Photocatalytic Decomposition of Atmospheric Toxic Substances on the TiO$_2$-loaded Glasses Set on the Roadside of a Highway

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ABSTRACT

The aims of the present study are to evaluate the effects of the photocatalytic decomposition of toxic atmospheric substances with TiO$_2$ in the actual atmospheric environment. Titanium dioxide loaded glass simulates the function of a sound-proof wall with photocatalysis, which was set on the roadside of a highway. The decomposition of attached substances on the glass was measured in warm and cold periods for polycyclic aromatic hydrocarbons (PAHs) and toxicity. From the measurements of the concentration decrease in PAHs artificially attached to the glass, a significant toxicity decrease by TiO$_2$ photocatalytic decomposition was observed. For the naturally attached toxic substances in the roadside, on the other hand, the decrease was observed less than that of artificial condition. Still, significant decreases were observed for PAHs and Ah-immunoassay in warm periods. For the toxicity of *V. fischeri*, on the other hand, no significant decrease was observed both in cold and warm periods.

Keywords: Ah-immunoassay, atmosphere, PAHs, photocatalysis, toxicity, *Vibrio fischeri*

INTRODUCTION

The load of toxic chemical substances from urban runoff has become a serious problem. These toxic chemicals include polycyclic aromatic hydrocarbons (PAHs), which are a group of organic compounds composed of two or more fused benzene rings that have been linked to carcinogenicity and mutagenicity (Dipple 1985; Vinggaard et al., 2000). In atmospheric environments, PAHs primarily originate from the incomplete combustion of fossil fuels, which results in their emission into the atmosphere and subsequently into water environments. Many researchers have extensively investigated atmospheric and aquatic PAHs pollution (Dickhut et al., 2000; Fernandez et al., 2000; Soclo et al., 2000; Kavouras et al., 2001; Schauer et al., 2001; Martinis et al., 2002; Yunker et al., 2002; Pengchai et al., 2004; Colombo et al., 2006). We have also been studying the behaviour of PAHs and related toxicities in atmospheric and aquatic environments in Hiroshima Bay area (Ozaki et al., 2007, 2012a, b; Iwasaki et al., 2009; Kojima et al., 2010).

In order to clean air pollutants on site, titanium dioxide (TiO$_2$) coating technology has been investigated (Ireland et al., 1995; Garcia-Martinez et al., 2005; Bizani et al., 2006; Woo et al., 2009), and one promising application involves coating road pavements and sidewalls. Studies focusing on NOx demonstrate the photocatalytic decomposition of atmospheric pollutants such as NOx, SOx and organic pollutants (Anpo, 2004). In these reaction processes, some unknown toxic chemicals can be generated due to the reaction
of other chemical compounds. To estimate the effect of TiO\textsubscript{2} in the actual environment, the decrease of PAHs, the toxicity to marine bacteria (\textit{Vibrio fischeri}), and dioxin-like toxicity (Ah-immunoassay) were measured for the atmospheric pollutants attached on the TiO\textsubscript{2}-loaded glasses set on the roadside of a highway. From the results, the effects of photocatalytic decomposition on the mixture of various actual atmospheric toxic substances attached on the TiO\textsubscript{2} surface were discussed.

**MATERIALS AND METHODS**

**Preparation of the photocatalysis glass**

Titanium dioxide loaded glass plate was used as a simulation of the sound-proof wall. Though glasses are not generally used for the sound-proof wall of highways, they are not reactive for photolytic or photocatalytic decomposition and the authors considered that glass would be a good substitute for actual wall surfaces both with or without TiO\textsubscript{2} coating. A solution dissolving TiO\textsubscript{2} (PSA-015, Photo-Catalytic Materials Co. Ltd, Japan) was applied on the glass plate. The major solvent of the solution was ethanol, and finely powdered titanium was suspended in the solution. Using this solution and a heatproof glass plate, TiO\textsubscript{2} glass was made by a method called dip coating. The heatproof glass was soaked into the TiO\textsubscript{2} solution, and was withdrawn vertically at a constant speed (2 mm/s). The glass was coated with the solution. The surface area of glass plate was 13.44 cm\textsuperscript{2} (48 × 28 mm) and the thickness was 2 mm. The coated glass was dried for one hour at 70°C, and was further burned for 1.5 hours at 600°C. After burning, TiO\textsubscript{2} was fixed on the surface of the glass. The blank glass was burned with the AP-7 solution. The solvent was the same as those of PSA-015, but the Ti powder was not contained in the solution.

