-octane may be used as a surrogate for describing the trend in fuel-water partition coefficient of organochlorine pesticides.

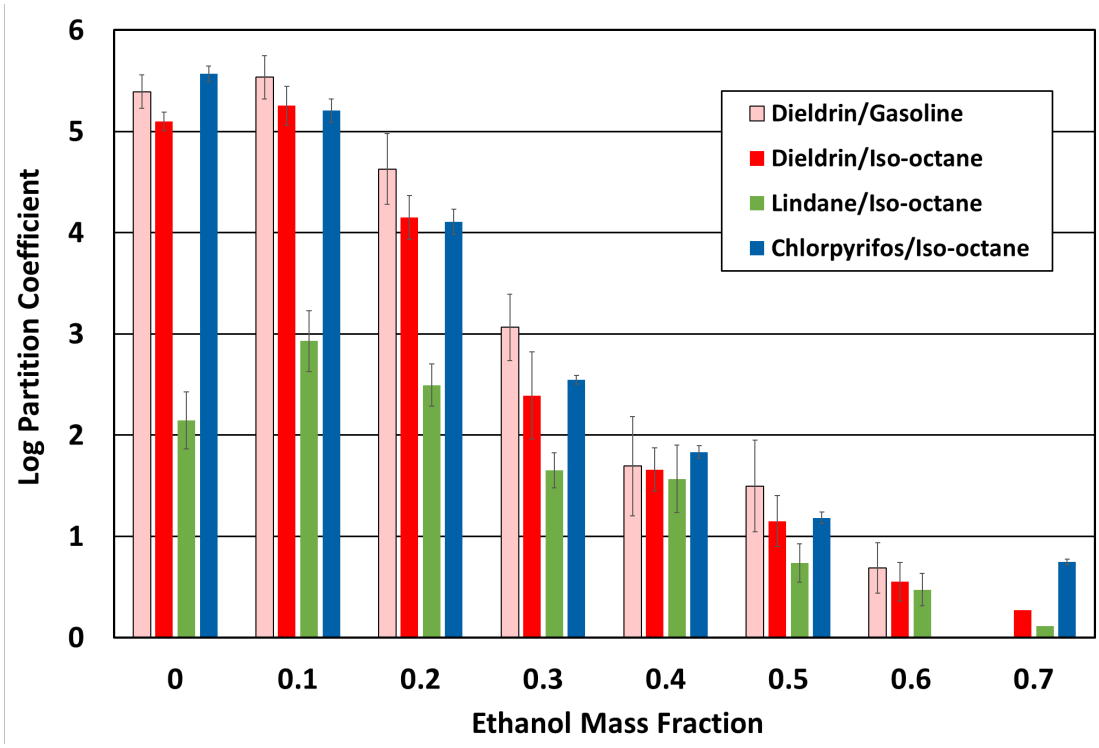


**Figure 3.5** Log of the partition coefficient (Eqn. 3.1) of several organochlorine pesticides between iso-octane or gasoline and water as a function of ethanol mass fraction in the system. *Note that the ethanol mass fraction does not take into account the ethanol that might have been originally present in the gasoline.

The decrease in the partition coefficient was greater for the more hydrophobic pesticides, dieldrin and chlorpyrifos, than for lindane. These data suggest that the effect of ethanol on partitioning is related to the enhancement of the aqueous solubility of the pesticides by the ethanol, as the cosolvency power was also greater for dieldrin and chlorpyrifos than for lindane (Figure 2.1 and Table 2.2). In line with this observation, the aqueous solubility of the pesticide was determined using Eqns. 2.3 and 2.6, at low and high ethanol mass fractions in the aqueous phase, respectively, using the parameters from Table 2.2. Then the measured fuel-water partition coefficients for the pesticides were replotted with the aqueous solubility of the pesticide at the corresponding ethanol mass fraction in the aqueous phase on the ordinate axis, as shown in Figure 3.6. This figure also shows linear regression fits to the data, excluding the data points

corresponding to 0% ethanol mass fraction. For all the pesticides, the slope was approximately equal to -1.0. Furthermore, the y-intercept seemed to be independent of the solute, with an average value (expressed as a log) of 4.82 ± 0.28 (Table 3.2). Based on this figure, it appeared that a log-log model similar in form to Eqn. 3.2:

$$\log K = -\log S_m + 4.82 \qquad (3.5)$$

was suitable to describe the fuel-water partition coefficient of organochlorine pesticides. In this context, the solubility of the pesticide in the water-ethanol mixture, $S_m$, must be known or predicted, using for example Eqns. 2.3 and 2.6.

While it appears that the form of Eqn. 3.2 is appropriate, the y-intercept is not given as it appears Eqn. 3.4. Using the system of dieldrin and iso-octane as the organic liquid as an example, the log of the product of $MW_{pesticide}$ and the ratio of $\rho_{org}$ to $MW_{org}$ for iso-octane is equal to 6.36, not 4.82 (Table 3.2). Nevertheless, in both Eqns. 3.2 and 3.5, the y-intercept is independent of the solute.

In a water/ethanol/organic liquid system, ethanol displays a high preference for the aqueous phase. With most of the ethanol partitioning into the aqueous phase, an increase in the aqueous solubility of the organic liquid phase can occur. Even though the increase in aqueous solubility of the organic liquid phase is over four orders of magnitude, the concentration of ethanol is over five orders of magnitude higher. The high concentration of ethanol in the aqueous phase enhances the aqueous solubility of the organochlorine pesticides, which, in turn, decreases the partition coefficient of the organochlorine pesticides between the organic liquid phase and the aqueous phase. The decrease observed in the partition coefficient was smaller than the increase observed in the aqueous solubility; however, a similar trend was observed in that the

impact was greater for the more hydrophobic pesticides. The behavior observed in the partition coefficient of the pesticides seems to be driven by the partitioning of ethanol into the aqueous phase, resulting in a "tracking" by the pesticide of the ethanol into the aqueous phase and a concomitant decrease of the fuel-water partition coefficient.

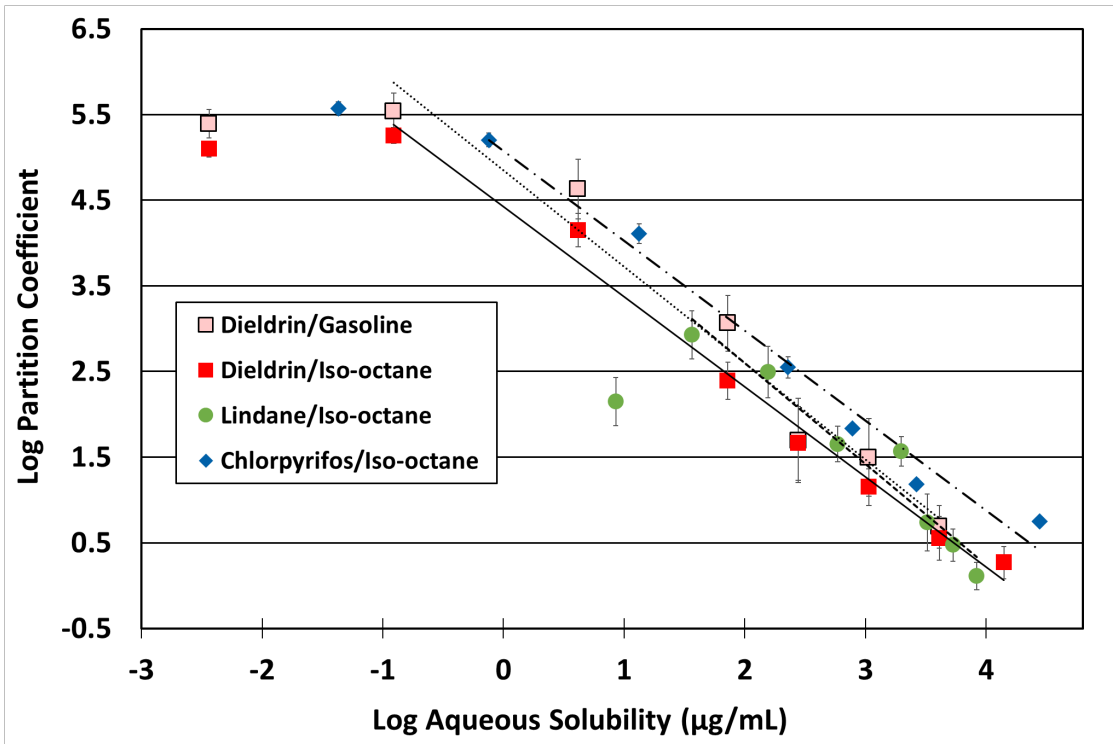


**Figure 3.6** Log of the partition coefficient (Eqn. 3.1) of several organochlorine pesticides between an organic liquid and water as a function of the log of the aqueous solubility of the pesticide at the corresponding ethanol mass fraction in the aqueous phase. The lines shown are best fit linear regressions for the various systems excluding the data points corresponding to 0% ethanol mass fraction. The values for the linear regression parameters are given in Table 3.2.

**Table 3.2** Properties and model parameters for fuel-water partition coefficients for several pesticides.

| Pesticide | Dieldrin ($C_{12}H_8Cl_6O$) | Dieldrin ($C_{12}H_8Cl_6O$) | Lindane ($C_6H_6Cl_6$) | Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) |
|---|---|---|---|---|
| Organic liquid | Gasoline | Iso-octane | Iso-octane | Iso-octane |
| Cosolvent | Ethanol | Ethanol | Ethanol | Ethanol |
| $MW_{pesticide}$ (g/mol) | 380.91 | 380.91 | 290.83 | 350.59 |
| log $S_w$ (µg/mL) | -2.44 | -2.44 | 0.93 | -1.37 |
| $\log\left(MW_{pesticide}\frac{\rho_{org}}{MW_{org}}\right)$ (µg/mL) | N/A | 6.36 | 6.25 | 6.33 |
| Slope from linear regression (Figure 3.6) | -1.13 | -1.05 | -1.18 | -1.05 |
| y-intercept | 4.85 | 4.43 | 4.94 | 5.07 |
| $R^2$ | 0.97 | 0.99 | 0.94 | 0.98 |

### 3.4 Conclusions

In a water/ethanol/organic liquid system, ethanol displays a high preference for the aqueous phase. With most of the ethanol partitioning into the aqueous phase, an increase in the aqueous solubility of the organic liquid phase can occur. Even though the increase in the solubility of the organic liquid was over 4 orders of magnitude, the concentration of ethanol was over five orders of magnitude higher. The high concentration of ethanol in the aqueous phase

enhanced the aqueous solubility of the organochlorine pesticides, thus affecting the partitioning behavior of organochlorine pesticides between the organic liquid phase and the aqueous phase by increasing the concentration of the pesticide in the aqueous phase. Essentially, the pesticide is "tracking" the ethanol into the aqueous phase, resulting in decreases in the fuel-water partition coefficient of dieldrin, lindane, and chlorpyrifos between iso-octane and water of about 4.83, 2.03, and 4.82 orders of magnitude, respectively, as the system ethanol mass fraction increased from 0.0 to 0.7.

