PHOTODEGRADATION OF PCDD/FS AND PAHS ON SURFACES OF SPRUCE (*PICEA ABIES* (L.) KARST.) NEEDLES

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Introduction

More than 80% of the Earth's land surface is covered with vegetation, and typically vegetation has a surface area that is 6-14 times greater than the land it covers[1,2]. Generally, the outer surfaces of vegetation are hydrophobic environments that can enrich persistent organic pollutants (POPs) mainly from atmosphere[3]. To facilitate understanding the fate of POPs sorbed on surfaces of vegetation, photodegradation of PCDD/Fs and PAHs on surfaces of spruce (*Pieca abies* (L.) Karst.) needles was studied.

Materials and Methods

PCDD/Fs and PAHs were produced and deposited on surfaces of spruce needles in a combustion system by burning polyvinyl chloride, wood, high-density polyethylene and styrene[4,5].

Live spruce trees contaminated by PCDD/Fs and PAHs were exposed to sunlight in Munich (latitude 48.2˚ N), in July 2001 during the time period 9:00-18:00. The local temperature was 25-33 ℃, and the local sunlight irradiation intensity was 70 - 950 W/m^2 with an average of 620 W/m^2 throughout the irradiation time. At the same time, some spruce trees masked from sunlight, served as dark controls.

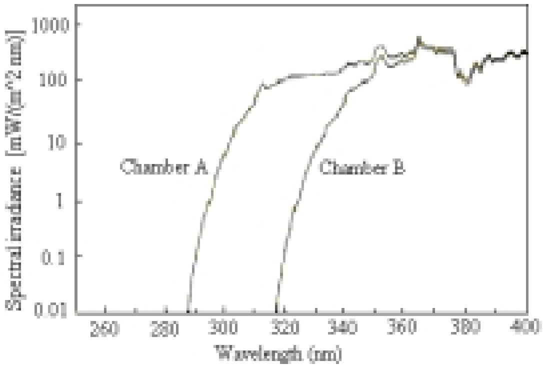

Figure 1. The spectral irradiance of simulated sunlight

Sun simulators included in controlled environmental chambers were also used to irradiate the contaminated spruce trees. The space of the controlled environmental chamber is

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1.4×1.4×1.4m^3 (L × W × H). The chambers were ventilated by filtered air at a temperature of 20ºC. The air pressure inside the chamber was $(9.65 \pm 0.05) \times 10^4$ Pa, relative humidity (70 ± 2)%. Two chambers (A and B) were involved. In Chamber A, the light intensities were 840-940μmol·m^{-2}·s^{-1} that corresponds to a total global irradiance in the order of 400 W·m^{-2} for photosynthetic active radiation (400 - 700 nm), 11-16 W·m^{-2} for UV-A, and 0.43-0.53 W·m^{-2} for UV-B. In Chamber B, the UV-B component was almost completely removed (<10^{-4} W·m^{-2}) using appropriate glass filters and the other light and radiation parameters were the same as in Chamber A. The irradiance spectra[6,7] of the sun simulators is shown in Figure 1. Periodically throughout the experiment, 10-20 g spruce needles were collected and analyzed using the methods described previously[4,5].

Results and Discussion

The recovery of 2,3,7,8-substituted PCDD/Fs is 77% - 104%, and the recovery of spiked PAHs is 85% - 101%, indicating the reliability of the analytical methods. PCDD/Fs and PAHs levels in uncontaminated spruce needles were not detectable or very low, and in the current study, they did originate from the combustion process.

The photolysis of PCDD/Fs and PAHs followed first-order kinetics. Two distinct kinetic phases were observed for PCDD/Fs under irradiation of the sun simulator in Chamber A, as shown in Figure 2 for selected 2,3,7,8-substituted PCDDs as an example. For the other degradation kinetics (PCDD/Fs irradiated by natural sunlight, PAHs irradiated by natural sunlight or simulated sunlight), no distinction of the kinetics was observed.

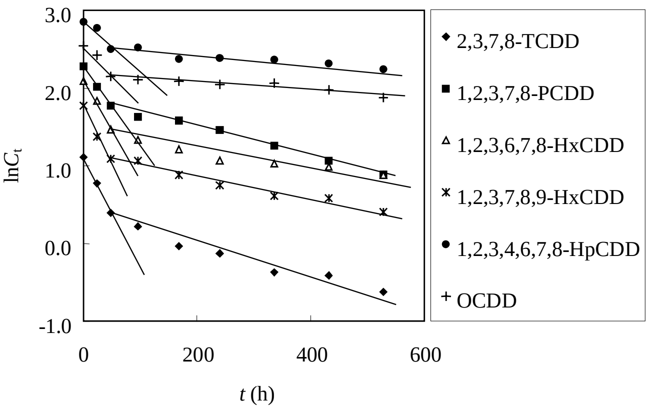

Figure 2. The two phases of degradation kinetics of PCDDs

The first-order photodegradation rate constants in Chamber B for PCDD/Fs and PAHs were so low that they are comparable with the dark control. Consistent half-lives ($t_{1/2}$) are observed from Figure 3, which compares $t_{1/2}$ of 2,3,7,8-substituted PCDD/Fs on 1-year-old spruce needles irradiated by the sun simulator in Chamber A (calculated from the first phase of kinetics) with those irradiated by natural sunlight. Figure 4 shows the first-order rate constants of 2,3,7,8-substituted PCDD/Fs on surfaces of spruce needles with different ages. It can be concluded from Figure 4 that the rate constants for the 3-year-old spruce needles are higher than for the 2-year-old spruce needles, and the 2-year-old spruce needles are higher than 1-year-old spruce needles.

