

FORMATION OF THE CHLORINATED FORMS OF SIX POLYCYCLIC AROMATIC HYDROCARBONS BY CHLORINATION IN THE WATER

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are discharged from various emission source in air environment and in aqueous environment¹. PAHs discharged in the atmosphere are flowed into aqueous environment through falling or rain water^{2,3}. It seems PAHs are received the changes (oxidation, reduction, decomposition, substitution, conjugation etc.) in the aqueous environment by chemical reaction, photoreaction, metabolism of the organism and various treatment processes. Especially, in the case of raw water for drinking water source, these compounds are exposed chlorine in the process for the disinfection in drinking water treatment plant and then are reacted oxidation and/or chlorine displacement. It is known that compounds in water are changed to various reaction products by chlorination. For instance, trihalomethanes and halo-acetic acids were found in the disinfection process as disinfection by products⁴. Among these disinfection by products, there are many compounds causing the adverse effect to the human⁵. However, there is not much information on the reaction products by chlorination in drinking water treatment plant. It is assumed that PAHs also are similarly changed to various reaction products by chlorination in the process for the disinfection. Additionally, it is afraid the reaction products effect on human health^{6,7}. There are few reports about behavior of PAHs during chlorine treatment in water treatment process.

At Dioxin 2005, we presented the identification method for chlorinated benzo[a]pyrene in water⁸. In this paper, we investigated the behavior of six PAHs, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, in chlorine water by gas chromatography with mass spectrometric detection.

Materials and Methods

Chemicals

Fluoranthene (FL), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[ghi]perylene (B[ghi]P), indeno[1,2,3-cd]pyrene (IP), dichloromethane and acetonitrile (pesticide residue PCB analysis grade), methanol (HPLC grade), sodium hypochlorite solution, and L(+)-ascorbic acid sodium salt were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Laboratory water was purified by a Milli-Q gradient A10 Elix system with an EDS polisher (Millipore, Bedford, MA, USA).

Individual stock solutions were prepared to 1000 mg/l in acetonitrile. All stock solutions were stored at -20 °C, whereas working solutions were prepared fresh for each use by dilution of the standard stock solution.

Gas chromatography with mass spectrometric detection (GC/MS)

GC was carried out using an HP6890 Series Gas Chromatograph system (Hewlett Packard, Wilmington, DE, USA) with an HP6890 Series auto-sampler and split/splitless injector. The analytical column was a DB-5 fused silica capillary column, 30 m × 0.25 mm ID, 0.25 mm film thickness (J&W Scientific, Folsom, CA, USA). The oven temperature program was as follows: 100 °C initial temperature for 1 min, ramped at 10 °C/min to 220 °C, at 3 °C/min to 280 °C, holding for 5 or 10 min at 280 °C. The carrier gas (helium) flow was set to 1.2 ml/min. Pulsed splitless injection of a 2 µl volume was carried out at 250 °C. The MS was carried out using a 5973 Mass Selective Detector (Hewlett Packard, Wilmington, DE, USA) in electron ionization mode with an ionization voltage of 70 V and ion source temperature of 280 °C. The instrument was operated in selected ion monitoring (SIM) mode. Two selected ions for each compound were monitored for identification by following mass number (*m/z*); FL:202, mono-chlorinated FL:236, di-chlorinated FL:270, B[b]F:252, mono-chlorinated B[b]F:286, di-chlorinated B[b]F:320, B[k]F:252, mono-chlorinated B[k]F:286, di-chlorinated B[k]F:320,

B[a]P;252, mono-chlorinated B[a]P;286, di-chlorinated B[a]P;320, B[ghi]P;276, mono-chlorinated B[ghi]P;310, di-chlorinated B[ghi]P;344, B[ghi]P;276, IP;276, mono-chlorinated IP;310, di-chlorinated IP;344.

