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Effects of UV-B on Photochemical Behavior of Fly Ash Particle-Associated PCDD/Fs

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Airborne particulate matter and fly ash from combustion contain polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) that are directly mutagenic without metabolic activation (Lohmann and Jones 1998; Oh et al. 2002). PCDD/Fs are typical persistent organic pollutants (POPs) and are highly lipophilic and chemically stable (Oh et al. 2002). Photolysis may be one of major abiotic transformations of the chemicals adsorbed to the particles in the atmosphere (Borwitzky and Schramm 1991). Some studies indicated that photochemical behavior of PCDD/Fs appeared to be dependent on the substrate to which they are adsorbed (Borwitzky and Schramm 1991) [3-5]. A common presumption was that atmospheric PCDD/Fs could undergo relatively difficult photodecomposition (Borwitzky and Schramm 1991; Tysklind and Rappe 1991; Koester and Hites 1992). However, so far the photochemical behavior of particle-associated PCDD/Fs has not been well understood.

The spectral composition of sunlight reaching the Earth's surface can be characterized by spectral bands, which include UV-B region (280–315 nm), UV-A region (315–400 nm), visible light (400–780 nm), and infrared band (> 780 nm). Approximately 4% of the total energy from sunlight reaching the Earth's surface occurs in the UV band and the minimum wavelength of terrestrial global radiation is about 290 nm. Although UV-B radiation contributes less than 1% of the total solar energy reaching the Earth's surface, it may play an important role on the photolysis of organic pollutants in the environment due to its high photonic energy of approx. 4 eV (Larson and Weber 1994; Mill 1999). In the present study, a sun-simulator designed for ecological research was used to investigate the photochemical behavior of fly ash particle-associated PCDD/Fs deposited on glass slides. The effect of UV-B radiation on PCDD/Fs photolysis was particularly studied.

MATERIALS AND METHODS

The fly ash samples were generated from a combustion system, which was described in detail previously (Niu et al. 2003). A mixture of polyvinyl chloride (PVC), wood, high-density polyethylene (HDPE), and styrene was used for combustion to produce exhaust gas containing fly ash and PCDD/Fs. Glass slides

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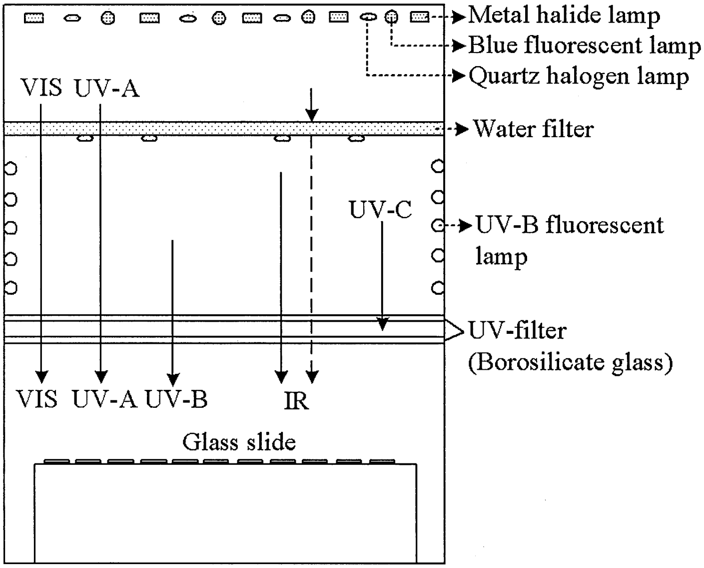

Figure 1. Schematic of the sunlight simulator to expose PCDD/Fs (Thiel et al. 1996)

