# Reaction of Polycyclic Aromatic Hydrocarbons Adsorbed on Silica in Aqueous Chlorine

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The reaction of polycyclic aromatic hydrocarbons (PAHs) previously adsorbed on silica gel or diatomaceous earth with sodium hypochlorite was carried out to elucidate their reactivity to aqueous chlorine. It was demonstrated that the PAHs adsorbed on silica reacted more rapidly than the PAHs themselves in water, leading to the formation of many chlorinated and oxidized derivatives. A similar reaction in the presence of potassium bromide was found to preferentially produce corresponding brominated derivatives. These reactions seem to proceed through PAHs adsorbed on the silica surface and halogenating agents, the electrophilicity of which may be raised by the catalytic effect of the silanol group of the silica surface. These findings from the environmental viewpoint suggest that the reaction of hydrophobic compounds adsorbed on sediment cannot be neglected.

### Introduction

A number of hydrophobic compounds are released into aquatic environments. The association of these organic compounds with sediments plays an important role in the distribution and dynamics of organic pollutants in the aquatic environments. Of these compounds polycyclic aromatic hydrocarbons (PAHs) have been found at high concentrations in sediments (1-4). Our interest is in the reactivity of adsorbed PAHs to aqueous chlorine, which is used in the disinfection processes of many water supply systems and sewage treatment plants.

PAHs are ubiquitous environmental pollutants. Many PAHs are suspected or known potent mutagens and carcinogens that may pose serious human and environmental risks (5, 6), and they have also been recognized as aryl hydrocarbon receptor (AhR) agonists (7–13). Therefore, many papers have recently been published highlighting their effects on health due to their endocrine-disrupting activities (14–18). PAHs are predominantly produced by anthropogenic activities such as the burning of fossil fuels or other combustion sources. The occurrence of PAHs in raw water is due to atmospheric fallout, urban runoff, municipal effluents, industrial effluents, and oil spillage or leakage (1–4, 19–22).

It is well-known that the disinfection process using aqueous chlorine leads to the formation of various chlorinated or otherwise oxidized byproducts. From the viewpoint of toxicity of halogenated PAHs, 1-chloropyrene was reported to be higher mutagenic than pyrene (23). Although reactions of PAHs with aqueous chlorine in the laboratory have been reported in several papers (24-27), such reactions seem not to proceed smoothly in water without a cosolvent due to their hydrophobic property. This paper describes that pyrene, fluorene, and fluoranthene, which are frequently detected in aquatic environments, adsorbed on silica easily react with aqueous chlorine in water to produce various chlorinated or brominated derivatives. Silica was used as a model adsorbent because of its prevalence in the environment and well characterized properties.

#### **Materials and Methods**

**Chemicals.** Pyrene, fluorene, 9-fluorenone, fluoranthene, and 1-bromopyrene [**5**] were purchased from Sigma-Aldrich Chem. Co. Ltd. (Tokyo, Japan). Sodium sulfite, sodium hypochlorite solution (>5% available chlorine), and sodium hypobromite solution (>9% available bromine) were purchased from Wako Pure Chemicals Industries Ltd. (Osaka, Japan). The available chlorine or bromine concentration in the solution was measured by iodometric titration. Ethyl acetate, methanol, and hexane used were purchased from Kanto Co. Ltd. (Tokyo, Japan). Deionized water was used for all the experimental procedures. Silica gel 60N (spherical, neutral) was obtained from Kanto Co. Ltd. (Tokyo, Japan). Diatomaceous earth (chemical grade) and all the other chemicals used were purchased from Wako Pure Chemicals Industries Ltd. (Osaka, Japan).

Syntheses of Chlorinated and Brominated Derivatives of Pyrene as Reference Materials. 1-Chloropyrene [1], 1,6dichloropyrene [2], 1,8-dichloropyrene [3], 1,3,6-trichloropyrene [4], 1,6-dibromopyrene [6], 1,8-dibromopyrene [7], and 1,3,6-tribromo-pyrene [8] were synthesized by the reaction of pyrene with sodium hypochlorite in methanol solution in the presence or absence of potassium bromide. The structures of chlorinated or brominated derivatives of pyrene shown in Figure 1 were determined by FAB-MS and NMR spectroscopy. The detailed synthetic procedures and the spectral data for chlorinated or brominated derivatives of pyrene are provided in the Supporting Information.

