

Sedimentary record of Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in a Dated Sediment Core from the Northern Arabian Gulf.

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are a class of ubiquitous environmental contaminants with a tricyclic aromatic structure, high chemical stability and poor aqueous solubility. They are unintentionally produced, mostly as byproducts of industrial activities such as cement manufacturing, metal smelting, processing of paper pulp, incineration of medical waste, and the backyard burning of household waste containing chlorinated materials such as plastics¹. They are also present as impurities during the manufacture of chlorinated aromatics such as pentachlorophenol (PCP), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs)²⁻³. Natural sources of PCDD/Fs include volcanic eruptions and forest fires. Since they are hydrophobic they preferentially associate with suspended particulate material and sediments upon entry into the marine environment and transported to bottom sediments where their incorporation can be delayed due to recycling processes like bioturbation and resuspension. Sediments can thus provide an important record of contamination. The use of dated sediment cores is a well-established means of reconstructing historical chronologies of contaminant inputs⁴. In the current study we reconstruct the input chronology of PCDD/Fs in sediments from a very remote area within Kuwait's territorial waters not influenced by any point sources of contaminants (Fig. 1) enabling us to investigate the historical trends in atmospheric concentrations of PCDD/Fs in Kuwait, and possibly the Arabian Gulf.

Materials and methods

A sediment core was collected using a freeze corer from the location in Fig. 1. The freeze corer comprised of a rectangular aluminium frame (16 x 8 x 150 cm) with a tapered end for easy penetration into sediment⁵⁻⁶. The corer was filled with dry ice and ethanol before lowering into the water. The corer was allowed to drop freely from approximately 5 m from the sediment-water interface into the sediment and left there for between 15 and 20 min. When retrieved thick slabs of sediment was frozen on both faces of the corer. The slabs of sediment were gently scraped off the metal plate, wrapped in aluminium foil, kept frozen on dry ice in coolers for transport back to the laboratory where it was stored at -18°C until sectioning. One side of the sediment core was used for the PCDD/F analysis and the other side for radiochemical dating. The core was sectioned at approximately 2 cm intervals. The sectioning materials were washed and solvent-rinsed between each section. The samples were stored in clean, solvent-rinsed, amber glass jars and kept at -20°C prior to analysis.

Dating. The unsupported ²¹⁰Pb (total – supported) radioisotopes was used to determine sedimentation rates. The specific activity of total ²¹⁰Pb and ¹³⁷Cs radioisotopes were determined using ultra low background γ -spectrometry with HPGE detectors. Supported ²¹⁰Pb was obtained by indirectly determining the activity concentration of the supporting parent ²²⁶Ra. The unsupported ²¹⁰Pb was calculated by subtracting the ²²⁶Ra activity from the measured ²¹⁰Pb. The mean sedimentation rate determined from the unsupported ²¹⁰Pb profiles in the upper portion of the sediment column was determined to be 0.7±0.17 cm y⁻¹. The dates shown in subsequent figures are those based on the ²¹⁰Pb-derived mean sedimentation rate.

Extraction and Analyses

The analytical method used to determine the PCDD/F concentrations in sediments is similar to that reported by Ma et al⁷ with slight modifications. Approximately 40 g of wet sediment were homogenized with approximately 160 g anhydrous sodium sulfate that has been previously baked at 650 °C to remove residual water. The mixture was Soxhlet-extracted with 400 mL dichloromethane:hexane (3:1 v/v) for 16 h. Prior to extraction the mixture was spiked with PCB congeners 30 and 204 to monitor analytical recovery. The extracts were rotary-evaporated

to 10 mL at 38 °C and spiked with $^{13}\text{C}_{12}$ -labeled internal standards (2378-TCDD/F, 12378-PeCDD/F, 123678-HxCDD/F, 1234678-HpCDD/F, OCDD; Wellington Laboratories, Guelph, Ontario, Canada). Elemental sulphur was removed using activated copper. The extracts cleaned on a multilayer silica gel column, packed in the following order: 2 g of silica gel, 2 g of 40% acidic-silica gel, 2 g of silica gel, 1 g of Na_2SO_4 (baked at 400 °C for 6 h) at the top. The column was pre-cleaned by passage of 100 mL of hexane. Sample extracts were then loaded and eluted with 150 mL of 30% dichloromethane in hexane, and rotary-evaporated to 5 mL. The extract was then passed through a glass column (10 mm i.d.) packed with 1 g of silica gel-impregnated carbon (Wako Pure Chemical Industries, Tokyo, Japan) and 1 g of Na_2SO_4 . PBDEs and PCBs were eluted with 150 mL of 20% dichloromethane in hexane (F1; discarded); PCDD/Fs were eluted with 200 mL of toluene (F2), and then concentrated to 50 μL under a gentle stream of ultra-pure nitrogen.