A log-log model has been previously proposed in order to describe the relationship between the aqueous solubility of an HOC and its fuel-water partition coefficient between an organic liquid phase and an aqueous phase. The model was evaluated in this study and the results indicated that a log-log model with a similar form is adequate to describe the decrease in the fuel-water partition coefficient as a function of the pesticide solubility in the aqueous phase at the corresponding ethanol mass fraction in the aqueous phase. In both cases, the slope is equal to -1.0; however, in the case of pesticides partitioning between water and iso-octane in the presence of alcohol, the value of the y-intercept of 4.82 was not predicted by a ratio of the density to the molecular weight of the organic liquid as suggested by previous studies. However, here as previously, the value of the intercept appeared to be independent of the solute.

The results reported thus far have considered water as a pure liquid. However, in the natural environment, surface waters are solutions, containing, for example, dissolved organic matter (DOM). Ethanol could also affect the aqueous concentration of such constituents, perhaps further enhancing the aqueous solubility of organochlorine pesticides. The following chapter examines the relationship of DOM, its concentration and composition, on the aqueous solubility of pesticides in the presence of ethanol.

# CHAPTER 4

# Aqueous solubility enhancement of organochlorine pesticides by dissolved organic matter in the presence of ethanol

## 4.1 Background

The work reported in Chapter 2 considered the impact of ethanol spills on the solubility of organochlorine pesticides in pure water. However, when considering spills in surface waters, this water is in contact with sediment and as such, may contain natural organic matter as well as contaminants dissolved from the sediment. Natura organic matter contains humic materials which are generally classified based on their solubility. Fulvic acid is the fraction soluble in acid, insoluble in alkali (Wershaw et al., 1969), completely soluble in aqueous solution (Kipton et al., 1992) and capable of forming water-soluble complexes with organic compounds (Schnitzer, 1986). Humic acid is the fraction soluble in alkali and insoluble in acid (Wershaw et al., 1969) and can be further divided into an alcohol-soluble acid fraction and an alcohol-insoluble fraction (Waksman and Stevens, 1928; Saiz-Jimenez and De Leeuw, 1986). Both fulvic and humic acids may contain carboxylic and phenolic hydroxyl functional groups, among others (Gevao et al., 2000; Ma et al., 2012), with fulvic acids containing a higher carboxylic group content than humic acids (Oliver et al, 1983; Chen and Wang, 2007).

The concentration, composition, and chemistry of dissolved organic matter (DOM) depends on the source of the organic matter (Leenheer and Croué, 2003). Under natural conditions, it is mainly composed of aromatic and aliphatic hydrocarbon structures that have,

predominantly, amide, carboxyl, hydroxyl, and ketone functional groups attached (Leenheer and Croué, 2003). The hydrophilic fractions of DOM may contain carbohydrates, aliphatics, and compounds resulting from the oxidative transformation of organic matter (Benner et al., 1992; Guggenberger et al., 1994; Kaiser et al., 2001). The hydrophobic fractions are mainly composed of microbially-altered lignin decomposition products and often contained strongly oxidized organic material (Benner et al., 1992; Guggenberger et al., 1994; Kaiser et al., 2001). Moreover, the hydrophobic acid fraction may contain a water-soluble polymer resulting from lignocellulose degradation (Guggenberger et al., 1994).

The composition of DOM may be influenced by anthropogenic activity. For example, road runoff constitutes a source for contaminants such as oil and tar products, dioxins, oxygenated compounds, halogenated phenols, metals, de-icing salts and asbestos (Boxall and Maltby, 1995). In the study done by Boxall and Maltby (1995), extractions of sediment contaminated with road runoff contained aliphatic hydrocarbons, PAHs, and substituted phenols. Van Metre and Mahler (2010) reported that coal tar-based sealcoats were the largest source for PAHs in the sediments of the 40 lakes they sampled; other sources included vehicle-related sources and coal combustion. Petroleum contamination can also lead to an additional source of hydrocarbons in watersheds near urban areas (Meyers and Teranes, 2002).

Previous studies have shown that DOM can enhance the aqueous solubility of HOCs, including PAHs (Landrum et al., 1984; Danielsen et al., 1995; Cho et al., 2002), PCBs (Landrum et al., 1984; Chiou et al., 1986; Chiou et al., 1987), and pesticides (Wershaw et al., 1969; Landrum et al., 1984; West, 1984; Chiou et al., 1986; Chiou et al., 1987; Burnison, 1994; Ma et al., 2012). For example, Chiou and others (1986) observed that the aqueous solubility of DDT increased by a factor of eight when 100 mg/L of humic acid was present. These studies suggest

that the enhancement in the aqueous solubility increases linearly with DOM concentration. But, the degree of enhancement also depends on both the structure of the solute and the composition of the DOM. Only small nonionic organic compounds with very low water solubilities are significantly affected by the presence of DOM (Hassett and Anderson, 1982; Kile and Chiou, 1989). Furthermore, humic acid influences the aqueous solubility more than fulvic acid, as Chiou and others (1986) observed an increase in the aqueous solubility of several PCBs and pesticides of about four times higher in the presence of the former.

The enhancement in the aqueous solubility of HOCs by dissolved organic matter occurs through a direct DOM-solute interaction (Chiou et al., 1986; Kile and Chiou, 1989). Hassett and Anderson (1982) suggested that soluble complexes could form between HOCs and DOM. Therefore, pesticides in the aqueous phase could be present in two forms: free dissolved and DOM-bound (Caron et al., 1985). Carter and Suffet (1982) looked at the amount of DDT that freely dissolved in the aqueous phase relative to that bound to the dissolved humic material and found that more than 75% of the total DDT was in the bound form. Chiou and others (1986) suggested that the aqueous solubility enhancement by DOM is due to a partition-like interaction of the solute with the "microscopic organic environment" of the DOM molecules. They proposed that the functional groups of DOM organize in such a way that the interior structure is hydrophobic and the exterior surface is hydrophilic, and the HOCs partition into the hydrophobic interior of the DOM aggregates, in an interaction that is similar to that with micelles (Chiou et al., 1986; Wershaw, 1986; Kile and Chiou, 1989).

To date, the work done on the enhancement of the aqueous solubility of HOCs by DOM have only looked at uncontaminated systems. It is conceivable that a higher concentration of DOM could be present in the aqueous phase if a cosolvent, like ethanol, is introduced into the

water column. In addition, in the case of a river contaminated with anthropogenic compounds, the ethanol might cause the dissolution of petroleum-like products. For example, Peters and Luthy (1993) observed that the presence of n-butylamine, acetone, and 2-propanol, as cosolvents, increased the dissolution of coal tar by orders of magnitude. Therefore, the presence of ethanol might result in a greater amount, as well as a different composition, of DOM in the water column that might further enhance the solubility of organochlorine pesticides.

The work on the enhancement of the aqueous solubility of pesticides by DOM has focused on the impact caused by a small concentration of the organic matter extracted by water; no studies have addressed the impact when an alcohol, like ethanol, is present. This research seeks to assess the impact of DOM on the aqueous solubility of organochlorine pesticides in the presence of ethanol. Moreover, this study investigates the relationship between the enhancement in the aqueous solubility of the pesticides and the composition and concentration of the DOM.

**4.2 Materials and Methods**

To investigate the effect of dissolved organic matter on the enhancement of the aqueous solubility of organochlorine pesticides in the presence of ethanol, the aqueous solubility of two of the representative organochlorine pesticides described in Chapter 2, dieldrin and lindane (Table 4.1), was determined at different water-ethanol ratios, in the presence of DOM, at room temperature (21.7 ± 0.8 ºC) and relative humidity (32 ± 8%). DOM was extracted from three soils, whose composition is summarized in Table 4.2. Two were natural soils dominated by humic materials, obtained from the International Humic Substances Society (IHSS) (Saint Paul, MN), Pahokee peat and Elliott soil. Pahokee peat is representative of an agricultural peat soil found in the Florida Everglades and Elliott soil is representative of a fertile prairie soil found in

Illinois. Both of these soils were prepared by grinding them with a mortar and pestle, and using the fraction that passed through a 250 µm sieve. Additionally, sediment, collected in 2008 for a sediment capping study (Cakir Kavcar, 2008), from the Anacostia River (Maryland), an urban river that flows into the Potomac River near Washington D.C., was used. The sediment was dried overnight in an oven at 200 °C prior to grinding it using the mortar and pestle.

The total organic carbon (TOC) and total organic matter (TOM) present in the soils was determined. The Walkley-Black Wet Combustion method, based on that presented by Nelson and Sommers (1982), was used for determining TOC. The amount of soil added was adjusted so that approximately less than 30 mg of total organic carbon was present. The weighed soils were placed in Erlenmeyer flasks and 10 mL of 1 N potassium dichromate ($K_2Cr_2O_7$) and 20 mL of concentrated sulfuric acid ($H_2SO_4$) were added to all the flasks, including a blank, and swirled for 30 seconds. After cooling for 30 minutes, 100 mL of Milli-Q water were added and mixed thoroughly. The aliquot was passed through a 0.20 µm PTFE filter into a plastic cuvette. The absorbance of the solution was measured using a spectrophotometer (Analytik Jena SPECORD 200 PLUS) at 620 nm, using the blank as a reference. The standards for calibration were prepared using sucrose.

The loss on ignition method presented by Dean (1974) was used to determine the TOM present in the soils. Approximately 10 mg of soil were weighed in a ceramic crucible and left overnight in an oven at 105 °C. After cooling to room temperature in a desiccator for 10 minutes, the sample and crucible were weighed. Then the samples were placed in a muffle furnace at 550 °C for three hours. After cooling to room temperature in a desiccator for 30 minutes, the sample and crucible were weighed again. The difference between two weights represents the amount of organic matter ignited (Dean, 1974).

**Table 4.1** Description of pesticides used for determining the impact of DOM on the aqueous solubility.

| Pesticide | Dieldrin ($C_{12}H_8Cl_6O$) | Lindane ($C_6H_6Cl_6$) |
|---|---|---|
| Longest dimension (Å)[a] | 7.52 | 5.69 |
| $MW_{pesticide}$ (g/mol) | 380.91 | 290.83 |
| log $S_w$ (μg/mL) | -2.44 | 0.93 |
| Classification[b] | Nonionic | Nonionic |

[a]Longest dimensions were obtained using the Automated Topology Builder (ATB) and Repository. [b]Classificaiton of the pesticides was based on Gevao and others (2000).

