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Interaction of Polychlorinated Biphenyls with Dissolved Humic Acid from Azraq, Jordan

Mahmoud A. Alawi, Fawwaz Khalili and Jafar Abd Elgani

Department of Chemistry, University of Jordan
P.O. Box 13003, Amman-11942, Jordan
✉ alawima@ju.edu.jo

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Abstract: Humic acid is an important component of soil which was the subject of several environmental studies. Humic acid interact widely with environmental pollutants, such as chlorinated pesticides. Until now, the mechanism of interaction of humic acid with chemicals in the environment is not well defined. In this work the interaction behaviour of polychlorinated biphenyls (PCBs) with humic acid (HA) which was isolated from the Azraq Oasis (Jordan) was studied at different HA concentrations, pH and temperature. The amounts of the remaining PCBs were determined by extraction and analyzed on a capillary gas chromatograph equipped with a ^{63}Ni-electron capture detector (ECD). Generally the interacted amount of PCBs is directly proportional to the increase of soluble humic acid and inversely proportional to the increase of pH. The changes in temperature have no significant effect on the interacted amount of PCBs. The more chlorinated the PCBs are, the more the interaction is and the less the sensitivity for the changes in pH and HA concentration.

Key words: PPCBs, humic acid, Azraq-Jordan.

Introduction

Humic substances are colloidal macromolecular systems, heterogeneous, polydispersed complexes that are poorly understood. They constitute a major fraction (60-70%) of soil organic matter and 30-50% of surface organic matter and possibly the most abundant of naturally occurring macromolecules on the earth (Tochiyama et al., 2000 and Bryan et al., 1998). Humic acid has high molecular mass and reported to range from several hundred to several hundred thousand Daltons and it is not possible to define a detailed molecular structure for humic acid as it is consisting of non-uniform distribution of functional groups joined by a variety of aliphatic and aromatic units (Choppin, 1999; Shin et al., 1999; Choppin and Labonne, 1997).

Polychlorinated biphenyls are considered as hazardous pollutants due to their toxicity and persistency in the environment. They are mixtures of synthetic organic chemicals with same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications (Robert and Diane, 1999).

The lipophilicity of PCBs is responsible for their ability to bioaccumulation, primarily in tissues and organs rich in lipids (Takao et al., 2007). It has been shown that PCBs cause enzyme and immune suppression in mammals and associated with heptacellular carcinoma in rats and mice (Safe, 1990).

The objective of this work is to study the interaction behaviour between some polychlorinated biphenyls (PCBs) represented through the priority pollutants (seven compounds), PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180, with dissolved humic acid (HA) isolated from the Azraq Oasis.

The effect of humic acid concentration, reaction time, different pH conditions, and different temperatures on

the interaction behaviour of PCBs with dissolved humic acid was studied.

All experiments were done under conditions similar to the environmental conditions of the Azraq Oasis.

Experimental Procedures

All experiments were carried out by varying one of the following parameters: humic acid concentration, pH, temperature, or reaction time. The concentrations of the studied PCBs were kept constant. Different experiments were done as described in Table 1.

Table 1: Experimental conditions

PCB No.	*pH*	*HA amount (mg)*	*PCBs amount (μg)*	*Reaction time (hours)*	*Temperature (°C)*
28				0	
52				3	
101	6	10		9	25
118	7	25	50	15	35
138	8	50		24	45
153					
180					

Results and Discussion

Study of the Reaction Time Effect

The results of the interacted percentage amount of the seven PCBs with humic acid (HA) at different reaction time 0, 3, 9, 15 and 24 hours were obtained, such as the one shown in Figure 1.

Almost all researchers in organochlorine-humic acid interaction did not study the reaction time effect. They adopt certain equilibration time without justification and only for the purpose of the comparison between results.

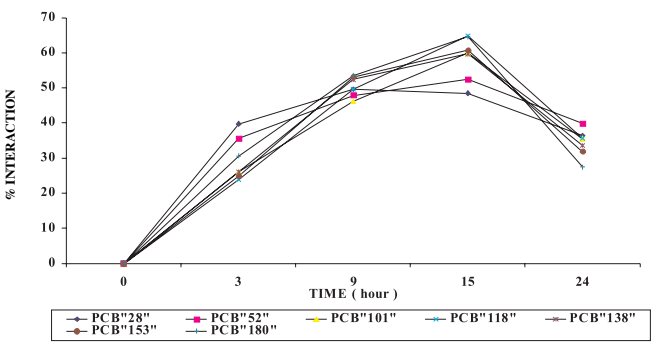

Figure 1: Effect of reaction time on the interacted amount of PCBs at pH 7, 10 ppm concentration of HA and at 25 °C.

