Photodegradation and dioxin-like endocrine potential of polychlorinated dibenzothiophenes(1)

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Introduction

Polychlorinated dibenzothiophenes (PCDTs) are sulfur analogues of polychlorinated dibenzofurans (PCDFs). PCDTs have been detected in environmental samples such as soil and sediment[1,2], and in some samples PCDT homologues are present at higher levels than the corresponding PCDD/DFs[3]. Owing to their structural similarity to PCDFs, PCDTs are suspected of causing dioxin-like endocrine disruption[4]. Although PCDTs are environmental contaminants of a great concern, limited information is available for their toxicity and persistency in the environment. Therefore, this research was carried out to estimate the dioxin-like endocrine-disruption potential and photodegradability of these compounds.

Materials and Methods

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) was poured into a 4-cm3 quartz cuvette and subjected to UV irradiation for 1 h with a low-pressure mercury lamp (Germipak GCL212/11.4/Cell/C, Light Sources, USA). During irradiation, a portion of the n-hexane solution was sampled and analyzed by high resolution gas chromatography/low-resolution mass spectrometry (HP6890/HP5973, Agilent, USA).

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 estimate the endocrine-disruption potential of PCDTs by comparing the Ah receptor–binding activities of PCDTs with the activity of 2,3,7,8-TeCDD. 2,3,7,8-TeCDT, 1,2,3,7,8-PeCDT, 1,2,3,7,8,9-HxCDT, 1,2,3,4,7,8,9-HpCDT, and OCDT were separately dissolved in dimethyl sulfoxide and then analyzed with an Ah-immunoassay kit (Paracelsian, USA) according to the instructions supplied with the kit. 2,3,7,8-TeCDD was used as a reference compound in the assay to determine the dioxin equivalency quantity (DEQ) of each isomer. Finally, an experimental toxicity equivalency factor (e-TEF) was calculated on the basis of the DEQ.

Results and Discussion

Photodegradation of PCDTs

Upon photodegradation of OCDT/DF in n-hexane (Fig. 1), the OCDT concentration fell below the detection limit (<10 pg/μl) after 0.5 h, whereas OCDF disappeared after only 0.1 h. This result indicates OCDT underwent photodegradation more slowly than did OCDF.

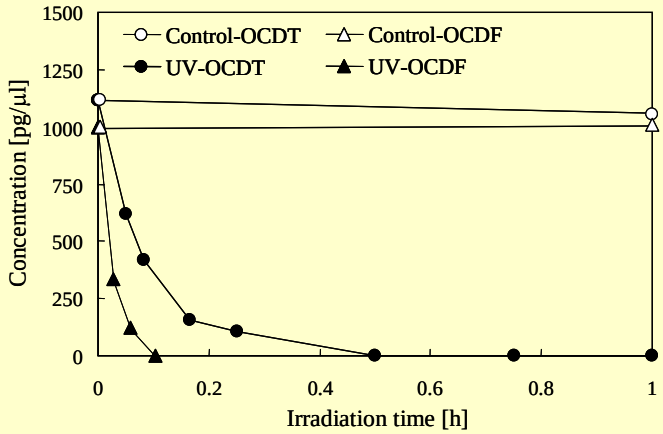

Fig. 1. Time course of OCDT and OCDF concentrations during UV irradiation.

Photodegradation of 2,3,7,8-TeCDT/DF and OCDT/DF followed pseudo-first-order kinetics (Fig. 2). The photodegradation rate of OCDF was about seven times that of 2,3,7,8-TeCDF, a result that agrees with the results of previous research on the photodegradability of 2,3,7,8-TeCDF and OCDF in n-hexane[5]. Photodegradation rates for 2,3,7,8-TeCDT and OCDT were lower than the rates for the corresponding PCDF isomers, and the difference between the octachlorinated isomers was bigger than that between the tetrachlorinated isomers, which indicates that PCDTs are more stable to photodegradation than PCDFs.

Figure 3 shows the total-ion chromatogram of the OCDT solution after 15 min of UV irradiation, at which point Tr–HpCDTs appeared. The presence of lower-chlorinated compounds confirmed that dechlorination of OCDT had occurred. Among the HpCDTs, 1,2,3,4,7,8,9-HpCDT showed the largest peak area, which reached a maximum at 15 min and then decreased (data not shown). 1,2,3,7,8,9-HxCDT was one of the two dominant HxCDTs isomers; the other dominant isomer detected at the same magnitude has not yet been identified.

