ENVIRONMENTAL TRANSPORT AND FATE

PHOTOLYTIC BEHAVIOR OF PCDD/FS ON SPRUCE (*PICEA ABIES* (L.) KARST.) NEEDLE SURFACES BY SUNLIGHT RADIATION

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants. Most PCDD/Fs are potent carcinogens and endocrine disrupting chemicals[1,2]. A few studies showed that photodegradation on vegetation significantly interacted in the transfer of PCDD/Fs from the atmosphere into the terrestrial food web[3,4]. Spruce (*Picea abies* (L.) Karst.) is one kind of the most widespread and typical vegetations in the environment. Spruce needle surfaces are covered with waxy or lipidic layers, which can accumulate many kinds of lipophilic organic compounds[5,6]. To date the fate of PCDD/Fs adsorbed on spruce needle surfaces has not been fully explored. Can they undergo photodegradation under sunlight irradiation? Is the photodegradation significant for the fate of PCDD/Fs in the environment? The purpose of this study is to answer these questions.

In the present study, spruce needles were exposed to the exhaust gas containing PCDD/Fs produced by actual combustion of polyvinyl chloride (PVC), wood, high-density polyethylene (HDPE), and styrene in a combustion chamber. Then sunlight photodegradation of PCDD/Fs absorbed to spruce needles was investigated.

Materials and Methods

A combustion system to generate PCDD/Fs was designed and constructed, as shown in Figure 1. A mixture with the following proportion was used for combustion to produce exhaust gas containing PCDD/Fs: PVC (2000 g), wood (1800 g, dry weight), HDPE (430 g), and styrene (200 g). The combustion process lasted for 4 h. Some 8-year-old spruce trees were placed in the exposure chamber, for which length × width × height is $6.5 \times 2.8 \times 2.8$ m³. The temperature in the chamber was ca. 32 ºC during the combustion. After the combustion, the spruce trees were placed in the exposure chamber for 96 h further to establish a uniform and constant concentration distribution of PCDD/Fs on the needle surfaces.

Periodically throughout the experiment, 10 g spruce needles at the height of around 1 m, exposed to sunlight, as well as needles from the control, were sampled for chemical analysis. The standard PCDD/F analysis method of GSF-Institute of Ecological Chemistry was followed[7,8].

UV-visible absorption spectrum of the wax and lipid extracted from the spruce needle surfaces was determined by using a Hewlett Packard 8452A diode array spectrophotometer.

Results and Discussion

All the PCDD/F congeners under study and their corresponding numbers are listed in Table 1.

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Table 1. PCDD/F congeners in this study

No.	Compounds	No.	Compounds	No.	Compounds
TCDD		24	1,2,3,4,6,9-	47	1,2,3,7,9-
1	2,3,7,8-	25	1,2,3,4,6,7-	48	1,2,3,6,7-
2	1,3,6,8-	HpCDD		49	1,2,6,7,9-
3	1,3,7,9-	26	1,2,3,4,6,7,8-	50	1,2,3,6,9-
4	1,3,7,8-	27	1,2,3,4,6,7,9-	51	2,3,4,6,8-
5	1,2,6,8-	28	OCDD	52	1,2,3,4,9-
6	1,4,7,8-	TCDF		53	1,2,4,8,9-
7	1,2,3,9-	29	2,3,7,8-	54	1,2,3,8,9-
8	1,2,6,9-	30	1,3,6,8-	55	2,3,4,6,7-
9	1,2,6,7-	31	1,4,6,8-	HxCDF	
10	1,2,8,9-	32	1,3,4,8-	56	1,2,3,6,7,8-
PeCDD		33	1,2,7,8-	57	1,2,3,7,8,9-
11	1,2,3,7,8-	34	1,2,6,7-	58	2,3,4,6,7,8-
12	1,2,3,6,8-	35	2,4,6,7-	59	1,2,3,4,6,8-
13	1,2,4,7,8-	36	1,2,6,9-	60	1,2,4,6,7,8-
14	1,2,3,7,9-	37	2,3,4,6-	61	1,2,4,6,7,9-
15	1,2,3,6,9-	38	2,3,6,7-	62	1,2,4,6,8,9-
16	1,2,4,6,7-	39	3,4,6,7-	63	1,2,3,4,6,7-
17	1,2,4,8,9-	PeCDF		64	1,2,3,6,7,9-
18	1,2,3,4,6-	40	2,3,4,7,8-	65	1,2,3,4,8,9-
19	1,2,3,6,7-	41	1,3,6,7,8-	HpCDF	
20	1,2,3,8,9-	42	1,3,4,7,8-	66	1,2,3,4,6,7,8-
HxCDD		43	1,2,4,7,8-	67	1,2,3,4,7,8,9-
21	1,2,3,4,7,8-	44	1,2,4,6,7-	68	1,2,3,4,6,7,9-
22	1,2,3,6,7,8-	45	1,3,4,6,9-	69	1,2,3,4,6,8,9-
23	1,2,3,7,8,9-	46	1,2,3,4,6-	70	OCDF

Recovery for the analysis was ca. 80%. The patterns for the initial concentrations of 2,3,7,8-substituted PCDD/Fs on spruce needle surfaces are shown by Figure 2. Several earlier experiments indicated that PCDD/Fs could not be detected on uncontaminated spruce needle surfaces. Thus the PCDD/Fs detected come from the combustion process.