Reaction of PAHs Adsorbed on Silica with Sodium **Hypochlorite.** A solution of appropriate PAH (25  $\mu$ mol) in acetone (0.2 mL) was added to silica gel or diatomaceous earth (0.5 g), the mixture was stirred for 30 min, and then acetone was completely removed under reduced pressure. Deionized water (10 mL) was added to the silica-adsorbed PAH, where it had not been detected in the aqueous laver after the suspension had been stirred for 1 h. An aqueous solution of sodium hypochlorite was added to the suspension prepared at pH 5 (by adding 2% hydrochloric acid) or pH 9 (by adding 2% sodium hydroxide), and the mixture (available chlorine, 1 ppm) was stirred at room temperature without serious fluctuation of the pH value. The reactions were started in six vessels at the same time and stopped by adding an aqueous solution of sodium sulfite (1 mM, 0.3 mL) after 1, 2, 3, 6, 12, and 24 h. After the mixture was acidified with 2% hydrochloric acid, ethyl acetate was added to the mixture, and the mixture was stirred for 30 min. After the solids had been removed by filtration, the organic layer of the filtrate was separated. The aqueous layer and the solids on the filter were extracted with ethyl acetate until no peaks due to the products in the extract could be detected by GC-MS analysis.

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pyrene :  $R_1$ =H,  $R_2$ =H,  $R_3$ =H,  $R_4$ =H 1-chloropyrene [1]:  $R_1$ =Cl,  $R_2$ =H,  $R_3$ =H,  $R_4$ =H 1.6-dichloropyrene [2]:  $R_1$ =Cl,  $R_2$ =H,  $R_3$ =Cl,  $R_4$ =H 1.8-dichloropyrene [3]:  $R_1$ =Cl,  $R_2$ =H,  $R_3$ =H,  $R_4$ =Cl 1.3,6-trichloropyrene [4]:  $R_1$ =Cl,  $R_2$ =Cl,  $R_3$ =Cl,  $R_4$ =H 1-bromopyrene [5]:  $R_1$ =Br,  $R_2$ =H,  $R_3$ =H,  $R_4$ =H 1.6-dibromopyrene [6]:  $R_1$ =Br,  $R_2$ =H,  $R_3$ =Br,  $R_4$ =H 1.8-dibromopyrene [7]:  $R_1$ =Br,  $R_2$ =H,  $R_3$ =Br,  $R_4$ =Br 1.3,6-tribromopyrene [8]:  $R_1$ =Br,  $R_2$ =H,  $R_3$ =Br,  $R_4$ =Br 1.3,6-tribromopyrene [8]:  $R_1$ =Br,  $R_2$ =Br,  $R_3$ =Br,  $R_4$ =H



 $\begin{array}{l} 9\text{-fluorenone}: R_9 \!\!=\!\! H, R_{10} \!\!=\!\! H, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! H \\ 2\text{-chloro-9-fluorenone} [14]: R_9 \!\!=\!\! CI, R_{10} \!\!=\!\! H, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! H \\ 4\text{-chloro-9-fluorenone} [15]: R_9 \!\!=\!\! R, R_{10} \!\!=\!\! CI, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! H \\ 2,5\text{-dichloro-9-fluorenone} [16]: R_9 \!\!=\!\! CI, R_{10} \!\!=\!\! H, R_{11} \!\!=\!\! CI, R_{12} \!\!=\!\! H \\ 2,7\text{-dichloro-9-fluorenone} [17]: R_9 \!\!=\!\! CI, R_{10} \!\!=\!\! H, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! H \\ 2,7\text{-dichloro-9-fluorenone} [18]: R_9 \!\!=\!\! CI, R_{10} \!\!=\!\! H, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! CI \\ 2,4,7\text{-trichloro-9-fluorenone} [18]: R_9 \!\!=\!\! CI, R_{10} \!\!=\!\! CI, R_{11} \!\!=\!\! H, R_{12} \!\!=\!\! CI \end{array}$ 