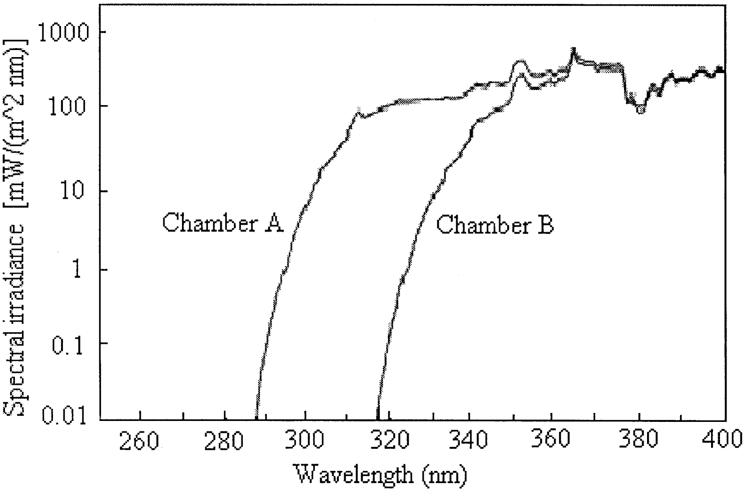

Figure 2. The spectral irradiance of simulated sunlight

with the size 76 × 26 mm^2 were placed in the exposure chamber where the temperature was held at 32°C and then particle-associated PCDD/Fs deposited on the glass slides. The slides were kept in the exposure chamber for 96 h after combustion so as to establish a uniform and constant concentration distribution of PCDD/Fs on fly ash.

The space of the controlled environmental chamber is $1.4 \times 1.4 \times 1.4$ m^3 (length × width × height) (Niu et al. 2003 and 2004). The controlled chamber was ventilated by filtered air at a temperature of 20 °C. The air pressure inside the chamber is $(9.65 \pm 0.05) \times 10^4$ Pa, relative humidity $(70 \pm 2)\%$. The schematic of the sunlight simulator is illustrated in Figure 1.

In the controlled environmental chambers, the fly ash containing PCDD/Fs was exposed to simulated sunlight. The experiments were conducted in two sun simulators, Chamber A and B. In Chamber A, the light and UV-radiation were set at moderate levels occurring at mid-latitudes. The spectral irradiance within the sun simulators was determined by a radiometric calibrated double monochromator system with a spectral resolution of 1 nm in the 280-400 nm band and 2 nm in the 400-850 nm band (Bentham DM300, U.K.). The integrated irradiance at canopy level was 840-940 $\mu mol \cdot m^{-2} \cdot s^{-1}$ for photosynthetic active radiation (400-700 nm) (which corresponds to a total global irradiance in the order of 400 $W \cdot m^{-2}$), 11-16 $W \cdot m^{-2}$ for UV-A (315-400 nm), and 0.43-0.53 $W \cdot m^{-2}$ for UV-B (280-315 nm). The range of irradiance values considers the spatial distribution of light and UV-radiation within the chamber. The irradiance spectral of the simulated sunlight is shown in Figure 2. In Chamber B, the UV-B component was almost completely removed ($< 10^{-4}$ $W \cdot m^{-2}$) using appropriate glass filters while the other light and radiation parameters were the same as in Chamber A. Periodically throughout the experiment, 10 slides fully exposed to sunlight, as well as slides from the control, were sampled for further analysis.

The standard PCDD/Fs analysis method of the GSF-Institute of Ecological Chemistry was followed (Niu et al. 2003). Briefly, $^{13}C_{12}$ labeled PCDD/F internal standards (For 2,3,7,8-TCDD/Fs, 100 ng/ml; For HpCDD/Fs, 400 ng/ml; For OCDD/F, 1000 ng/ml; For the other 9 PCDD/Fs, 200 ng/ml) (Cambridge Isotope Laboratory, Woburn, Massachusetts, USA) were spiked before extraction that was carried out using chloroform/toluene. Purification of the extract was performed using a sandwich-column, an alumina-column, and a florisil-column in turn. The eluent was concentrated to about 1 mL and then the recovery standard $^{13}C_{12}$-1,2,3,4-TCDD was added. The final extract was concentrated to ca. 10 μL using a stream of nitrogen at 46.0 ± 0.5°C.

Quantification was performed on a high-resolution gas chromatography (60 m Rtx-2330 polar capillary column, Restek) coupled with a high-resolution mass spectrometer (Finnigan MAT95s, $R = 10\ 000$) in EI mode by tracing the two most abundant signals of the isotope clusters. For each GC run, a 1 μL sample was injected on a cold injection system (KAS 4, Gerstel) operated in splitless mode.