The spruce trees contaminated with PCDD/Fs were exposed to full sunlight in Oberschleissheim, Munich, Germany (latitude 48.2º N) in July 2001 from the time period between 9:00 a.m. and 6:00 p.m. under clear sky conditions. The parts higher than 1 m of the spruce trees were cut off before sunlight exposure to assure uniform sunlight exposure. The experiments were conducted over an 8-day period with a daily air temperature varying between 25ºC and 33ºC, air pressure $(9.65 \pm 0.05) \times 10^4$ Pa, relative humidity (50 ± 10) %, and the global irradiation intensity varying between 70 W/m^2 and 950 W/m^2 with an average of 620 ± 50 W/m^2 throughout the irradiation time. At the same time, some spruce trees shielded with aluminum foil were used as control.

It was found that disappearance of PCDD/Fs follows pseudo-first-order kinetics. The general pseudo-first- order disappearance rate constants (k_T) for PCDD/Fs are shown in Figure 3. The disappearance rate constants of PCDD/Fs in the control (k_E) were also calculated assuming the pseudo-first- order kinetics (Figure 3). The variation of TEQ (WHO) of PCDD/Fs for the control and sunlight irradiation is shown in Figure 4. As shown by Figure 4, because of the sunlight irradiation, the decrease of TEQ (WHO) on spruce needle surfaces over the irradiation time is obvious. Therefore, photolysis plays a major role on the fate of PCDD/Fs on spruce needle surfaces.
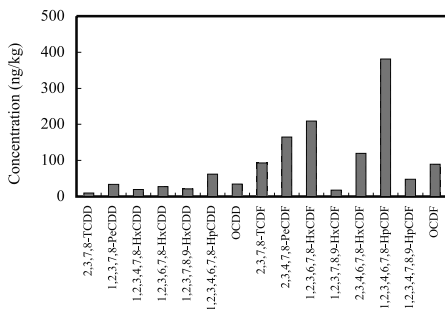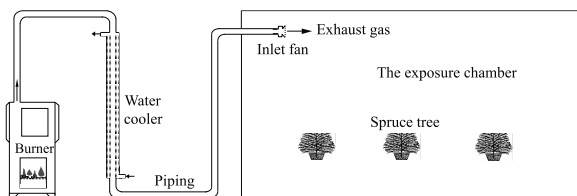
Figure 1. Combustion system for PCDD/F emission.

**Figure 2.** The initial concentration of 2,3,7,8-substituted PCDD/F homologues

The results indicate that the photolysis rates of PCDD/Fs absorbed on spruce needle surfaces are much faster than on fly ashes[9] or in air[10]. The UV-visible absorption spectrum of wax and lipid extracted from the spruce needles (Figure 5) shows that wax and lipid have strong absorption in the 250-320 nm region. Therefore, needle surfaces can absorb most of the sunlight UV photons with the wavelength value below 320 nm. Moreover, spruce needle surfaces are covered by a cuticle (1-5 µm thick) consisting mainly of saturated aliphatic components, long chain esters, polyesters and paraffins[11], some of them are capable of sensitizing photochemical reactions[12,13]. As a result of sunlight absorption by these compounds, free electrons and reactive radicals may be formed on the needle surfaces, leading to indirect or sensitized degradation of PCDD/Fs absorbed on needle surfaces. Thus the photolysis rates of PCDD/Fs may be enhanced on spruce needle surfaces relative to its direct photolysis rates in air or absorbed to fly ash.

