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Polychlorinated dibenzothiophenes in Japanese environmental samples and their photodegradability and dioxin-like endocrine-disruption potential

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Abstract

Polychlorinated dibenzothiophenes (PCDTs) in sediment, soil, and fly ash samples collected in Japan were analyzed and their dioxin-like endocrine-disruption potential and photodegradability investigated. PCDTs were detected in all three types of sample, although the concentrations were lower than those of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). An Ah-immunoassay confirmed that 2,3,7,8-TeCDT, 1,2,3,7,8-PeCDT, 1,2,3,7,8,9-HxCDT, and 1,2,3,4,7,8,9-HpCDT had Ah receptor-binding activities, which means that these PCDTs have the potential to cause dioxin-like endocrine-disruption. Photodegradation of PCDTs by UV irradiation was accompanied by dechlorination. The photodegradation rates of 2,3,7,8-TeCDT and OCDT were lower than the rates for the corresponding PCDF isomers (2,3,7,8-TeCDF and OCDF), which indicates that PCDTs are more stable than PCDFs to photodegradation.

Keywords: Ah receptor; Fly ash; Photodegradation; Polychlorinated dibenzothiophenes; Sediment; Soil

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1. Introduction

Polychlorinated dibenzothiophenes (PCDTs) are sulfur analogues of polychlorinated dibenzofurans (PCDFs). PCDTs have been detected in environmental samples such as soil and sediment (Peterman et al., 1986, 1988; Buser and Rappe, 1991; Pruell et al., 1993; Claus et al., 1998; Sinkkonen et al., 1994a, 1995, 2001), and in some samples PCDT homologues are present at higher levels than the corresponding PCDD/DFs. Pruell et al. (1993) found that the concentration of 2,4,6,8-TeCDT (3680 pg g^{-1}) was five times that of 2,3,7,8-TeCDD (656 pg g^{-1}) in sediment that was collected from the Passaic River (NJ, USA) and had been contaminated with 2,4,5-T containing 2,3,7,8-TeCDD as an impurity. Cai et al. (1994) reported that blue crabs (*Callinectes sapidus*) collected from Newark Bay, at the mouth of the Passaic River, contained more 2,4,6,8-TeCDT than 2,3,7,8-TeCDD in their muscle and hepatopancreatic tissues. These results indicate the necessity for monitoring PCDTs as a class of environmental pollutants.

Unfortunately, information on the environmental levels and emissions of PCDTs is limited. Although incineration of municipal waste and polychlorinated biphenyls (Peterman et al., 1986; Buser et al., 1991; Sinkkonen et al., 1991), pulp bleaching (Sinkkonen et al., 1994a), metal reclamation (Sinkkonen et al., 1994b, 2003), and production of chlorinated thiophenols (Benz et al., 1992) have been reported as emission sources of PCDTs, the high level of 2,4,6,8-TeCDT in the Passaic River has not been explained. In addition, there have been no reports of PCDTs in environmental samples collected in Japan, because Japanese environmental samples have not been tested for PCDTs.

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Owing to their structural similarity to PCDFs, PCDTs are suspected of causing dioxin-like endocrine-disruption. Kopponen et al. (1994) measured aryl hydrocarbon hydroxylase and ethoxyresorufin-*O*-deethylase (AHH/EROD) activities induced by 2,3,7,8-TeCDT in mouse hepatoma cell cultures and calculated its toxic equivalency factor (TEF) with respect to 2,3,7,8-TeCDD. The experimental TEF was 0.001, indicating that 2,3,7,8-TeCDT has the potential to cause dioxin-like endocrine-disruption. However, no data are available for more highly chlorinated dibenzothiophenes.

To determine whether or not PCDTs are environmental pollutants that require high priority for monitoring, the toxicity, environmental levels, and persistence of PCDTs must be evaluated. However, information on the environmental levels, sources, and endocrine-disruption potency of PCDTs is limited, and the degradability of PCDTs in the environment has not yet been investigated. Therefore, we analyzed PCDTs in sediment, soil, and fly ash samples collected in Japan and estimated the dioxin-like endocrine-disruption potential and photodegradability of these compounds.