Analytical procedures

The working solutions were prepared from the stock solution with acetonitrile before use. The 6 mg/L working solution was dropped into purified water with 10 mM phosphate buffer (pH 7.0) as mimic tap water. The final concentration of PAH was 3 mg/L and that of acetonitrile was 0.05 % (v/v). After stirring 10 min at room temperature, five hundreds mL was divided as the original water sample, the reaction time at 0 hour. Then, the sodium hypochlorite solution was added to the solution so that the concentration of free chlorine became 1 mg/L. With stirring at 20 °C, five hundreds mL of the solution was taken at the reaction time of 1, 2, 4, 6 and 24 hours, respectively. One mL of 10 g/L sodium ascorbic acid solution was added into five hundreds mL of the sample water solution in order to remove chlorine. The sample water adjusted to pH 3.5 with 9 % (v/v) nitric acid.

The fortified water samples were concentrated according to the SPE method as described below with Oasis HLB Plus Extraction Cartridge (Waters, Milford, MA, USA) prepacked with *N*-vinyl-pyrrolidone polymer resin as described previously¹⁰. The cartridges were equilibrated with 5 ml dichloromethane, 5 ml methanol and 5 ml water, respectively. Extraction of water samples was carried out at a flow rate of approximately 10 ml/min. Air was then passed through the cartridges for 5 min, and nitrogen gas for 10 min. The analytes were eluted from the cartridges with 5 ml dichloromethane. After evaporating the samples to less than 1 ml under a gentle nitrogen steam, the eluate was adjusted to a final volume of 1.0 ml with dichloromethane for GC/MS analysis. The automatic concentrator used was a Sep-Pak Concentrator Plus (Waters, Milford, MA, USA).

Results and Discussion

Condition of Chlorination

The pure water was fortified with 10 mM phosphate buffer (pH 7.0) and 1mg/L free chlorine on the assumption of the quality of tap water. The concentration of free chlorine is ten fold of the drinking water quality standard value in Japan. However, at the exit of the water treatment plant, the concentration of free chlorine in water may be adjusted at 1mg/l to retain the concentration of free chlorine on the tap. If PAHs remain in the treated water without removing under the water treatment process, PAHs might react with chlorine at this concentration or less. So, the concentration of free chlorine was decided at 1 mg/L. The final concentration of PAHs in the experimental water was decided considering the solubility at 3.0 µg/l. In this condition, non-chlorinated PAHs dissolved in water were recovered from 80 % to 120 % by SPE in Materials and Methods.

The concentration of free chlorine was decreased with time-dependent and reached about 0.8 mg/l (80 %) after 24 hours in all case of six kinds of PAH. This means that the quantity of chlorine for the reaction had sufficiently remained after 24 hours and that the reaction had almost perfectly advanced. It indicates the detected reaction products might be a compounds formed under actual water distribution.

Identification of Chlorinated PAHs

The GC/MS system in selected ion monitoring mode was used for the analysis of PAHs and chlorinated PAHs. PAHs decreased with time-dependent in the case of all six kinds of PAH, FL (Fig.1), B[b]F (Fig. 2), B[k]F (Fig. 3), B[a]P (Fig. 4), B[ghi]P (Fig. 5), IP (Fig. 6). FL, B[b]F and B[ghi]P were slowly decomposed in comparison with B[k]F, B[a]P and IP. The time in which the initial concentration decreased to the half was 0.6 hours in B[a]P, 1.5 hours in B[k]F and IP, 3.2 hours in B[b]F, 3.8 hours in B[ghi]P and 4.1 hours in FL (Table). As the initial speed of the reaction, these PAHs can be classified two groups. However, FL, B[ghi]P and IP were

