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Fluorescence Based Detection of Polychlorinated Biphenyls (PCBs) in Water Using Hydrophobic Interaction

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Abstract

Despite increasing controls in their production and disposal, persistent organic pollutants in water, even at concentrations below parts per million, represent an ongoing environmental health risk. Despite this concern, the detection of these compounds in water sources rely upon expensive, time consuming approaches that do not permit frequent monitoring and evaluation. In this work, a new fluorescence-based technique is presented for the detection of Polychlorinated biphenyls (PCBs) in water. Benzopyrene (BaP) fluorescence was shown to increase with trace concentrations of aromatic organic pollutants. BaP forms a hydrophobic complex with PCB, which has allowed for the successful detection of pollutants including PCB-126, PCB-153 and PCB-118. To determine the selectivity and robustness of this response, the impact of pH, ionic strength and humic acid to mimic surface water conditions is explored. While suppression of signal was seen, these factors' impact on PCBs detection was minor, suggesting a potential sensing strategy can be developed through this interaction. It is seen that the number and location of chlorine atoms are important along with the geometric orientation of molecule's structure.

Introduction

Polychlorinated biphenyls (PCBs), man-made persistent organic pollutants (POPs), represent a class of compounds that possess anywhere from 1 to 10 chlorine atoms, resulting in 209 unique congeners, based upon the exact number and orientation of chlorines. PCBs have some unique properties, including resistance to high pressure, high temperature, and are chemically stable to acid and bases. These properties made them attractive for a variety of applications in heat transfer fluids, plasticizers, dielectric fluids, flame-retardants, organic diluents and solvent extenders.^{1–4} However, this stability also means they do not readily degrade, and therefore accumulate in the environment. Although, PCBs production was banned in the 1970s, there are still readily accessible contact sources, including caulking material in old buildings.^{1,2} In more modern systems, according to NIEHS (National Institute of Environmental Health), PCBs are also linked to printing inks, which can be

[†]Footnotes relating to the title and/or authors should appear here.

Conflicts of interest

There are no conflicts to declare

released into the wastewater during the recycling process of newspapers, magazines, mailing materials, and packaging.³ The improper disposal of large amounts of electrical parts and dumping of chemicals containing PCBs cause their leakage into the water and soil, from where they enter the food chain and finally into the human body. Environmental Protection Agency (EPA) has set a limit of 0.0005 ppm of PCBs in the drinking water, Food and Drug Administration (FDA) has a range of 0.2 to 3.0 ppm of PCBs in all foods and for paper food-packaging its limit is 10 ppm.⁴ Whereas, World Health Organization (WHO) allows PCB intake of 6 µg/kg per day.⁴ PCBs bioaccumulate in the fatty tissues in the body⁵ and cause adverse health effects including inflammatory and cardiovascular diseases. The ideal is to have a system that promptly sense their presence at high selectivity and sensitivity within the water bodies because of health-related issues.

There are multiple techniques being studied to detect PCBs including screen-printed electrodes (SPCEs), surface-enhanced Raman scattering (SERS), surface plasmon resonance (SPR), electrochemical impedance sensors, whole cell sensors, gas chromatography–mass spectrometry (GC-MS) and micro-flow immunosensor chips.^{6–10} Among these, GC-MS remains the most common technique used to measure PCBs.¹¹ GC-MS is beneficial because it provides explicit identification of organic molecules in complex mixtures.¹² Given the safety needs, it is very important to detect PCBs in dilute conditions and for which, GC-MS is serving as a gold standard technique (EPA method 8082A).¹³ However, GC-MS possesses some limitations, as it requires high vacuum that needs maintenance which, is a time consuming and expensive technique. Additionally, GC-MS needs organic solvent extraction⁶, to concentrate PCBs for analysis and these solvents can pose additional environmental and health risks.