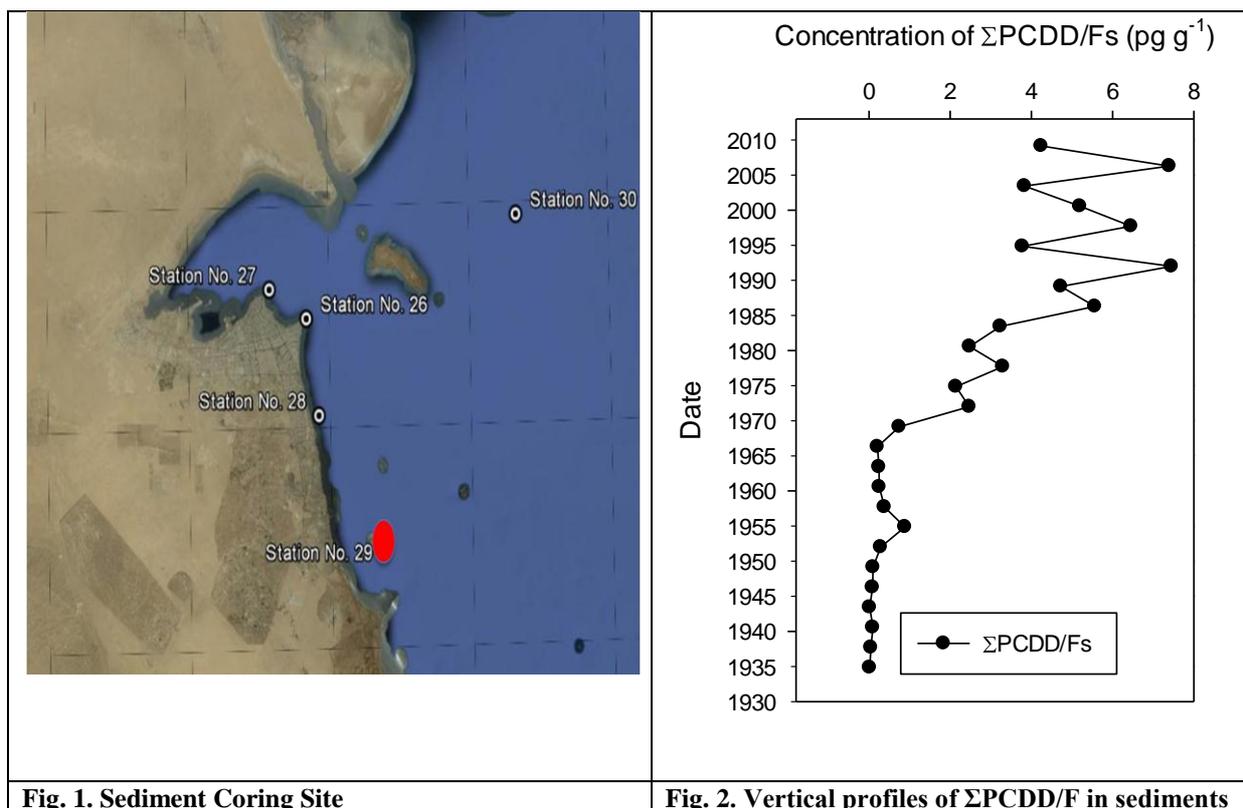


Fig. 1. Sediment Coring Site

Fig. 2. Vertical profiles of ΣPCDD/F in sediments

Identification and Quantification. Extracts from the carbon column (F2) were injected into a high-resolution gas chromatograph (HRGC; Thermo Trace GC Ultra; Thermo Electron Corporation, Bellefonte, PA, USA) coupled with a high-resolution double-focusing mass selective detector (HRMS; Thermo DFS; Thermo Fisher Scientific, Bremen, Germany) at a resolving power of >10000 (10% valley) for the determination of PCDD/F congeners. The GC column used was a DB-5 (0.25 mm \times 60 m \times 0.1 μm film thickness; J&W Scientific Inc, Folsom, CA). The column oven temperature was programmed from 140 °C (2 min) to 190 °C at a rate of 20 °C/min, and then to 216 °C at a rate of 1 °C/min, then to a final temperature 290 °C (10 min) at a rate of 10 °C/min. The HRMS was operated in a positive electron impact (40 eV), selected ion monitoring mode. All of the congeners were quantified using the isotope dilution method based on the responses from the corresponding $^{13}\text{C}_{12}$ -labeled congeners. Identification of 17 2,3,7,8-substituted PCDD/F congeners was accomplished by injection of corresponding external standards of each of the congeners (Wellington Laboratories Inc, Guelph, ON).

Quality Assurance/Quality Control. Procedural blanks were analyzed with every 10 samples. The reported concentrations in samples have been corrected for blank values, when applicable. Limits of quantification (LOQs) were estimated as 3 times mean value of blank measurements (0.00-0.94 pg/g dw for TCDD/F, 0.00-

1.29 pg/g dw for PeCDD/F, 0.00-1.17 pg/g dw for HxCDD/F, 0.49-1.74 pg/g dw for HpCDD/F, 1.47-1.77 pg/g dw for OCDD/F). For TEQ calculations, values below the LOQ were assigned a value of one-half of the LOQ, and the non-detects were set to zero. Recoveries of $^{13}\text{C}_{12}$ -labeled PCDD/Fs spiked into individual samples were $105\pm 29\%$ for TCDD/F, $105\pm 28\%$ for PeCDD/F, $106\pm 30\%$ for HxCDD/F, $101\pm 33\%$ for HpCDD/F, and $84\pm 31\%$ for OCDD. Quality control standards for PCDD/Fs were analyzed after every five samples, to monitor instrument stability. All of the concentrations presented are given on a dry weight (dw) basis.

