

Article

Photocatalytic Degradation of Polycyclic Aromatic Hydrocarbons in Fine Particulate Matter (PM_{2.5}) Collected on TiO₂-Supporting Quartz Fibre Filters

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Abstract: Airborne fine particulate matter (PM_{2.5}) pollution is known to have adverse effects on human health, and owing to their carcinogenic and mutagenic nature, polycyclic aromatic hydrocarbons (PAHs) are of particular concern. This study investigated the effect of ultraviolet (UV)-induced photocatalysis on the degradation of PAHs in PM_{2.5}, employing titanium dioxide (TiO₂)-supporting quartz fibre filters. A TiO₂ layer was formed on the quartz fibre filters, and airborne PM_{2.5} was collected using an air sample at a flow rate of 500 L/min for 24 h. The PM_{2.5} samples were subsequently irradiated with ultraviolet rays at 1.1 mW/cm². The amounts of nine targeted PAHs (phenanthrene, PHE; anthracene, ANT; pyrene, PYR; benzo[a]anthracene, BaA; chrysene, CHR; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene, BkF; benzo[a]pyrene, BaP; and benzo[g,h,i]perylene, BgP) gradually decreased during the treatment, with half-lives ranging from 18 h (PHE) to 3 h (BaP), and a significantly greater reduction was found in comparison with the PAHs collected in the control (non-TiO₂ coated) quartz fibre filters. However, the degradation rates were much faster when the PAHs were in direct contact with the TiO₂ layer. As PM_{2.5} is a mixture of various kinds of solids, co-existing components can be a rate-determining factor in the UV-induced degradation of PAHs. This was demonstrated by a remarkable increase in degradation rates following the removal of co-existing salts from the PM_{2.5} using water treatment.

Keywords: polycyclic aromatic hydrocarbons (PAHs); particulate matter (PM_{2.5}); photocatalysis; quartz fibre filter; TiO₂; degradation



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1. Introduction

The air pollution caused by particulate matter with a size of 2.5 µm or less (PM_{2.5}) is one of the main health risks globally, causing significant excess mortality and reductions in life expectancy [1]. Increased mortality associated with exposure to PM_{2.5} has been documented in numerous epidemiological studies, linked to pulmonary and cardiovascular diseases [2–7]. PM_{2.5} is a mixture of various solids and droplets emitted and/or generated from natural and anthropogenic sources and, therefore, the possibility of adverse health effects may depend on the chemical contaminants in the PM_{2.5} at a receptor site [8].

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds containing two or more fused rings of carbon and hydrogen atoms, and represent ubiquitous contaminants in the environment [9]. These compounds are generated mainly from anthropogenic sources, such as fossil-fuel burning, coal production, oil manufacturing, oil spills, wood preservation, tobacco smoke, various forms of cooking, and occasionally from natural sources such as volcanoes and forest fires [10,11]. When emitted into the air, PAHs readily condense onto the PM_{2.5} owing to the lower vapour pressure. PAHs have been identified as important mediators of adverse health effects due to their carcinogenic and mutagenic nature [12–15]. For example, the International Agency for Research on Cancer (IARC)

has classified several PAHs into the groups A (carcinogenic to humans), 2A (probably carcinogenic to humans), and 2B (possibly carcinogenic to humans) [16] depending on their level of carcinogenicity. Of the hundreds of known PAHs, 16 have been designated as high-priority pollutants by the United States (U.S.) Environmental Protection Agency (EPA) [17] because of their potential toxicity to humans and other organisms as well as their prevalence and persistence in the environment [18].

The photocatalysis of titanium dioxide (TiO_2) has been extensively studied for its application in environmental remediation [19], which relies on the generation of active oxidants (e.g., OH radicals) to trigger the oxidative degradation of a broad range of organic compounds. Although photocatalytic oxidation has been applied to the degradation of PAHs in soil and water samples [20,21], no previous studies have reported its application for the treatment of PAHs in atmospheric $\text{PM}_{2.5}$.

Air-filtration technology (e.g., filter masks and air-cleaning devices) is widely used to prevent personal exposure to $\text{PM}_{2.5}$. However, the $\text{PM}_{2.5}$ trapped on the surface of the filters still has hazardous properties if not subsequently treated owing to its potentially toxic constituents, including PAHs. Therefore, there is a potential risk of human contact with the condensed $\text{PM}_{2.5}$ when replacing or cleaning filter-units. We previously developed a TiO_2 -supporting quartz fibre filter (TiO_2 filter) for the collection of $\text{PM}_{2.5}$ and subsequently applied this to the degradation of the carbonaceous components in $\text{PM}_{2.5}$ [22]. Our results showed that the total carbon content in $\text{PM}_{2.5}$, measured by a carbon analyser, gradually decreased with time during ultraviolet (UV) irradiation, and carbon dioxide (CO_2) was the major product [22]. However, the application of this kind of treatment remains untested for individual organic compounds such as PAHs. Therefore, here, we aimed to investigate the effect of UV-induced photocatalysis on the degradation of PAHs in $\text{PM}_{2.5}$ following its collection on a TiO_2 filter (Figure 1).

