

Dioxin '97, Indianapolis, Indiana, USA

Profile of Chlorinated and Brominated Dioxins and Furans in Soil and Sediments Collected at a Former Chlor-Alkali Plant

Kurunthachalam Kannan¹, Isao Watanabe², and John P. Giesy¹, ¹Pesticide Research Center, Michigan State University, East Lansing, MI 48824-1222, USA, ²Osaka Prefectural Institute of Public Health, 1-3-69 Nakamichi, Higashinari-ku, Osaka 537, Japan

Abstract

Soil and sediments collected at a former chlor-alkali plant in coastal Georgia (United States), contained total PCDF concentrations as great as 82 ng/g, dry wt. PCDF concentrations in marsh sediments declined gradually with distance from the source. Of PCDDs/DFs, 2,3,7,8-substituted PCDFs accounted for 94-98% of the TCDD-like activity. Concentrations of PCDDs in sediments were as great as 17 ng/g. Reduction in PCDD concentrations with distance from the source was less than that for PCDFs. PBDDs and PBDFs were not detected. Polybrominated biphenyl ether (PBBE) and monobromo-heptachloro dibenzo-*p*-dioxins and dibenzofurans (PXDDs/DFs) were detected at less concentrations and their spatial distribution was similar to those of PCDDs.

Introduction

A former chlor-alkali plant in coastal southeastern Georgia (United States) utilized Aroclor 1268, an uncommon, more chlorinated polychlorinated biphenyl (PCB) mixture to lubricate graphite electrodes used in process equipment. Disposal of process wastes into large holding pits as well as directly into adjacent marshlands has resulted in extensive contamination of soils on-site and also of sediments in the coastal marsh. While studies have shown extensive contamination by PCBs ^{1,2}, no reports of dioxins and furans in soil and sediments from the site are available. Graphite electrodes used in the chlorine production in chlor-alkali process have been identified as a potential source of PCDDs and PCDFs in the environment ³. In this study, on-site soil and sediments collected along a contamination gradient were analyzed for chlorinated-, brominated- and mixed bromo-polychlorinated dibenzo-*p*-dioxins (PCDDs, PBDDs, PXDDs) and dibenzofurans (PCDFs, PBDFs, PXDFs) and polybrominated biphenyl ethers (PBBEs) to characterize their occurrence and distribution.

Materials and Methods

Surficial sediments (0-5 cm) were collected during low tide, at two intertidal locations - one in the contaminated marsh close to industrial site (marsh sediment) and the other about 500 m away from the site, at Purvis creek (creek sediment). Details and map of sampling locations are given elsewhere¹. A grab sample of soil excavated from the industrial site was also collected. Samples were collected with a stainless scoop pre-rinsed with acetone and hexane, homogenized, immediately placed in I-Chem jars and transported to the laboratory in ice-filled portable

containers and stored at -20°C prior to analysis. Sediments were freeze dried and passed through a 500 µm sieve prior to chemical analysis.

Soil and sediment samples (10 to 20 g) were Soxhlet extracted with a mixture of *n*-hexane and acetone (1:1, 150 mL) for 20 h. The extract was transferred to a separatory funnel containing hexane-washed water (500 ml) and re-extracted twice with 100 mL of *n*-hexane. The extract was dried over anhydrous sodium sulfate (50 g) and spiked with ¹³C-labeled 2,3,7,8-substituted PCDDs/DFs as internal standards, which was then Kuderna-Danish concentrated to 15 mL and treated three times with 5 mL volumes of conc. sulfuric acid. Extracts were cleaned on a multi layer column chromatography (20 mm i.d. X 25 cm) packed with 2 g of 10% AgNO₃-silica (w/w), 3 g of 44% H₂SO₄-silica, and 2 g of 2% KOH-silica eluting with 180 mL of 5% dichloromethane in hexane, following the method described elsewhere ^{4,5}. The eluate was concentrated and passed through 3 g of neutral alumina (10 mm i.d. X 30 cm), which had been activated at 230°C (12 h) for fractionation. The first fraction eluted with 25 mL of 4% dichloromethane in *n*-hexane contained contained PBBEs except decabromobiphenyl ether (DBBE) and the second fraction eluted with 20 mL of 50% dichloromethane in *n*-hexane contained PCDDs/DFs, PBDDs/DFs and PXDDs/DFs.