As shown by Figure 5, the degradation rates of PAHs on 1-year-old spruce needles irradiated by natural sunlight are faster than by simulated sunlight, and the degradation rates in Chamber B are the lowest.

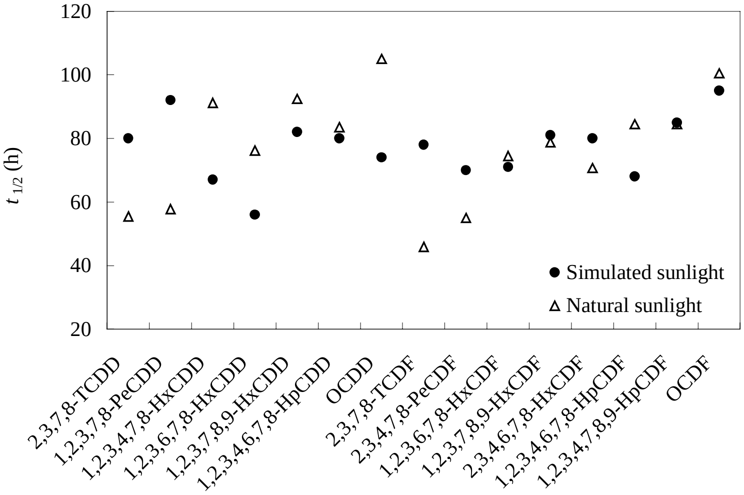

Figure 3. A comparison between $t_{1/2}$ values for the first phase of photodegradation for 2,3,7,8-substituted PCDD/Fs on the 1-year-old spruce needle surfaces in Chamber A and those irradiated by natural sunlight

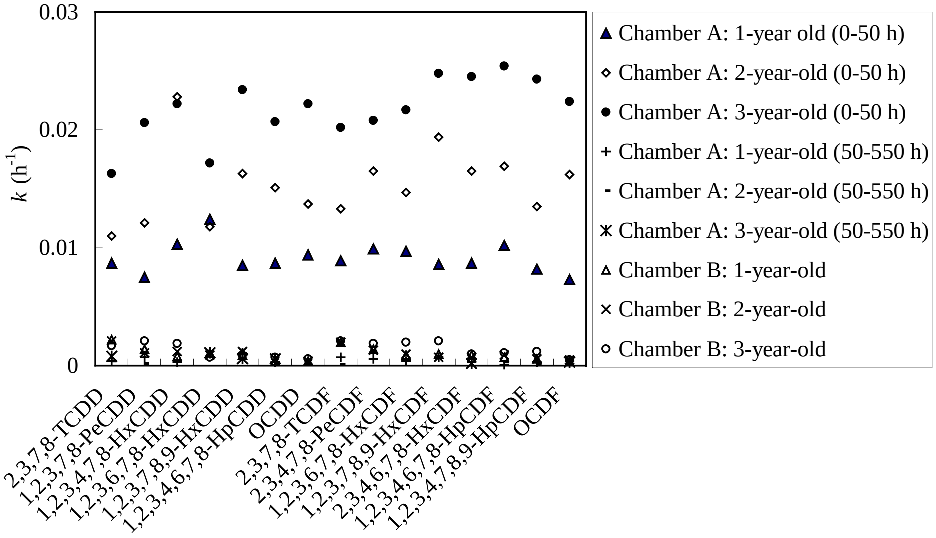

Figure 4. The first-order photolysis rate constants for 2,3,7,8-substituted PCDD/Fs irradiated by simulated sunlight

Most PCDD/Fs absorb UV photons with a wavelength below 315 nm[8,9], whereas PAHs absorb both UV-A and UV-B[10,11]. Thus UV-B plays a more important role on the photodegradation for PCDD/Fs than for PAHs, in view of direct photolysis for which the absorption of photons by the candidate molecules is a prerequisite. The phenomena were observed from the current study indeed, which implies that direct photolysis dominates the photodegradation of PCDD/Fs and PAHs on surfaces of spruce needles.

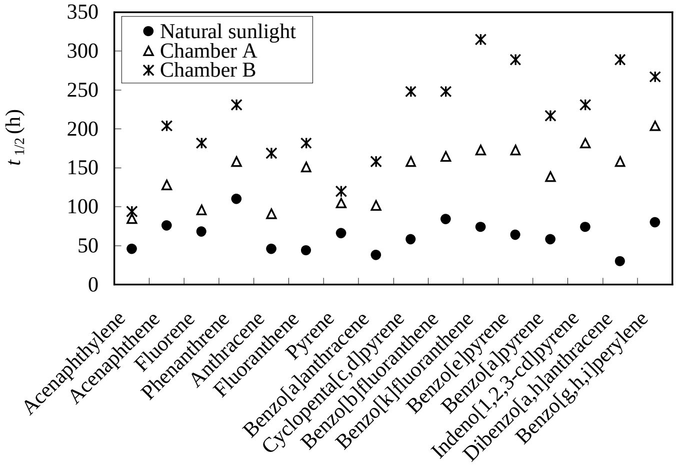

Figure 5. The degradation half-lives of PAHs irradiated by simulated sunlight and natural sunlight

Acknowledgments

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