Detection techniques involving fluorescence spectroscopy is highly sensitive, rapid and simple to employ.¹⁴ This technique is already being used for environmental and bio applications in terms of sensing precious metal ions¹⁵, explosives¹⁶, hazardous gas molecules¹⁷, cancer biomarkers, cells, and tissues.¹³ While other methods and techniques are limited by the cost, time and sample handling, the ubiquitous use of fluorescence techniques in a wide range of industries and applications make their application to environmental pollutant detection plausible. There are various fluorescence-based techniques listed in literature to sense molecules e.g. intensity-based sensing, lifetime-based fluorescence response, Förster resonance energy transfer, wavelength shift, wavelength ratiometric response and anisotropy-based sensing and polarization assays.¹⁸

In this work, hydrophobic interactions of sensing molecules are explored as a means of detecting dilute quantities of PCBs in aqueous environments. Benzo[a]pyrene (BaP) is a fluorescent molecule, whose fluorescence signal is strongly enhanced in non-polar environments. It was found that BaP intensity increases in water beyond the highest intensity in organic solvent through interactions with PCBs, potentially providing a rapid sensing technique for the detection of PCBs. Furthermore, this work will show that hydrophobic sensor can sense PCBs in water by using surface water conditions such as pH, ionic strength and humic acid.

Experimental section

Materials

Unless otherwise stated, chemicals and reagents were used as received without any additional purification. 3,3',4,4',5 Penta-chlorobiphenyl (PCB-126), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB-153), 2,3',4,4',5 Pentachlorobiphenyl (PCB-118) and biphenyls were purchased from AccuStandard Inc., New Haven, Connecticut. 4, 4-dihydroxy biphenyl was purchased from Sigma Aldrich. Sodium hydroxide was purchased from fisher scientific. Sodium chloride was obtained from VWR. Humic acid and benzo[a]pyrene were purchased from Alfa Aesar. Dichloromethane (DCM), iso-octane, n-Hexane and Dimethyl sulfoxide (DMSO) was purchased from Pharmaco. Deionized (DI) water was obtained from Milli-Q water purification system.

Method

Stocks solutions of PCBs, biphenyl, 4, 4-Dihydroxybiphenyl and BaP were prepared in DMSO. Whereas, humic acid was solubilized in water. A total five studies were carried out in this work with similar steps. For all studies, in order to minimize PCB loss, all PCBs and sample transfer were performed using glass syringes. During each experiment 0.08 μM of BaP was added to the solvent (water or DMSO), the solution was then spiked with analytes based upon the study to be evaluated. Solutions were mixed for 5 seconds to make sure that DMSO layer is disappeared. The solutions become homogeneously dispersed and then characterized. In the first study, only DI water is used as a solvent for the hydrophobic interaction. DMSO was kept constant at 1.6 vol%. In second study, organic solvent effect was evaluated. BaP was introduced to DMSO along with PCBs, biphenyl and 4, 4-Dihydroxybiphenyl. In third study, the effect of pH was observed on the interactions of BaP and PCBs. Sodium hydroxide was used to adjust the pH. Samples of BaP and PCBs were prepared using high pH water. In fourth experiment, effects of ionic strength of water was evaluated. Sodium chloride was selected to change the ionic strength, as its molar concentrations and ionic strength are identical. Ionic strength of

DI water was varied from 1mM to 20M. BaP along with PCBs were added to different ionic strength water. In fifth study, hydrophobic interaction of BaP and PCBs is studied in the presence of humic acid in water followed by the addition of BaP and PCBs. Water solution was spiked with Zero to 20 ppm of humic acid. In addition to this, the data from the humic acid study is used to perform the regression analysis to endorse the effectiveness of the fluorophore.

Characterization

All the samples were characterized using Cary Eclipse spectrophotometer. It has maximum spectra intensity of 1000 a.u. All the samples were scanned at medium scanning rate (600nm/min) with medium voltages (600 volts) of PMT detector. Samples were introduced to spectrophotometer using quartz Micro Fluorometer Cell of 0.7 ml volume and 10 mm path length from Starna Cells, Inc.

Results

Change in BaP intensity in organic solvents and with PCB

Maximum intensity of BaP in organic solvents was evaluated and compared to BaP intensity in water with PCBs. For this study, five organic solvents (n-hexane, DMSO, chloroform, DCM and isooctane) were used. BaP concentration was kept at 0.08 μM in all samples. For BaP study in water, its stock was prepared in DMSO. The spectra of BaP were characterized using fluorescence spectroscopy. The spectra and bar graphs in figure 3, represents the intensity peaks of BaP in organic solvents with and without PCB-153 in water. Table 1 summarize the properties of solvents that can potentially impact BaP fluorescence.