 $\begin{array}{l} \label{eq:result} fluorene: R_5=H, R_6=H, R_7=H, R_8=H\\ 2-chlorofluorene [9]: R_5=Cl, R_6=H, R_7=H, R_8=H\\ 4-chlorofluorene [10]: R_5=H, R_6=Cl, R_7=H, R_8=H\\ 2,5-dichlorofluorene [11]: R_5=Cl, R_6=H, R_7=Cl, R_8=H\\ 2,7-dichlorofluorene [12]: R_5=Cl, R_6=Cl, R_7=H, R_8=Cl\\ 2,4,7-trichlorofluorene [13]: R_5=Cl, R_6=Cl, R_7=H, R_8=Cl\\ \end{array}$ 



 $\begin{array}{l} \label{eq:constraint} fluoranthene: R_{13}=H, R_{14}=H, R_{16}=H, R_{17}=H, R_{18}=H\\ 3-chlorofluoranthene [19]: R_{13}=H, R_{14}=Cl, R_{15}=H, R_{16}=H, R_{17}=H, R_{18}=H\\ 3,4-dichlorofluoranthene [20]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=H, R_{18}=H\\ 3,8-dichlorofluoranthene [21]: R_{13}=H, R_{14}=Cl, R_{15}=H, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 1,3,8-trichlorofluoranthene [22]: R_{13}=Cl, R_{14}=Cl, R_{15}=H, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 3,4,7-trichlorofluoranthene [23]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=Cl, R_{17}=H, R_{18}=H\\ 3,4,8-trichlorofluoranthene [24]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 3,4,7-trichlorofluoranthene [25]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 3,4,7-trichlorofluoranthene [26]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 3,4,8-trichlorofluoranthene [26]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=Cl, R_{18}=H\\ 3,4,8-tetrachlorofluoranthene [27]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=H, R_{17}=Cl, R_{18}=Cl\\ 3,4,8,9-tetrachlorofluoranthene [27]: R_{13}=H, R_{14}=Cl, R_{15}=Cl, R_{16}=Cl, R_{17}=Cl, R_{18}=Cl\\ 3,4,8,9-tetrachlorofluoranthene [27]: R_{13}=H, R_{14}=Cl, R_{15}=Cl\\ 3,4,8,9$ 

FIGURE 1. Structures of pyrene, fluorene, 9-fluorenone, fluoranthene, and their halogenated derivatives.

After the combined organic solution was dried over sodium sulfate, the ethyl acetate was removed under reduced pressure. The residue obtained was subjected to GC-MS analysis.

The reaction of adsorbed pyrene with sodium hypochlorite in the presence of excess potassium bromide ( $125 \mu$ mol) and the reaction with sodium hypobromite were carried out with a method similar to that described above.

Isolation of Chlorinated and/or Oxidized Fluorene and Fluoranthene. To isolate the chlorinated and/or oxidized products, large scale reactions were carried out as follows. The reaction of fluorene or fluoranthene ( $250 \mu$ mol) adsorbed on silica gel (5 g) in deionized water (100 mL) was undertaken with a method similar to that described above. The extract was subjected to preparative HPLC using an ODS-A column ( $50 \times 250 \text{ mm}$ , YMC Co. Ltd., Kyoto, Japan; 80% acetonitrile). The structures of the isolated products were determined by MS and NMR spectroscopy. The spectral data for chlorinated and/or oxidized derivatives of fluorene and fluoranthene are provided in the Supporting Information.

**Analytical Procedure for PAHs.** The gas chromatography (GC) and the gas chromatography/mass spectrometry (GC-MS) measurements were done on a SHIMADZU 14-A gas chromatograph (GC) using flame ionization detector (FID) and a Hewlett-Packard HP-6890 gas chromatograph/HP-5972 mass selective detection (MSD) system for GC-MS. The MSD system was run in the electron impact ionization mode, and the electron energy was 70 eV. Nitrogen was used as the carrier gas for GC and helium for GC-MS. The capillary columns used were either a SUPELCO SPB-35 (35% diphenyl and 65% dimethylsiloxane, coating film thickness 0.25  $\mu$ m, 30 m × 0.32 mm i.d., Sigma-Aldrich Chem. Co. Ltd.) or a DB-5 (5% phenylmethylpolysiloxane, coating film thickness 0.25  $\mu$ m, 30 m × 0.32 mm i.d., J & W Scientific).