**Set-up of the glasses**

Toxic atmospheric substances were collected on Sanyo Highway in Higashi Hiroshima, Japan. An average of 2.4 million vehicles use Sanyo Highway per month, according to West Nippon Express Company Limited, which is in charge of the Highway. In this study, in order to simulate a sound-proof wall with photocatalysis, two kinds of glass (TiO\textsubscript{2} and blank) were set vertically beside the highway for naturally attached PAHs experiments. The glass surface areas were 13.44 cm\textsuperscript{2}. The temperature, humidity, rainfall, and intensity of total radiation were obtained from the data of the nearest station of the samplings using Automated Meteorological Data Acquisition System (AMeDAS). The intensity of UV (UV-A + B) was manually measured with a UV-A + B meter at noontime (average was taken for two days sampling). The UV-A + B meter was set horizontally for the measurements. Table 1 summarizes the sampling information for both artificial and natural attachment experiments. Other than the weak rainfall (0.9 mm) in S1, no rainfall occurred during each sampling.
Extraction of toxic chemical substances from the glass

For particulate PAHs, a sample was extracted with dichloromethane (DCM) in an ultrasonic water bath, and the extract was concentrated into 2 mL by N₂-gas. After concentration, the PAH concentration was analyzed using a gas chromatograph equipped with a mass selective detector (GC-17A/MS-QP5050; Shimadzu Co., Japan). The details of the extraction and analysis are shown elsewhere (Iwasaki et al., 2009). Sixteen unsubstituted PAHs were measured (Table 2). The detection limit was set at level 3 in the SN ratio. Instrument detection limits (IDL) ranged from 0.1 – 1 pg for each species. Within this level, the coefficient of variation of each of the compounds was less than 20%.

**Table 1 - Sampling conditions.**

<table>
<thead>
<tr>
<th>Cold</th>
<th>Warm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>A2</td>
</tr>
<tr>
<td>Sampling date</td>
<td>Duration hrs</td>
</tr>
<tr>
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<td>13.8</td>
</tr>
<tr>
<td>24</td>
<td>9.1</td>
</tr>
<tr>
<td>24</td>
<td>9.5</td>
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</table>

**Table 2 - Details of extraction and analysis.**

Extraction of toxic chemical substances from the glass

For particulate PAHs, a sample was extracted with dichloromethane (DCM) in an ultrasonic water bath, and the extract was concentrated into 2 mL by N₂-gas. After concentration, the PAH concentration was analyzed using a gas chromatograph equipped with a mass selective detector (GC-17A/MS-QP5050; Shimadzu Co., Japan). The details of the extraction and analysis are shown elsewhere (Iwasaki et al., 2009). Sixteen unsubstituted PAHs were measured (Table 2). The detection limit was set at level 3 in the SN ratio. Instrument detection limits (IDL) ranged from 0.1 – 1 pg for each species. Within this level, the coefficient of variation of each of the compounds was less than 20%.