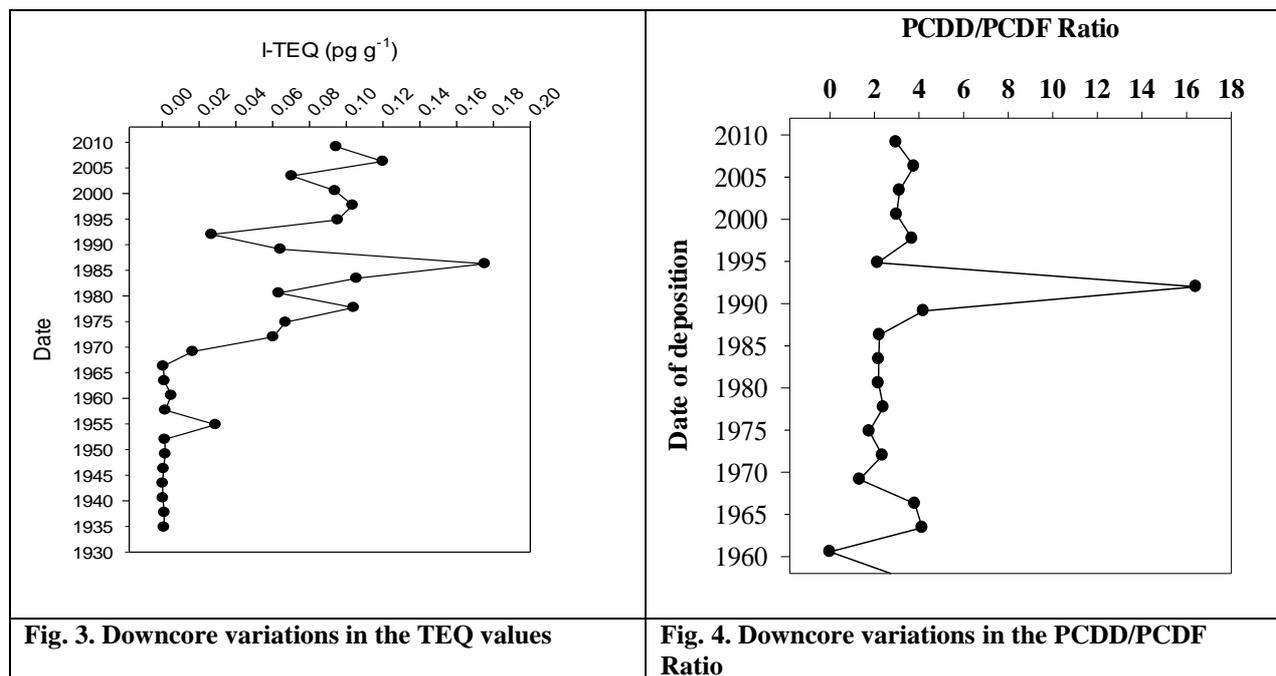
Results and discussion

The downcore variations in $\Sigma\text{PCDD/Fs}$ concentrations is summarized in Fig. 2 illustrating the time trends in the atmospheric records of dioxin contamination in Kuwait. The historical record shows that PCDD/F concentrations started to increase above pre-industrial background levels in the mid 1960s. This was followed by an exponential increase in concentrations attaining a maximum of 7.5 pg g^{-1} in the early 1990s and fluctuated between 3.5 and the 7.5 pg g^{-1} thereafter. The presence of PCDD/Fs before the mid 1960s is likely to be from natural processes, backyard burning, burning of wood, and other small scale industrial activities such as metal smelting that may have been occurring within the catchment. The PCDD/F profile seems to parallel economic developments and armed conflicts in the Middle East. Oil exploration in Kuwait began in the early 1950s and became the largest oil exporting country by the mid-1960s when the PCDD/F concentrations started to increase above background concentrations. A major war was fought between Iraq and Iran started in 1980 and lasted until 1988. During this period there were over 520 attacks on commercial oil tankers which appear to coincide with the rapid increase in PCDD/F concentrations in the sediment core.

In order to compare the findings in this study with other similar studies the concentrations measured in the samples were expressed in terms of their total toxicity, represented by their toxic equivalency (TEQ). This was calculated by multiplying the absolute concentration of each of the seventeen 2,3,7,8-substituted dioxin and furan by a toxic equivalency factor (TEF). The sedimentary profile of the I-TEQs, representing the 17 most persistent, carcinogenic and potentially toxic congeners of PCDD/Fs in sediments obtained in this study are shown in Fig.3. The downcore variations in the I-TEQs in the sediment were very low in deeper sediments and started to increase in the mid-1960s to a maximum of 0.18 pg I-TEQ/g in the mid-1980s and a decrease to present day levels of 0.08 pg I-TEQ/g . The concentrations of PCDD/Fs in recent sediments are among the lowest reported in the literature for coastal marine sediments and estuaries.

