

Persistence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in Ya-Er Lake area, China

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Abstract

The concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in surface sediment, soil, human hair, and fish muscle from Ya-Er Lake area, China, were analyzed. The results showed that there were very high concentrations of PCDD/F existing in these samples. The results also indicated that Ya-Er Lake, which received a large amount of waste water from a nearby chloroalkali plant, was heavily polluted by PCDD/F. The present study demonstrated that those congeners, which possess at least three chlorine atoms in the lateral position with a fourth chlorine atom in the neighborhood bond of the third single chlorine atom, such as 1,2,7,8-TCDF and 2,3,6,7-TCDF, were very resistant to biodegradation due to the “neighbor effect” of every two chlorine atoms. The present study suggested that human hair may be a suitable alternative bioindicator for detecting PCDD/F exposure. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) have been globally distributed and can be found in all environmental media (Somogyi, 1997; Li et al., 1999). They are chemically stable, have low solubilities in water, and have been shown to be accumulated in the foodweb (Geyer et al., 1990; Bonn, 1998; Landi et al., 1998). Those isomers with chlorines substituted in the 2,3,7,8 positions are thought to pose a risk to human health due to their toxicity, carcinogenic potency, and potential effects on animal reproductive and immunological systems (Safe, 1990; US-EPA, 1993; Boening, 1998; Vos et al., 1997). It has been reported recently that PCDD/F possess the toxicity of endocrine disrupting (Mocarelli et al., 1996; Safe, 1998).

Humans are consumers of fish, and exposure assessments now routinely consider fish ingestion as a potential route of human exposure to chemicals in the environment. Body fluids and tissues are commonly used to characterise human exposure, which integratively describe the long-term expo-

sure in the past without enabling us to identify distinct body burdens. It was reported that hair monitoring could provide useful monitoring information for human and animal samples (Schramm, 1997; Klein et al., 1992).

Ya-Er Lake has been heavily polluted by the large amount of waste water from the chloroalkali industry nearby, therefore the concentrations of PCDD/F and other chemical pollutants are relatively high in the sediment. Early studies focused on HCH isomers (Xu, 1994), while in recent years, studies were focused on PCBs and PCDD/F (Wu, 1999). The residents in Ya-Er Lake area are mainly living on rice-planting, fishery, and other aquatic products. A substantial number of residents in this area have hepatitis and skin diseases, and the reasons of causing these diseases are unclear. In the present study, the concentrations of PCDD/F in sediment, soil, fish muscle (common carp), and human hair samples of the region were analyzed in order to obtain a clearer picture.

2. Materials and methods

2.1. Sampling

Surface sediment, soil, fish muscle, and human hair were collected from Ya-Er Lake area, China in September 1997.

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Before 1962, Ya-Er Lake was an oligotrophic lake. During 1962–1978, the lake was seriously polluted by the effluent of hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB) from a large chemical plant. In 1979, a series of five ponds were built for treating the effluent by self-oxidative purification (Wu, 1999). The water depth of the lake is 2–3 m and the pH of the water is 7.5–7.9.

2.2. PCDD/F analysis

After homogenization, except for human hair, all the other samples were freeze-dried and ground. The PCDD/F analysis was performed using the isotope dilution technique. About 2 g dried sample was spiked with $^{13}\text{C}_{12}$ labeled 2,3,7,8-substituted PCDD/F internal standards. Extraction was carried out by Soxhlet using 180 ml toluene for 24 h. Thirty liters of lake water were enriched by XAD (Suplco), then freeze-dried and extracted as 20 g fish sample. Details including the validation and quality assurance of the method are described elsewhere (Wu et al., 1998). Quantification and detection were performed on a high-resolution gas chromatography coupled with mass spectrometry in EI mode by tracing the M^- , $(\text{M}+2)^-$, or the most intensive ions of the isotope cluster (Finnigan MAT95s, $R=10,000$).