Dioxins and furans were quantified using a high resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). A Hewlett-Packard 5890 series II gas chromatograph equipped with a JEOL JMS-700 mass spectrometer and a fused silica capillary column coated with DB-5 (60 m X 0.25 mm i.d., 0.1 µm film thickness) (J&W Scientific, Folsom, CA) was used to quantify PCDDs/DFs, PBDDs/DFs and PXDDs/DFs. 2,3,7,8-substituted PCDDs/DFs were quantified with a SP-2331 coated capillary column (60 m X 0.25 mm i.d., 0.2 µm film thickness) (Supelco, Bellefonte, PA). The mass spectrometer was operated at EI mode with an ionization voltage of 50 eV and was held at 280°C. The masses monitored for each analyte were chosen at two most intensive ions of molecular ion cluster. Recoveries of internal standards were between 67 and 89%. To avoid photodegradation of PBDDs/DFs and PXDDs/DFs during analysis, amber color glassware was used. A Shimadzu 15A gas chromatograph equipped with a ⁶³Ni-electron capture detector (ECD) and a DB-5 column (30 m X 0.25 mm i.d.; 0.1 µm film thickness) were used for the analysis of decabromobiphenyl ether (DBBE).

Results and Discussion

Concentrations of total PCDDs and PCDFs in soil and sediments were in the range of 6-17 and 1.9-82 ng/g, dry wt, respectively (Fig. 1). PCDFs concentrations in excavated soil was 7-fold greater than that of PCDDs. Graphite electrodes used in the chlor-alkali industry are made of wood-pitch, a material providing aromatic precursors from which PCDFs are formed during electrolysis. Because of the lack of appropriate precursors in the pitch, however, PCDDs are not formed in appreciable quantities ⁶. The relative abundance of PCDFs in marsh sediment was in the order of, HxCDF > OCDF > PnCDF ≥ HpCDF > TeCDF (Fig. 1). Creek sediment contained comparable concentrations of TeCDF through OCDF. An altered PCDF homolog composition in sediments relative to soils suggests physico-chemical and biologically-mediated transformation processes in sediments. Concentrations of PCDFs declined along a gradient with increasing distance from the source. PCDF concentrations in marsh sediment were 2-fold less than those in soil, whereas concentrations in creek sediments were 44-fold less.

Dioxin '97, Indianapolis, Indiana, USA

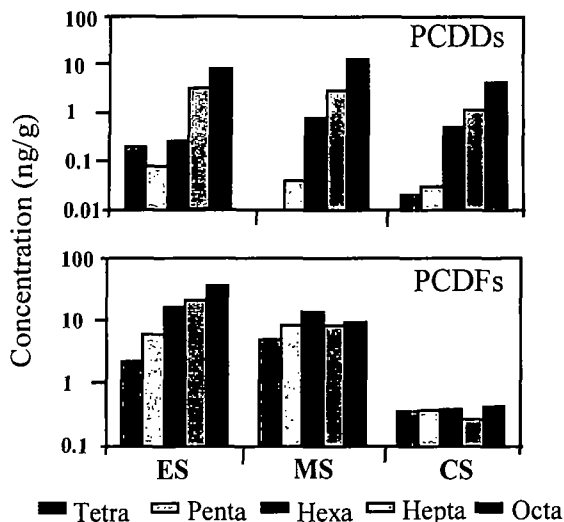


Fig.1. Concentrations (dry wt) of PCDDs and PCDFs in soil and sediments collected at a chlor-alkali plant. (ES-Excavation soil, MS-Marsh sediment, CS-Creek sediment)

Concentrations of PCDDs in soil and marsh sediment were 12 and 17 ng/g, dry wt, respectively. The spatial distribution of PCDDs was different from those of PCDFs. Marsh sediment contained greater concentrations of PCDDs than the excavation soil, while the creek sediments had 3-fold less concentration than of marsh. In contrast to PCDFs, the decline in concentrations of PCDDs along the contamination gradient was less prominent. This suggests the presence of other sources of PCDDs in or near the marsh. An electric power utility that occupied the site prior to construction of the chlor-alkali facility is a potential source. OCDD was the dominant congener accounting for >70% of the total PCDDs concentration (Fig. 1). HpCDD and HxCDD accounted for 17-27 and 2.2-8.7% of the total PCDDs, respectively.