**Table 4.2** Composition of the three soils used in this study.

| | Pahokee Peat, FL | Elliott Soil, IL | Anacostia River Sediment, MD |
|---|---|---|---|
| C[a] (wt%) | 46.90 | 2.90 | 6.54 |
| O[a] (wt%) | 30.30 | N/A | 9.98 |
| N[a] (wt%) | 3.42 | 0.25 | 0.29 |
| S[a] (wt%) | 0.58 | N/A | 0.32 |
| Ash[a] (wt%) | 12.70 | N/A | 83.63 |
| Total Organic Carbon[b] (wt%) | 38 | 2 | 6 |
| Total Organic Matter[c] (wt%) | 77 | 7 | 12 |

[a]Elemental analysis was performed by Huffman Hazen Laboratories (Golden, CO) for the Anacostia River sediment; data for Pahokee Peat and Elliott Soil were obtained from the IHSS (Saint Paul, MN). The method used to determine the [b]total organic carbon (TOC) and [c]total organic matter (TOM) present in the soils were based on those presented by Nelson and Sommers (1982), and Dean (1974), respectively.

Figure 4.1 shows a schematic of the experimental procedure used to determine the effect of DOM on the enhancement of the aqueous solubility of organochlorine pesticides in the presence of ethanol. In order to extract the DOM, water and ethanol were first mixed in 10 mL PTFE centrifuge tubes on a rotator overnight, after which approximately 100 mg of soil was added and then left to equilibrate on a rotator for 72 hours. The samples were subsequently centrifuged at 600 g for 20 minutes to separate the liquid from the solid. The supernatant was filtered using a 0.20 µm PTFE filter. The filtrate was then split in three ways: one part was analyzed for the relative concentration of DOM, another was freeze dried for the characterization of total dissolved solids (TDS), and the last was placed into a clean 10 mL centrifuge tube along with an excess amount of pesticide.

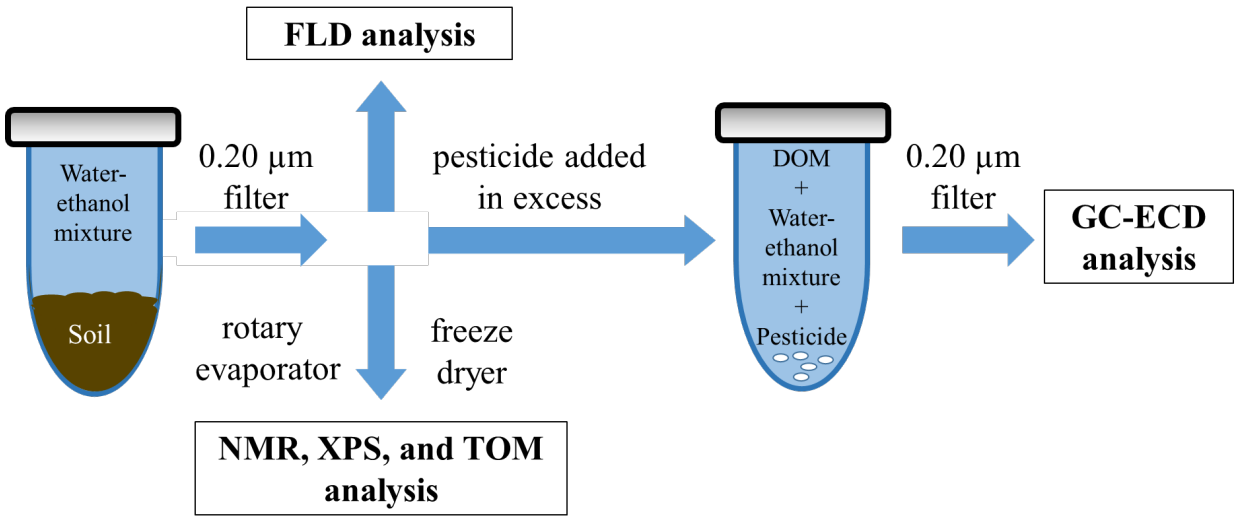


**Figure 4.1** Overall experimental procedure to determine the effect of dissolved organic matter on the enhancement of the aqueous solubility of organochlorine pesticides in the presence of ethanol.

The same methodology described in Chapter 2 was used to determine the aqueous solubility of the organochlorine pesticides, where after a total of 96 hours of equilibration with the pesticides, three sets of samples were withdrawn, each set approximately one day apart. Each sample was passed through a 0.20 μm PTFE filter to remove undissolved pesticide, after which 2 μL of methanol were added to maintain the pesticide in solution during analysis. The samples were analyzed using a GC-ECD. At higher ethanol fractions, the samples were diluted prior to analysis to reduce the potential of saturating the gas chromatograph column.

To obtain a relative concentration of DOM, a fluorescence detector (Hewlett Packard G1321A) was used. The humic-like fraction absorbs light from 250 to > 450 nm and emits light (fluoresces) from 395-430 nm (Coble et al., 2014). The concentration of fluorescent DOM was obtained as the intensity at an excitation and emission wavelengths of 252 and 445 nm, respectively. Samples at higher concentrations were diluted in methanol in order to avoid saturating the detector. The amount of the humic-like fraction dissolved was reported in relative fluorescence intensities based on the areas under the peak from the fluorescence detector spectra.

The extracted total dissolved solids (TDS) was characterized by solid-state $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy and x-ray photoelectron (XPS) spectroscopy. In order to obtain the dissolved solids present in the aqueous phase, a rotary evaporator (BUCHI, R-134) was used to remove the ethanol and then the sample was freeze-dried using a freeze dryer (LABCONCO FreeZone 6) to remove the water. The resulting TDS samples were fine powder, except for the sample extracted from the sediment of the Anacostia River at an ethanol mass fraction of 1.0, which was more of a tar-like substance (Figure 4.2). The same method used on the bulk soils to determine TOM was used on the freeze-dried samples. Moreover, the TOC

present in the freeze-dried samples extracted with water was determined using a TOC analyzer (Shimadzu TOC-V CSH).

Solid-state NMR spectra were acquired with a Bruker Advance-III HD 500 MHz spectrometer operating at 125 MHz for $^{13}C$ using cross polarization (CP), magic-angle spinning (MAS), and high power $^{1}H$ decoupling. A Bruker triple resonance E-Free probe with a Vespel spinning module housing a 3.2 mm zirconia rotor with Kel-F drive tip and caps was used. Approximately 25 mg of the freeze-dried sample was packed into the zirconia rotor with a Kel-F cap. All $^{13}C$ CP-MAS spectra were acquired at a MAS speed of 12.0 kHz, a contact time of 2.5 ms, and a recycle time between subsequent acquisitions of 3 s. 2048 data points were acquired using a spectral width of 50 kHz, corresponding to acquisition times of 20.48 ms. To quantify the solid-state $^{13}C$ CP-MAS NMR spectra, they were integrated using the TopSpin 3.5pl6 software. The peaks in the spectra were identified according to the chemical shifts suggested by IHSS (2017), which grouped them into the following: aliphatic carbon (0-60 ppm), heteroaliphatic carbon (60-90 ppm), acetal carbon (90-110 ppm), aromatic carbon (110-165 ppm), carboxyl carbon (165-190 ppm), and carbonyl carbon (190-220 ppm).

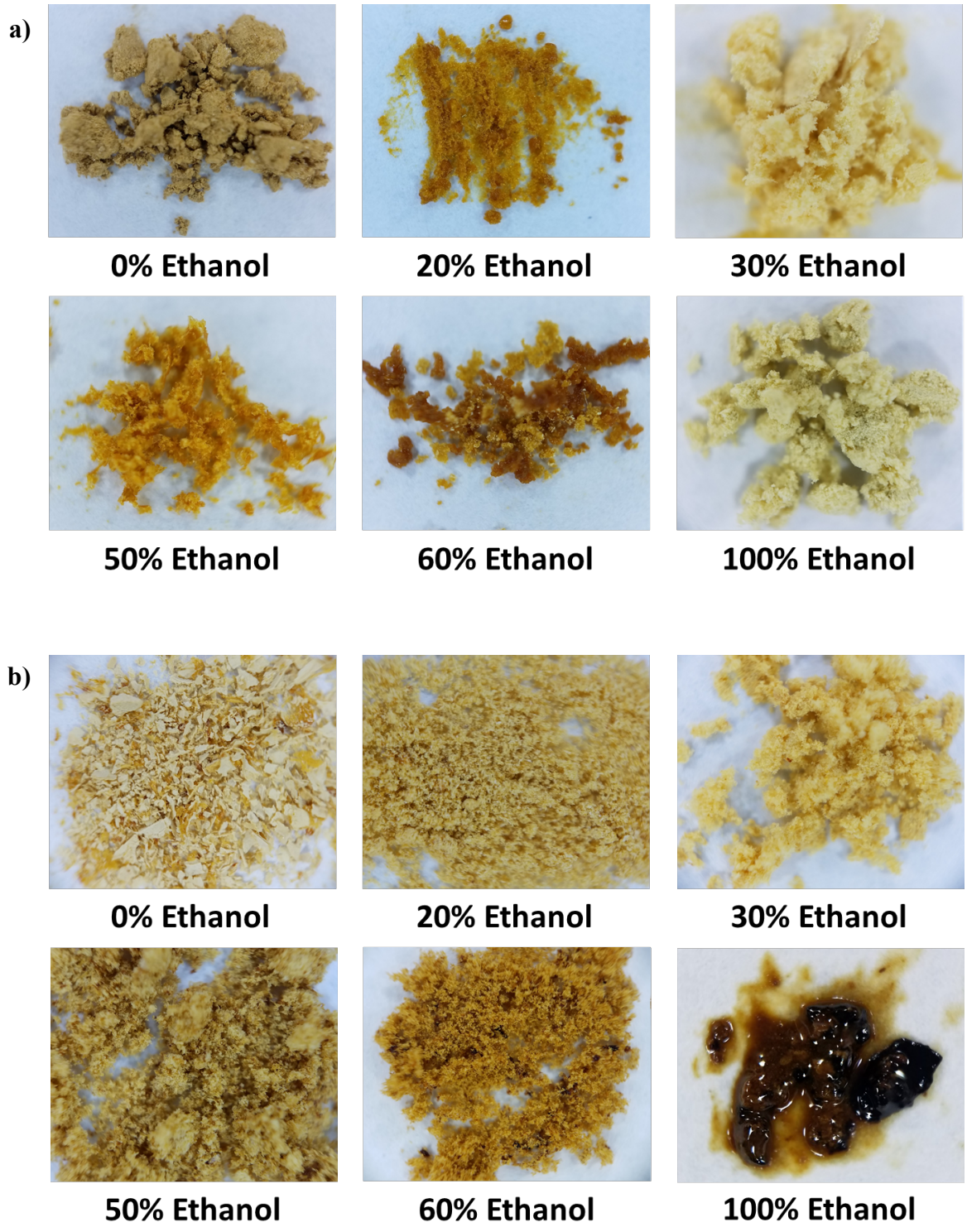


**Figure 4.2** TDS extracted from a) Pahokee peat, a soil dominated by humic materials, and b) sediment from the Anacostia River, as a function of ethanol mass fraction in the aqueous phase. *Pictures were not taken at the same magnification**.**

XPS data were collected using a Kratos axis ultra XPS under vacuum at $5\times10^{-9}$ Tor, using a monochromatic ray Kα of Al source (1486.6 eV). The X-ray gun was operated at 14 kV and 8 mA. For the high resolution spectra, the pass energy was 20 eV and the step size was 0.1 eV. TDS samples were pressed onto indium foil (Sigmal-Aldrich, 99.999% trace metals basis) using a piece of glass. Spectra were recomposed using CasaXPS software. The binding energies were calibrated for charging effects using the $Ca2p_{3/2}$ peak of the carbonate structure (346.6 eV). Gaussian-Lorentzian peaks and Shirley-type background subtraction were used to fit the peaks.