The qualitative and quantitative analysis of the chlorinated or brominated pyrene was carried out by GC and GC-MS

using the SPB-35 column. GC-MS analysis was at a flow rate of 1.5 mL/min and an injection temperature of 280 °C. The column temperature was initially maintained at 50 °C for 1.5 min, then was programmed from 50 to 280 °C at a rate of 2 °C /min, with a final hold time of 24 min. The column temperature for GC analysis was programmed from 150 to 250 °C at a rate of 10 °C /min, with a final hold time of 20 min.

GC-MS analysis using the DB-5 column was performed on the products of fluorene, 9-fluorenone, and fluoranthene at a flow rate of 1 mL/min and an injection temperature of 280 °C. The column temperature was initially held at 50 °C for 1.5 min, then was programmed to 150 °C at a rate of 20 °C/min, from 150 to 310 °C at a rate of 8 °C/min, with a final hold time of 15 min.

Ethyl acetate extracts were prepared for analysis by diluting them (1/500) with ethyl acetate. Aliquots (1  $\mu$ L) were then injected on the GC or GC-MS. The yields were shown as a percentage of the mole of chlorinated pyrene, which was provided by calibration curves with a correlation coefficient ( $r^2$ ) ranging from 0.979 to 0.999, to the mole of starting pyrene (25  $\mu$ mol).

## Results

**Reaction of Pyrene Adsorbed on Silica.** We carried out the reaction of PAHs previously adsorbed on silica, where silica gel and diatomaceous earth were adopted as model adsorbents, with aqueous chlorine.

The chromatogram (GC-FID) of the raw products, which were obtained by reacting of pyrene adsorbed on silica gel in water at pH 5 and 9 for 24 h, are shown in Figure 2. The peaks due to monochloro-, dichloro-, and trichloropyrene were observed with a small peak of pyrene at pH 5 and 24 h contact time. Each peak was identified by comparing it with authentic samples, which were synthesized by the



FIGURE 2. Chromatograms (GC-FID) of raw products obtained by reaction of pyrene adsorbed on silica gel or diatomaceous earth (D.E.) in water with sodium hypochlorite (at pH 5 or 9 for 24 h) 1: 1-chloropyrene, 2: 1,6-dichloropyrene, 3: 1,8-dichloropyrene, 4: 1,3,6-trichloropyrene.

reaction of pyrene with sodium hypochlorite in methanol. In the reaction of pyrene itself in water, a large peak due to nonreacted pyrene was found along with very small peaks due to monochloro- and dichloropyrene. The reactivity of pyrene adsorbed on diatomaceous earth was slightly lower than that on silica gel. The difference in reactivity between pH values may be attributed to that the more reactive HOCl prevails at pH 5, and OCl<sup>-</sup> at pH 9. These results suggest that the adsorption of hydrophobic PAHs on silica greatly increased the reactivity of aqueous chlorine. To clarify these adsorption effects, we conducted more detailed studies of the production and the reactions of several other PAHs.

**Time-Course for Reaction of Pyrene Adsorbed on Silica.** The time-course of reaction of the adsorbed pyrene showing formation of its chlorinated derivatives at pH 9 is displayed in Figure 3. In the reaction at pH 9, pyrene adsorbed on silica gel was consumed gradually and decreased to 17% after 24 h. At the same time, 1-chloropyrene [1], 1,6-dichloropyrene [2], 1,8-dichloropyrene [3], and 1,3,6-trichloropyrene [4] gradually increased to 26%, 29%, 19%, and 1% yield, respectively. The reaction behavior of pyrene adsorbed on diatomaceous earth was slightly different from that on silica gel; pyrene rapidly decreased to 27% and product 1 increased to 36% after 3 h. Products 2, 3, and 4 were produced in 15%, 9%, and 1%, respectively, and the yields of these products were similar even after 24 h.

Pyrene adsorbed on silica gel was consumed rapidly at an initial stage of the reaction at pH 5 (data not shown). The production of chlorinated derivatives, not only product 1, but also 2 and 3, started at the same time. The adsorbed pyrene decreased to 5% after 1 h and to below 1% after 24 h resulting in 1 (4%), 2 (22%), 3 (12%), and 4 (12%). Furthermore, peaks with molecular ions corresponding to

trichloropyrene, tetrachloropyrene, and hydroxylchloropyrene were observed in the TIC in addition to the four products described above. Time-course for reaction of pyrene adsorbed on diatomaceous earth was analogous to that on silica gel at pH 5 (data not shown).