**Table 1 - Sampling conditions.**

- **Artificial attachment**
  - A1: 2008/11/02-03
  - A2: 2008/11/10-11
  - A3: 2008/11/11-12

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Duration hrs</th>
<th>Average temp. °C</th>
<th>Average humidity %</th>
<th>UV-A+B W/m²</th>
<th>Total radiation MJ/m²</th>
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<tr>
<td>2008/11/10-11</td>
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<td>9.1</td>
<td>70.6</td>
<td></td>
<td>6.2</td>
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<td>9.5</td>
<td>71.3</td>
<td></td>
<td>24.1</td>
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</table>

- **Highway TiO₂-loaded sound-proof wall experiments (natural attachment).**
  - Cold:
    - S1: 2008/12/09-10
    - S2: 2008/12/10-11
    - S3: 2009/01/05-07
    - S4: 2009/01/14-16
    - S5: 2009/09/18-20
    - S6: 2009/09/20-22
    - S7: 2009/10/20-22
    - S8: 2009/10/22-24
  - Warm:
    - S1: 2008/12/10-11
    - S2: 2009/01/05-07
    - S3: 2009/01/14-16
    - S4: 2009/09/18-20
    - S5: 2009/09/20-22
    - S6: 2009/10/20-22
    - S7: 2009/10/22-24

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Sampling duration hrs</th>
<th>Average temp. °C</th>
<th>Average humidity %</th>
<th>UV-A+B W/m²</th>
<th>Total radiation MJ/m²</th>
</tr>
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<td>2009/09/18-20</td>
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<td>2009/09/20-22</td>
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<td>21.9</td>
<td>66.9</td>
<td>5.4</td>
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<tr>
<td>2009/10/20-22</td>
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<td>12.8</td>
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<td>15.9</td>
<td>61.6</td>
<td>4.6</td>
<td>23.9</td>
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Bioassay methods
The toxicity of organic solvent extracts from the glasses were measured based on the Ah-immunoassay and the attenuation of luminescence of the marine luminescent bacteria *Vibrio fischeri* (NRRL B-11177). To measure them, sample glasses were extracted with DCM using a method similar to that used for PAHs, and the solvents were subsequently transferred by N₂ gas to dimethyl sulfoxide (DMSO), which is less toxic to bacteria.

The AhR immunoassay test was conducted using a measurement kit (Ah IMMUNOASSAY® kit; Paracelsian Inc., USA). The Ah-immunoassay method simulates an important stage in the exertion of the toxicity of dioxins in human bodies, in which dioxins bond with aryl hydrocarbon receptors in human bodies; this process is considered to be the initial important stage of dioxin toxicity.

The toxicity to *V. fischeri* was measured using the ISO 11348-1 (2007) method. Briefly, the bacteria were supplied in a standard freeze-dried state by Strategic Diagnostics Inc. and then cultivated with the designated substrates prior to the experiments. The luminescence was measured using a luminescence microplate reader (LP-5000; Microtech-Nichion Co. Ltd., Japan).

The inactivation ratio was determined by the luminescence attenuation after the 15-minute exposure to the sample solution, and the 1/EC50 was determined from the results by exposure to a series of dilution (Ozaki *et al.*, 2012b).

**RESULTS AND DISCUSSION**

**Photodecomposition of artificially attached PAHs on TiO₂ glass**
The photodecomposition of 16 PAHs artificially attached on the TiO₂ glass was confirmed by preliminary experiment. The 16 PAHs were added on the TiO₂ glass and the blank glass. For the addition, the PAHs solution in DCM was evenly spread on the glass surface and DCM was gently dried with N₂-gas in the dark. The glasses with PAHs were set beside the highway for 24 hours similar to the experiments. One hundred ng of each PAH species (7.4 ng/cm² or 74,400 ng/m²) were spiked on the plate (119 ng/cm² totally for 16 PAHs). The effect of the mass attached naturally was considered to be negligible because the amount of naturally attached PAHs was estimated to be far lower (–10⁻³ times) than that of artificially attached. Figure 1 shows an example of the
decrease of PAH after one day of exposure to sunlight.
From the results, we can see that the amounts of lower molecular weight PAHs (Acty – B(a)A) reduced to almost nothing both on the TiO$_2$ glass and the blank glass. This is probably due to both vaporization and direct photodecomposition. From the results, the ratio of the amount of PAHs after one day to that of PAHs attached initially on blank glass (reflecting the effects of vaporization and direct photodecomposition by the radiation) and the ratio of the amount of PAHs on TiO$_2$ glass to that on blank glass after one day (reflecting the photocatalytic decomposition by the TiO$_2$) were taken for each PAH species. Figure 2 shows the summarized result (A1 – A3) of the ratios. For vaporization + direct photodecomposition (Fig. 2a), the ratio was lower for lower molecular weight species, suggesting enhanced vaporization. The ratio approximated to unity for higher molecular weight species, suggesting the vaporization and direct photodecomposition is less for higher molecular weight species. The ratios for B(a)A and B(a)P were exceptionally lower than the other species. We have also conducted the laboratory experiments of photolysis under UV-A irradiation (black light) (Ozaki et al., 2012a), and when compared (Fig. 3), the decomposition was fairly similar to those obtained under actual sunlight other than the higher decomposition rate of evaporation +