3. Results and discussion

Fig. 1 shows the results of homologue profiles of PCDD/F of human hair, surface sediment, and fish samples collected from Ya-Er Lake. The concentrations of PCDD/F

F in human hair were not related to human age. Fig. 2 shows the results of PCDD/F homologues and 2,3,7,8-substituted PCDD/F in two human hair and soil samples near the chloroalkali plant. Fig. 3 compares the average concentrations of PCDD/F of hair and surface sediment samples. The high concentrations of PCDD/F in these samples indicated that the Ya-Er Lake, which received a large amount of waste water from the nearby chloroalkali industry, was heavily polluted by PCDD/F.

If the congeners of PCDD/F are further compared, we can find 1,2,7,8-TCDF and 2,3,6,7-TCDF are unusual. They are also bioaccumulated as 2,3,7,8-substituted PCDD/F in hair. Their chemical structures are the same as 2,3,8,9-TCDF and 3,4,7,8-TCDF, respectively. These congeners possess at least three chlorine atoms in the external rings and the fourth chlorine atom must be located at the neighbor bond of the third atom (Fig. 4). Because of their chemical structures, these congeners have no special biological toxicity, but they are very resistant to biodegradation due to the “neighbor effect” of the two chlorine atoms (Wu, 1999). Among pentachlorinated dibenzofurans, 1,2,4,7,8-PeCDF, 1,2,3,6,7-PeCDF, 1,2,6,7,7-PeCDF, and 2,3,4,6,7-PeCDF show relatively high ability of bioaccumulation, due to the reason mentioned above. Ingested and inhaled PCDD/F are completely metabolised, except the 2,3,7,8-substituted PCDD/F and the above persistent congeners which are accumulated in the mammalian body (Wu, 1999). An external exposure of hair leads to a congener pattern that also contains the nonpersistent isomers. Using the information from the PCDD/F pattern, the source and pathway of exposure can be identified. Based on the present results,