The retention time and recovery of analysed 2,3,7,8-substituted PCDD/Fs are listed in Table 1. As shown in Table 1, the recovery of PCDD/Fs varies from 75% to 106%, and for most PCDD/Fs the recoveries are more than 80%, indicating the reliability of the analytical method used in the study. The analysis results showed the relative standard deviation for duplicate samples was lower than 10%.

Table 1. The retention time, TEQ, initial concentration (C_0, pg/dm^2 fly ash) and recovery of 2,3,7,8-substituted PCDD/Fs.

PCDD/Fs	PCDD/Fs	^{13}C-labelled PCDD/Fs	WHO-TEQ	C_0 (pg/dm^2)	Recovery (%)
Compounds	*RT* (min)	*RT* (min)			
2,3,7,8-TCDD	18:04	18:03	1	16.95	77
1,2,3,7,8-PeCDD	22:41	22:40	1	40.85	99
1,2,3,4,7,8-HxCDD	27:19	27:18	0.1	27.11	87
1,2,3,6,7,8-HxCDD	27:29	27:28	0.1	38.86	89
1,2,3,7,8,9-HxCDD	28:45		0.1	25.53	
1,2,3,4,6,7,8-HpCDD	32:37	32:36	0.01	79.04	75
OCDD	38:16	38:15	0.0001	56.83	96
2,3,7,8-TCDF	21:21	21:20	0.1	122.73	102
2,3,4,7,8-PeCDF	26:32	26:31	0.5	172.43	103
1,2,3,6,7,8-HxCDF	26:03	26:02	0.1	190.57	105
1,2,3,7,8,9-HxCDF	30:06	30:04	0.1	18.92	84
2,3,4,6,7,8-HxCDF	31:26	31:25	0.1	121.51	80
1,2,3,4,6,7,8-HpCDF	30:06	30:06	0.01	357.81	86
1,2,3,4,7,8,9-HpCDF	33:43	33:42	0.01	48.42	92
OCDF	37:53	37:52	0.0001	75.19	104

RESULTS AND DISCUSSION

The total mass of fly ash determined from 10 glass slide surfaces was about 0.008 g. As the mass of fly ash is so low, high errors may be involved if the mass of fly ash is is adopted to express the concentration of PCDD/Fs on fly ash. It is observed that the thickness of fly ash on the slides was very thin, thus it can be regarded that the thickness of fly ash on slides was consistent. Thus, the mass of PCDD/Fs per square decimetre of slide surface (pg/dm^2 fly ash) was used as the concentration unit to calculate the photolysis kinetics.

The initial concentrations (C_0, pg/dm^2 fly ash) of 2,3,7,8-substituted PCDD/F congeners sorbed to fly ash are shown in Table 1. Table 1 indicates that the total concentration of PCDFs is higher than that of PCDDs, and the concentration of PCDF congeners is higher than that of PCDD congeners with the same chlorinated substitutions.

For the experiments conducted in Chamber A, it was found that the degradation kinetics could be divided into two phases, as shown by Figure 3 for 2,3,7,8-TCDD (Figure 3a) and 2,3,7,8-TCDF (Figure 3b). For the first phase (about 0-50 h), the photolysis rates are considerably fast. The degradation rates declined in the second phase (about 50-550 h). The plots of the natural logarithms of PCDD/Fs concentration (lnC_t) versus time (t) are essentially straight lines for the two phases (Figure 3). Therefore, the first-order kinetics can be applied to the photolysis. As the concentrations of PCDD/Fs in the fly ash samples are low, the assumption of first-order kinetics is reasonable. The kinetics for the loss of PCDD/Fs in fly ash exposed to simulated sunlight was shown in Figure 4.