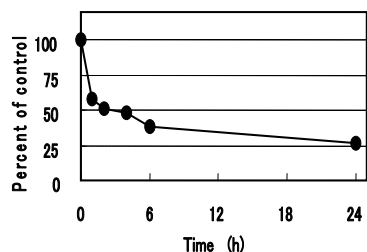


Fig.1 Concentration of FL

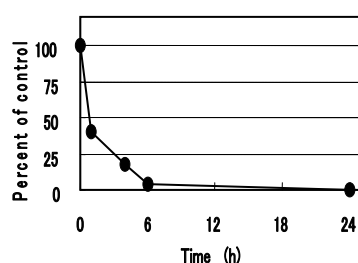


Fig.2 Concentration of B[b]F

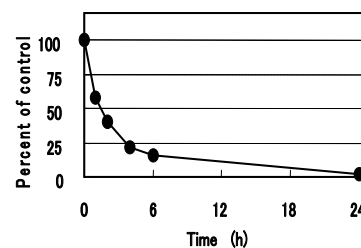


Fig.3 Concentration of B[k]F

Formation, sources and source inventories

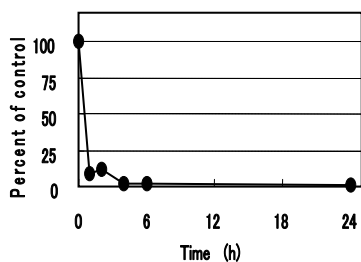


Fig.4 Concentration of B[a]P

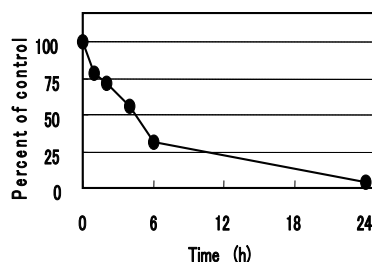


Fig.5 Concentration of B[ghi]P

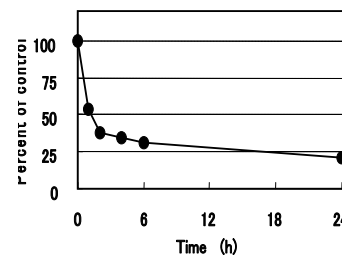


Fig.6 Concentration of IP

detected the original compounds after 24 hours. From these results, the reactivity for the chlorine was sensitive in order of B[a]P>B[k]F>B[b]F=IP>B[ghi]P>FL. If the concentration of the chlorine in reaction solution is higher, the original compounds decompose more quickly (data not shown). The mole ratio of the target compound and free chlorine concentration may be an important element. Mono-chlorinated PAHs were formed in the case of all six kinds of PAH, FL (Fig.7), B[b]F (Fig. 8), B[k]F (Fig. 9), B[a]P (Fig. 10), B[ghi]P (Fig. 11), IP (Fig. 12). Di-chlorinated PAHs were detected in the case of B[k]F and B[a]P. However, tri-chlorinated forms were not detected in this condition. The peak area of mono-chlorinated FL increased with time-dependent until 24 hours. FL remained 27.3 % of the initial concentration after 24 hours. From these results, FL reacted gradually with chlorine for long period

Table Time Decomposing the Half of PAHs by the Chlorination

| Compound | Hours |
|------------------------|-------|
| Fluoranthene | 4.1 |
| Benzo[b]fluoranthene | 3.2 |
| Benzo[k]fluoranthene | 1.5 |
| Benzo[a]pyrene | 0.6 |
| Benzo[ghi]perylene | 3.8 |
| Indeno[1,2,3-cd]pyrene | 1.5 |

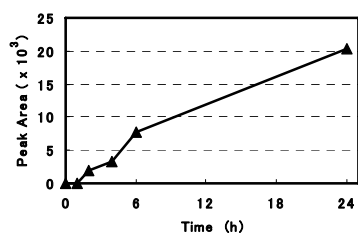


Fig.7 Concentration of chlorinated FL
▲ ;mono-chlorinated form

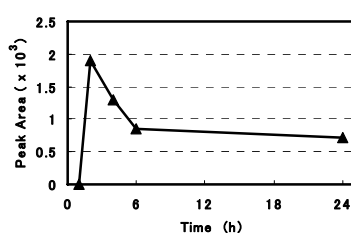


Fig.8 Concentration of chlorinated B[b]F
▲ ;mono-chlorinated form

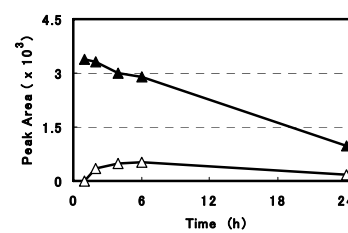


Fig.9 Concentration of chlorinated B[k]F:
▲ ;mono-chlorinated form
△ ;di-chlorinated form