In this work, the equilibrium time was adopted to be 15 hr where it shows the maximum interaction amount.

Study of Humic Acid Concentration

The results of interacted percentage amounts of seven PCBs with HA at different concentration of 10, 25 and 50 ppm were obtained, such as the one shown in Figure 2.

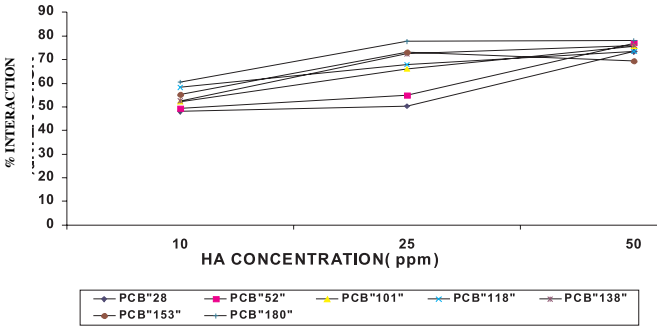

Figure 2: Effect of HA concentration on the interacted amount of PCBs after 15 hr at pH 6 and at 25 °C.

The experiments indicate that at pH 6, 7 and 8, the interacted amount of PCBs increases significantly with the increase of humic acid (HA) concentration from 10 ppm to 25 ppm, as shown in Figure 2. This is due to the increase in the interacting hydrophobic sites as the concentration of HA increases.

In the case of pH 6 and 7, the interacted amount of PCBs exhibit only slight increase upon increasing the concentration of HA from 25 ppm to 50 ppm. This is due to the competitive effect of humic-humic (aggregates) interaction and humic-hydrophobic interaction that reduce the number of available hydrophobic sites for PCBs interaction.

In case of pH 8, humic acid will change from fibrous to a more sheet-like one due to the presence of more anionic groups (Zappoli et al., 1997), so the effect of humic-humic interaction observed in the case of pH 6 and pH 7 (HA = 25 to 50 ppm) is reduced. Thus the interacted amount is significantly increased by the increase in the concentration of HA.

Effect of pH

The results of interacted percentage amount of seven PCBs with humic acid (HA) at different pHs 6, 7 and 8 are shown in Figure 3.

Figure 3 indicates that the interacted amount of PCBs decreases as the pH increases. The highest interacted amount of PCBs is at pH 6 and the lowest is at pH 8. The

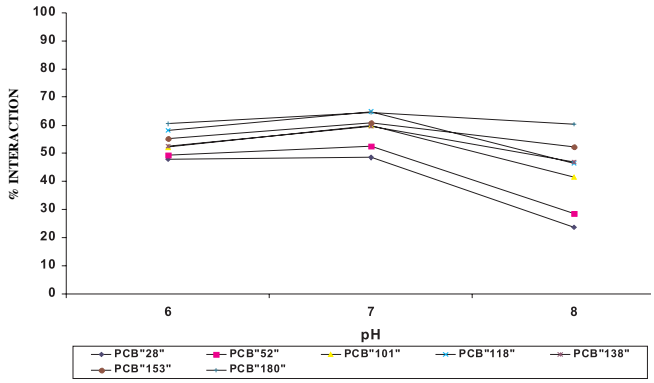

Figure 3: Effect of pH on the interacted amount of PCBs after 15 hr at 10 ppm concentration of HA and at 25°C.

difference in the interacted amount between pH 6 and pH 7 is small, because HA at these pH does behave as uncharged (or partially charged) polymer. As the pH increases to pH 8, HA behaves as a strong polyelectrolyte (Alawi et al., 1995).

Reducing the pH from pH 8 to pH 7 will lead to a dramatic increase in the interacted amounts of PCBs because of increasing H-bonding between polymeric chains; therefore, the possibility for trappings PCBs increases in the HA aggregate.

Effect of Temperature

The results of interacted percentage amount of seven PCBs with humic acid (HA) at different temperatures 25, 35 and 45°C are shown in Figure 4.

As shown in Figure 4, there was no significant change in the interacted amount of PCBs upon increase in temperature. So the interaction is entropy-driven since enthalpy is about zero. This finding emphasizes the fact that the interaction is neither an adsorption nor desorption process but a form of weak hydrophobic bonding between the PCBs and humic acid.

