Solubility Enhancement of Hexachlorobenzene
in the Presence of Aldrich Humic Acid

by
Lori Susan Ellinger
The Ohio State University

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Dr. Yu-Ping Chin
Department of Geological Sciences
Abstract

The binding of hexachlorobenzene to Aldrich Humic Acid was measured using the solubility enhancement method. In comparison with $K_{\text{doc}}$ values from previous studies, the value for $K_{\text{doc}}$ measured in this experiment shows that the affinity of a contaminant for binding DOM does not always obey the relationships observed between $K_{\text{doc}}$ and aqueous solubility or octanol/water partition coefficients. These results suggest that physicochemical properties other than those related specifically to nonpolar organic compounds play an important role in their binding to dissolved organic matter.
Introduction

Humic substances are formed from the degradation of biogenic materials and are present in virtually all terrestrial and aquatic environments. They constitute a significant fraction of the dissolved organic matter (DOM) phase present in all natural waters. These materials are capable of participating in a number of chemical reactions of environmental significance including the complexation of heavy metals and the binding of nonpolar synthetic compounds. Several studies have shown that the aqueous solubilities of hydrophobic organic contaminants (HOCs) can be significantly enhanced by humic substances (Carter, et al., 1982, Chiou, et al., 1986, 1987, Gauthier, et al., 1987, Danielsen, et al., 1995, Chin, et al., 1996). The binding of HOCs to humic substances in the aqueous phase can increase their mobility in groundwater and surface waters, and impact their bioavailability to organisms. Moreover, humic substances may impact the remediation of HOCs by making them less susceptible to treatment strategies.

The physicochemical properties of a pollutant (e.g., solubility, octanol-water partition coefficients) are some of the most important factors in determining its fate and transport in aquatic environments. Water solubilities and $K_{\text{ow}}$ (octanol-water partition coefficient) values are often used in modeling the mobility and fate of pollutants in aqueous environments. Because the presence of humic materials can increase the solubility of a substance by as much as several factors, they must be treated as a separate phase. As a consequence, traditional 2-box models can be inaccurate and ineffective. Therefore, a better understanding of the factors which control HOC binding to humic substances is necessary for improving our ability to predict their environmental fate (Chiou, et al., 1986, 1987, Gauthier, et al., 1986,1987, Chin, et al., 1992, 1996).

In the past, partitioning experiments conducted by a number of investigators (Carter, et al.,1982, Chin, et al., 1996, Chiou, et al., 1986,1987, Danielsen, et al., 1995, Gauthier, et al., 1986, 1987) resulted in what appeared to be a relationship between the HOC binding coefficient to dissolved organic matter ($K_{\text{dom}}$) and its octanol-water partition coefficient ($K_{\text{ow}}$). Chiou and others (1986) observed relationships between $K_{\text{dom}}$ and $K_{\text{ow}}$ values for a series of chlorinated
hydrocarbons where those substances with large octanol-water partition coefficients were more intensely bound by humic substances. Similarly, an inverse correlation was observed between their aqueous solubilities and $K_{dom}$. Observations by these investigators (Chiou et al., 1986, 1987) indicated that the polarity of HOCs is an important factor influencing its ability to be bound by humic materials.

More recent studies have shown, however, that solute polarity may not be the only mechanism controlling HOC partitioning into DOM. Gauthier and others (1987) showed that an increase in the degree of aromaticity of the sorbent (DOM) results in an increase in the solubility of pyrene (a 4-ring polynuclear aromatic hydrocarbon). Another study by Chin and others (submitted, 1996) also showed that steric effects may influence the sorption of HOCs. A bulky HOC may not fit into the DOM matrix as easily as smaller HOCs. It has become clear that the chemical structure and characteristics of both the solvent and solute play an important role in HOC-DOM binding.

The objective of this experiment is to measure the partition coefficient between hexachlorobenzene and Aldrich humic acid using the solubility enhancement method developed by Chiou and others (1986). The results of this experiment can be compared to results from previous work in order to provide some insights into how compounds of different structures, but similar polarities can interact with the same type of dissolved organic matter.

Materials and Methods

The solubility enhancement used in this experiment is similar to that used by Chiou and others (1987). This method is designed to measure partition coefficients of a specific organic compound with dissolved organic matter by analyzing the changes in the solubility of an organic compound in varying concentrations of dissolved organic material.

Hexachlorobenzene (HCB) (Aldrich Chemicals, 99%), a polyhalogenated aromatic hydrocarbon, was chosen because it is an EPA “priority pollutant” present in a number of locations in the U. S. , and possesses a low water solubility (~5 µg/L). The HCB working
solution was prepared in hexane (Baxter, UV grade) at a concentration of 50 mg/L in a Pyrex volumetric flask.