A batch extraction method based on Chen and others (1996) was used to determine the amount of four PAHs (anthracene, fluoranthene, phenanthrene, and pyrene) that could be desorbed from the Anacostia River sediment. Approximately 9.5 g of sediment were placed in a 30 mL PTFE centrifuge tube. Three consecutive extractions were carried out using 1:1 v/v methanol-methylene chloride as the extractant. The first extraction step involved equilibration with 16.5 mL of the contact liquid on a rotary shaker for 3 days. The two remaining extractions involve the equilibration of the same sediment with 10 mL of the contacting liquid for 18 hours for each. After each extraction, the samples were centrifuged at approximately 626 g for 30 minutes. Then the supernatant was passed through a 0.20 μm PTFE filter. Samples from each individual extraction were analyzed separately using a gas chromatography mass spectroscopy (Hewlett Packard 5972 Series Mass Selective Detector) (GC-MS). A DB-5 1 μm column (J & W Scientific) was used with hydrogen as the carrier gas. The reported concentrations are based on a summation of the three sequential extractions.

### 4.3 Results and Discussion

Figure 4.3 shows the measured aqueous solubility of a) dieldrin and b) lindane as a function of ethanol mass fraction in the presence and absence of TDS extracted from the two soils dominated by humic materials (Pahokee peat and Elliot soil) and from Anacostia River sediment. A linear regression analysis suggested that the data were best fit when divided into two parts, similar to the behavior presented in Chapter 2 in the absence of TDS (Figure 2.1). The presence of TDS had no appreciable effect on the aqueous solubility of dieldrin. However, there was a substantive effect on the aqueous solubility of lindane, which differed depending on the source of the TDS. The TDS extracted from the Anacostia River sediment impacted the aqueous solubility of lindane over the entire range of ethanol mass fractions, with a maximum of 1.5 orders of magnitude increase over the aqueous solubility in the absence of TDS. On the other hand, the humic-derived TDS only had an appreciable impact on the aqueous solubility of lindane at high ethanol mass fractions, with a maximum of approximately 1.0 and 0.6 orders of magnitude increase over the aqueous solubility in the absence of TDS for the TDS extracted from Pahokee peat and Elliot soil, respectively.

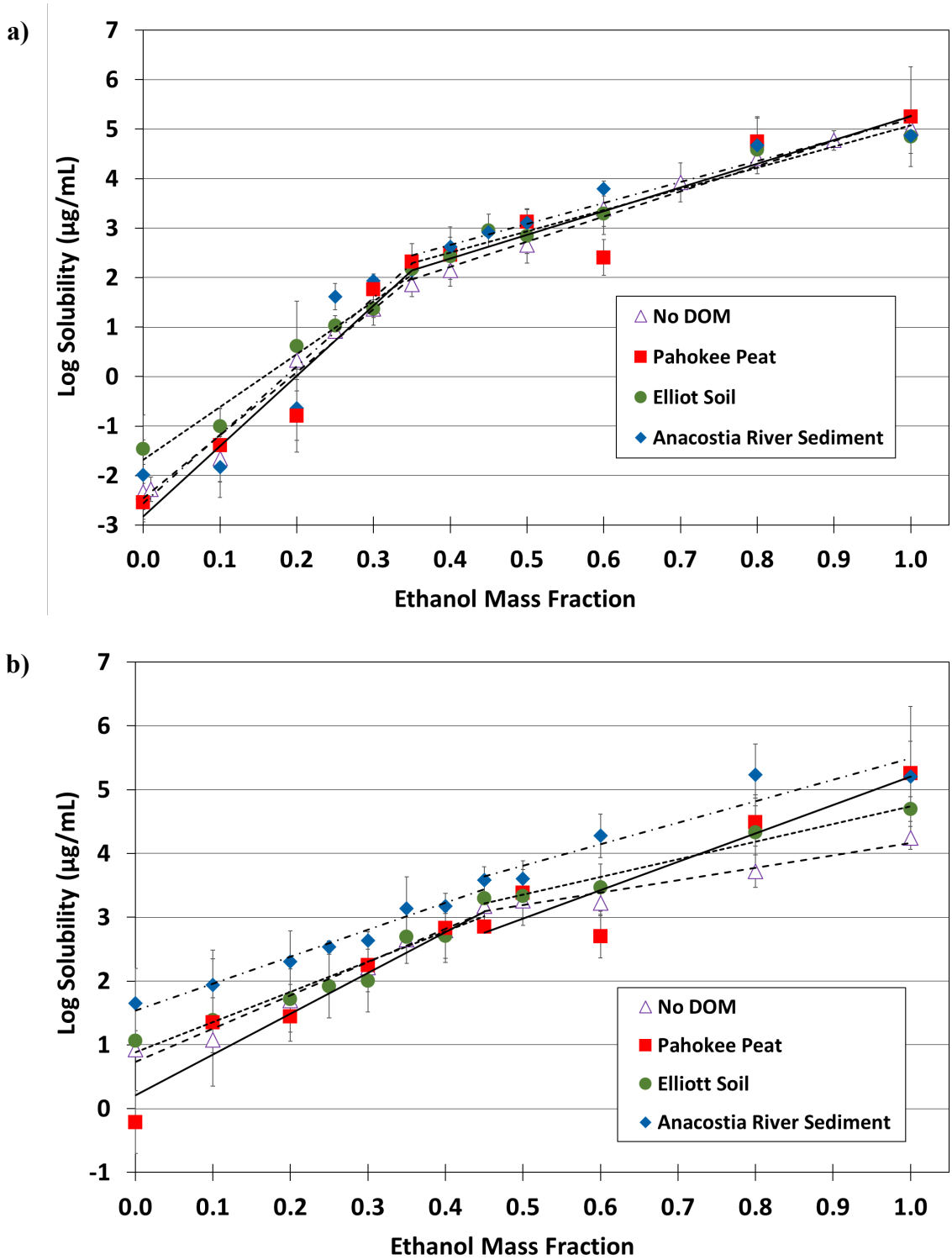


**Figure 4.3** Log of the aqueous solubility of a) dieldrin and b) lindane as a function of ethanol mass fraction in the presence and absence of dissolved matter extracted from two soils dominated by humic materials (Pahokee peat and Elliot soil) and from sediment from the Anacostia River. The lines shown are best fit linear regressions for the various systems.

The variation in the increase of the aqueous solubility of the pesticide in the presence of TDS might be attributable to the variation in concentration of the DOM, the difference in chemical structure of the DOM, or both. Table 4.3 shows the TOC and TOM present in the bulk and in the extract obtained with water as the extractant for Pahokee peat and the Anacostia River sediment. This table shows that a higher concentration of organic matter is present, both in the bulk soil and in the dissolved material extracted by water, for Pahokee peat than for the Anacostia River sediment. Figure 4.4 shows the TOM extracted from Pahokee peat and from the Anacostia River sediment, as a function of ethanol mass fraction in the aqueous phase. The trends for the two soils are opposite in that, for Pahokee peat, water extracted the greatest amount of organic matter, whereas for the Anacostia River sediment, alcohol extracted the greatest. In fact, as the ethanol mass fraction increased from 0.0 to 1.0, the TOM extracted from the Anacostia River sediment increased by approximately 137%, whereas the TOM extracted from the humic-based soil decreased by approximately 66%. These data suggest that more water-soluble organic matter is present in Pahokee peat, whereas more alcohol-soluble organic matter is present in the Anacostia River sediment.

**Table 4.3** Total organic carbon (TOC) total organic matter (TOM) for the bulk Pahokee peat and Anacostia River sediment and the total dissolved solids (TDS) extracted from both soils with water.

| | Pahokee Peat | Anacostia River Sediment |
|---|---|---|
| TOC (g) per bulk soil (g) (wt%) | 38 | 6 |
| TOM (g) per bulk soil (g) (wt%) | 77 | 12 |
| TOC of TDS extracted with water (g) per total mass of extracted solid (g) (wt%) | 32 | 11 |
| TOM of TDS extracted with water (g) per total mass of extracted solid (g) (wt%) | 73 | 40 |

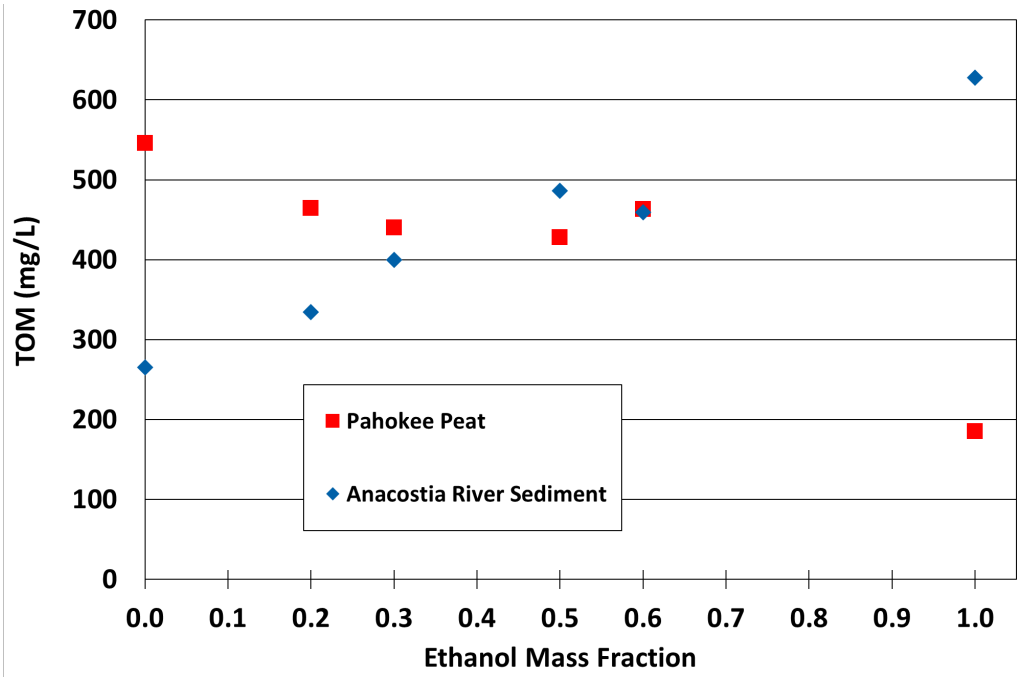


**Figure 4.4** The total organic matter (TOM) in the aqueous phase extracted from Pahokee peat and Anacostia River sediment as a function of ethanol mass fraction in the aqueous phase.

