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Preliminary Study of the Photolysis of Fluorene in Rainwater

Yasmin Wai Fon Tham · H. Sakugawa

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic pollutants in the environment. In this preliminary study, photolysis of fluorene, a three-ring PAH, in rainwater collected in Higashi–Hiroshima, Japan, was studied. The photolysis kinetic was observed to be of first order under our experimental conditions. It was found that the photolysis rate constant was approximately 0.091 min^{-1} with a half-life of 8.0 min. The photolysis kinetic of fluorene in rainwater was found to be very much faster than for particulate atmospheric PAHs reported in the literature.

Keywords Photolysis · Fluorene · Rainwater · Half-lives

Polycyclic aromatic hydrocarbons (PAHs) are a group of harmful pollutants in the environment. Many of them demonstrate mutagenic, teratogenic and carcinogenic activities. They are ubiquitous in the ecosphere (Jacek and Dorota 2001). It is difficult for most PAHs to undergo biodegradation and photolysis is one of the major transformation processes for PAHs in the environment (Sabate et al. 2001). Research has shown that the derivatives of PAHs under photolysis could be more toxic than the parent compounds. Therefore, studies on the processes of photolysis of PAHs in the environment are extremely important in order to evaluate the fate and transformation of these hazardous compounds in the environment.

The fall of rainwater is an important deposition process for air pollutants including PAHs (Arantzazu et al. 2004). The toxicity of the rain matrix could pose a negative effect to the final receiving body on the earth (e.g. surface water, soil, vegetation). Photolysis may transform PAHs into other photoproducts which could be more toxic than the parent compounds (Jacek and Dorota 2001). However, to date the photolysis data of PAHs in rain is scarce although it could be a very important atmospheric process in terms of toxicity. Therefore, this study examines the photolysis of PAHs in rainwater in order to understand the fate and transformation of these hazardous compounds. This work reports our preliminary data on the photolysis of fluorene in rainwater. Fluorene, a three ring PAH that is designated a United States Environmental Protection Agency (USEPA) priority PAH, was chosen as a representative due to its relatively high solubility (1.68×10^{-3} g dm^{-3} according to Jacek and Dorota 2001) compared with other high ring PAHs.

Materials and Methods

Fluorene reagents (analytical grade) were purchased from Fluka Co. Ltd. Acetonitrile of HPLC grade was obtained from Kanto Chemicals Co. Ltd. The rainwater samples used in this study were collected on 15 April 2006 at a rooftop location of Hiroshima University in Higashi–Hiroshima city, Japan. The total rainfall collected was 5.7 mm with a pH of 4.93. Ions found in the rain samples included Cl^- (22.9 µM), NO_3^- (9.53 µM), SO_4^{2-} (7.2 µM), Na^+ (34.7 µM) and NH_4^+ (7.6 µM). Fluorene was directly dissolved in rainwater for 3 h under gentle stirring with a magnetic stirrer. The spiked rainwater was filtered with a PALL Ekicrodisc 25 mm syringe membrane filter (0.45 µm pore size) to screen out unsoluble fluorene powder.

Y. W. F. Tham (✉) · H. Sakugawa
Graduate School of Biosphere Science, Hiroshima University,
1-7-1, Kagamiyama, Higashi–Hiroshima 739-8521, Japan
e-mail: waifon@hotmail.com

Under room temperature and atmospheric pressure in the laboratory, it was found that the spiked rainwater had a fluorene concentration of 1.2 mg L^{-1}. In addition, fluorene was directly dissolved in Milli-Q water using the same procedure as above to produce a Milli-Q fluorene aqueous solution with the same concentration (1.2 mg L^{-1}).

The spiked rain samples and the fluorene aqueous solution in Milli Q water served as working solutions for the irradiation experiment. Based on our preliminary investigation, the solutions prepared in this way remain stable for 1 day if stored under 4°C in capped dark brown bottles. Therefore, working solutions were prepared freshly for every experimental batch to minimize any biological, physical or chemical transformation due to prolonged storage. The irradiation experiment was conducted using a solar simulator (Oriel, Model 81160-1000) equipped with a 300 W Xenon lamp (ozone free, Oriel Model 81160) and special glass filters that restricted the transmission of wavelengths below 300 nm. The light intensity was calculated by measuring the degradation rate of a 7.96 μM standard of 2-nitrobenzaldehyde (2-NB) solution in a 60 mL quartz cell. The degradation rate of 2-NB for the lamp employed in the study was 0.0024 s^{-1} whilst natural sunlight on 6 July 2004 at the Hiroshima University campus (at noon under clear sky conditions) was 0.00783 s^{-1} (Khan et al. 2005). Irradiation was carried out for 15 min under gentle stirring in a round shaped 60 mL quartz cell. Sample measuring 500 μL was removed at certain time intervals. Samples were then subjected to immediate analysis.