2. Materials and methods

2.1. Environmental samples and PCDT standard compounds

Soil samples were collected from Japanese sites (in Nose, Osaka, and Hachiouji, Tokyo) contaminated with dioxins from municipal waste incineration. A fly ash sample was obtained from a municipal waste incineration plant located on the Tamagawa River in Tokyo, Japan, and a sediment sample was taken from the mouth of the same river, about 35 km downstream from the incineration plant. 2,3,7,8-TeCDT (Wellington Laboratories, Canada) and 1,2,3,7,8-PeCDT, 1,2,3,7,8,9-HxCDT, 1,2,3,4,7,8,9-HpCDT, and OCDT (EnBio Tec Laboratories, Japan) were used as standard PCDTs. 2,3,7,8-TeCDF and OCDF were purchased from Cambridge Isotope Laboratories (USA). Because ^{13}C-labeled PCDTs were not available, the corresponding ^{13}C-labeled PCDFs (NK-LCS-I, Wellington Laboratories, Canada) and a mixture of ^{13}C-1,2,3,4-TeCDD and ^{13}C-1,2,3,7,8,9-HxCDD (NK-IS-A, Wellington Laboratories, Canada) were used as internal standards for quantification of PCDTs in the samples.

2.2. Analysis of PCDTs in environmental samples

Prior to qualification and quantification of PCDTs, the environmental samples were extracted and purified. Because previous research has shown that PCDTs behave similarly to dioxins during conventional extraction and purification processes designed for dioxins (Sielex and Andersson, 1997; Sinkkonen et al., 2001), we used the Japanese standard analytical methods for dioxins in soil and sediment (Water Quality Bureau, 2000a,b), and waste (Environmental Health Bureau, 1997) to analyze PCDTs in the environmental samples. The purified samples were then analyzed for PCDTs by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; JMS700, Jeol, Japan; see Table 1 for operating conditions). To quantify the PCDTs, we assumed that their mass spectrometry responses were equal to those of the corresponding ^{13}C-labeled PCDFs.

2.3. Photodegradation of PCDTs

To investigate the persistence of PCDTs, we compared the photodegradabilities of 2,3,7,8-TeCDT and OCDT with those of 2,3,7,8-TeCDF and OCDF. Briefly, an *n*-hexane solution of each compound (1000 pg µl^{-1}) was poured into a 4-cm^3 quartz cuvette (S11-UV-10, GL Science, Japan) and subjected to UV irradiation for 1 h with a 5.3 W low-pressure mercury lamp that emits mainly 254 nm (Germipak GCL212/11.4/Cell/C, Light Sources, USA) (Fig. 1). During irradiation, a portion of the *n*-hexane solution was sampled and analyzed by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS) (HP6890/HP5973, Agilent, USA; see Table 2 for operating conditions).

2.4. Estimation of Ah receptor-binding activities of PCDTs

Dioxins are known to cause endocrine-disruption by binding to Ah receptors in cells. Therefore, we decided to

Table 1
HRGC/HRMS operating conditions

Homologue	Te-HxCDTs	Hp-OCDTs
Resolution	22000	24000
Column[a]	DB-5MS 0.25 mm ID × 30 m, 0.25 µm (J&W Scientific, USA)	
Oven temperature[a]	80 °C (2 min), 8 °C min^{-1} to 320 °C (5 min)	
Ion source temperature	275 °C	
Ionization	Electron impact	
Ionization current	500 µA (42 keV)	
Injection	1 µl (splitless)	
Masses for SIM	TeCDTs: 319.8788, 321.8758	PeCDTs: 355.8369, 357.8339
	HxCDTs: 389.7979, 391.7949	HpCDTs: 423.7589, 425.7560
	OCDT: 457.7199, 459.7170	

[a] The column and temperature program were used by Sielex and Andersson (1997).