Fig. 2 - Effect of vaporization, direct photodecomposition, and photocatalysis. (geometric mean ± std)
direct photodecomposition for lower molecular weight species (green plots of Acty – B(a)A in Fig. 3a). These differences would be due to the enhancement of vaporization for lower molecular weight species. For B(a)A and B(a)P (and also Ant in some extent), exceptional higher decomposition rates were observed in the laboratory experiment using black light also, suggesting these three species would more easily be degradable by the irradiation directly. Overall, the PAHs attached on the TiO₂ surface is considered to be substantially degradable in the order of a day, under the actual sunlight (Fig. 2b)

**Photocatalytic decomposition of naturally attached PAHs on the TiO₂ glass**

In order to evaluate the photocatalytic decomposition of naturally attached PAHs on TiO₂ along the roadside, TiO₂ and blank glasses were set vertically by the roadside for one to two days, the attached substances were extracted, the amount of PAHs was measured, and the bioassay test was conducted. Figure 4 shows examples of the amount of extracted PAH on the glass for a cold period (S1: 2008/12/09 – 10) and a warm period (S6: 2009/09/20 – 22). From the data, the ratio of the amount of PAHs on the TiO₂ glass to the blank glass was calculated for all the samplings (Fig. 5). This ratio indicates the extent of photocatalysis.

**Fig. 3 - Comparison of UV-A irradiation experiments (black light).**

a) S1 (cold; 2008/12/09 – 10)

**Fig. 4 - Amount of naturally attached PAHs on the glass after 24 or 48 hours.**

(S1 and S6)
Unlike the case of artificially attached PAHs, the difference was not so distinct for the TiO$_2$ glass for each PAH species. The PAHs naturally attached on the TiO$_2$ glasses were not considerably decomposed within one or two days. For cold periods, almost no photocatalysis was observed (Fig. 5a). For warm periods, several PAHs were decomposed (Fig. 5b). However, the tendency for each species was not similar to that of artificially attached (Fig. 3b) and the rate of decomposition seems to be restricted for all the species other than some lower molecular weight species (Acty – Ant). Unlike the case of artificially attached PAHs, other chemical species would also attach on the glasses and these species would possibly influence (in our case, hinder) the decomposition. These species would also attach on the glasses for artificially attached PAHs experiments similarly but the relative amount to the artificially attached PAHs was probably extremely lower than that of naturally attached PAHs experiments, and the effect to the PAHs decomposition would possibly be limited. Another possible difference is the condition of attachment. Since the radicals generated by the irradiation have very short life span, the decomposition reaction would be restricted at only the very surface of the coating. If the naturally attached chemicals were not strongly combined with the surface, e. g., if PAHs attached were contained in particulate matters and not directly attached to the TiO$_2$ surface, the rate of the reaction would also be limited.