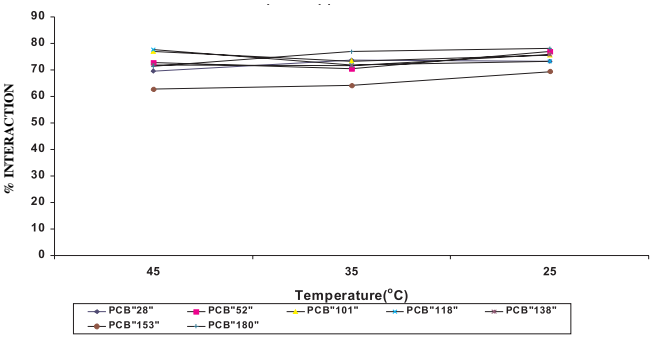

Figure 4: Effect of temperature on the interacted amount of PCBs after 15 hr at 50 ppm HA concentration and pH 6.

Effect of Chlorine Substitution

As shown in Figure 5, the experiments indicate that the interacted amount of PCB increases with number of chloro substituents. On account of higher molecular mass of PCB, its water solubility decreases.

It was observed that penta-, hexa- and hepta-chlorinated PCBs are slightly affected by the change in pH and the change of concentration; the opposite is observed of PCBs which has lower chlorine substitution, and lower molecular mass.

Tri- and tetra-chlorinated PCBs are more sensitive to the change in pH or increase in HA concentration, because forming humic-humic aggregates increases by decreasing pH and increasing HA. This will decrease the aggregate size available for large size PCBs and become suitable only for small size PCBs.

Considering the PCBs which have the same number of substitution of chlorine, there is another parameter that affects the interacted amounts of PCBs with HA, which is the ortho-substitution of 2,3,6-chlorinated PCBs. Increasing the o-substitution of PCBs makes them non-coplanar and more polar and so increases their solubility in water. This will lead to less hydrophobic interaction with HA.

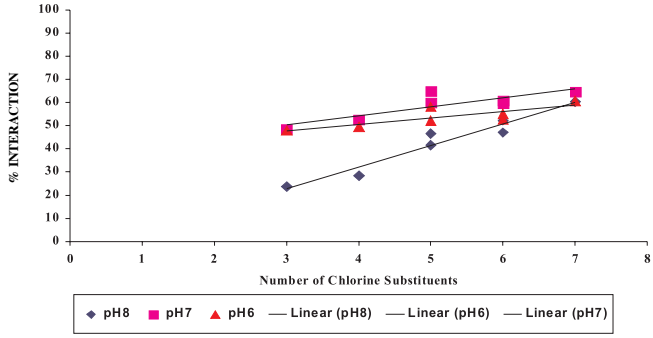

Figure 5: Effect of the number of chlorine substituents in the interacted amount of PCBs at pH 6, 7 and 8, 15h and 25°C.

Effect of Humic Acid in the Environmental PCBs

- From the results shown, humic acid can be used to remove or decrease the PCBs' pollution from the environment. The presence of humic acid in water will enhance the solubility of PCBs which are hydrophobic organic compounds.
- Lakes and rivers contain much more soluble organic matter than ground water, so we expect PCBs to reside more in the lakes and rivers and so taken by fishes, plankton and near plants. Thus, lakes and river water is expected to be much more contaminated with PCBs

than ground water, and it will be interesting to test this idea by further research.

- PCBs enter the environment through two ways. The first is the dumps and landfills and the second is the disposal of industrial fluids into rivers and coastal waters.
- The effect of these two sources on the environment will be evaluated in the light of the results of the present study.
- Ground water is not expected to be effected by PCBs pollution. Though the rain water passes through dumps and landfills that contain PCBs, the PCBs will be filtered through soil that contains particulate humic acid interacting with PCBs.
- If soils contaminated with PCBs are taken away from dumps and landfills and reach agricultural soil, PCBs may be absorbed by plants and then the concentration of PCBs increases along the food chain (biomagnified). More acidic soils or aquatic systems that contain humic substances are expected to be richer in PCBs due to the higher interaction with PCBs as it has been shown by the present study.
- One of the environmental techniques that can be developed depending on this study is to make filters that contain humic acid which are useful in reducing the concentration of PCBs and other hydrophobic pollutants from water.

Conclusions

- The increase in humic acid concentration generally causes an increase in the interacted amount of PCBs. Furthermore, the higher the pH, the stronger the effect.
- With respect to pH (more than 7), there was a decrease in the interacted amount of PCBs, the lower the pH the more the interaction.
- Interacted amounts of PCBs increase as the number of chlorine atoms increases (i.e. the more chlorinated PCBs interact more with HA).
- With respect to temperature changes, there were no significant changes in the interacted amount of PCBs.
- The more chlorinated PCBs are less sensitive to the change of HA and pH.
- From the results shown, humic acid can play a good role in reducing the concentration of PCBs in ground water.

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