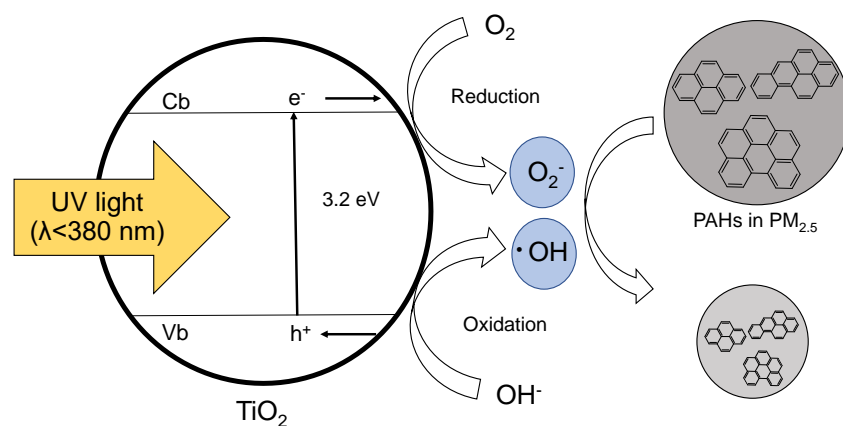


Figure 1. Conceptual schematic of the photocatalytic degradation of polycyclic aromatic hydrocarbons (PAHs) in fine particulate matter ($\text{PM}_{2.5}$).

2. Results and Discussion

2.1. $\text{PM}_{2.5}$ Collection Using the TiO_2 Filter

As a quartz fibre filter is commonly used for sampling $\text{PM}_{2.5}$ and withstands temperatures up to 1000°C , it was used as the supporting material for the TiO_2 . Following the method of Misawa et al. [22], a TiO_2 layer was formed on the surface of the individual quartz fibres by calcinating titanium tetraisopropoxide (TTIO). By considering the suction pressure of the air sampler and adjusting the TTIO concentration, the amount of TiO_2 supported on the filter was estimated as approximately 0.05 g/filter [22]. The actual amount was subsequently determined as the difference in mass before and after calcination, which was calculated to be $0.0478 \pm 0.0051 \text{ g/filter}$ ($n = 3$).

The $\text{PM}_{2.5}$ samples were collected using a high-volume air sampler to pass outdoor air through the TiO_2 and quartz filters at a flow rate of 500 L/min for 24 h on the roof

of the Tokai University building, Kanagawa, Japan. Figure 2 shows the high-volume air samplers used and the typical appearance of PM_{2.5} collected on the TiO₂ filter. The photocatalytic degradation rate is dependent on the UV intensity. Based on Misawa et al.'s [22] observations of significant decreases in the carbonaceous content of the PM_{2.5} at a peak wavelength of 365 nm at 1.1 mW/cm², we employed the same irradiation conditions in this study. Figure 3 shows the scanning electron microscope (SEM) images of individual PM_{2.5} particles collected on the quartz and TiO₂ filters before and after UV-irradiation for 72 h. While no remarkable changes were observed for the PM_{2.5} collected on the quartz filter (as a control), numerous particles disappeared from the TiO₂ filter, which we attributed to the photocatalytic degradation of organic compounds. To quantify this effect, the PAH contents in the PM_{2.5} were measured before and after the UV-irradiation treatment.

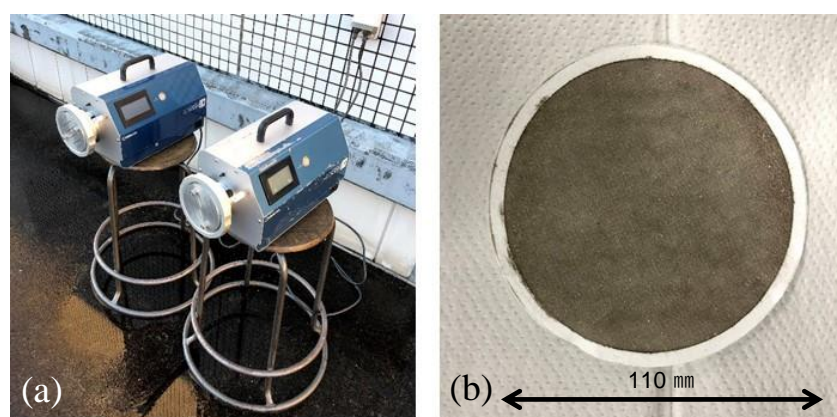
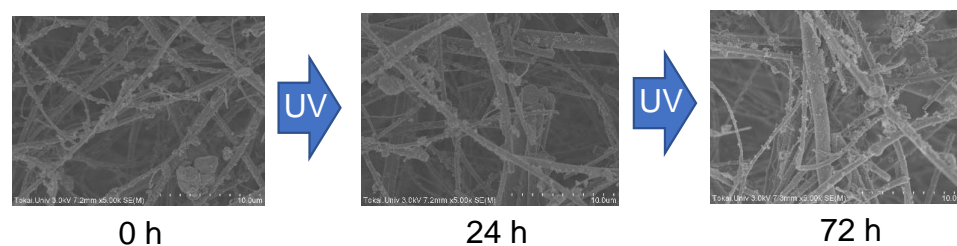


Figure 2. (a) High-volume air samplers and (b) typical PM_{2.5} samples collected on the titanium dioxide-supporting quartz fibre filter (TiO₂ filter).

a) Quartz filter



b) TiO₂ filter

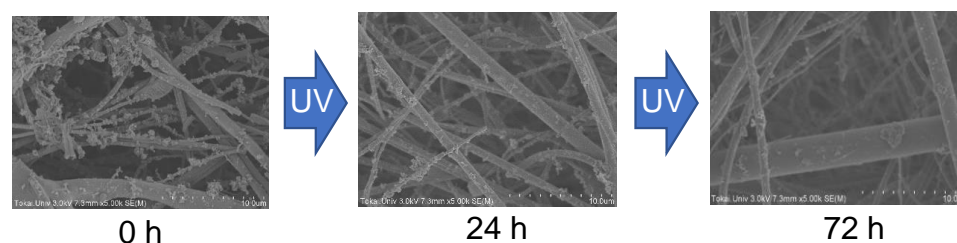


Figure 3. Scanning electron microscope (SEM) images of PM_{2.5} particles collected on (a) quartz filter and (b) TiO₂ filter before and after ultraviolet (UV) irradiation (365 nm, 1.1 mW/cm²).