Figure 4.5 shows the relative fluorescence intensity of the humic-like fraction of the TDS extracted from Pahokee peat and from Anacostia River sediment as a function of the TOM concentration. An analysis of these data suggests that the chemical composition of the DOM extracted by water is different from that extracted by ethanol as evidenced by the increase in fluorescence intensity with the increase of TOM extracted. Moreover, these data suggest that the organic matter extracted from the Anacostia River sediment differs in chemical composition from that extracted from the Pahokee peat as evidenced by the difference in the trend of the fluorescence intensity, with a greater increase observed with the Anacostia River sediment.

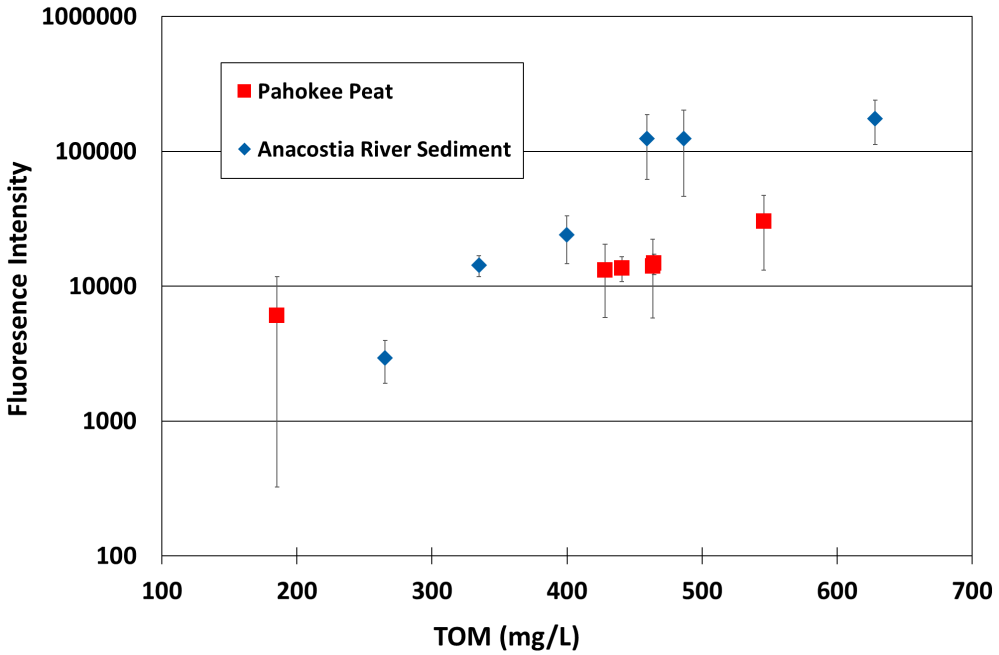


**Figure 4.5** Relative fluorescence intensity of the humic-like fraction of the dissolved organic matter (expressed in log scale) extracted from Pahokee peat and from Anacostia River sediment as a function of the total organic matter (TOM) from the corresponding extract in the aqueous phase.

Figures 4.6 and 4.7 show the XPS $C^{1s}$ spectra of the TDS extracted from Pahokee peat and from Anacostia River sediment, respectively, as a function of ethanol mass fraction. Figure

4.6 shows that at an ethanol mass fraction of 0.0, approximately 50% of the carbon present in the extract from Pahokee peat is present in the form of C-O bonding. However, as the ethanol mass fraction increased to 1.0, the compounds containing C-O bonds decreased to approximately 16% and the compounds containing C=O bonds decreased from approximately 23% to 3%. On the other hand, as the ethanol mass fraction increased, the relative abundance of compounds containing C-C bonds in the extract increased. In fact, at an ethanol mass fraction above 0.5, the organic content of the TDS is dominated by C-C bonds and, at an ethanol mass fraction of 1.0, approximately 81% of the carbon source is present in the form of C-C bonding.

On the other hand, Figure 4.7 suggests that the organic content of the TDS extracted from the Anacostia River sediment is dominated by compounds containing C-C bonds at every ethanol mass fraction, with the relative abundance increasing with the ethanol mass fraction. In this case, approximately 54% and 92% of the carbon is present in the form of C-C bonding at the two ends of the range of ethanol content. The relative abundance of carbon present in the form of C-O bonding decreased from approximately 27% to 6%; similarly the relative abundance of C=O bonds decreased from approximately 18% to 2%, as the ethanol mass fraction increased from 0.0 to 1.0. There is some experimental evidence that not all the ethanol present is completely removed after using the rotary evaporator (Sánchez-González et al., 2012); consequently, a portion of the shift observed in the spectra may be attributable to the presence of ethanol. Nevertheless, a difference in the distribution of the carbon bonding is observed between that extracted from Pahokee peat and that extracted from the Anacostia River sediment at the same system ethanol content, corroborating the evidence presented in Figure 4.5 that organic matter extracted from the two sources are different in chemical composition.

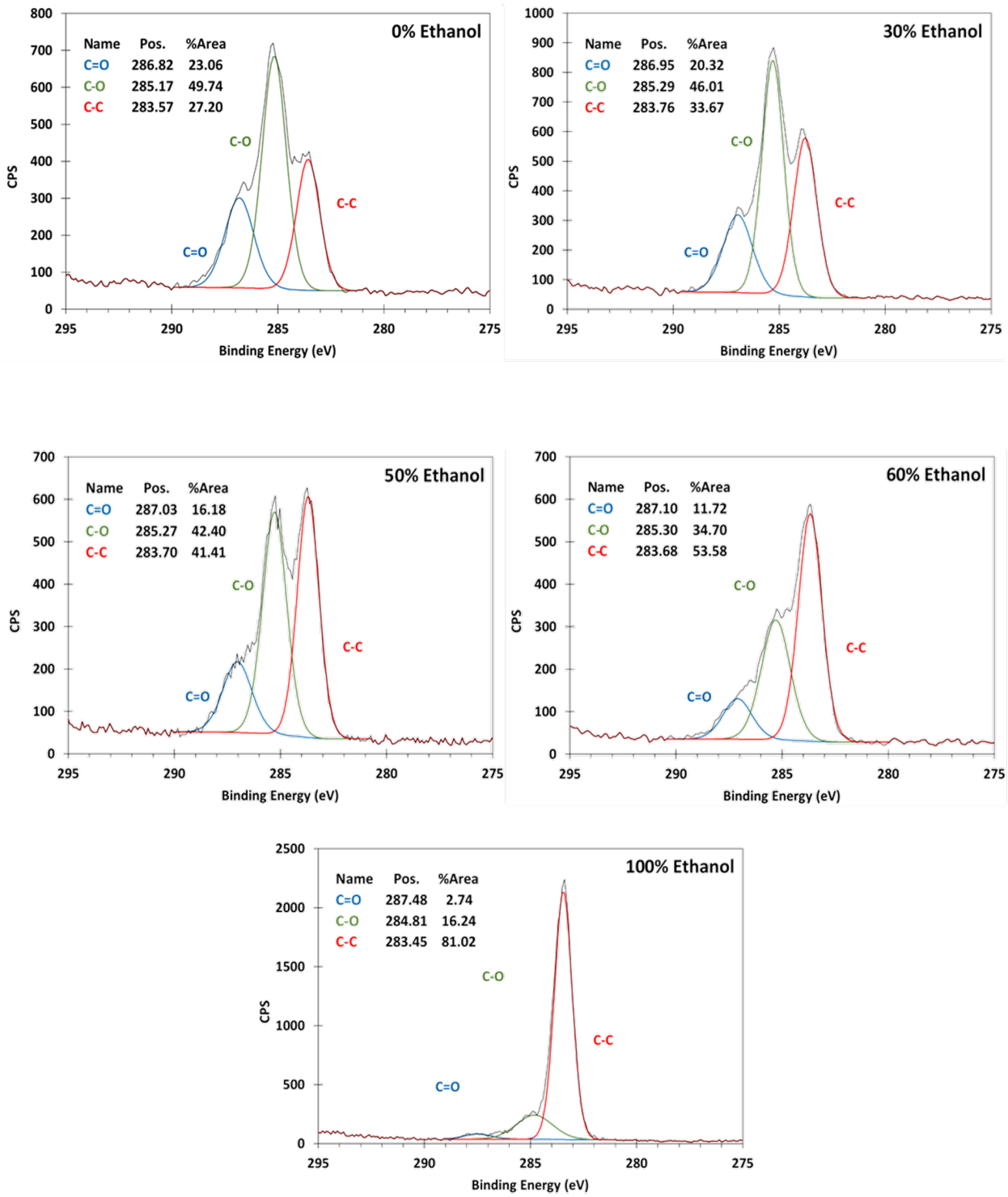


**Figure 4.6** XPS $C^{1s}$ spectra of dissolved organic matter extracted from Pahokee peat, a soil dominated by humic materials, at different ethanol mass fractions.