Samples were analysed by high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector. The adsorption wavelength of the detector was 254 nm. A C18 reverse-phase column (Supelco, LC-18 5 μm × 4.6 mm i.d. × 150 mm length) was used for separation. The instrument was operated in isocratic mode. The mobile phase used was $CH_3CN:H_2O = 60:40$ (v/v) with a flow rate of 1.5 mL min^{-1}. Under this analytical condition, fluorene was found to have a retention time of 12.3 min. Quantitative analysis was carried out by the external standards method. Prior to the analysis, linear calibration was done using standard fluorene solution ranging from 0.06 to 0.20 mg L^{-1}, and gave a regression coefficient higher than 0.99. The quantitative analysis of the fluorene concentration was based on the calibration curve established. Under the analytical conditions, the detection limit for the diluted standard solutions was 0.0024 mg L^{-1}. Milli-Q and rainwater samples that were found to be free of fluorene contamination were spiked with a known amount of standard fluorene solution. These spiked solutions were then analysed by the same procedure as for the other samples. The recoveries obtained were 97.9% and 98.5%, respectively, for spiked Milli-Q and spiked rainwater solutions.

Prior to the experiments, the PALL Ekicrodisc 25 mm syringe membrane filters used were examined for possible fluorene contamination. Milli-Q water free from chemicals (blank solutions) was passed through three new filters and the filtered blank solutions were analysed by the same procedure given above. The fluorene concentrations of the blanks were found to be under the detection limit, indicating that contamination by the filters is negligible. Reproducibility of the analysis was calculated based on a five replicate analysis of diluted standard fluorene solutions with known concentrations. Reproducibility obtained as a relative standard deviation was 5%.

Results and Discussions

Figure 1 shows the photolysis of fluorene under dark and irradiated conditions. It was found that the fluorene concentration in the control (pure water) solutions remained fairly constant under the dark condition with only a slight decrease of not more than 2% (Fig. 1a). This agrees with theory that photodegradation does not occur in the dark (Laifer 1988). On the other hand, biodegradation of a PAH is difficult in a short time period less than 10 days (Degao

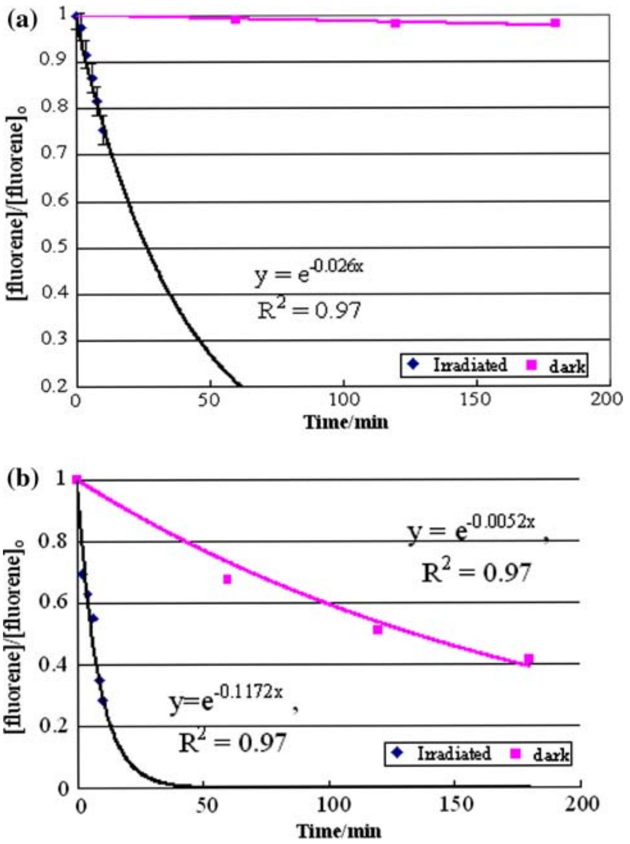

Fig. 1 Degradation trend of fluorene in **a** control, **b** rain water under irradiated and dark conditions

et al. 2005). We believe that the slight decrease in fluorene concentration is probably due to the evaporation of fluorene during sampling at each time interval. However, based on Fig. 1b, it is obvious that there was a significant decrease in the fluorene concentration in rainwater even under dark conditions. The existence of Fenton's reagent, namely hydrogen peroxide and ferrous ion, in rainwater collected in Higashi–Hiroshima has been well-documented by Kim et al. (2002) and PAHs could degrade in the dark by Fenton reaction (Michelle and Matthew 2000; Vanina et al. 2005). We believe that the Fenton reaction was possibly responsible for the decrease in fluorene concentration in this context.