2.2. Photocatalytic Degradation of PAHs in PM_{2.5}

Simultaneous sampling of the PM_{2.5} was conducted using two co-located high-volume air samplers with the TiO₂ and quartz (non-TiO₂ coated) filters, respectively. The concentrations of PM_{2.5} collected on the TiO₂ and quartz filters were very similar at $20 \pm 7.0 \mu\text{g}/\text{m}^3$ ($n = 3$) and $19 \pm 7.5 \mu\text{g}/\text{m}^3$ ($n = 3$), respectively. As these 24 h mean concentrations were slightly lower than the World Health Organisation (WHO) air quality guidelines ($25 \mu\text{g}/\text{m}^3$), the status of the PM_{2.5} air pollution at the study site was not severe.

Among the 16 PAHs designated as high-priority pollutants by the U.S. EPA, 9 were targeted in this study (phenanthrene, PHE; anthracene, ANT; pyrene, PYR; benzo[a]anthracene, BaA; chrysene, CHR; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene, BkF; benzo[a]pyrene, BaP; and benzo[g,h,i]perylene, BgP), considering the higher volatility (i.e., a lower fraction in the particle phase) of PAHs containing 2–3-member rings [23] and the analytical sensitivity of each compound. Table 1 shows the average amount of these different PAHs detected in the three pairs of PM_{2.5} samples before UV-irradiation (the initial amount of the PAHs, m_0). No significant differences were found between the amounts on the two types of filters. Generally, the PAHs detected as trace components: in total, the nine PAHs accounted for only 0.006% of the collected PM_{2.5} material.

Table 1. Amounts of nine PAHs collected on quartz filters and TiO₂ filters (ng/filter) before UV-irradiation.

	Quartz Filter	TiO ₂ Filter
PHE	182 ± 47	196 ± 45
ANT	8.7 ± 2.0	9.3 ± 2.0
PYR	142 ± 39	151 ± 41
BaA	48 ± 15	61 ± 28
CHR	97 ± 34	111 ± 25
BbF	113 ± 47	148 ± 19
BkF	38 ± 17	45 ± 18
BaP	70 ± 32	89 ± 41
BgP	99 ± 29	121 ± 46

The PM_{2.5} samples were subsequently irradiated with UV light ($1.1 \text{ mW}/\text{cm}^2$) and the amounts of the nine target PAHs (m) were measured at 6, 12, and 24 h after irradiation. Figure 4 shows the trends in the PAHs after being normalised by the initial amounts (m/m_0 , %). In the case of the quartz filter, a slight decrease was observed for each PAH and the m/m_0 percentages after 24 h were as follows: PHE, $60 \pm 4.2\%$; ANT, $75 \pm 5.0\%$; PYR, $74 \pm 9.9\%$; BaA, $69 \pm 6.0\%$; CHR, $82 \pm 9.2\%$; BbF, $84 \pm 9.7\%$; BkF, $83 \pm 11\%$; BaP, $85 \pm 9.3\%$; and BgP, $83 \pm 97\%$. These reductions likely resulted from a combination of heat-induced evaporation by UV-irradiation and UV-induced decomposition [24,25].

In comparison with the quartz filters, significantly greater decreases in m/m_0 were found for the PAHs collected on the TiO₂ filters ($p < 0.05$, at 24 h), as follows: PHE, $37 \pm 8.2\%$; ANT, $50 \pm 2.1\%$; PYR, $46 \pm 3.1\%$; BaA, $45 \pm 5.2\%$; CHR, $46 \pm 0.38\%$; BbF, $56 \pm 2.2\%$; BkF, $58 \pm 3.3\%$; BaP, $60 \pm 4.3\%$; and BgP, $48 \pm 8.2\%$. This shows that the photocatalysis of TiO₂ is effective at enhancing the degradation of nine of the most harmful PAHs present in PM_{2.5}.

By assuming first-order kinetics, the half-lives ($t_{1/2}$) of the PAHs in the PM_{2.5} can be obtained based on the obtained degradation rates (k (/h)), using the m/m_0 trends shown in Figure 4, where the following applies:

