Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Laurentian Trough Sediments, Lower St. Lawrence Estuary

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are released in the environment as undesirable by-products of various anthropogenic activities[1]. Combustion of organochlorine-based products is one of the most significant sources of these compounds[2]. Other sources of PCDD/Fs in the environment include production of paper products from chlorine-bleached wood pulp and chemically manufactured chlorinated organic compounds[3-5]. However, there is still a lack of information on the environmental fate of these compounds, especially in coastal marine systems.

This study describes the levels and the sedimentary records of PCDDs and PCDFs in two sediment cores from the Laurentian Trough, the main zone of accumulation of fine-grained sediment and associated contaminants in the Estuary and Gulf of St.Lawrence[6,7]. Depth distribution profiles of individual congeners and distribution patterns of PCDD/F homolog groups are examined in an attempt to trace and characterize historical changes in sources of PCDD/Fs to the St.Lawrence Estuary.

2. Methods

Sampling. In June 1992, sediments from two stations in the St.Lawrence Estuary (23 and 24A) at water depths greater than 300 m were collected using a box corer . The sediment cores were immediately sliced on board in 0.5 cm increments at the top, gradually increasing to 3 cm increments at the 40 cm depth. Aliquots of each slice were transferred to solvent-cleaned glass jars and kept frozen at -20°C for later analysis.

PCDD/F analysis. Sediment samples were air-dried at room temperature and ground to a fine powder in a mortar. Approximately 10 g of each sediment sample were spiked with a surrogate mixture of nine [$^{13}C_{12}$]-labelled dioxins and furans and then soxhlet extracted overnight with toluene. The extraction solutions were evaporated to about 1 ml, solvent exchanged to hexane and further reduced in volume to 1 ml. The residues were eluted through a multi-layer column

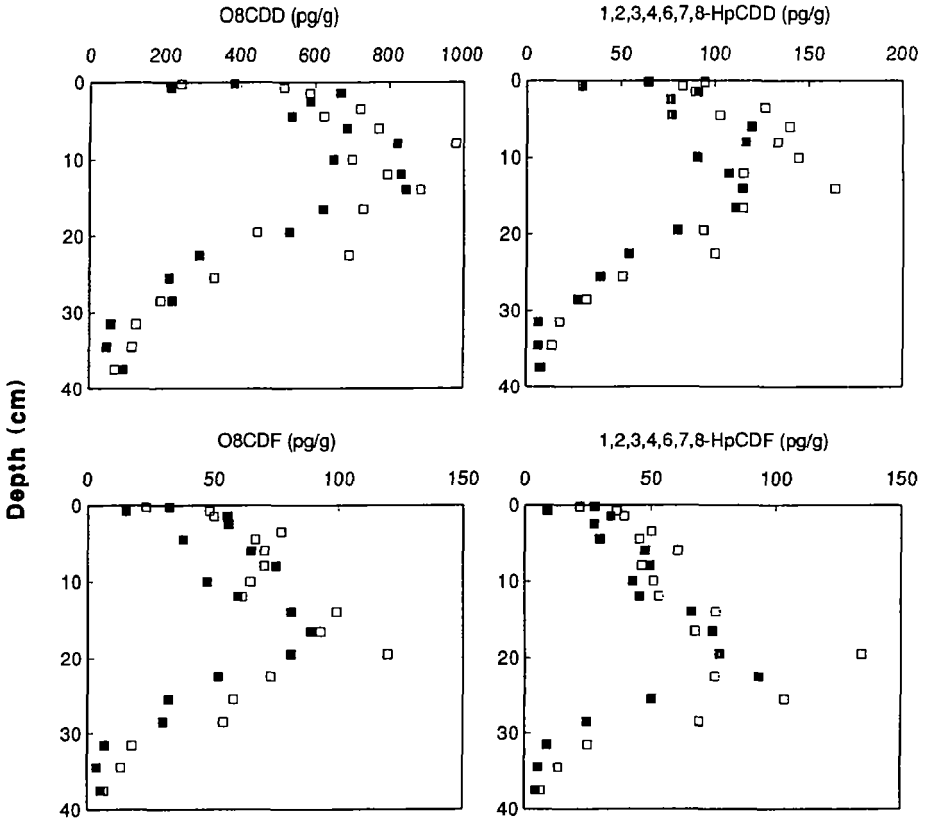

Figure 1. Depth distribution profiles of the most abundant PCDD/F congeners at stations 23 (■) and 24A (□).

packed with sodium sulphate, acidic silica, neutral silica, basic silica and silver nitrate-impregnated silica. The clean extracts were evaporated to about 1 ml and fractionated on a freshly activated alumina column. The fractions containing the PCDD/Fs were evaporated to dryness and dissolved in a mixture of four [$^{13}C_{12}$]-labelled dioxins and furans. Measurements were performed on a high resolution gas chromatography (HRGC)- high resolution mass spectrometry (HRMS) system operated at 10,000 resolution. All the results were corrected on the basis of the recovery of the [$^{13}C_{12}$] surrogates. Precision and accuracy were verified with reference material EDF-2513 (CIL) and confirmed within 30% of the consensus values[8] .