HCB was plated onto the inside of 50mL Corex centrifuge tubes by adding enough of the stock solution into the centrifuge tubes to maintain a saturated solution and allowing the solvent to evaporate. Solutions containing various concentrations (0, 5, 10, 15, 20, 30 mg/L) of Aldrich humic acid (AHA), a commercial humic acid obtained from Aldrich Chemicals, were added to the centrifuge tubes in 40mL volumes. Actual concentrations of the dissolved organic matter were measured using a Shimadzu TOC-5000 Total Organic Carbon Analyzer. Dilutions of the humic and fulvic acids were prepared in Milli-Q water. All solutions were placed on a rotating shaker overnight and were allowed to sit for at least two days to attain equilibrium.

Humic acid solutions were subsequently centrifuged at 2500 rpm for one hour so that any excess HCB in the centrifuge tube would no longer be suspended in the solution. Four mL of each solution was pipetted into a separate glass vials and extracted with an equal volume amount of hexane. HCB is much more soluble in the hexane than in the humic acid solutions, and will readily partition into the hexane phase. The hexane phase was then pipetted into a second glass vial.

The HCB solutions were assayed using a Fisons Instruments 8000 series Gas Chromatograph (GC) equipped with an electron capture detector. The GC was calibrated using HCB standards of 2, 5, 10, and 20 µg/L concentrations. One µL of each hexane solution was injected into the GC. Fisons Chrom-Card software was used to calculate the concentrations of the HCB in each solution based on the calibration curve generated previously.

Results and Conclusions

The solubility enhancement method is used to quantify the binding of HOCs to dissolved organic material by comparing the solubilities of the sorbent in the absence and presence of dissolved organic matter. The partition coefficient for the binding of the sorbate and the organic matter can be determined using the relationship derived by Chiou, et al. (1986):
\[ S_{w}^* = S_w + XC_0 \]  \hspace{1cm} (1)

where \( S_{w}^*(\mu g/L) \) is the solubility of the solute in water containing dissolved organic material, \( S_w \) is the solubility of the solute in water without dissolved organic carbon (kg/L), \( X \) is the concentration of the dissolved organic carbon, and \( C_0 \) is the mass of the solute partitioned into a unit mass of the DOC.

The quantity \( C_0 \) can be elucidated from the partition coefficient between dissolved organic matter and pure water \( K_{doc} \), where,

\[ K_{doc} = \frac{C_0}{S_w} \]  \hspace{1cm} (2)

Combining the two equations gives

\[ S_{w}^* = S_w (1 + XK_{doc}) \]  \hspace{1cm} (3)

Thus, the solute solubility in the presence of organic matter would be greater than its solubility in pure water if the value of \( XK_{doc} \) is significant (Chiou, et al., 1986). Rearranging the previous equation gives
A plot of $S_{w}^*/S_{w}$ versus $X$ yields a straight line where the slope is $K_{\text{doc}}$. High $K_{\text{doc}}$ values are indicative of a greater affinity of the HOC to the dissolved organic matter phase. Please note that I have chosen to express our HOC-DOM partition coefficients as a function of a measurable quantity (i.e., DOC), and this is reflected in my choice of using $K_{\text{doc}}$ rather than $K_{\text{dom}}$.

Figure 1 shows the enhancement of HCB solubility in the presence of the Aldrich humic acid cosolute. The values shown are averages of two sets of duplicate experiments. The linear regression for the data of $S_{w}^*/S_{w}$ has an average slope of 1.15351 which is equivalent to the $K_{\text{doc}}$ value.

The values for the slopes of the two experiments show considerable variation. Some of this variation can be attributed to the heterogeneity of the humic acid. The variance in the structure of the humic acid molecules could cause a significant difference in the degree of sorption of the HOCs resulting in a large range in the magnitude of the measured HOC-DOM partition coefficient. Variability may also be a result of analytical errors. For example, the analysis of the solutions with the GC were performed on separate days with the instrument recalibrated each time. The change in the calibration curves might have caused a significant change in the calculations of the concentrations of each solution. Because of the variability in the data, the reported value for the HCB-Aldrich Humic Acid partition coefficient needs to be verified. However, the data can be used as an approximate range for comparison with other HOC-DOM partition coefficients.

Literature values reported for the binding of HCB to dissolved organic matter is sparse. Values of the Log $K_{\text{doc}}$ for a variety of sources of dissolved organic matter are reported in Table 1. These results do not follow the trend observed by Chiou and others (1986) where they show that the binding of HOCs is greater for soil organic matter than aquatic DOM. Also, several studies (Carter, et al., 1982, Chiou, et al., 1986,1987, Gauthier, et al., 1986, 1987) have shown that the $K_{\text{doc}}$ values for HOCs binding to Aldrich humic acid is considerably higher than those
measured using natural aquatic dissolved organic matter. For these reasons, it is difficult to compare our $K_{\text{doc}}$ value with those reported previously.

Pyrene, a fused ring pollutant, has been well studied and serves as a good comparison for the results of these experiments. The Log $K_{\text{ow}}$ value for pyrene is smaller than that of hexachlorobenzene (5.13 and 5.50 respectively) and its solubility is significantly larger (~130 $\mu$g/L versus ~5$\mu$g/L respectively) (Schwarzenbach, 1993) (Table 2). Thus, based upon the hypothesis that those substances that posses a higher $K_{\text{ow}}$ would partition more strongly into DOM, one might expect initially that the $K_{\text{doc}}$ values of HCB should be greater than that of pyrene. Table 2 shows $K_{\text{doc}}$ values for pyrene and Aldrich humic acid work reported by Chin et al. (1996). The $K_{\text{doc}}$ values for pyrene are all larger than the HCB value measured in this experiment.