$$\ln(m/m_0) = -kt \quad (1)$$

$$t_{1/2} = \ln 2/k \quad (2)$$

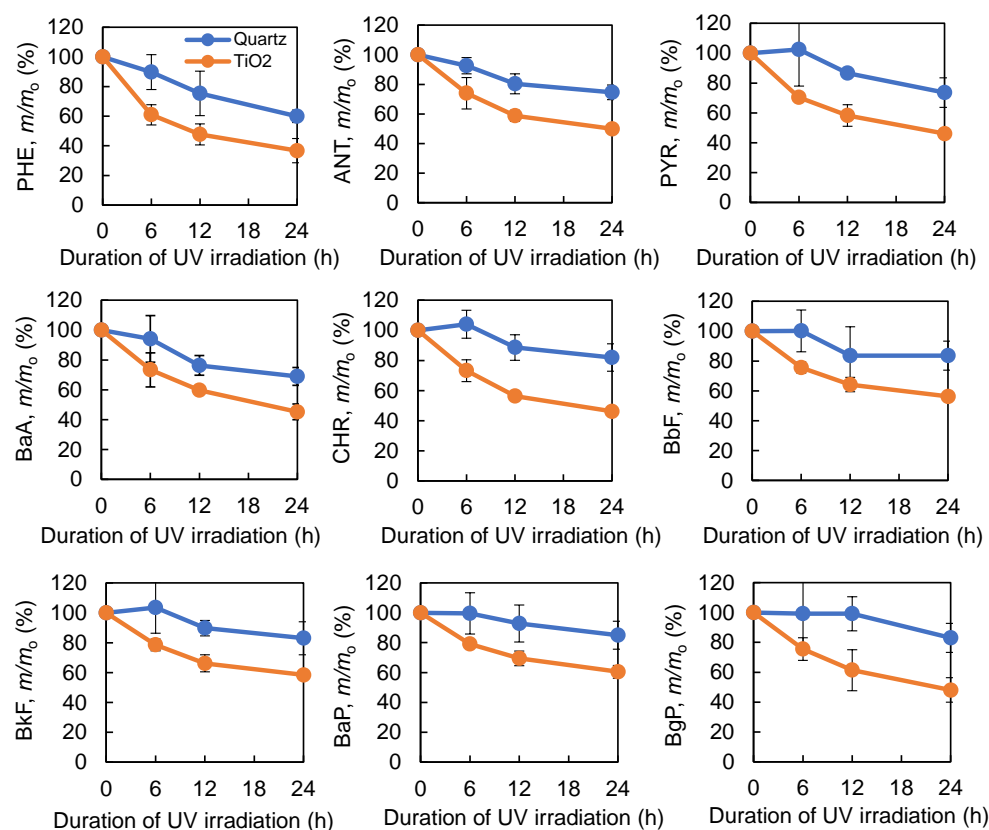


Figure 4. UV-induced degradation of PAHs in PM_{2.5} collected on quartz filters and TiO₂ filters. Plots show the averages of three samples and error bars show the standard deviations.

This yields the following half-lives for the studied PAHs: PHE, 18 h; ANT, 25 h; PYR, 23 h; BaA, 20 h; CHR, 22 h; BbF, 31 h; BkF, 31 h; BaP, 33 h; and BgP, 21 h. However, these times appear to be too long for this method to be effectively employed as a practical remediation strategy. As a comparison, the molecules of the nine PAHs were placed in direct contact with the TiO₂ and quartz filters by adding an aliquot of standard PAH solution (acetonitrile/methanol) and subjected to UV light at 1.1 mW/cm². The initial amounts of the PAHs were as follows: PHE, 85 ng/filter; ANT, 38 ng/filter; PYR, 176 ng/filter; BaA, 96 ng/filter; CHR, 98 ng/filter; BbF, 38 ng/filter; BkF, 40 ng/filter; BaP, 93 ng/filter; and BghiP, 150 ng/filter. These amounts were comparable to those present in the PM_{2.5} samples collected from the field (Table 1). As shown in Figure 5, after UV-irradiation for just 0.5 h, the amounts of the target PAHs immediately decreased to below or close to detection limits in the case of the TiO₂ filter. As several PAHs are known to be labile to UV [24,25], the amounts of the PAHs—especially ANT and BaP—immediately decreased, even in the case of the quartz filters. This indicates the action of a rate-regulating factor in the degradation of PAHs in PM_{2.5}.

2.3. Effect of Water-Soluble Salts on the Photocatalytic Degradation of PAHs

When the catalytic degradation of environmental contaminants is conducted on a homogeneous interface (solid–solid), the efficiency potentially depends on the contact between the targets and the catalyst. Di Sarli et al. [26] showed the importance of strategies that avoid or minimise the segregation between soot particles and the catalyst to regenerate diesel particulate filters. Lee and Choi [27] conducted the solid-phase photocatalytic reaction on the soot/TiO₂ interface and described that the migrating nature of the active oxidants should be taken into account in the quantitative understanding of photocatalytic reaction mechanisms. As shown in Figure 2, a few particles remained on the TiO₂ filter surface even after UV-irradiation. These particles mainly consisted of inorganic constituents

including sulphates, nitrates, metal oxides, elemental carbon (which is inert to TiO_2 photolysis), and porous carbonaceous particles [22]. Mayama et al. [28] observed the structure and composition of individual aerosol particles using a time-of-flight secondary mass spectrometer (TOF-SIMS) and found black carbon, which is an incomplete-combustion effluent that usually contains PAHs, present on the surface of sulphate surrounded by organic matter, probably non-volatile fatty acids [29]. Based on these observations, the PAHs in $\text{PM}_{2.5}$ that are not in direct contact with the TiO_2 layer, and co-existing solid components may prevent active oxidants from reacting with the PAHs. Therefore, we attempted to change the structure of the $\text{PM}_{2.5}$ collected on the TiO_2 filter by removing water-soluble salts.