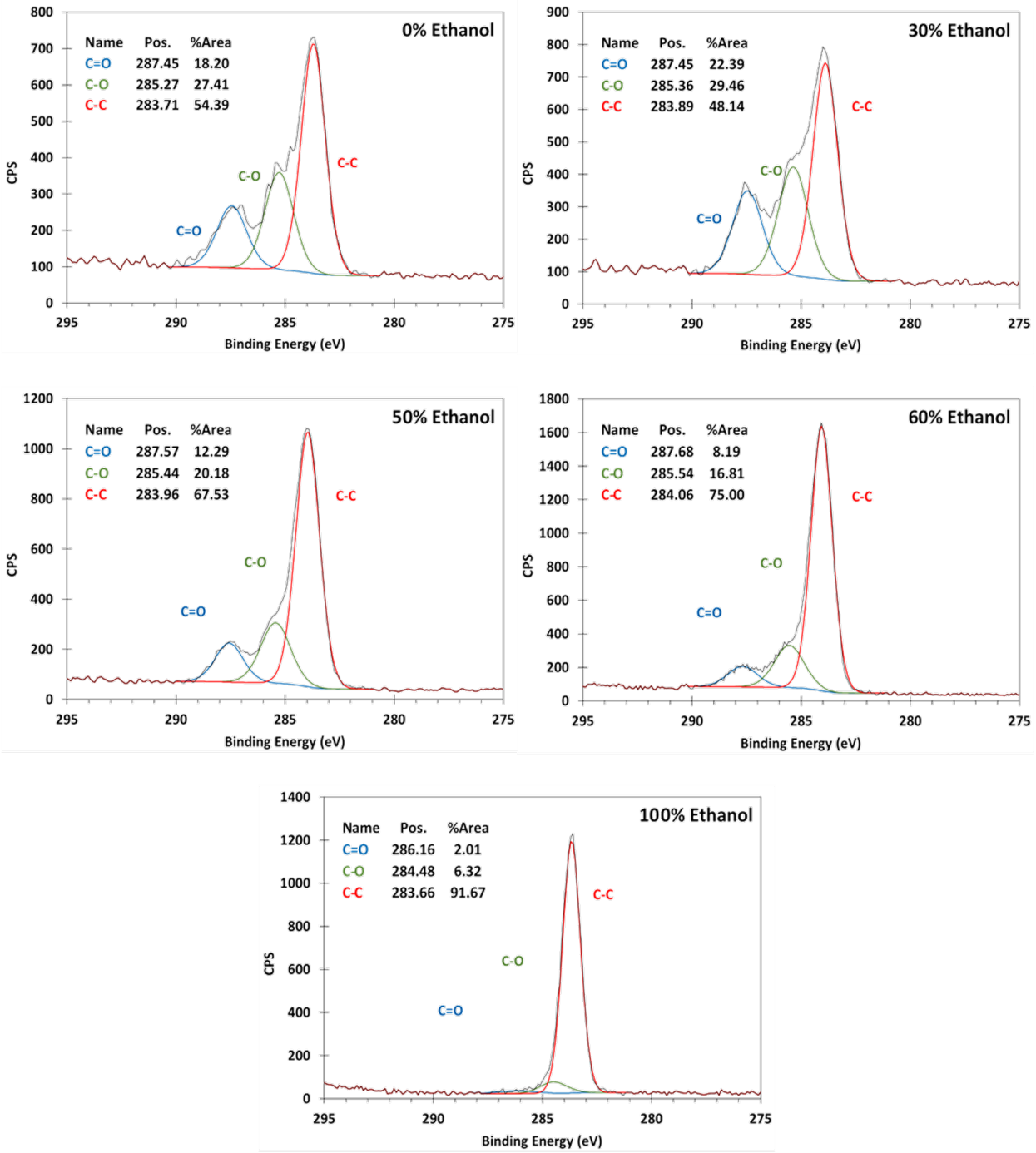


**Figure 4.7** XPS $C^{1s}$ spectra of dissolved organic matter extracted from sediment from the Anacostia River at different ethanol mass fractions.

Figure 4.8 shows the area distributions of the peaks in the $C^{13}$ NMR spectra present in the bulk Pahokee peat and Anacostia River sediment, and in the TDS extracted by water from both

soils. This figure indicates that the predominant carbon functional group in the humic acid derived from the Pahokee peat is aromatic and that in the TDS extracted by water from the Pahokee peat is hetero-aliphatic. The predominant functional groups in the bulk Anacostia River sediment are aliphatic and aromatic whereas that in the TDS extracted by water from the Anacostia River sediment is aliphatic followed by hetero-aliphatic and carboxyl.

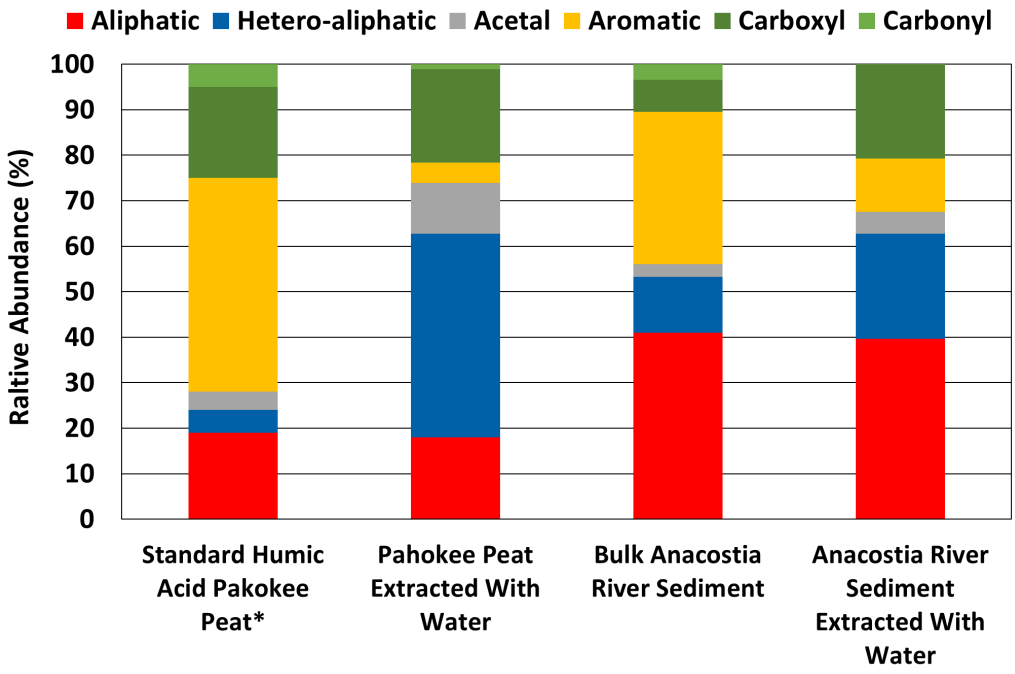


**Figure 4.8** Area percentages of the carbon moieties present in the standard humic acid sample from Pahokee peat as presented by IHSS (2017), the TDS extracted by water from the Pahokee peat, the bulk Anacostia River sediment, and the TDS extracted by water from the Anacostia River sediment based on the solid-state $^{13}C$ NMR spectra presented in Figures 4.9 and 4.10. *Note that the characterization provided by IHSS (2017) for the standard humic and fulvic acid present in the Pahokee Peat were analyzed using solution-state $^{13}C$ NMR.

Figures 4.9 and 4.10 show the $^{13}C$ NMR spectra of the TDS extracted from Pahokee peat and from Anacostia River sediment, respectively, as a function of ethanol mass fraction. The area distributions of the peaks in the $^{13}C$ NMR spectra are shown in Table 4.4. Figure 4.8 and Table 4.4 show that in the absence of ethanol, approximately 45% of the carbon present in the

extract from the humic-based soil is present in the form of heteroaliphatic functional groups. As the ethanol mass fraction increased to 1.0, the relative abundance of heteroaliphatic groups decreased to approximately 5%. Similarly, the compounds containing carboxyl functional groups decreased from approximately 20% to 2%. On the other hand, the relative abundance of compounds containing aliphatic functional groups in the extract from the humic-based soil increased from approximately 20% to 89%. Similar to the data presented in Figure 4.6, at ethanol mass fractions above 0.5, the extract is dominated by compounds containing aliphatic functional groups (Table 4.4).

Figure 4.10 shows that the TDS extracted from the Anacostia River sediment is dominated by compounds containing aliphatic functional groups at every ethanol mass fraction, with the relative abundance increasing with the ethanol mass fraction, similar to the trends presented in Figure 4.7. In addition, the relative abundance of compounds containing aromatic functional groups increased as the ethanol mass fraction increased. On the other hand, the relative abundance of carbon present in the form of heteroaliphatic and carboxyl functional groups decreased as the ethanol mass fraction increased.

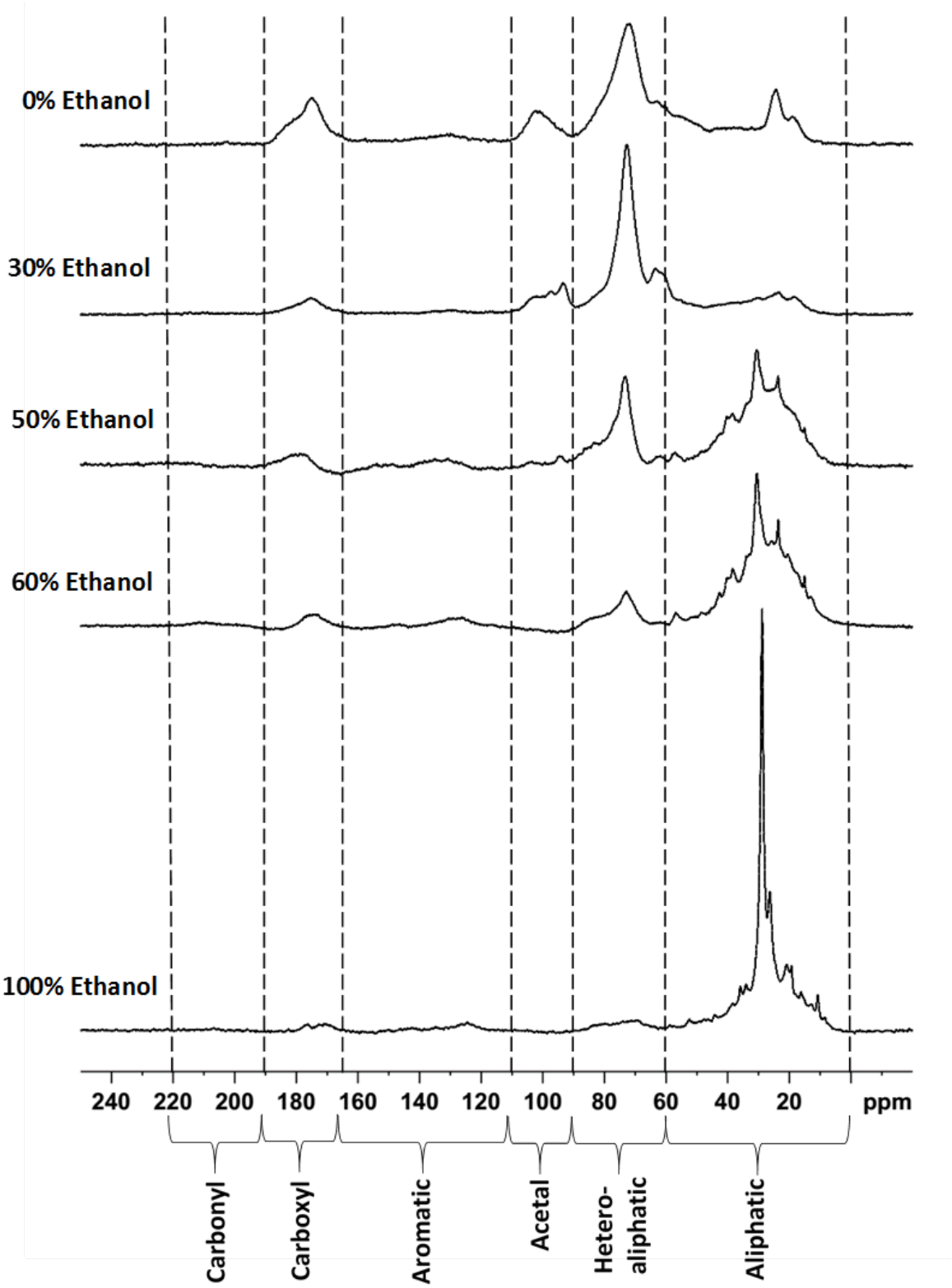


**Figure 4.9** Solid-state $^{13}C$ NMR spectra of dissolved organic matter extracted from Pahokee Peat at different ethanol mass fractions.