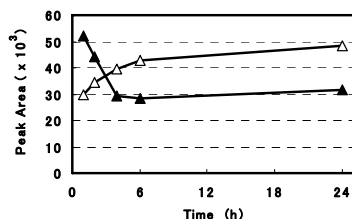


Fig.10 Concentration of chlorinated B[a]P
▲ ;mono-chlorinated form
△ ;di-chlorinated form

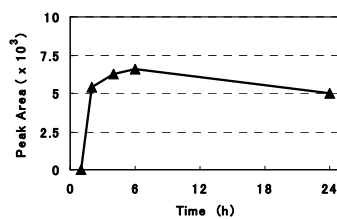


Fig.11 Concentration of chlorinated B[ghi]P
▲ ;mono-chlorinated form

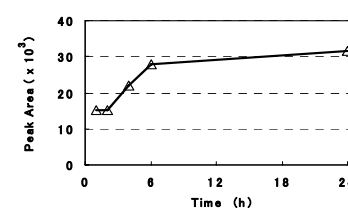


Fig.12 Concentration of chlorinated IP
▲ ;mono-chlorinated form

and changed to a mono-chlorinated form, but it was hard that the mono-chlorinated form changed to a di-chlorinated and a tri-chlorinated forms in this condition. The mono-chlorinated form produced might be stable in chlorine water.

The peak area of mono-chlorinated B[b]F increased maximally within 2 hours after contact with chlorine and decreased gradually until 6 hours and then kept constantly from 6 hours to 24 hours. B[b]F changed to a mono-chlorinated form and the mono-chlorinated form was decomposed gradually to other compounds, because B[b]F decreased immediately (Fig.2). A mono-chlorinated B[b]F may be no so stable in chlorine water. A di-chlorinated B[b]F and a tri-chlorinated B[b]F were not detected.

Unlike B[b]F, B[k]F changed to both a mono-chlorinated form and a di-chlorinated form. The mono-chlorinated B[k]F was detected immediately and decreased with time-dependent. The di-chlorinated B[k]F was detected after 2 hours and increased until 6 hours. B[k]F changed easily to a mono-chlorinated form but the mono-chlorinated form was not stable in chlorine water. The mono-chlorinated form changed gradually to a di-chlorinated form and/or decomposed compounds.

B[a]P rapidly decreased and then reached to 6.6 % of the initial concentration after 2 hour (Fig.3). The peak area of a mono-chlorinated B[a]P increased with time-dependent. The concentration of the mono-chlorinated B[a]P kept constantly from 6 hours to 24 hours. The di-chlorinated B[a]P was detected at 2 hours and increased until 6 hours. The di-chlorinated B[a]P kept from 6 hours to 24 hours at the constant concentration. From these results B[a]P reacted rapidly with the chlorine and changed to the chlorinated forms. First, B[a]P changed to a mono-chlorinated form and gradually changed to a di-chlorinated form. In addition, it seemed di-chlorinated form was substituted more with chlorine or was decomposed.

B[ghi]P changed a mono-chlorinated form. The peak area of the mono-chlorinated form reached maximally between 2 hours and 4 hours. Though the reactivity of B[ghi]P with the chlorine is not high, the mono-chlorinated form formed exists stably for a long period in chlorine water. A di-chlorinated form was not detected in this condition.

IP changed a mono-chlorinated form, but not a di-chlorinated form. The peak area of mono-chlorinated IP increased with time-dependent until 6 hours and kept constantly until 24 hours. Though the reactivity of IP with the chlorine was not high, the mono-chlorinated IP formed gradually for a long time and the mono-chlorinated IP might exist stably for a long period in chlorine water.

In this paper, we show PAHs react with chlorine and change to chlorinated form. It is considered that the chlorination mechanism of PAHs is individually different. It is important to advance the elucidation of the mechanism of the chlorination reaction of PAHs and the evaluation of effects on organism.

Acknowledgements

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