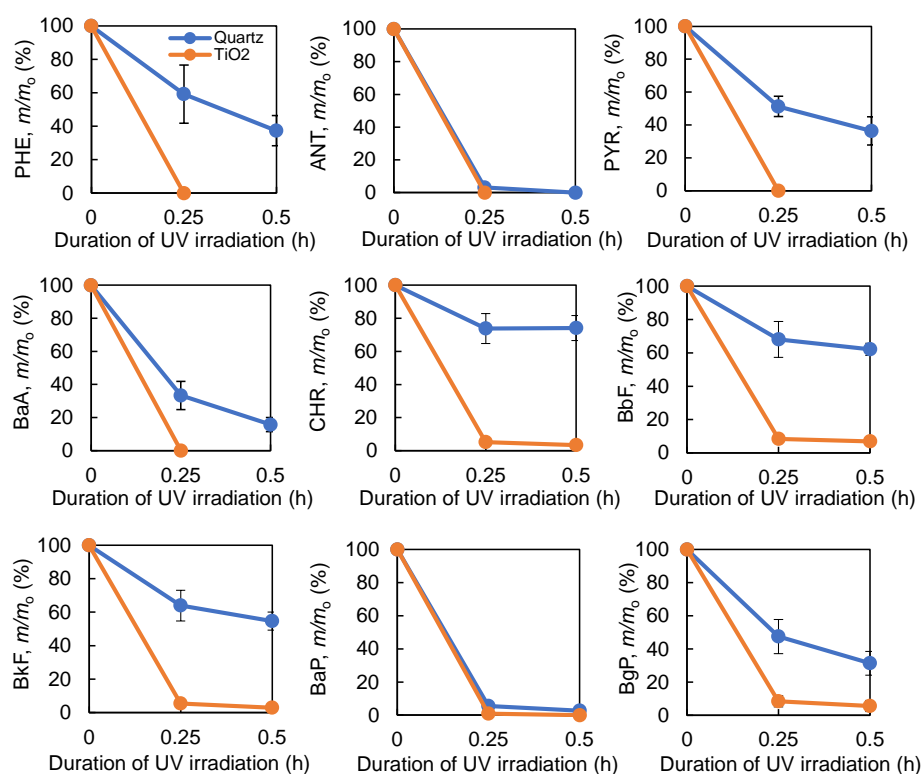


Figure 5. UV-induced degradation of PAHs in direct contact with quartz filters and TiO_2 filters following addition of a PAH solution. Plots are the average of three samples and the error bars show the standard deviations.

Figure 6 shows the changes in the amounts of water-soluble ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) before and after treatment with Milli-Q water (0.5 L). Overall, 93% of the ions were easily removed by the water treatment. Even though PAHs are insoluble in water, 30% of the nine targeted PAHs were removed by the water treatment, probably due to volatilisation by the subsequent drying process (40°C for 1 h) and/or co-elution with finer particles. The $\text{PM}_{2.5}$ samples with and without the water treatment were then irradiated with UV at $1.1\text{ mW}/\text{cm}^2$ and the target PAHs were measured at intervals of 2.5 h for 7.5 h. Compared to the TiO_2 filter without the salts removed, remarkable decreases in m/m_0 were observed for all PAHs in the treated (salt-removed) $\text{PM}_{2.5}$ samples (Figure 7). This demonstrates that co-existing solid components in $\text{PM}_{2.5}$ can act as a rate-regulating factor in the UV-induced degradation of PAHs, likely by reducing the light intensity reaching photo-labile PAH molecules and preventing the diffusion of active oxidants generated by the TiO_2 layer. As such, the overall degradation rate of the PAHs was affected by the structure of the solid mixture of $\text{PM}_{2.5}$ collected on the TiO_2 filter.

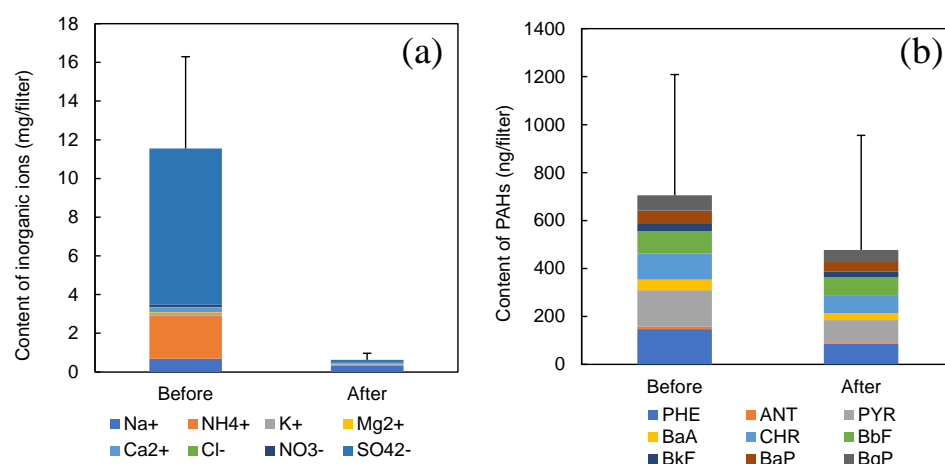


Figure 6. Effect of water treatment on the contents of (a) water-soluble ions and (b) nine PAHs. Bars show the averages and standard deviations of three repeat experiments.