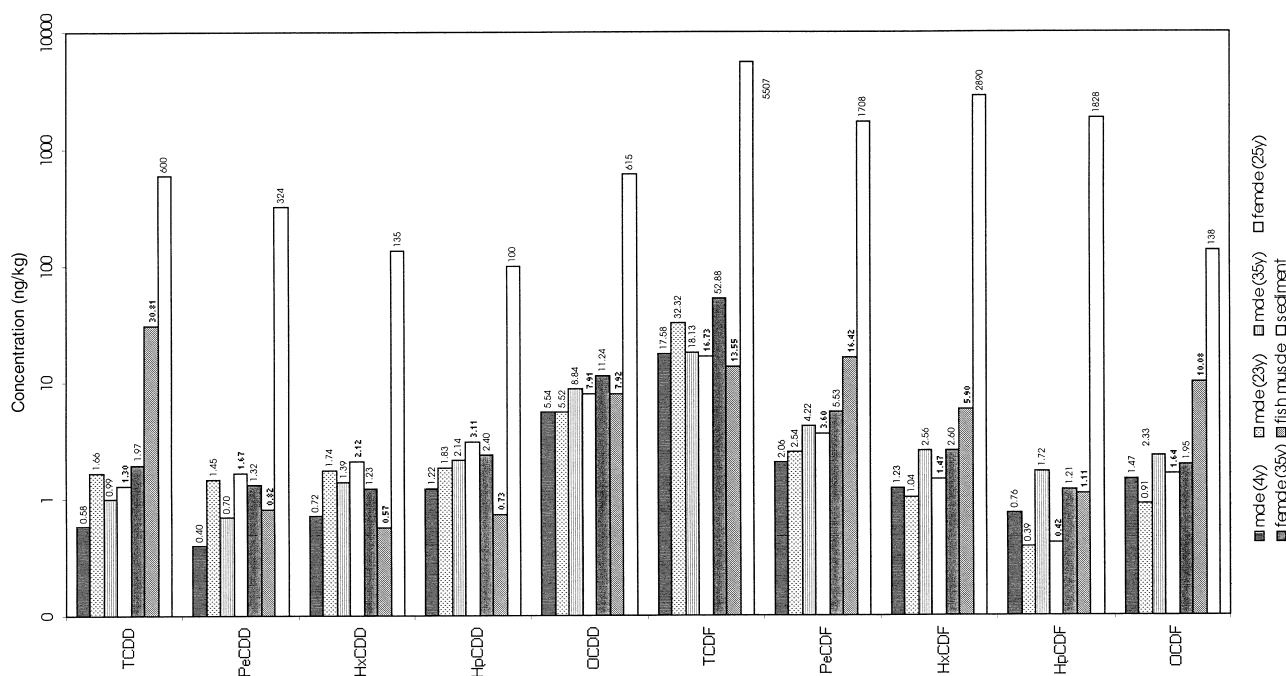


Fig. 1. PCDD/F homologue profiles in surface sediment (0–12 cm), fish (common carp) muscle, and human hair.