Toxicity evaluation based on the Ah-immunoassay and *V. fischeri* test

Table 3 shows the PAHs concentrations, Ah-immunoassay test results and *V. fischeri* test results for all the samples. The PAHs concentrations attached on the glass were $1311 – 3081$ and $2079 – 3685$ ng/(m$^2$·day) for TiO$_2$ and blank glass, respectively. The Ah-immunoassay results were $10.7 – 139.3$ and $36.9 – 145.1$ ng TCDD/(m$^2$·day) for TiO$_2$ and blank glass, respectively. The toxicities to *V. fischeri* were $0.11 – 34.25$ and $0.17 – 23.35$ L/(m$^2$·day) for TiO$_2$ and blank glass, respectively. The concentrations were compared between the TiO$_2$ and blank glasses for the PAHs and toxicities using a paired t-test for the cold, warm, and whole periods. The significant concentration differences were found for PAHs and Ah-immunoassay for the warm periods and the whole periods. For the cold periods, on the other hand, no significant differences were found for all the indices. This was supposedly due to the lower irradiation for the winter seasons. For the *V. fischeri* toxicity, on the other hand, no significant difference was
found for both the cold and warm periods. Overall, PAHs and dioxin-like toxicity (Ah-immunoassay) can be considered as photocatalytically decomposed. Some PAH species, e.g., B(b)F, B(k)F, B(a)P, Ind, are known to be reactive to aryl hydrocarbon receptor (Kobayashi and Uechi, 2002). From the data of cross-reactivity to the aryl hydrocarbon receptor of PAHs (Kobayashi and Uechi, 2002), the contribution of five PAHs (B(a)a, B(b)f, B(k)f, B(a)p, and Ind) to the whole AhR reactivity was evaluated. However, the sum of the reactivity of the five PAHs was not simply correlated to AhR reactivity. Still, the sum of five PAHs reactivity contribution was calculated to be comparable to the whole toxicity (10 – 90%), and the PAHs would possibly behave as the representatives of the dioxin-like toxic substances.

The higher stability of *V. fischeri* toxicity on the TiO₂ compared with the blank glass means the refractory to photocatalytic decomposition of toxic substances. The one possible explanation of different tendencies between the PAHs and *V. fischeri* toxicity is that the contribution of PAHs toxicities to *V. fischeri* was far lower than the other attached toxic substances, and the other toxic substances were not easily decomposed on TiO₂ surface. The toxicity of individual PAHs has been obtained for several species (Jacobs *et al.*, 1993). From the results, the contribution of the sum of the evaluated PAHs (Acty, Acen, Flu, Phe, Ant, Flt, Pyr, B(a)a, Chr, and B(a)p; Pyr toxicity was measured by the authors (EC50 = 9.65 mg/L)) was calculated under the assumption of linearity and additivity of 1/EC50, and the contribution of 10 PAHs was only 1 – 10%. Hence, other toxic substances, which are not easily decomposed by the irradiation, would possibly influence the toxicity results for *V. fischeri*.

**CONCLUSIONS**

The attachment and photocatalytic decomposition of PAHs or other toxic chemical substances were evaluated for a simulated TiO₂-loaded soundproof wall set beside a highway. For the experiments, two types of glasses, with/without TiO₂ were applied as simulated soundproof walls. From the measurements, the PAHs artificially attached on the TiO₂ glasses were decomposed with TiO₂. From the experiments of naturally attached PAHs on the glasses, the significant decreases in the amounts of PAHs and dioxin-like toxicity were found on the TiO₂ glasses. On the other hand, no significant decrease was found for *V. fischeri* toxicity. This implies that PAHs and dioxin-like toxicity can be decomposed photocatalytically, but toxic substances against *V. fischeri* are not easily decomposed. The photocatalytic decomposition rate of PAHs was
different between the artificially and naturally attached conditions. The different attachment status would possibly influence the decomposition but the reason was not clarified in this study. The status of attachment of the pollution should be investigated in the actual environments for the further studies.

REFERENCES