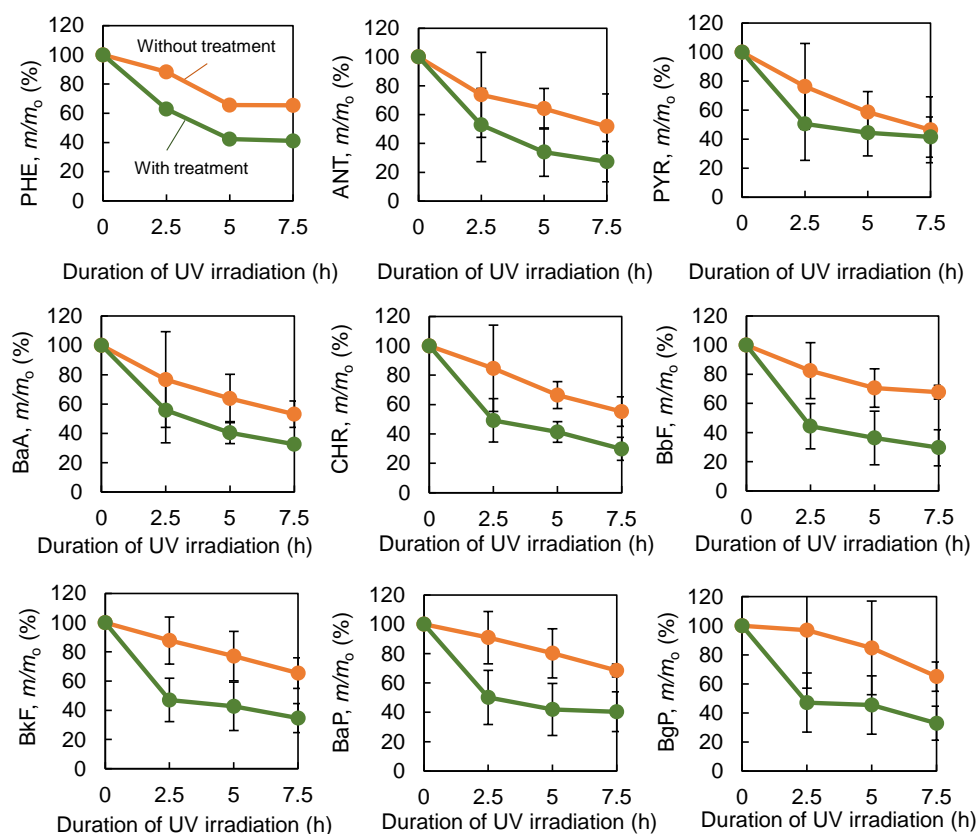


Figure 7. UV-induced degradation of PAHs in PM_{2.5} collected on TiO₂ filters with and without water treatment to remove co-existing water-soluble salts. Plots show the averages of three samples and the error bars show the standard deviations.

3. Experimental Details

3.1. Preparation of TiO₂ Filter

The TiO₂ filter was prepared following the method described by Misawa et al. [22]. Briefly, a piece of quartz fibre filter (Advantec, Tokyo, Japan, diameter = 110 mm ϕ , thickness = 0.38 mm, SiO₂ > 99%) was added to 2% titanium tetraisopropoxide (Kanto Chemical, Tokyo, Japan, reagent grade) in 2-propanol (Kanto Chemical, reagent grade) solution for 1 h. After drying at ambient air temperature, the filter was calcined at 500 °C

for 2 h in an electronic furnace (Thermo Fisher Scientific, Waltham, MA, USA, FB1400) to obtain a TiO_2 layer supported on the quartz fibre filter. The morphology of the TiO_2 layer was observed using a field-emission SEM (Hitachi, Tokyo, Japan, S-4800) after coating with a thin Au/Pt film to obtain higher-quality secondary electron images. The crystalline structure of the TiO_2 was also observed using X-ray diffraction instrument (Rigaku, Tokyo, Japan, Gaiger Flex RAD-C).

3.2. Sampling $\text{PM}_{2.5}$ on the TiO_2 Filter

The airborne $\text{PM}_{2.5}$ was collected on the TiO_2 filter using a high-volume air sampler (Shibata, Tokyo, Japan, HV-500R) attached to a particle-size selector for the $\text{PM}_{2.5}$, with a flow rate of 500 L/min. The sampler was positioned on the roof of the Tokai University building, Kanagawa, Japan ($35^\circ 21' 42.4''$ N, $139^\circ 16' 29.0''$ E) approximately 20 m above the ground for 24 h. All sampling was conducted between May 2018 and September 2019. Before and after sampling, the filters were conditioned for more than 24 h at a constant temperature (21°C) and relative humidity ($40 \pm 4\%$). Thereafter, weight measurements were obtained using a microbalance. The concentrations of $\text{PM}_{2.5}$ were subsequently determined from the weight difference and the total sampling volume of air. As a control, the $\text{PM}_{2.5}$ was collected and measured in the same manner using uncoated quartz filters whose collection efficiency was 99.99% for $0.3\ \mu\text{m}$ of diethyl phthalate at a rate of 5 cm/s [30].

3.3. Photocatalytic Degradation of PAHs

3.3.1. PAHs in $\text{PM}_{2.5}$

As both the concentration and chemical composition of $\text{PM}_{2.5}$ vary daily, simultaneous sampling on the TiO_2 -coated and non-coated fibre filters was conducted three times using two adjacent samplers. The photocatalytic degradation of the $\text{PM}_{2.5}$ was carried out in ambient air at room temperature ($\sim 20^\circ\text{C}$). Three UV black lights (Toshiba Lighting & Technology, Kanagawa, Japan, FL15BLB, peak wavelength = 365 nm) were placed in parallel, 10 cm above the surface of the $\text{PM}_{2.5}$ samples collected on the TiO_2 or quartz filters to ensure uniform irradiation. To quantify the nine target PAHs on the filter samples, two 25 mm \varnothing pieces were cut from the filters and used for the high-performance liquid chromatography (HPLC) analysis described in Section 3.4. The sampling was performed after 6, 12, and 24 h of irradiation. During this process, the UV intensity at the surface of the filters was $1.1\ \text{mW}/\text{cm}^2$ (Custom, Tokyo, Japan, UVA-365) and the surface temperature during the experiment was $34.2\text{--}37.3^\circ\text{C}$.