BaP interaction with PCBs, biphenyls and humic acid in water

BaP concentration in water was selected based on its excimer formation ability. A stock solution of BaP was prepared in DMSO to help enhance the solubility of BaP in the water. To avoid the excimer formation, the BaP concentration of 0.08 μM was selected, as it was found to be the maximum concentration in water, which did not form an excimer signal nor precipitate out.

The excitation and emission spectra of BaP are shown in figure 2. BaP concentration was kept constant at 0.08 μM in water along with numerous concentrations of PCBs, biphenyls and humic acid. Small concentration of DMSO from the stock solution helped to solubilize the BaP in the water. The effect of PCB-126 on BaP spectra and PCB-126 control in water are shown in figure 4a and 4b. All the samples were excited at 294nm, excitation and emission slits were kept constant at 5nm. In figure 4a, BaP intensity increases as PCB-126 concentration increases. In a parallel study, the intensity of the PCB-126 emission spectra (Without BaP) in water was very low (Figure 4b) and did not increase significantly. Figures 4c represents the change in peak intensity at 407 nm of BaP in the presence of PCBs (126,153 and 118) in water.

Similarly, biphenyl, 4, 4-dihydroxy biphenyl and humic acid were studied with BaP in water as a control molecule. Peak intensities of BaP with these three molecules are given in figure 4d. Humic acid molecular weight was calculated using the average chemical formula $\text{C}_{187}\text{H}_{186}\text{O}_{89}\text{N}_9\text{S}_1$.²⁰ Biphenyl does not show any change in the intensity. Whereas, 4, 4-dihydroxy biphenyl and humic acid increase the intensity of BaP. Intensity signals of these two chemicals are also displayed without BaP in water.

BaP interaction with PCBs and other molecules in organic solvent

To determine the impact of solvent on the fluorescence signal, PCB/BaP interaction studies were carried out in DMSO. Figure 5 represents the impact of PCB-126, 153 and 118 on BaP fluorescence intensity. As shown, in an organic solvent, PCB/BaP interaction is inhibited, resulting in a loss of fluorescence signature. Note that while baseline intensity is higher fluorescence within the concentration range studied.

Effect of water properties and environmental contaminants on BaP-PCB interaction

pH effects—Ground water pH can range from ~6 to 8.5, while surface water is around 6.5 to 8.5.²¹ The DI water used in these experiments has an unbuffered pH of 5.8, close to the lower limits. In this section of the work, pH of the solvent is changed to the higher end and its effects on sensing are studied. Figures 6 shows the interaction of BaP and PCB-126, PCB-153 and PCB-118 in pH 5.8 (DI water pH) and in pH 8.5.

Ionic strength—Surface water's ionic strength typically spans from 1mM to 5mM. Whereas, ground water has ionic strength ranges from 1mM to 20mM. The sensing interaction of BaP and PCBs are studied using three ionic strength values of 1 mM, 5 mM and 20 mM. Ionic strength was set using sodium chloride salt. Figures 7 represents the interaction of BaP and PCBs in ionic strengths values and their comparisons with pure DI water. As demonstrated, within the scope of surface water, fluorescence response was not strongly affected by ionic strength.

Natural organic matter (NOM)—The concentration of natural organic matter (NOM) in surface water runs from 0.1 ppm to 20 ppm and consists mainly of humic acid substance.²² Evaluating the compounds' impact on PCB detection, five concentrations of humic acid (0.1, 3, 5, 10 and 20 ppm) were selected.

These concentrations change the fluorescence signals of BaP and PCBs, as shown in figure 8. Since humic acid has background fluorescence (See Figures S4), background signals of humic acid were subtracted from the respective intensity to get the BaP specific intensity in the presence of humic acid.