**Reactions of Fluorene and Fluoranthene.** Our findings on the reaction behavior of pyrene prompted us to study the reactions of PAHs adsorbed on silica with aqueous chlorine in detail. We carried out the reactions of fluorene and fluoranthene that have frequently been detected in the environment. The TIC of the raw products obtained by the reactions of fluorene and fluoranthene adsorbed on silica gel at pH 5 after 24 h are shown in Figure 4.

The reaction of fluorene adsorbed on silica gel at pH 5 produced many kinds of chlorinated derivatives. The main products were 2-chlorofluorene [9], 2,5-dichlorofluorene [11], and 2,7-dichlorofluorene [12]. Chlorinated derivatives of 9-fluorenone were also produced. They seem to be produced by the oxidation of the corresponding chlorinated fluorenes that are formed first, because the adsorbed 9-fluorenone did not react with aqueous chlorine under similar conditions. 4-Chlorofluorene [10], trichlorofluorene [13, 18], and fluorene dimer were tentatively identified by their MS spectra as minor products.

Many chlorinated derivatives were also produced by the reaction of fluoranthene adsorbed on silica gel at pH 5. The main products were 3-chlorofluoranthene [**19**], 3,8- dichlorofluoranthene [**21**], and 3,4,8-trichlorofluoranthene [**24**], which show the ease of the chlorine substitution at the 3-, 4-, and 8-position.

Bromination of Pyrene with Sodium Hypochlorite in the Presence of Potassium Bromide. Many investigators have reported that bromination takes place in preference to





FIGURE 3. Time-courses for reaction of pyrene (a) suspended in water, adsorbed on (b) silica gel and (c) diatomaceous earth at pH 9;  $\bullet$ , pyrene;  $\diamond$  1-chloropyrene;  $\triangle$  1,6-dichloropyrene;  $\bigcirc$  1,8-dichloropyrene;  $\Box$ , 1,3,6-trichloropyrene.

chlorination in the presence of  $Br^-$  (26, 28–30). We investigated such bromination of adsorbed PAHs. As was expected, the bromination of pyrene adsorbed on silica gel or diatomaceous earth continues to preferentially yield mono-, di-, and tribromopyrene in the presence of potassium bromide (Figure 5), where none of the chlorinated derivative was detected after 24 h.

When this reaction was compared with that using sodium hypobromite, the reaction in the KBr/NaOCl system was observed to be much faster (Figure 6). It is thought that the reaction species in the KBr/NaOCl system is not NaOBr but BrCl which was reported to be very active bromination species (*31, 32*).

#### Discussion

It was reported (*25*, *26*) that 2-chlorofluorene, 2,7-dichlorofluorene, and 9-fluorenone were produced by the reaction of fluorene with aqueous chlorine, and only 3-chlorofluoranthene was detected from fluoranthene. However, in the reaction of silica-adsorbed PAHs we could isolate many chlorinated derivatives as described above. Table 1 illustrates the recovery (%) of used PAHs in the reactions after 24 h. Although the reaction rate estimated roughly depended on the structure of PAHs, especially on pH value, it is obvious that silica-adsorbed PAHs react more rapidly than those in water.

Ringwald et al. (*33*) reported that they estimated the adsorption of gaseous benzene or toluene on silica to occur via  $\pi$ -system—hydrogen bonding with silanol groups on the silica surface on the basis of Raman and FTIR spectroscopy. A silanol group on silica, on the other hand, has acted as a catalyst in organic reactions (*34*–*37*). Therefore, we consider that the electrophilicity of chlorine of hypochlorous acid



FIGURE 4. TIC (GC-MS) of byproducts obtained from reaction with hypochlorous acid (pH 5 for 24 h). (a) Reaction of fluorene suspended in water, (b) reaction of fluorene adsorbed on silica gel, (c) reaction of fluoranthene suspended in water, and (d) reaction of fluoranthrene adsorbed on silica gel. Peak numbers correspond to the compound numbers in Figure 2.