3.3.2. PAHs in Direct Contact with the Filters

As a reference comparison, the molecules of the nine target PAHs were placed in direct contact with the TiO_2 and quartz filters by adding a standard PAH solution (Sigma-Aldrich, Supelco, St. Louis, MO, USA, TCL PAH Mix certified reference material; acetonitrile: methanol (9:1), varied) and irradiated with UV light ($1.1\ \text{mW}/\text{cm}^2$). Two 25 mm \varnothing pieces were then cut from the filters and used for HPLC analysis. As the degradation of PAHs was rapid, the PAHs were analysed within 0.5 h of irradiation.

3.3.3. PAHs in $\text{PM}_{2.5}$ after Salt Removal

To investigate the effect of water-soluble salts on the degradation of PAHs in $\text{PM}_{2.5}$, three pairs of $\text{PM}_{2.5}$ samples were collected on the TiO_2 filters using two adjacent samplers. The $\text{PM}_{2.5}$ samples collected by the first sampler were used for the degradation tests described in Section 3.3.1 following treatment with water. These samples were vacuum filtrated with deionised water (0.5 L), dried in an oven for 1 h at 40°C , and subsequently used for the degradation test. For the second set of samples, the $\text{PM}_{2.5}$ samples were dried in an oven for 1 h at 40°C without water treatment. In both cases, PAH contents were measured 2.5 and 7.5 h after UV-irradiation.

3.4. Determination of PAHs

Two 25 mm ϕ pieces of the filters were cut into small fragments and transferred into a centrifuge tube. The PAHs were then extracted in 10 mL of dichloromethane (Kanto Chemical, reagent grade) for 20 min (two cycles of 10 min each) using an ultrasonic bath to ensure complete extraction. Each extract was then centrifuged for 10 min at 3000 revolutions per minute (rpm). The resulting supernatant (5 mL) was transferred into another centrifuge tube to which 30 μ L of dimethyl sulfoxide (FUJIFILM Wako Pure Chemical, Osaka, Japan, reagent grade) was added. After evaporating the dichloromethane under a gentle nitrogen flow, 0.97 mL of acetonitrile was mixed with the residue. The final samples were dissolved in acetonitrile (Kanto Chemical, HPLC grade), filtered using a disposable cellulose acetate membrane filter (Advantec, DISMIC-25CS, pore size = 0.20 μ m), transferred to brown vials, and stored at -20°C until further analysis.

The amounts of target PAHs in the extracts of two 25 mm ϕ filter pieces were determined using high-performance liquid chromatography with fluorescence detection (HPLC-FL), and subsequently converted to those in a whole filter (100 mm ϕ , an effective sampling area) by multiplying by a factor of 8, $(100/2)^2/[2(25/2)^2]$, to have a unit of ng/filter. The HPLC-FL system consisted of a Shimadzu (Kyoto, Japan) LC-6A pump, an RF-20A fluorescence detector, a CTO-10A column oven, and a C-R6A recorder. The following analytical conditions were used: column $\phi = 4.6 \times 250$ nm; particle size = 5 μ m (GL Science, Tokyo, Japan, Inertsil ODS-P); the eluent consisted of the mixed solution containing 80% acetonitrile and 20% ultrapure water (Milli-Q), at a rate of 1.2 mL/min (isocratic); oven temperature = 40°C ; injection volume = 20 μ L. The excitation (Ex) and emission (Em) wavelengths were programmed as follows: 0–16 min = Ex 250 nm and Em 400 nm; and 16–40 min = Ex 286 nm and Em 433 nm. The nine targeted PAHs consisted of 3-member ring (PHE and ANT), 4-member ring (PYR, BaA, and CHR), 5-member ring (BbF, BkF, and BaP), and 6-member ring (BgP) types. A five-point calibration was performed using a dilution series of certified reference material (Sigma-Aldrich, Supelco, TCL PAH Mix certified reference material; acetonitrile: methanol (9:1), varied). The typical HPLC chromatograms are shown in Figure 8. Correlation coefficients (r) for linear regressions of the calibration curves were >0.99 for all PAHs. The limit of detection (LOD) for each PAH was defined as three times the standard deviation of the blank samples. The LODs were 4.5 ng/filter for PHE, 0.26 ng/filter for ANT, 0.13 ng/filter for PYR, 0.13 ng/filter for BaA, 0.26 ng/filter for CHR, 0.15 ng/filter for BbF, 0.04 ng/filter for BkF, 0.04 ng/filter for BaP, and 0.18 ng/filter for BgP.