Under irradiated conditions, the photolysis kinetic was observed to be of first-order under our experimental conditions. The decrease in fluorene concentration was drastic for both control and spiked rain solutions compared with those under dark conditions (Fig. 1a, b). The decrease in fluorene concentration seems to have been faster in the irradiated spiked rain solution than in the irradiated control solution. In order to further evaluate the fluorene degradation processes in the spiked rain solution, the kinetic constants and the respective half-lives were computed and are listed in Table 1 together with the findings of other studies.

The photolysis kinetic constant of fluorene in rainwater is approximately 0.091 min^{-1} with a half-life of 8 min. The photolysis kinetic of fluorene in rainwater is approximately three times higher than in pure water (control) (kinetic constant of 0.026 min^{-1} and a half-life of 26.7 min). This strongly suggests the rainwater matrix has a significant effect on the photolysis of fluorene. The existence of various active species such as nitrites, nitrates, hydrogen peroxide and iron species in the rainwater of Higashi–Hiroshima had been well-documented by Kim et al. (2002). In a spiked rain solution, it is believed that photolysis is greatly enhanced by the existence of these species. Nitrates and nitrites can produce hydroxyl radicals after excitation by solar ultraviolet light (Nelieu et al. 2004). Photo-Fenton reaction involving hydrogen peroxide and iron (III)–organic ligand complex gave a significant contribution to OH radical formation in the rainwater collected at our sampling site (Nakatani et al. 2007). The radicals generated could be involved in the photolysis of organics, resulting in an elevation of the kinetic rate (Michelle and Matthew 2000; Nelieu et al. 2004).

PAHs such as fluorene exist in gas, liquid and particulate phases in the atmosphere (Arantzazu et al. 2004). Information on the photolysis of atmospheric gaseous PAHs is scarce in the literature. Ozaki et al. (2005) has studied the photolysis of PAHs in atmospheric particulates collected in Higashi–Hiroshima. They reported half-lives of 52, 171 and 210 h, respectively for fine, coarse and deposited particles under natural solar irradiation at the same sampling site (Table 1). Obviously, the photolysis kinetic in rainwater is very much faster than those in particles with a half-life of only 8 min although both studies involve different methodology which might not be comparable directly. This result suggests that photolysis is a more important transformation process in rainwater than in particles. On the other hand, there have been many studies on the photolysis of fluorene in various media including aqueous solutions. Table 1 lists some reports with half-lives of aqueous fluorene solutions obtained between 2 and 7 min. Compared to these results, the photolysis kinetic of fluorene in our control solution is much slower with a half-life of 26.7 min. We believe the difference is due to different experimental designs and conditions. For instance, the experimental design of other studies involves the addition of organic solvents (Sabate et al. 2001; Jacek and Dorota 2001), acids or alkali solutions (Trapido et al. 1995; Jacek and Dorota 2001) that might alter their systems and allow induced photolysis to occur, whereas in our control solution, fluorene is the only chemical that exists.

Based on our preliminary study, the photolysis of fluorene in rainwater is fast with a kinetic constant of only 0.091 min^{-1}. The fast photolysis kinetic might enable the generation of a significant amount of toxic photoproducts that could have an adverse impact on the receiving environment. Thus, further study is essential, particularly on product identification and the toxicity effect. Our work will

Table 1 Comparison of kinetic constants and half-lives of fluorene degradation processes in rainwater with other samples

Reference	Samples	k (min^{-1})	Half-life, $t_{1/2}$ (min)
This study	Spiked rain	0.091 ± 0.027^{a}	8.0 ± 2.0^{a}
This study	Pure aqueous solution (control)	0.026 ± 0.002^{a}	26.8 ± 1.5^{a}
Ozaki et al. (2005)	Fine particles	9.25×10^{-5}	7,500 (52 h)
	Coarse particles	6.74×10^{-5}	10,300 (171 h)
	Deposited particles	5.48×10^{-5}	13,000 (210 h)
Sabate et al. (2001)	Aqueous solutions	0.35	2.0
Trapido et al. (1995)	Aqueous solutions	0.105	6.6
Jacek and Dorota (2001)	Aqueous solutions	0.099	7.0

[a] Values reported represent mean ± SD

also be expanded to cover other USEPA priority PAHs to obtain a full picture of the ultimate fate and possible effects of PAHs in rainwater.

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