TABLE 1. Rec	overy of	PAHs	(%)	in	the	Reaction	with	Sodium
Hypochlorite	for 24 h							

	silica gel		diatomac	water		
compound	pH 5	pH 9	pH 5	pH 9	pH 5	pH 9
pyrene	0	17	18	29	77	101
fluorene	0	71	34	68	91	89
fluoranthene	5	81	27	58	95	103

increases by hydrogen bonding with silanol on the surface and the interaction between silanol group and  $\pi$ -electron system of PAHs increases the chance of contact with PAHs molecules (Figure 7). The photocatalyzed reaction can be neglected, because we obtained the same result as shown in Figure 2 when a reaction of silica gel-adsorbed pyrene was carried out in a dark place. The difference in reactivity between silica gel and diatomaceous earth can be mainly affected by the structure of silicon dioxide.

The concentrations of PAHs in sediments are generally higher than those in the surrounding water because of their low solubility in water (1-4). Although the chlorination of PAHs in aqueous chlorine has often been reported, little



FIGURE 5. TIC (GC-MS) of brominated products obtained by reaction of pyrene adsorbed on (a) silica gel or (b) diatomaceous earth and (c) suspended in water on adding both sodium hypochlorite and potassium bromide (pH 9 for 24 h). Peak numbers correspond to the compound numbers in Figure 2.



FIGURE 6. Time-courses for decrease in pyrene adsorbed on silica at pH 9;  $\diamond$  on silica gel, with NaOCI+KBr;  $\blacklozenge$  on silica gel, with NaOBr;  $\bigcirc$  on diatomaceous earth, with NaOCI+KBr;  $\blacklozenge$  on diatomaceous earth, with NaOCI+KBr;  $\blacklozenge$  on diatomaceous earth, with NaOBr;  $\times$ , pyrene suspended in water.



#### FIGURE 7. Hypothesized interaction between pyrene adsorbed on silica and hypochlorous acid leading to chlorinated pyrene

attention has been paid to the reaction behavior of PAHs adsorbed on sediment. The reactivity of silica-adosorbed PAHs in this study was demonstrated by employing silica gel and diatomaceous earth as model adsorbents. The reactions of PAHs on such adsorbents with aqueous chlorine proceed rapidly to produce many kinds of chlorinated or brominated PAHs, which seem to again associate with silica (or sediment)

2194 ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 41, NO. 7, 2007

due to their high hydrophobicity. Byproducts adsorbed on sediment, including those generated with an aqueous chlorine or other reactive chemicals, should be investigated from the viewpoint of aquatic environmental pollution.

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## Supporting Information Available

Detailed synthetic procedure for standard chlorinated or brominated pyrene, spectral measurements by FAB-MS and NMR, and spectral data for chlorinated, brominated, and/or oxidized derivatives of pyrene, fluorene, and fluoranthene. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **Literature Cited**