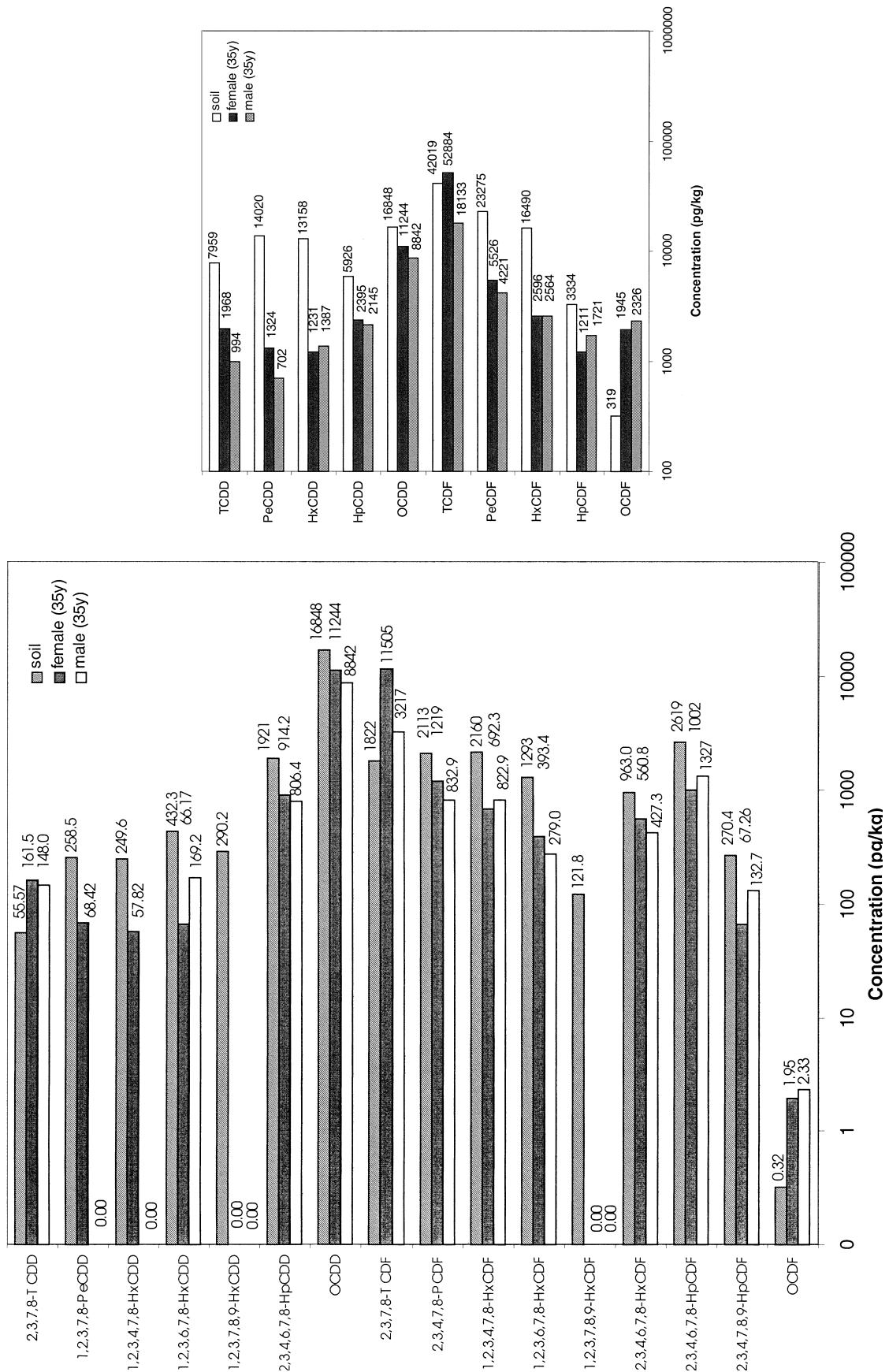


Fig. 2. Two human hair and soil samples near chloroalkali industry area: (a) PCDD/F homologue; (b) 2,3,7,8-substituted PCDD/F.

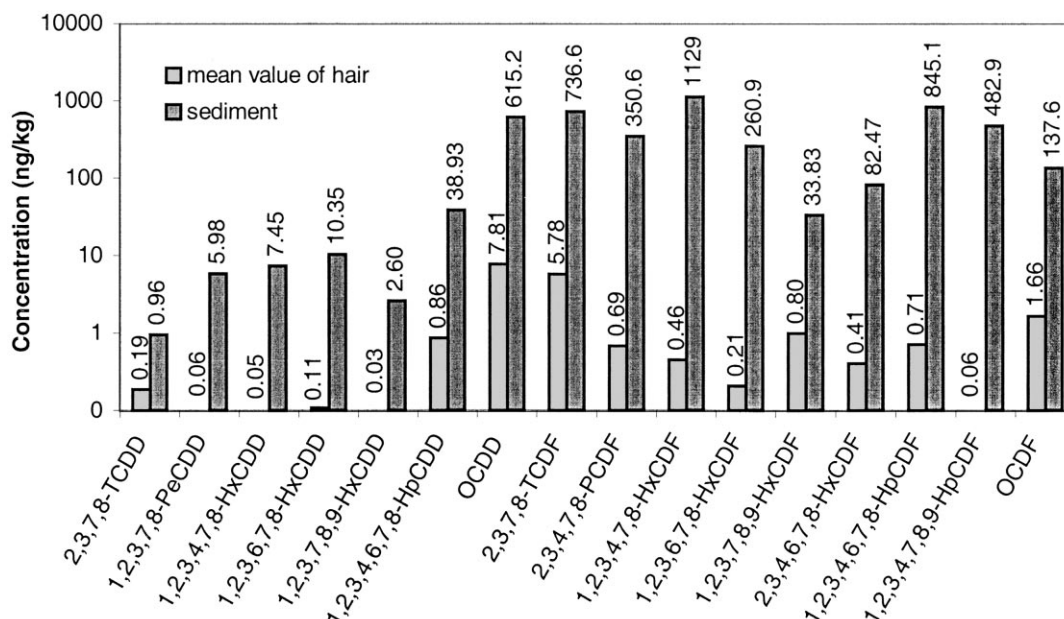


Fig. 3. The concentrations of 2,3,7,8-substituted PCDD/F in sediment and the mean value in human hair.

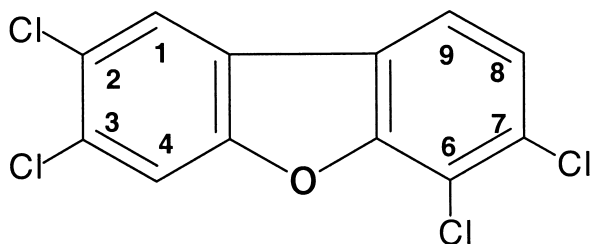


Fig. 4. The structure of special persistent congeners in human hair, such as 2,3,8,9-TCDF, 3,4,7,8-TCDF, 1,2,7,8-TCDF, and 2,3,6,7-TCDF, respectively, which have at least three chlorine atoms in the external rings and the fourth chlorine atom must be in neighbor bond of the third atom.

human hair may be used as an alternative bioindicator for detecting PCDD/F exposure.

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