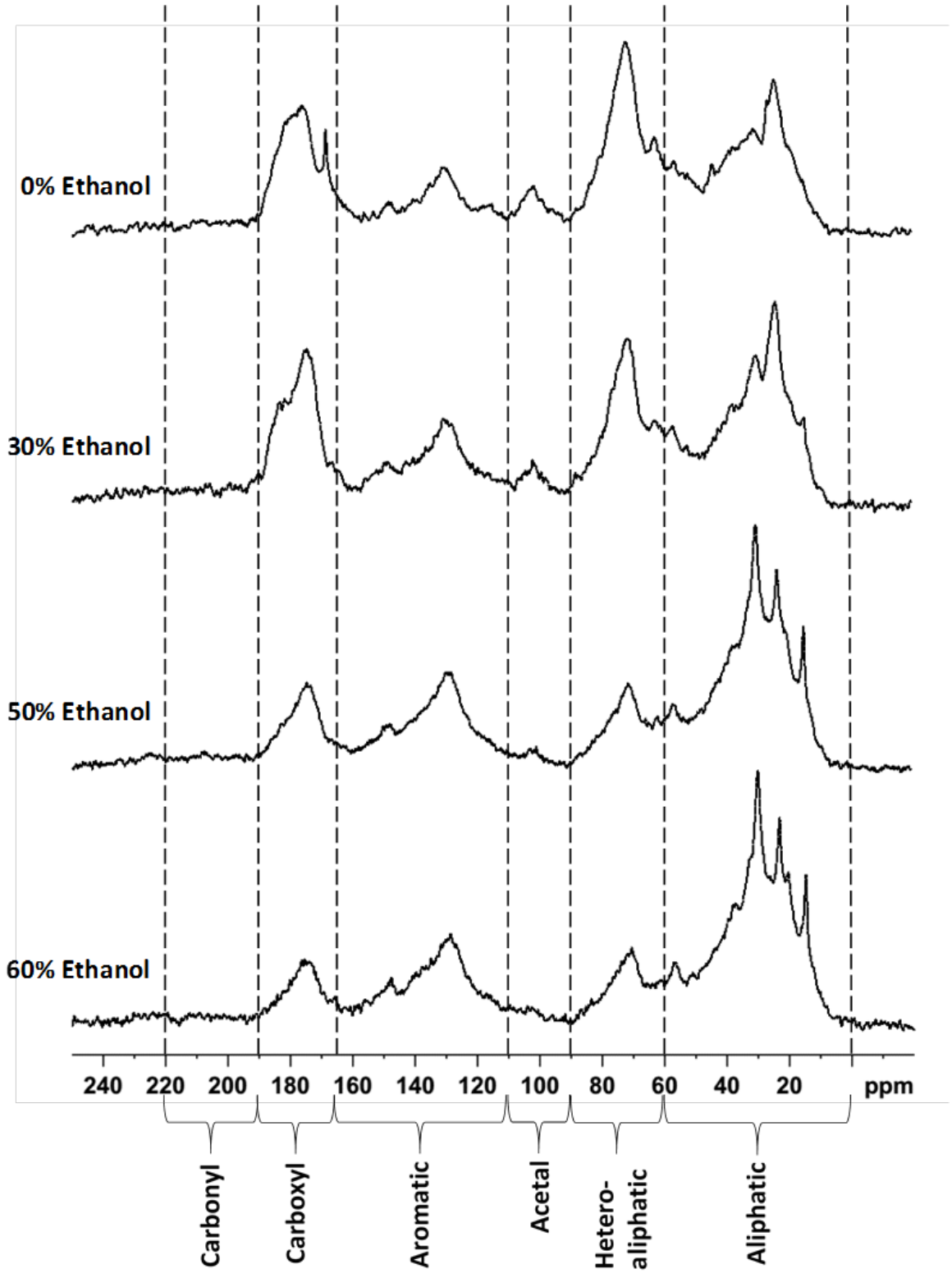


**Figure 4.10** Solid-state $^{13}C$ NMR spectra of dissolved organic matter extracted from Anacostia River sediment at different ethanol mass fractions.

**Table 4.4** Area percentages of the carbon moieties present in the TDS extracted from Pahokee peat and Anacostia River sediment as a function of ethanol mass fraction based on the solid-state $^{13}C$ NMR spectra presented in Figures 4.8 and 4.9.

| TDS extracted from: | Ethanol mass fraction | Carbon moieties (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Aliphatic 0-60 ppm | Hetero-aliphatic 60-90 ppm | Acetal 90-110 ppm | Aromatic 110-165 ppm | Carboxyl 165-190 ppm | Carbonyl 190-220 ppm |
| Pahokee Peat | 0.0 | 17.94 | 44.84 | 11.15 | 4.48 | 20.48 | 1.11 |
| | 0.3 | 12.82 | 62.81 | 11.52 | 2.04 | 9.67 | 1.14 |
| | 0.5 | 64.5 | 20.71 | 1.52 | 7.05 | 6.1 | 0.12 |
| | 0.6 | 75.86 | 11.27 | 0.84 | 4.81 | 5.06 | 2.16 |
| | 1.0 | 88.77 | 4.72 | 0.00 | 3.70 | 2.37 | 0.44 |
| Anacostia River Sediment | 0.0 | 39.69 | 23.05 | 4.75 | 11.77 | 20.64 | 0.1 |
| | 0.3 | 43.48 | 16.19 | 2.81 | 13.14 | 23.82 | 0.56 |
| | 0.5 | 60.35 | 6.9 | 1.16 | 21.06 | 10.17 | 0.36 |
| | 0.6 | 62.77 | 6.87 | 1.21 | 21.97 | 7.15 | 0.03 |
| | 1.0* | N/A | N/A | N/A | N/A | N/A | N/A |

*The freeze-dried TDS sample extracted from the sediment of the Anacostia River at an ethanol mass fraction of 1.0 was not truly a solid, but more of a soft tar-like substance; therefore solid-state $^{13}C$ NMR could not be performed on this sample.

Figures 4.3 through 4.9 suggest that organic carbon with different characteristics is extracted by water versus ethanol. Furthermore, a higher alcohol-soluble fraction is present in the extract from the Anacostia River sediment than in that from Pahokee peat. Contamination present in the Anacostia River sediment may be an additional source of aliphatic and aromatic hydrocarbons. Boxall and Maltby (1995) observed that extracts of sediment contaminated with road runoff contained aliphatic hydrocarbons, PAHs, and substituted phenols. Figure 4.11 shows concentrations of PAHs (anthracene, phenanthrene, fluoranthene, and pyrene) extracted using methylene chloride, the concentrations observed are in line with that observed by McGee and others (2009) in the Anacostia River sediment. These PAHs were present at concentrations above background, providing evidence of the presence of anthropogenic inputs in the Anacostia River sediment.

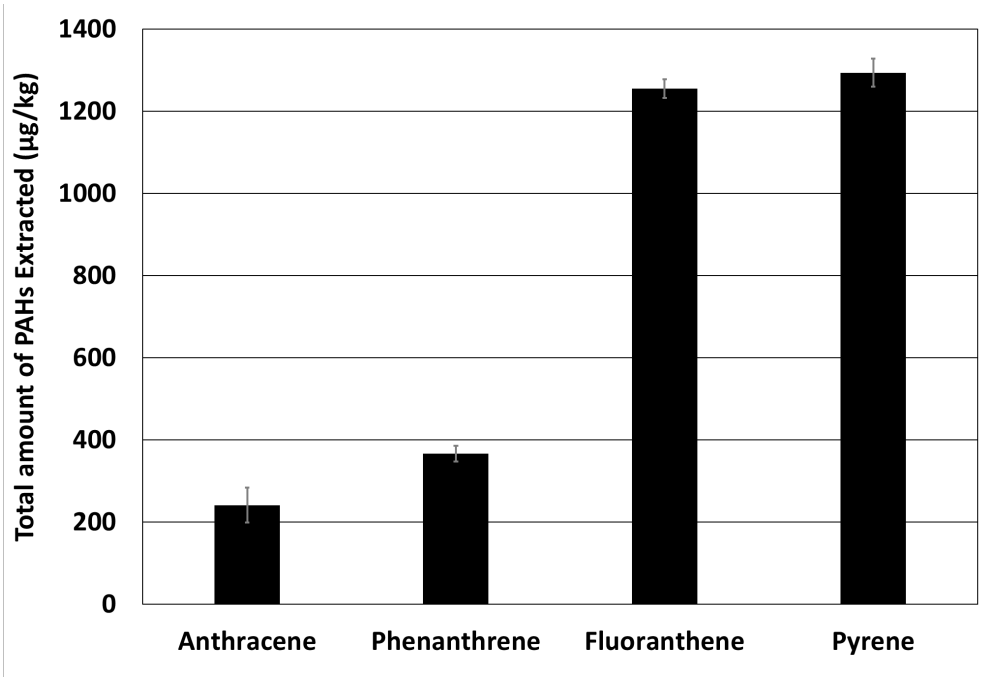


**Figure 4.11** Total amount of four PAHs, anthracene, phenanthrene, fluoranthene, and pyrene, extracted by 1:1 v/v methanol-methylene chloride over three consecutive batch extractions from the Anacostia River sediment per mass of bulk soil.

The data obtained in this study suggest that both differences in composition and concentration of DOM from the natural soils and the Anacostia River sediment contribute to the differential increase observed in the aqueous solubility of lindane (Figure 4.3). In addition to the composition and concentration of the DOM, the effect on the aqueous solubility of pesticides of DOM depends on the solute's aqueous solubility and polarity compatibility with the DOM (Chiou et al., 1986). According to previous studies, only relatively small nonionic organic compounds with very low water solubilities would be significantly affected by the presence of DOM (Hassett and Anderson, 1982; Kile and Chiou, 1989). Both dieldrin and lindane are classified as nonionic pesticides (Table 4.1). Based on the solute's aqueous solubility, a greater effect would be expected for dieldrin versus lindane given that dieldrin has a lower solubility in water by over three orders of magnitude (Table 4.1). However, an increase was observed in the aqueous solubility of lindane in the presence of DOM of over one order of magnitude, whereas no appreciable increase was observed for dieldrin. Lindane has a smaller and more symmetric configuration among the two pesticides (Table 4.1); additionally dieldrin contains oxygen, suggesting that lindane may be more compatible with the DOM structure.