- Simpson, C. D.; Mosi, A. A.; Cullen, W. R.; Reimer, K. J. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. *Sci. Total Environ.* **1996**, *181*, 265– 278.
- (2) Simpson, C. D.; Harrington, C. F.; Cullen, W. R.; Bright, D. A.; Reimer, K. J. Polycyclic aromatic hydrocarbon contamination in marine sediments near Kitimat, British Columbia. *Environ. Sci. Technol.* **1998**, *32*, 3266–3272.
- (3) Busetti, F.; Heitz, A.; Cuomo, M.; Badoer, S.; Traverso, P. Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant. *J. Chromatogr.*, A 2006, 1102, 104–115.
- (4) King, A. J.; Readman, J. W.; Zhou, J. L. Dynamic behaviour of polycyclic aromatic hydrocarbons in Brighton marina, UK. *Mar. Pollut. Bull.* **2004**, *48*, 229–239.
- (5) National Recommended Water Quality Criteria: 2002; 822-R-02-047; Health and Ecological Criteria Division, Office of Science and Technology, U.S. EPA: 2002.
- (6) Environmental Health Criteria 202. Selected Nonheterocyclic Polycyclic Aromatic Hydrocarbons; World Health Organization/ International Program on Chemical Safety: Geneva, 1998.
- (7) Bigelow, S. W.; Nebert, D. W. The Ah regulatory gene product. Survey of nineteen polycyclic aromatic compounds' and fifteen benzo[a]pyrene metabolites' capacity to bind to the cytosolic receptor. *Toxicol. Lett.* **1982**, *10*, 109–118.
- (8) Jones, J. M.; Anderson, J. W. Relative potencies of PAHs and PCBs based on the response of human cells. *Environ. Toxicol. Pharm.* **1999**, *7*, 19–26.
- (9) Machala, M.; Vondracek, J.; Blaha, L.; Ciganek, M.; Neca, J. V. Aryl hydrocarbon receptor-mediated activity of mutagenic polycyclic aromatic hydrocarbons determined using in vitro reporter gene assay. *Mutat. Res.* 2001, 497, 49–62.
- (10) Piskorska-Pliszczynska, J.; Keys, B.; Safe, S.; Newman, M. S. The cytosolic receptor binding affinities and AHH induction potencies of 29 polynuclear aromatic hydrocarbons. *Toxicol. Lett.* **1986**, *34*, 67–74.
- (11) Ziccardi, M. H.; Gardner, I. A.; Denison, M. S. Application of the luciferase recombinant cell culture bioassay system for the analysis of polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* 2002, *21*, 2027–2033.
- (12) Willett, K. L.; Gardinali, P. R.; Sericano, J. L.; Wade, T. L.; Safe, S. H. Characterization of the H4IIE rat hepatoma cell bioassay for evaluation of environmental samples containing polycyclic polynuclear aromatic hydrocarbons. *Arch. Environ. Contam. Toxicol.* **1997**, *32*, 442–448.
- (13) Fent, K.; Batscher, R. Cytochrome O4501A induction potencies of polycyclic aromatic hydrocarbons in a fish hepatoma cell line: Demonstration of additive interactions. *Environ. Toxicol. Chem.* 2000, 19, 2047–2058.
- (14) Santodonato, J. Review of the estrogenic and antiestrogenic activity of polycyclic aromatic hydrocarbons: Relationship to carcinogenicity. *Chemosphere* **1997**, *34*, 835–848.
- (15) Arcaro, K. F.; O'Keefe, P. W.; Yang, Y.; Clayton, W.; Gierthy, J. F. Antiestrogenicity of environmental polycyclic aromatic hydrocarbons in human breast cancer cells. *Toxicology* **1999**, *133*, 115–127.
- (16) Chaloupka, K.; Krishnan, V.; Safe, S. Polynuclear aromatic hydrocarbon carcinogens as antiestrogens in MCF-7 human

breast cancer cells: Role of the Ah receptor. *Carcinogenesis* **1992**, *13*, 2233–2239.

- (17) Gozgit, J. M.; Nestor, K. M.; Fasco, M. J.; Pentecost, B. T.; Arcaro, K. F. Differential action of polycyclic aromatic hydrocarbons on endogenous estrogen-responsive genes and on a transfected estrogen-responsive reporter in MCF-7 cells. *Toxicol. Appl. Pharm.* **2004**, *196*, 58–67.
- (18) Charles, G. D.; Bartels, M. J.; Zacharewski, T. R.; Gollapudi, B. B.; Freshour, N. L.; Carney, E. W. Activity of benzo[*a*]pyrene and its hydroxylated metabolites in an estrogen receptor –a reporter gene assay. *Toxicol. Sci.* 2000, 55, 320–326.
- (19) Monoli, E.; Samara, C. Polycyclic aromatic hydrocarbons in natural waters: Sources, occurrence and analysis. *Trends Anal. Chem.* **1999**, *18*, 417–427.
- (20) Shiraishi, H.; Pilkington, N. H.; Otsuki, A; Fuwa, K. Occurrence of chlorinated polynuclear aromatic hydrocarbons in tap water. *Environ. Sci. Technol.* **1985**, *19*, 585–590.
- (21) Kveseth, K.; Sortlant, B.; Bokn, T. Polycyclic aromatic hydrocarbons in sewage, mussels and tap water. *Chemosphere* 1982, *11*, 623–639.
- (22) Nagai, A.; Kano, Y.; Funasaka, R.; Nakamuro, K. Mutagenic characteristics and contribution of polycyclic aromatic hydrocarbons to mutagenicity of concentrates from municipal river water by blue chitin column. *J. Health Sci.* 2002, *48*, 232–241.
- (23) Colmsjö, A.; Rannug, A.; Rannug, U. Some chloro derivatives of polynuclear aromatic hydrocarbons are potent mutagens in *Salmonella typhimurium. Mutat. Res.* **1984**, *135*, 21–29.
- (24) Onodera, S.; Igarashi, K.; Fukuda, A.; Ouchi, J.; Suzuki, S. Chemical changes of organic compounds in chlorinated water. VXI. Gas chromatographic-mass spectrometric studies of reactions of tricyclic aromatic hydrocarbons with hydrochlorite in dilute aqueous solution. J. Chromatogr., A 1989, 466, 233–249.
- (25) Oyler, A. R.; Liukkonen, R. J.; Lukasewycz, M. K.; Cox, D. A.; Peake, D. A.; Carlson, R. M. Implications of treating water containing polynuclear aromatic hydrocarbons with chlorine: A gas chromatographic mass spectrometric study. *Environ. Health Perspect.* **1982**, *46*, 73–86.
- (26) Oyler, A. R.; Liukkonen, R. J.; Lukasewycz, M. T.; Heikkila, K. E.; Cox, D. A.; Carlson, R. M. Chlorine disinfection chemistry of aromatic-compounds-polynuclear aromatic-hydrocarbons-Rates, products, and mechanisms. *Environ. Sci. Technol.* **1983**, *17*, 334–342.
- (27) Mori, Y.; Goto, S.; Onodera, S.; Naito, S.; Matsushita, H. Aqueous chlorination of tetracyclic aromatic hydrocarbons: Reactivity and product distribution. *Chemosphere* **1991**, *22*, 495–501.