Photodegradation and dioxin-like endocrine potential of polychlorinated dibenzothiophenes(2)

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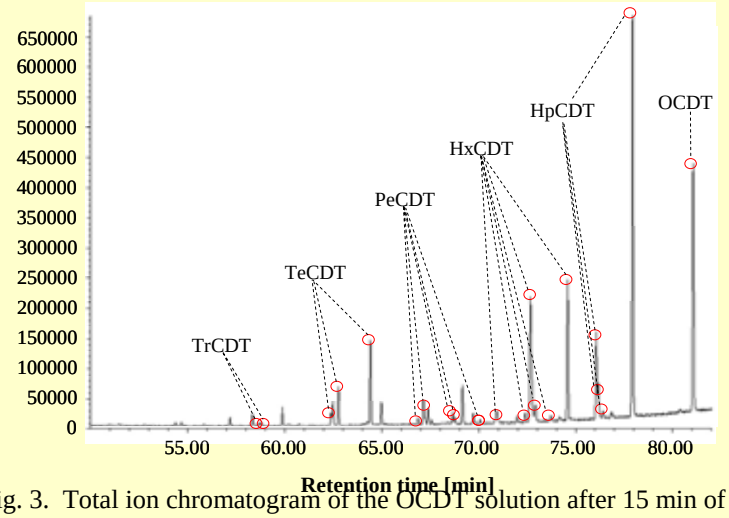

Fig. 3. Total ion chromatogram of the OCDT solution after 15 min of UV irradiation.

In OCDF molecules, the C–Cl bonds at the ortho positions are the weakest bonds, and therefore the C–Cl bonds at the 1- and 9-positions are preferably dissociated during the photodegradation of OCDF[6,7]. In contrast, photodegradation of OCDT produces 1,2,3,4,7,8,9-HpCDT preferentially, which allows us to hypothesize that the C–Cl bonds at the 4- and 6-positions may be the weakest of the eight C–Cl bonds of OCDT. The predominance of 1,2,3,7,8,9-HxCDF supports this hypothesis. To verify this hypothesis, further research is necessary to identify the unknown isomers.

Ah receptor-binding activity

Table 1 summarizes the responses of the five isomers relative to the response of 2,3,7,8-TeCDD in the Ah-immunoassay. All the tested isomers, except for OCDT, demonstrated Ah receptor–binding activities, which indicates that PCDTs have the potential to cause dioxin-like endocrine disruption. Of the five isomers, 2,3,7,8-TeCDT and 1,2,3,7,8-PeCDT showed the highest e-TEF values, at 0.1. This value is substantially different from the value of 0.001 that Kopponen et al. obtained for 2,3,7,8-TeCDT by measuring the induced AHH/EROD activities in Hep1c1c 7 cell[4]. The large difference may be due to the difference in the assay systems used.

Table 1 Response of PCDTs relative to 2,3,7,8-TeCDD

Isomer	2,3,7,8-TeCDD [pg-DEQ/g]	e-TEF [-]
2,3,7,8-TeCDT	111	0.1
1,2,3,7,8-PeCDT	117	0.1
1,2,3,7,8,9-HxCDT	44	0.04
1,2,3,4,7,8,9-HpCDT	50	0.05
OCDT	N.D.	-*

* Value could not be calculated.

Kobayashi investigated the Ah receptor–binding activities of PCDF isomers and reported the following e-TEF values: 0.06 for 2,3,7,8-TeCDF, 0.04 for 1,2,3,7,8-PeCDF, 0.6 for 1,2,3,7,8,9-HxCDF, 0.07 for 1,2,3,4,7,8,9-HpCDF, and 0.008 for OCDF[8]. Note that the e-TEF values for 2,3,7,8-TeCDT and 1,2,3,7,8-PeCDT were higher than the values for the corresponding PCDF isomers, whereas the opposite relationship was observed for the hexa- and octachlorinated isomers. In addition, the e-TEF value of 1,2,3,4,7,8,9-HpCDT was nearly identical to that of 1,2,3,4,7,8,9-HpCDF. These results indicate that PCDTs have dioxin-like endocrine-disruption potential comparable to that of PCDFs.

References

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