The smaller $K_{\text{doc}}$ value of HCB (reported by me) is most likely due to the structural differences between the two molecules and how these differences can affect their interactions with humic substances. Studies by Gauthier and others (1987) and Chin and others (1996) indicate that the electron interaction between the aromatic structures of the organic solute and the dissolved organic matter may be the primary mechanism for the binding of the two materials. Pyrene's fused rings give it a much greater degree of aromaticity than the single benzene ring of HCB. This would make the former substance more polarizable and amenable to interactions with the aromatic skeleton of the humic molecule. Thus, pyrene’s more abundant $\pi$ electrons would be made available for interaction with the $\pi$ electrons associated with the humic acid. Also, the electronegative chlorine atoms of the HCB could also pull the $\pi$ electrons away from the benzene ring causing them to be less available for interactions with the aromatic moieties of the humic acids.

The size of the molecules may also have an effect on how the solutes interact with the humic materials. The chlorine atoms on the HCB molecule would make it a much bulkier molecule than the planar geometry of the pyrene molecule. Thus, the HCB molecule may be more
sterically hindered in its ability to partition into the dissolved organic material relative to planar 
HOCs.

My results appear to be in agreement with the findings of Gauthier and others (1987) who 
concluded that the degree of aromaticity in the humic materials correlated strongly with 
measured $K_{\text{dso}}$ values. This is also in agreement with the hypothesis of Chin and others (1996) 
which states that both the degree of aromaticity of both the solute and dissolved organic material 
and steric effects influence the binding reactions of HOCs and dissolved organic material.

Further studies should focus on isolating variables such as aromaticity and size in order to 
establish the roles that these two variables play in these types of binding interactions. Previous 
work (Gauthier and others, 1987 and Chin and others, 1996) has focused on the properties of the 
humic materials and their effects on the binding interactions. Future experiments should attempt 
to determine the relationships between the structure of the hydrophobic organic compounds and 
the binding constants by observing the solubility enhancement of various types of organic 
compounds that possess major differences in structure, but have similar polar/nonpolar properties 
(i.e., solubilities and octanol/water partition coefficients). These results give preliminary 
evidence that the structure of the organic compound plays a major role in the partition 
interactions between HOCs and dissolved organic material.

Acknowledgments

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Wang, and Monique Meier for their advice not only about research, but also about life. Finally, 
to my family and friends, thank you for your love and support.
References


Figure 1: Solubility Enhancement of Hexachlorobenzene in the presence of Aldrich Humic Acid
Table 1: HCB Log Kdoc values for aquatic and natural humic substances and PMA. (from Hess, 1995)

<table>
<thead>
<tr>
<th>Source</th>
<th>Log Kdoc</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Dextran</td>
<td>3.08</td>
<td>Enfield, et al., 1989</td>
</tr>
<tr>
<td>OSU PMA</td>
<td>3.14</td>
<td>Hess, 199</td>
</tr>
<tr>
<td>Soil DOC</td>
<td>4.66</td>
<td>Enfield, et al., 1989</td>
</tr>
<tr>
<td>Suspended Particulate Matter</td>
<td>4.8</td>
<td>Wilken and Wirth, 1986</td>
</tr>
<tr>
<td>Freshwater Wetland DOC</td>
<td>4.86</td>
<td>Pardue, et al., 1993; Hassett and Milicic, 1985</td>
</tr>
<tr>
<td>Activated Sewage Sludge</td>
<td>4.94</td>
<td>Wilken and Wirth, 1986</td>
</tr>
<tr>
<td>Peat</td>
<td>5.12</td>
<td>Wilken and Wirth, 1986</td>
</tr>
<tr>
<td>Groundwater DOC</td>
<td>5.65</td>
<td>Enfield et al., 1989</td>
</tr>
<tr>
<td>Humic Acid DOC</td>
<td>5.98</td>
<td>Enfield et al., 1989</td>
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Table 2: Aqueous solubility, octanol-water partition coefficient, and dissolved organic matter partition coefficient for pyrene and hexachlorobenzene.

<table>
<thead>
<tr>
<th></th>
<th>Aqueous Solubility</th>
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<th>log $K_{dom}$</th>
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<tr>
<td></td>
<td>[-log $C_w^{**}$ (mol/L)]</td>
<td>[(mol/L octanol)*(mol/L water)]</td>
<td>(L/kg-OC)</td>
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<tr>
<td>Pyrene</td>
<td>6.17*</td>
<td>5.13*</td>
<td>5.17*</td>
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<tr>
<td>HCB</td>
<td>7.69*</td>
<td>5.5*</td>
<td>5.06</td>
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* Schwarzenbach et al., 1993.
* Chiou et al., 1987.