The homolog profiles in sediments remained fairly consistent throughout the core with PCDD contributing 75% (range, 55-100%) to the $\Sigma\text{PCDD/F}$ concentrations. The homolog profile was dominated by OCDD which contributed approximately 55% (range, 35-70%) of the total dioxins throughout the core. The vertical variations in the PCDD/PCDF ratio shown in Fig. 4 supports the theory that the source of PCDD/Fs have remained fairly consistent throughout the sedimentary history covered by the length of the core except for sediments deposited in the early 1990s. The consistency in the homolog patterns throughout the core suggests that the source of dioxins have remained practically unchanged throughout the sedimentary record represented by the core. This congener profile dominated largely by OCDD and other highly chlorinated dioxins and furans have been linked primarily to inputs indicative of the use of pentachlorophenol in industrial applications and/or the atmospheric conversion of dioxins released from other processes but photochemically altered during atmospheric transport to the study area.

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The ratio fluctuates between 1.5 and 4 for the most part except in sediments dated as been deposited in the early 1990s having a ratio of 16.4. This pulse in the PCDD/PCDF ratio corresponded to the 1991 invasion of Kuwait by Iraq. The source of dioxins during the conflict may have been entirely different during this period. During the invasion of Kuwait an estimated 11 million barrels (1749 Tm³) of oil was released into the Arabian Gulf in addition to the torching of 727 oil wells which started in February and lasted until November 1991 releasing massive amounts of smoke and other chemicals into the environment.

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