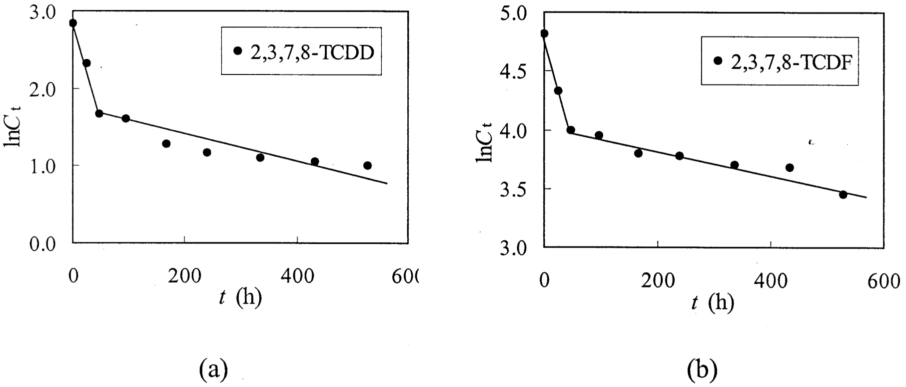

Figure 3. Degradation kinetics of 2,3,7,8-TCDD (a) and 2,3,7,8-TCDF (b) on fly ash surfaces

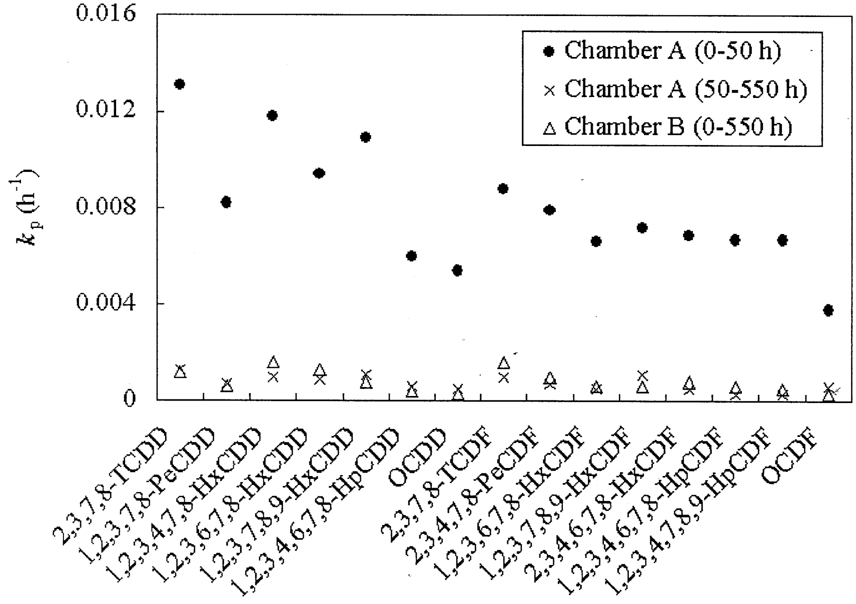

Figure 4. The first-order degradation rate constants of 2,3,7,8-substituted PCDD/Fs on fly ash irradiated by simulated sunlight

However, for the experiments performed in Chamber B, no distinction of the phases was observed for the kinetics. Furthermore, the decreases of PCDD/F were not obvious. Supposing that the disappearance of PCDD/Fs follows the first-order kinetics, the first-order degradation rate constants were also calculated, which are shown in Figure 4 for 2,3,7,8-substituted PCDD/Fs. The degradation rate constants in Chamber B are much lower than those of the first phase in Chamber A. These values indicate that UV-B radiation plays a key role on the photolysis of PCDD/Fs.

In this study, half-lives ($t_{1/2}$) of the first phase of photolysis determined in Chamber A for PCDD/Fs on fly ashes range from 53 h for 1,3,6,8-TCDF to 182 h for OCDF. The photolysis rate constants for the second phase of kinetics determined in Chamber A are about the same magnitude as those determined in Chamber B. For the second phase in Chamber A, $t_{1/2}$ values range from ca. 300 h to >1000 h, whereas $t_{1/2}$ values determined in Chamber B range from ca. 400 h to >1000 h.