PBDDs and PBDFs were not detected in soil or sediments at the chlor-alkali plant. PBBEs were detected in excavated soil and sediments at concentrations ranging from 0.28 to 1.02 ng/g, dry wt. Similar to that of PCDDs, marsh sediment contained greater concentrations compared to excavated soil and creek sediments. Tetrabrominated biphenyl ether (TeBBE) was the most prevalent congener.

PXDDs were encountered at concentrations ranging from 0.03-0.1 ng/g, dry wt. Monobromo-heptachloro dibenzo-*p*-dioxin (OXDD) was the only congener detected. The spatial distribution of OXDD was similar to those of PCDDs, with marsh sediment containing greater concentrations relative to excavated soil, while creek sediments had 3-fold less concentration than of the marsh. This suggests that OXDD and PCDDs may have originated from a common source.

2,3,7,8-TCDD Equivalents

Concentrations of 2,3,7,8-substituted PCDDs accounted for 79-87% of the total PCDDs in soil and sediments. The percentage of 2,3,7,8-substituted PCDFs in soil, marsh and creek sediments was 76, 43 and 52% of the total PCDFs, respectively. The estimated 2,3,7,8-TCDD equivalents

in soil, marsh and creek sediments were 1.34, 0.66 and 0.05 ng/g, respectively (Fig. 2). PCDFs accounted for 94-98% of the TCDD like-toxicity in soil and marsh sediments. Contribution by PCDDs to the concentrations of toxic equivalents was relatively greater in creek sediments than in soil and marsh sediments. Generally, corresponding with the reduction in total PCDF concentrations, toxic potential of these media also declined by 25-fold along the contamination gradient.

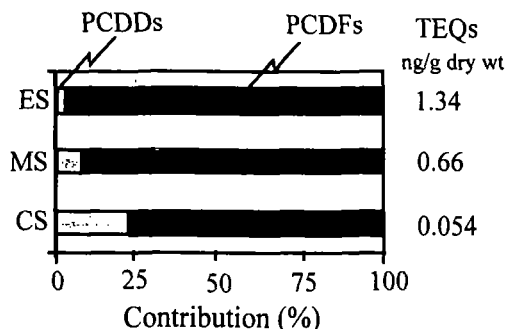


Fig. 2. Contribution of PCDDs and PCDFs to 2,3,7,8-TCDD EQs in soil and sediments collected at a chlor-alkali plant. (ES-Excavation soil, MS-Marsh sediment, CS-Creek sediment)

Graphite electrodes have been used internationally for the production of chlorine, by chlor-alkali plants. Thus, PCDDs/DFs contamination at this site may be an issue for the entire industry. In most modern plants the use of graphite electrodes was discontinued during the 1980s³⁾. However, sediments from industrialized areas and sludge from water treatment facilities exhibit the "chlorine pattern" of PCDD/DF contamination even in recent years⁷⁾, which suggests inputs of PCDDs/DFs from chlor-alkali process.

Literature Cited

- (1) Kannan, K.; Maruya, K.A.; Tanabe, S. *Environ. Sci. Technol.* **1997**, (in press).
- (2) USEPA. Analytical Report - LCP Chemical Site, Brunswick, Georgia. United States Environmental Protection Agency, Emergency Response Team, 1995, p.72.
- (3) Rappe, C.; Kjeller, L.-O.; Kulp, S.-E.; de Wit, C.; Hasselsten, I.; Palm, O. *Chemosphere* **1991**, 23, 1629-1636.
- (4) Watanabe, I.; Kawano, M.; Tatsukawa, R. *Organohalogen Compounds, Dioxin'95*, **1995**, 24, 337-340.
- (5) Loganathan, B.G.; Kannan, K.; Watanabe, I.; Kawano, M.; Irvine, K.; Kumar, S.; Sikka, H.C. *Environ. Sci. Technol.* **1995**, 29, 1832-1838.
- (6) Zook, D.R.; Rappe, C. *Dioxins and Health*, (A. Schecter, ed.), Plenum Press; London, 1994; pp. 79-113.
- (7) Evers, E.H.G.; Klamer, H.J.C.; Laane, R.W.P.M.; Govers, H.A.J. *Environ. Toxicol. Chem.* **1993**, 12, 1583-1598.