Discussion

Results from PCBs, Di-OH BiP, BiP, BaP and humic acid are presented in figure 1. Three PCBs were selected as they represent the three different possible structural orientations of the molecules (PCB-126 is coplanar, PCB-153 is non-coplanar and PCB-118 is mix-coplanar). The main goals of this work is to study the interaction of BaP with one PCB from each category.

All the PCBs including six congeners fall in one of the three categories studied here. BaP fluorescence is a strong function of the solvent system being used. Table 1 summarizes the properties of the solvents evaluated and the respective intensities of BaP in these solvents. As shown in Figure 3 fluorescence is lowest in n-hexane and greatest in DMSO. Comparing results (figure 3) to solvent properties in table 1, intensity of BaP increases as the dipole moment, dielectric constant and solubility parameter of these solvents increases. BaP intensity exhibited a strong dependency on the solvent polarity, with non-polar solvents showing a very low intensity of BaP. There is less spectral shift (figure 3), implying that the fluorophore and solvent have very low interaction in the ground state.²³ whereas, polar aprotic solvents, the intensity is higher for DMSO as it has high dipole moment, viscosity and solubility parameter. There is more than one factor (e.g. dipole moment for solvent-solute interaction at excited state and viscosity for local environment) enhancing the BaP intensity. As water is a unique polar protic solvent with the presence of hydrogen bonding, it

doesn't follow the fluorescence trend observed with the other studied organic solvents. It is possible that the low fluorescence in water is due to the hydrogen bonding inhibiting water to interact with the excited state BaP (figure 9a). Alternatively, it may be possible that BaP is not very strongly polarized by the incident light. Despite the low fluorescence of BaP in water, when PCBs are added, the fluorescence intensity increases to values beyond what is seen for PCBs in other solvents. This enhancement was only observed in water and not the organic solvents. While the exact mechanism for this effect is not known, it is likely that the PCB aides in enhancing BaPs excitation potential by suppressing water interactions. PCBs and BaP are both hydrophobic and have low aqueous solubility. The solubility PCBs in pure water range from 0.0012 to 4830 $\mu\text{g/L}$.²⁴ For the PCBs used in this study, the solubility of PCB-126, 153 and 118 in water are 7.4 $\mu\text{g/L}$ (0.023 μM), 0.91 $\mu\text{g/L}$ (0.003 μM) and 13.4 $\mu\text{g/L}$ (0.04 μM), respectively.^{25, 26} The stock solutions of PCBs and BaP were prepared in DMSO. The final concentration of DMSO in water was set at 1.6 Vol% in the water, which enhanced PCB solubility. When BaP was introduced in water, the water molecules are likely readjusted to accommodate BaP by forming a clathrate cage (hydrophobic hydration) around the molecule as shown in figure 9a. When the concentrations of hydrophobic molecules (BaP and PCBs) increase in water, the molecules in the clathrate hydrate start to interact with each other and forming a cage around hydrophobic complex that leads to the hydrophobic interaction demonstrated in figure 9b. When both reagents were mixed in the water, no white precipitates were observed which suggests that PCB is not precipitating out of solution. This was further verified from figure 4, where BaP shows an increasing trend with increasing the concentrations of PCBs. White precipitates were only observed for ionic strength study in figure 7 at higher concentration of PCB-153. The hydrophobic complex of BaP and PCB possesses its own unique properties that are distinctive from both PCBs and BaP. The chlorine atoms in PCBs having a high electron withdrawing potential, resulting in increasing the PCB dipole moment. As such, the BaP and PCB complex may have an increased dipole moment, enhancing the quantum yield of BaP in water. Figure 4a illustrates the fluorescence spectra of BaP with and without PCB-126. Importantly, as shown in Figure 4(b), PCB alone possessed slight fluorescence, below the intensities being studies. Figure 4(c) indicates the change in intensity of BaP with PCBs. The $\log K_{ow}$ values of PCB-126, PCB-118 and PCB-153 are 7.09, 7.26 and 7.79.²⁷ As non-planar PCB gave the highest intensity and has high hydrophobicity based on the number of chlorine atoms it is likely that PCB 206 will result in the greatest fluorescence increase as it has a $\log K_{ow}$ 10.83.²⁷