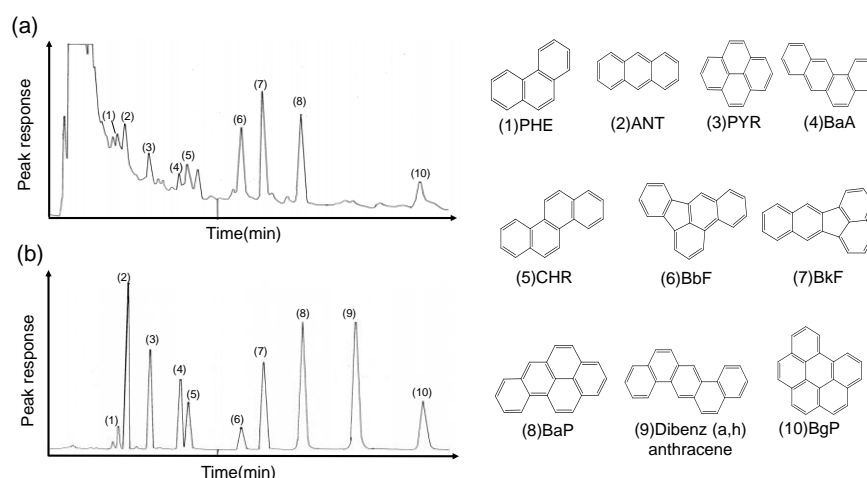


Figure 8. Typical high-performance liquid chromatography (HPLC) chromatograms of (a) extracts from PM_{2.5} before UV-irradiation and (b) standard solution at a dilution ratio of 10,000 times.

3.5. Determination of Water-Soluble Ion

Following the method described by Ota et al. [31], inorganic ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were determined using ion chromatography (IC). These ions are major components of the water-soluble salts in the $\text{PM}_{2.5}$ samples in Japan. For the samples with and without water treatment, the filters were cut into 14 mm ϕ pieces using a pierce punch. These were transferred into a 50 mL test tube and the water-soluble inorganic ions were extracted in 10 mL of ultrapure water (Milli-Q) using a shaker (As-One, Osaka, Japan, SR-1) at 170 rpm for 60 min. After filtration using a disposable cellulose acetate membrane filter, the filtrate was used for the IC analysis.

The IC system used for Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} measurement consisted of a Shimadzu LC-20AD pump, an SIL-10Ai auto-sampler, and a COD-10AVP conductivity detector. The following conditions were used: column $\phi = 4.6 \times 150$ mm; particle size = 7 μm (Showa Denko, Tokyo, Japan, ShodexTM IC YS-50); the eluent consisted of a 5.0 mM oxalic acid solution, with a flow rate of 1.0 mL/min (isocratic); oven temperature = 40 °C; and injection volume = 20 μL . A dilution series of $(\text{NH}_4)_2\text{SO}_4$ (Kanto Chemical) was used for calibration and determination.

For the Cl^- , NO_3^- , and SO_4^{2-} measurements, the analytical system consisted of a Thermo Fisher Scientific DionexTM AquionTM machine with a chemical suppressor (AMMS 3000) and an AS-AP auto-sampler. The following conditions were used during the measurements: separation column $\phi = 4.0 \times 250$ mm (Thermo Fisher Scientific, IonPac AS9-HC) with a guard column (Thermo Fisher Scientific, IonPac AG4); the eluent consisted of a 5 mM sodium carbonate solution, with a flow rate of 1.0 mL/min (isocratic); 15 mM of sulfuric acid as the scavenger for the chemical suppressor; oven temperature = 40 °C; and the injection volume = 25 μL . The dilution series of reagent-grade NaCl, NH_4Cl , KCl, MgCl_2 , CaCl_2 , NaCl, NaNO_3 , and Na_2SO_4 in ultrapure water were used for calibration and determination. All of the reagents were obtained from Kanto Chemical. The LOD was defined as three times the standard deviation of the blanks for anions and 1.0 $\mu\text{g/mL}$ of the standard solutions for cations. The LODs were 5.4 $\mu\text{g}/\text{filter}$ for Na^+ , 3.0 $\mu\text{g}/\text{filter}$ for NH_4^+ , 2.3 $\mu\text{g}/\text{filter}$ for K^+ , 3.2 $\mu\text{g}/\text{filter}$ for Mg^{2+} , 13 $\mu\text{g}/\text{filter}$ for Ca^{2+} , 1.0 $\mu\text{g}/\text{filter}$, 2.9 $\mu\text{g}/\text{filter}$ for NO_3^- , and 3.6 $\mu\text{g}/\text{filter}$ for SO_4^{2-} .

4. Conclusions

The photocatalytic degradation of hazardous PAHs in $\text{PM}_{2.5}$ was carried out by coupling air filtration and UV-induced TiO_2 technologies. A TiO_2 layer was formed on the surfaces of the quartz filters, and the airborne $\text{PM}_{2.5}$ was collected on the filter using a high-volume air sampler. The amounts of nine targeted PAHs on the TiO_2 filters gradually decreased with time during the photo-induction (1.1 mW/cm^2), and a significantly greater reduction was observed in comparison to non-coated quartz filter controls. However, degradation rates were much lower compared to the photolysis of the PAHs in direct contact with the TiO_2 layer. As $\text{PM}_{2.5}$ is a mixture of various kinds of solids, co-existing components including soluble salts can act as a rate-determining factor in the UV-induced degradation of PAHs. Thus, the overall degradation rates of the $\text{PM}_{2.5}$ collected on the TiO_2 filters are affected by the nano- and micro-structures of the samples. To highlight this, we found that degradation rates were remarkably improved after removing the co-existing salts in the $\text{PM}_{2.5}$ samples using simple water-treatment. As our goal is to investigate the practical application of this principle in air-cleaning devices to remove the most toxic components from $\text{PM}_{2.5}$, the efficacy for the decomposition of other health-related chemicals should be further investigated.

Author Contributions: Y.S., K.M. and K.S. designed and conceived this study. K.S. conducted the experiments. K.Y. and X.S. conducted the HPLC-FL and IC analysis, respectively. All authors have read and agreed to the published version of the manuscript.

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