- (28) Nikolaou, A. D.; Golfinopoulos, S. K.; Lekkas, T. D. Formation of organic byproducts during chlorination of natural water. *J. Environ. Monit.* 2002, *4*, 910–916.
- (29) Cowman, G. A.; Singer, P. C. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. *Environ. Sci. Technol.* **1996**, *30*, 16–24.
- (30) Hu, J.; Jin, X.; Kunikane, S.; Terao, Y.; Aizawa, T. Transformation of pyrene in aqueous chlorination in the presence and absence of bromide ion: Kinetics, products, and their aryl hydrocarbon receptor-mediated activities. *Environ. Sci. Technol.* 2006, 40, 487–493.
- (31) Voudrias, E. A.; Reinhard, M. Reactivities of hypochlorous and hypobromous acid, chlorine monoxide, hypobromous acidium ion, chlorine, bromine, and bromine chloride in electrophilic aromatic substitution reactions with *p*-xylene in water. *Environ. Sci. Technol.* **1988**, *22*, 1049–1056.
- (32) Voudrias, E. A.; Reinhard, M. A kinetic model for the halogenation of *p*-xylene in aqueous HOCl solutions containing Cl<sup>-</sup> and Br<sup>-</sup>. *Environ. Sci. Technol.* **1988**, *22*, 1056–1062.
- (33) Ringwald, S. C.; Pemberton, J. E. Adsorption interactions of aromatics and heteroaromatics with hydrated and dehydrated silica surfaces by Raman and FTIR spectroscopies. *Environ. Sci. Technol.* **2000**, *34*, 259–265.
- (34) Kropp, P. J.; Breton, G. W.; Craig, S. L.; Crawford, S. D.; Durland, W. F., Jr.; Jones, J. E., III: Raleigh, J. S. Surface-mediated reactions.
  6. Effects of silica gel and alumina on acid-catalyzed reactions. *J. Org. Chem.* 1995, 60, 4146–4152.
- (35) Patil, V. J.; Mavers, U. Wittig reactions in the presence of silica gel. *Tetrahedron Lett.* **1996**, *37*, 1281–1284.
- (36) Kotsuki, H.; Shimanouchi, T.; Ohshima, R.; Fujiwara, S. Solventfree organic reactions on silica gel supports. Facile transformation of epoxides to β-halohydrins with lithium halides. *Tetrahedron* **1998**, *54*, 2709–2722.
- (37) Das, B.; Banerjee, J.; Ravindranath, N. A simple and facile stereoselective synthesis of (*Z*)- and (*E*)-allyl halides catalyzed by silica supported sodium hydrogen sulfate: factors influencing the yields and stereochemistry of allyl halides. *Tetrahedron* **2004**, *60*, 8357–8361.

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