For comparison, figure 4(d) demonstrates the interaction of BaP with humic acid (H.A), biphenyl (BiP) and 4, 4-Dihydroxy biphenyl (Di-OH BiP). BiP and Di-OH BiP molecules were selected due to their PCB like structure, hydrophobic nature and absence of chlorine atoms. H.A was selected, as it is one of the main impurities in the surface water. Interestingly, BiP does not display any capacity to enhance BaP fluorescence, while the other compounds did possess a slight ability to increase the fluorescence signal. The absence of chlorine atoms on the BiP makes it less hydrophobic and more soluble in water as compared to PCBs. Importantly, both Di-OH BiP and HA did have a slight autofluorescence that was adding to the signal with BaP and the fluorescence spectra which is illustrated in figures S1a to S1d within supplementary material. The subtracted values of H.A intensities in water with and without BaP show that beyond 3 μM , the fluorescence signals are

completely shadowed by H.A alone. The interaction of BaP with HA, BiP and Di-OH BiP shows that the system highly depends on the presence of chlorine atoms in the molecules. Background signals of Di-OH BiP and HA can be noted in the control in figure 4(d). These background signals can be subtracted to show that BaP is not interacting with Di-OH BiP and HA, and resultant increase in the intensity is almost zero. This sensing technique can be used for different PCBs and distinguish them based on the change in the intensity of BaP which will be different for each PCB. It can be seen that PCB-126 and PCB-118, both have same numbers of chlorine atoms of five. However, both have different responses in the fluorescence intensity.

Aqueous

pH is known to play an important role in fluorescence, as a slight change in pH can radically influence fluorescence intensity.²⁸ BaP and PCBs interactions in water at different pH is shown in figure 6. PCB-126 and PCB-153 intensities decrease as the pH is changed from 5.8 (DI water) to 8.5. The intensity for PCB-118 increases with increasing the pH. The BaP control (zero μM PCBs) is almost same (around 16 a.u) in both 8.5 and 5.8 pH.

The interaction of PCBs and BaP in various ionic strength is shown in figure 7. NaCl (Sodium Chloride) was selected to control the ionic strength of the water. It is expected that with increasing ionic strength, the solubility of hydrophobic compounds to decrease. Due to this, we would anticipate a potential increase in PCB BaP interaction, resulting in increased fluorescence. As shown, there is only a slight increase at lower concentrations of PCB, but the fluorescence response remains largely unaffected by Ionic strength.

Humic acid is amphiphilic molecule. It has carboxyl and hydroxyl groups that makes it partially hydrophilic. Humic acid is the reason PCBs and other pollutants are soluble in water and in soil due to its hydrophobic pockets. In capturing and sensing system of these pollutants, humic acid serves as an impurity. Figure 8 represents the effect of humic acid's presence in water for PCB-126,153 and 118. BaP and PCBs are sticking to humic acid and making three molecular complexes. While interacting, BaP and PCBs should be present within close approximately. It changes the binding environment that can lead to the change in the intensity. For PCB-126 and PCB-153, increasing the humic acid concentration provides additional pockets that allow more distribution of molecules (decrease in the number of molecules in the hydrophobic complex). However, for PCB-118, the number of molecules in the hydrophobic complex doesn't change much by increasing the concentration of humic acid. PCB-126 and PCB-153 has profound effects on the BaP in the presence of humic acid whereas, PCB-118 and BaP has very low effect in the presence of humic acid.

To confirm the effectiveness of BaP fluorescence as a sensing scheme for each PCB, a linear regression model with each PCB, as well as humic acid concentration and BaP, as explanatory variables and their significant interactions was fitted. At first, all the three way interactions are included in the model. Then we used backward elimination to remove non-significant variables. Figures S5, S6 and S7 show the predicted intensities for different concentrations of humic acid (colors) as PCB concentration increases with and without BaP. For PCB-126, without BaP (Figure S5b), PCB-126 has a quadratic relationship with the logarithm of intensity for each humic acid concentration. While for PCB-118 without BaP

(Figure S6b), PCB-118 has linear relationship with the logarithm of intensity for each humic acid concentration. However, for PCB-153 without BaP (Figure S7b), PCB-118 is constant for each humic acid concentration. With BaP (Figures S5a, S6a, S7a), each PCB has a quadratic relationship with the logarithm of intensity but with different shapes for PCB-126, PCB-118 and PCB-153. Hence, these models shows that each PCB has its own unique interaction with BaP in the presence of humic acid, emphasizing the ability of PCB to interact with BaP even in the presence of competing molecules. This further emphasizes the potential of designing a sensing methodology that can detect PCBs, even in complex environmental samples.