Absorption of photons by the candidate molecules is a prerequisite for photochemical reaction. It can be concluded from Figure 4 that the photolysis rate constants of PCDD/Fs sorbed to fly ash for the initial phase (about 0-50 h) are far greater than for the second phase (about 50-550 h). In this experiment, it is mainly the surface of fly ash that is exposed to the simulated sunlight. As fly ash may strongly attenuate light below their surfaces, PCDD/Fs in the interior of fly ash can hardly exposed to the simulated sunlight, resulting in low photolysis rate. On the other hand, for the second phase of photolysis kinetics in Chamber A, the migration of particle-associated PCDD/Fs from the interior to exterior of fly ash can be the rate-limiting step.

A previous investigation (Niu et al. 2003) showed that the photolysis rates of PCDD/Fs sorbed on spruce (*Picea abies* (L.) Karst.) needle surfaces decrease with the increase of the degree of chlorination. In the present study, most PCDD/Fs in Chamber A also exerted the same trends (Figure 4). Thus, particle-associated PCDD/Fs containing more chlorine atoms are expected to have sufficiently long lifetimes to undergo long-range transport. Niu et al. (2003) found that the photolysis rate constants for PCDF homologues are higher than for PCDD homologues with the same degree of chlorination on spruce needle surfaces under sunlight irradiation. However, the photolytic behavior for most PCDD/Fs on fly ash surfaces showed that the photolysis rate constants for PCDFs are lower than for PCDDs with the same degree of chlorination. This difference indicates that the photolysis of PCDD/F homologues is dependent on the substrate to which they are sorbed (Chen et al. 2001).

Toxic equivalent (TEQ) levels based on the toxic equivalency factors for humans and mammals established by the World Health Organization (WHO) (Van den Berg et al. 1998) were calculated, which are shown in Figure 5. Figure 5 shows that the decrease of the TEQ values on fly ash in Chamber A over the irradiation time is obvious and the variation of TEQ values in Chamber B is not distinct. It can be concluded that UV-B radiation plays an important role on the decrease of TEQ levels on fly ash.

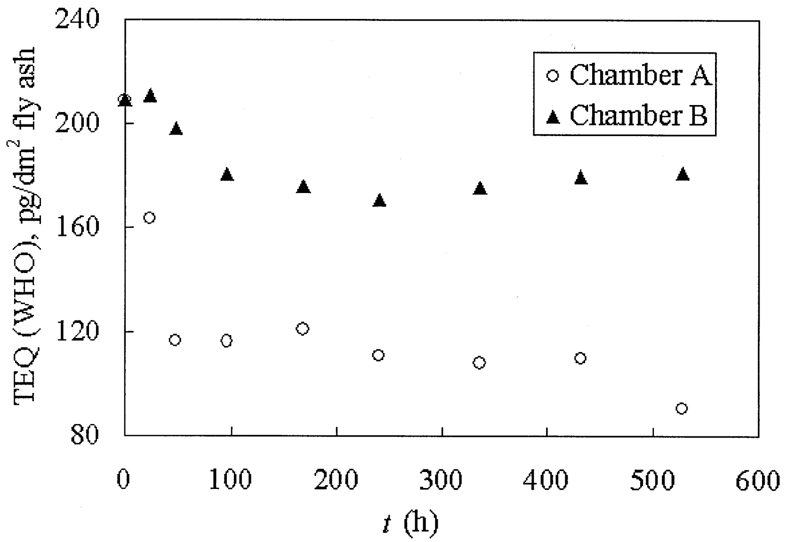

Figure 5. The variation of PCDD/Fs TEQ (WHO) values versus the irradiation time

Except for the differences in UV-B intensity, the other experimental conditions were the same between Chamber A and B. As most PCDD/Fs can only absorb UV photons with the wavelength below 315 nm (Podoll et al. 1986; Choi et al. 2000), the low amount of UV-B irradiation in Chamber B led to low degradation rates of PCDD/Fs. UV-B plays an important role on the fate of PCDD/Fs on fly ash surfaces. Thus it is mainly direct photolysis that is responsible for the degradation and PCDD/Fs sorbed on the surfaces of fly ash.

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