**4.4 Conclusions**

The presence of DOM may affect the environmental fate of organochlorine pesticides in the presence of ethanol. River sediment contains organic matter that, if dissolved, can act as a cosolvent, increasing the aqueous solubility of organochlorine pesticides. Ethanol can increase the concentration of DOM, thus increasing the aqueous solubility of organochlorine pesticides above that caused by just the presence of ethanol. This study showed that DOM can increase the aqueous solubility of organochlorine pesticides, like lindane, over one order of magnitude over the enhancement caused by the presence of ethanol. The DOM extracted from contaminated

river sediments, like the Anacostia River, has an impact at all ethanol mass fractions whereas that extracted from a natural soil only has an appreciable impact at high ethanol mass fractions. The magnitude of the increase depended on the concentration and composition of DOM. The organic matter extracted by water from the natural soils contained a higher amount of organic matter than the extract from the Anacostia River sediment under the same conditions. However, as the ethanol mass fraction increased from 0.0 to 1.0, the increase in the organic matter extracted from the Anacostia River sediment was greater than that extracted from the natural soils. Therefore, it appeared that the DOM extracted from the sediment of the Anacostia River contained a higher alcohol-soluble fraction than that extracted from the natural soils. The chemical composition of the DOM extracted by water is different from that extracted by ethanol, as indicated by the increase in the relative fluorescence intensity with an increase in TOM concentration. Moreover, the chemical composition of the DOM extracted from the Anacostia River sediment differed from that extracted from the natural soils, as suggested by multiple lines of evidence: the differential increases in relative fluorescence intensity with an increase in TOM concentration, the differences in the distribution of the carbon bonding as suggested by the XPS spectra and the differences in the functional groups from the organic matter extracted by water as suggested by the NMR spectra. The differences in concentration and composition of the extracted DOM from the Anacostia River may be due to, in part, to the presence of anthropogenic inputs. Analyses of the extracts using methylene chloride show the presence of several PAHs. Compounds such as these may be an additional source of aliphatic hydrocarbons and aromatic that contribute to the enhancement of pesticide solubility.

In addition to the composition and concentration of DOM, the aqueous solubility enhancement of pesticides by DOM may depend on the solute's aqueous solubility and polarity

compatibility with the DOM. In this study, it appeared that the compatibility with the DOM was a more important factor than the solute's aqueous solubility, as a more appreciable increase was observed in the aqueous solubility of lindane in the presence of DOM relative to that observed for dieldrin. Based on the solute's aqueous solubility, a greater effect would be expected for dieldrin versus lindane given that dieldrin has a lower water solubility of over three orders of magnitude. The main differences among these two pesticides is that lindane has a smaller and more symmetric configuration between the two and that dieldrin contains oxygen (Figure 2.1), making lindane more compatible with the DOM structure.

# CHAPTER 5

## Conclusions and recommendations for future work

### 5.1 Conclusions

In order to meet renewable energy mandates, the use of ethanol-blended fuels has increased dramatically. Since the majority of ethanol is produced in the Midwest and then transported to the coasts in tanker trucks, by railroad and on barges, the possibility of spills exists. In fact, with the increased consumption, the rate of ethanol spills has grown to the point where one occurs every two days on average. The coincidence of ethanol spills and high pesticide usage in agricultural watersheds raises the concern that ethanol might enhance the concentration of regulated organochlorine pesticides in surface waters. Therefore, this research assessed the aqueous solubility and partitioning of organochlorine pesticides in surface waters impacted by spills of ethanol and ethanol-blended fuels.

The research reported in this dissertation first addressed the aqueous solubility of organochlorine pesticides, specifically dieldrin, lindane, and chlorpyrifos, in the presence of ethanol. The results showed that the aqueous solubility of these pesticides increased by three to seven orders of magnitude as the ethanol mass fraction increased from 0.0 to 1.0. Models have been previously proposed in order to describe the enhanced aqueous solubility of HOCs as a function of alcohol concentration. These models were evaluated in this study and the results indicated that two-part models are necessary to describe the aqueous solubility behavior of organochlorine pesticides in the presence of an alcohol. All the pesticides examined here

displayed about the same breakpoint, at an alcohol mass fraction of about 0.35. Therefore, it appeared that the breakpoint is independent of the solute and dependent only on alcohol-water interactions. It was found that, at low alcohol mass fractions ($\leq 0.35$), a log-linear model can satisfactorily describe the behavior (Eqn. 2.3). The use of this model requires a knowledge of the solubility of the solute in pure water and in the pure cosolvent, the mass fraction at the breakpoint (which can be taken as 0.35), and the parameter $\beta$ representing the cosolvent-water interactions at low fractions. The solubilities can be determined independently, or located in the literature. However, the parameter $\beta$ must be determined empirically. At high alcohol mass fractions ($> 0.35$), two options are available: the log-linear model may be used which requires a value of $\beta$ suitable for high fractions and an additional empirical coefficient, $\delta$, which describes the change in slope at the breakpoint (Eqn. 2.7). Alternatively, the Heermann and Powers (1998) model for high fractions, can be utilized with no further parameters needed (Eqn. 2.6).

Ethanol is often blended with gasoline in the production of renewable fuels. If an ethanol-blend fuel were spilled, the presence of gasoline, which is sparingly miscible in water, would result in a two-phase system. The next portion of the research reported in this dissertation addressed the partitioning behavior of organochlorine pesticides between an organic liquid phase and water, as a function of ethanol content. In this study, a decrease of two to four orders of magnitude was observed for the partition coefficient of dieldrin, lindane, and chlorpyrifos between iso-octane and water. In the absence of ethanol, the majority of the pesticides is present in the organic liquid. However, ethanol partitions strongly into the aqueous phase in an organic liquid-water system. With most of the ethanol in the aqueous phase, the aqueous solubility of the organic liquid increased by orders of magnitude, but its concentration was still considerably lower than that of ethanol. The aqueous solubility of the pesticides also increased, resulting in a

situation where, at high ethanol mass fractions, the concentration of the pesticide in the organic liquid and in water were about equal. In order to describe the behavior of the partition coefficient as a function of ethanol mass fraction, an empirical log-log model was evaluated (Eqns. 3.2 - 3.4). This study suggests that, with the exclusion of the data point corresponding to the partition coefficient at a 0% ethanol mass fraction, an empirical log-log model with slope of approximately -1.0 and y-intercept independent of the solute can describe the relationship between the fuel-water partition coefficient and the aqueous solubility of the pesticides as a function of alcohol content (Eqn. 3.5).

When considering ethanol spills in surface waters, organic matter and contaminants dissolved from the sediment may be present. DOM has been previously shown to increase the aqueous solubility of HOCs. Ethanol could also potentially increase the concentration of DOM, thus creating a synergistic effect, where the aqueous solubility of organochlorine pesticides is increased above that caused by the presence of ethanol or the presence of DOM alone. This study suggested that DOM can increase the aqueous solubility of lindane over one order of magnitude over the enhancement caused by just the presence of ethanol. The effect was more pronounced for DOM extracted from contaminated river sediments, like the Anacostia River, than for natural soils. The DOM extracted from the sediment of the Anacostia River contained a higher amount of an alcohol-soluble fraction of organic matter. Moreover, the DOM extracted from the Anacostia River sediment differed in chemical composition from that extracted from a natural peat soil. Consequently, the higher capacity for enhancing the aqueous solubility of pesticides of the DOM observed in the case of the Anacostia River sediment may be due to both the composition and concentration of the extracted dissolved solids. The solute's aqueous solubility and polarity compatibility with the DOM need to be considered as well. According to

previous studies, only relatively small nonionic organic compounds with very low water solubilities would be significantly affected by the presence of DOM. Based on the solute's aqueous solubility, a greater effect would be expected for dieldrin versus lindane; however here, an appreciable increase was observed in the aqueous solubility of lindane in the presence of DOM of over one order of magnitude, whereas no appreciable increase was observed for dieldrin. Lindane has a smaller and more symmetric configuration among the two pesticides; additionally dieldrin contains oxygen, making lindane more compatible with the DOM structure. Therefore, for this study, it appeared that the compatibility with the DOM was a more important factor than the solute's solubility.

This research was carried out due to concerns about possible environmental consequences of biofuel spills in surface waters. In the case of a barge carrying ethanol spilling approximately 300,000 gallons of ethanol into a 1-meter deep and 100-meter wide river, an ethanol mass fraction of approximately 0.1 could be reached, if the complete mixing is achieved within 80 meters downstream of the spill. With this concentration of ethanol, pesticide concentrations of approximately 30 mg/kg could conceivably be desorbed, from the top 2 cm of the sediment, based on the observations by Smith and others (2004). Concentrations of approximately 500 mg/kg could be desorbed if the ethanol mass fraction reached about 0.44. Moreover, additional pesticide could be introduced through agricultural runoff, for example, Donald and others (1999) found a lindane concentration of approximately 0.02 μg/L in a wetland resulting from agricultural runoff. In the presence of ethanol, the pesticide would primarily remain in solution, rather than partitioning into the sediment. Consequently, under this scenario, an aqueous concentration of approximately 550 μg/L of a pesticide like lindane could be present

in the water column. This concentration is well above the permissible level of lindane in water of 4.2 μg/L (U.S. Environmental Protection Agency, 2017).

Following an ethanol or ethanol-blend fuel spill, the addition of ethanol into the water column creates a driving force that can increase the aqueous phase concentration of organochlorine pesticides over orders of magnitude. Given the low permissible levels of such pesticides in water, even a small increase in the concentration might result in regulatory standards being violated. Therefore, with the move towards ethanol-blended fuels, the impact of ethanol on the aqueous concentration of sparingly soluble organic compounds in surface water, such as organochlorine pesticides, needs to be considered.

## 5.2 Future Work

This study suggests that the presence of ethanol can enhance the aqueous solubility of organochlorine pesticides over orders of magnitude in surface waters. The enhancement in the aqueous solubility of the pesticides can occur through two mechanisms: by changing the overall solvency of the solution (the cosolvent effect caused by ethanol itself) or through a direct DOM-pesticide interaction (a partition-like interaction of the pesticide with DOM molecules). It was also observed that this enhancement of the aqueous solubility can affect other properties that influence the fate of such pesticides in the water column, like the partitioning behavior between an organic liquid phase and water. The pesticides could enter the water column from different sources. For example, they may be discharged directly into the waterway through runoff from agricultural fields. Alternatively, they may be desorbed from historically contaminated sediments. However, the actual desorption of the pesticides from historically contaminated sediments was not addressed in this study. Sorption isotherms should be measured to assess the

extent of the effect of ethanol on the solid-water partition coefficient of organochlorine pesticides.

The studies performed in this research were controlled batch experiments performed in the lab. It would be invaluable to take field samples downstream from an actual accident to determine the concentrations of ethanol, DOM, and pesticides in the water column. Such measurements would help in assessing the degree of ecosystem threat posed by recurring ethanol spills. A key concern might be the quality of the raw water entering a drinking water plant. In addition to potential violations of pesticide regulatory standards, ethanol could affect other parameters of concern in drinking water treatment. For example, DOM has been identified as a precursor for disinfection by-products (DBPs). The potential risk posed by increased concentrations of DOM due to the presence of ethanol may need to be considered in communities, for example along the Mississippi River, where spills occur routinely.

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