Conclusions

We have demonstrated the ability of PCB to enhance BaP fluorescence in water, suggesting a potential detection method for PCB contaminants in water. This fluoresce signal is unique for each PCB molecule that depends on the numbers of chlorine atoms, their orientation and the geometry of the molecule. It was also found that this unique interaction is observed in water, but not in organic solvents. Importantly, changes in ionic strength and pH of water slightly effected the signal response, while humic acid did attenuate the observed signals. Based on the intensity and unique trends, it is possible to detect variety of PCBs in water in the presence of allowable limits of impurities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Figure 1 :
Structure of biphenyls with and without chlorine atoms, Benzo[a]pyrene and humic acid used in this work

Figure 2:

Excitation and emission spectra of BaP in water. Dotted line shows the excitation spectra and solid lines show the emission spectra at two different excitation wavelengths.

Figure 3:
Increase in BaP (0.08 μ M) intensity in different organic solvents, in water and with PCB-153 in water.

Figure 4:

(a)- BaP Fluorescence intensity in the presence of PCB-126 in water, (b)- PCB-126 intensity by itself in water, (c)- increase in the intensity of BaP around 407 nm with the addition of PCBs (PCB-126, PCB-118 and PCB-153) in water, intensity of BaP is increasing with increasing the concentration of PCB, whereas, there is no change in PCBs intensity in water without BaP, (d)- change in intensity of BaP around 407 nm with the addition of humic acid, biphenyl (BiP) and 4,4-Dihydroxy biphenyl (Di-OH BiP) and their control in water, humic acid and Di-OH BiP control show an increase in its intensity in water.

Figure 5:

PCBs interaction with BaP in organic solvent. .

It was also noted that biphenyl and 4, 4-Dihydroxy biphenyl do not interact with BaP in DMSO.

Figure 6:

(a) - PCB-126 and BaP in DI water and at pH 5.8, (b) - PCB-153 and BaP in DI water and at pH 5.8. (c)- PCB-118 and BaP in DI water and at pH 5.8. Y-axis has same scale in all three figures for comparison.

Figure 7:

(a) - PCB-126 and BaP in different ionic strengths, (b) - PCB-153 and BaP in different ionic strengths. (c)- PCB-118 and BaP in different ionic strengths.

Figure 8:

(a) - BaP and PCB-126 interaction in the presence of humic acid, (b) - BaP and PCB-153 interaction in the presence of humic acid. (c)- BaP and PCB-1118 interaction in the presence of humic acid.

Figure 9:

Water forms the clathrate cage to accommodate the hydrophobic molecule, if there are two different hydrophobic molecules surrounded by the water then these two molecules can bind together to make a complex based on their hydrophobicity and affinity.

Table 1 :

Different organic solvents with their dipole moment, dielectric constant and BaP intensity in these solvents, BaP (n=3 with standard deviation).

Solvent	Dipole moment (D) ^{43,44,45}	Viscosity (mPa.s) ^{46,61}	Dielectric constant(ϵ) ^{46,47}	Polarity Index	Solubility parameter	BaP fluorescence intensity (a.u)
n-hexane	0.00	0.29	1.9	0.1	14.9	10.79 $\pm$ 0.33
Isocetane	0.00	0.47	2.2	0.4	15.1	18.18 $\pm$ 0.50
Chloroform	1.04	0.54	4.8	4.1	18.7	44.28 $\pm$ 0.38
DCM	1.62	0.42	9.1	3.1	20.2	66.97 $\pm$ 2.30
DMSO	3.96	2.0	47.24	7.2	26.4	84.71 $\pm$ 1.40
water	1.58	0.89	80.1	9.0	48.0	17.14 $\pm$ 0.7