As shown by Figure 3, photolysis rate constants for highly chlorinated PCDD/Fs are lower than for lowly chlorinated PCDD/Fs, implying that highly chlorinated PCDD/Fs are recalcitrant for photodegradation[14,15]. The photolysis rates are higher for PCDF homologues than for PCDD homologues with the same number of chlorine substitution (Figure 3), which implies PCDDs are slightly more resistant to photodegradation than PCDFs. As PCDF molecules have only one oxygen atom, they are more polarized than PCDDs and may be more reactive on spruce needle surfaces that contain many kinds of polarized compounds[11]. In the present study, the results indicated that the residual concentrations of most of tetra- and penta- chlorinated PCDD/Fs were higher at 72 h than at 54 h, while the concentrations of the higher chlorinated PCDD/Fs, such as HxCDD/Fs, HpCDD/Fs and OCDD/F, decreased over the irradiation time. The increase of the concentrations for lowly chlorinated congeners (tetra- and penta-chlorinated PCDD/Fs) with the sunlight irradiation time may be due to photoreductive dechlorination of higher chlorinated PCDD/Fs[3,16-17]. In the presence of sunlight, homolysis of C-Cl bonds of PCDD/Fs generates an aryl radical, which can rapidly abstract a hydrogen atom from proton donors such as the saturated hydrocarbon chains on spruce needle surfaces, leading to temporary increase of lowly chlorinated PCDD/Fs. Accordingly, photolytic reductive dechlorination may be an important photodegradation route for PCDD/Fs absorbed to spruce needles under sunlight irradiation.
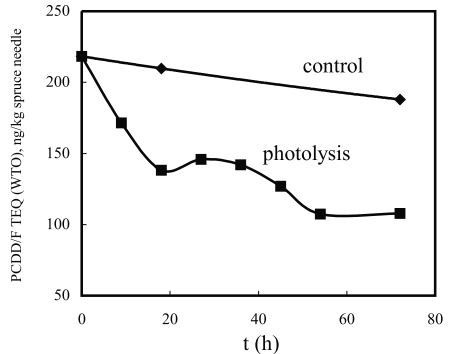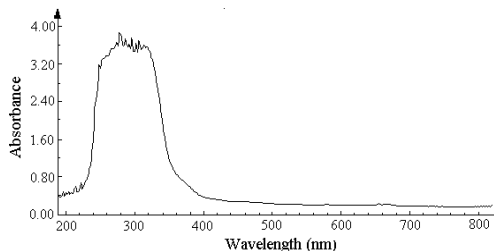
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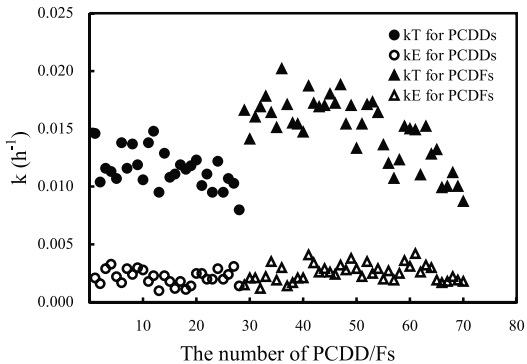
Figure 3. Disappear kinetics constants of PCDD/Fs on spruce needle surfaces

Figure 4. The variation of PCDD/F TEQ (WHO) values vs. the sunlight irradiation time

Figure 5. UV-visible absorption spectrum of the wax and lipid extracted from current spruce needles in chloroform

References

1. Boening D.W. (1998) Ecotoxicol Environ Safety, 39, 155
2. Fossi M.C., Casini S. and Marsili L. (1999) Chemosphere, 39, 1273
3. Crosby D.G. and Wong A.S. (1977) Science, 195, 1337
4. McCrady J.K. and Maggard S.P. (1993) Environ Sci Technol, 27, 343
5. Reischl A., Reissinger M. and Hutzinger O. (1987) Chemosphere, 16, 2647
6. Umlauf G., Hauk H. and Reissinger M. (1994) Chemosphere, 28, 1689
7. Schramm K.-W., Henkelmann B. and Kettrup A. (1995) Water Res, 29, 2160
8. Henkelmann B., Schramm K.-W., Klimm, C. and Kettrup A. (1996) Fresenius Z Anal Chem, 354, 818
9. Koester C.J. and Hites R.A. (1992) Environ Sci Technol, 26, 502
10. Podoll R.T., Jaber H.M. and Mill T. (1986) Environ Sci Technol, 20, 490
11. Matìjka P., Plešerová L., Budínová G., Havíøová K., Mulet X., Skácel F. and Volka K. (2001) J Mol Struct, 565-566, 305
12. Tuveson R.W., Larson R.A., Marley K.A., Wang G.-R. and Berenbaum M.R. (1989) Photochem Photobiol, 50, 733
13. Isosaari P., Tuhkanen T. and Vartiainen T. (2001) Environ Sci Technol, 35, 1259
14. Crosby D.G., Wong A.S., Plimmer J.R. and Woolson E.A. (1971) Science, 173, 748
15. Choi W., Hong S.J., Chang Y.-S. and Cho Y. (2000) Environ Sci Technol, 34, 4810
16. Buser H.-R. (1979) Chemosphere, 8, 251
17. Friesen K.J., Foga M.M. and Loewen M.D. (1996) Environ Sci Technol, 30, 2504