3. Results and Discussion

Levels and sedimentary records. The most abundant 2,3,7,8-substituted PCDD/F congeners in Laurentian Trough sediments at both stations are O8CDD, 1,2,3,4,6,7,8-HpCDD, O8CDF, and 1,2,3,4,6,7,8-HpCDF. The concentrations of these compounds increase from the bottom of the cores, reach maximum values between 10 and 20 cm, depending on the congeners, and decrease toward the sediment surface (Figure 1). The maximum concentrations of these

compounds are very similar for both stations, ranging from about 100 pg/g for O8CDF and 1,2,3,4,6,7,8,-HpCDD/F to about 900 pg/g for O8CDD. Most of the other congeners occur in the Trough sediments but at concentrations below 10 pg/g. Depth distribution profiles of these compounds are also characterized by a subsurface maximum similar to that of the dominant congeners. Subsurface maxima of the PCDD/F's revealed by the sedimentary records of the Laurentian Trough indicate a general reduction of the inputs in the recent years. However, the broad range of depths (about 10 cm) where these subsurface maxima are found in the sediment cores suggests that the pollution history has been different for certain congeners.

Enrichment (or depletion) profiles. Differences in depth distribution profiles among PCDD/F congeners are best evaluated when normalized to a nondiffusive and resistant congener in sediment cores[9]. For PCDD/Fs, it is particularly appropriate to choose O8CDD as the reference congener since it has a high affinity for particles and resists degradation[10-11]. In other words, sedimentary records of O8CDD are believed to be altered only by particle mixing. In order to examine systematically PCDD/F congener sedimentary profiles from the Laurentian Trough sediment cores, enrichment (or depletion) plots of selected PCDD/F congeners are calculated

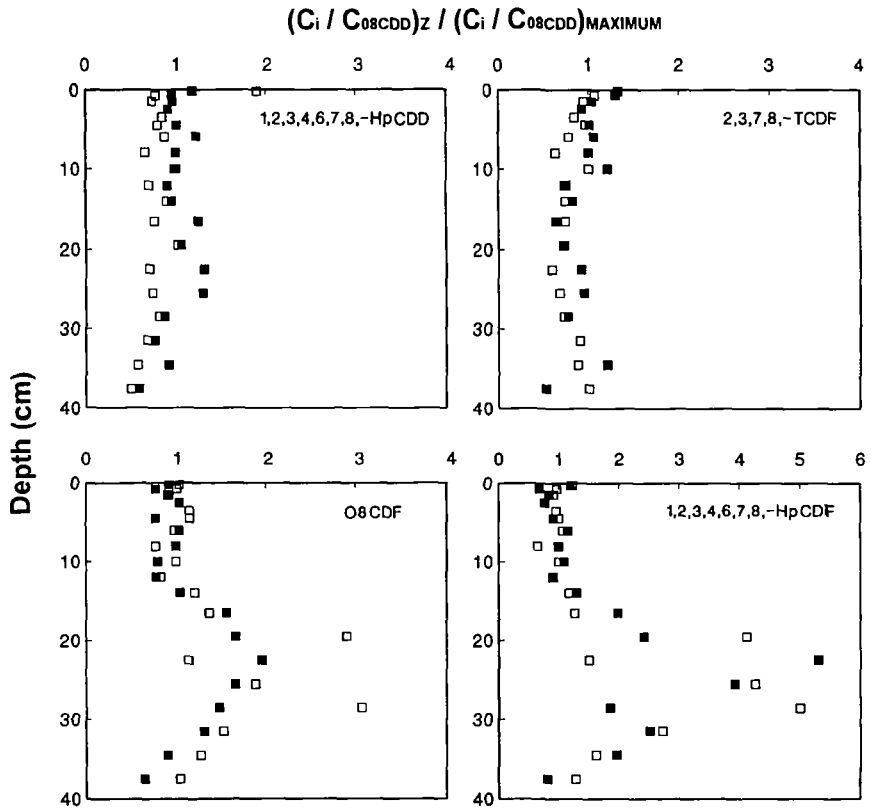

Figure 2. Enrichment (or depletion) of individual PCDD/F congeners relative to O8CDD in Laurentian Trough sediment cores 23 (■) and 24A (□).

and displayed in Figure 2. Enrichment (or depletion) is defined as the ratio of congener i concentration to congener O8CDD concentration at a given depth, normalized to the same ratio at depth of maximum O8CDD concentration. Plots of this ratio are commonly used to evaluate transformation and/or mobility of individual congeners[9]. The results show that the high chlorinated congener 1,2,3,4,6,7,8-HpCDD and the low chlorinated congener 2,3,7,8-TeCDF are neither enriched nor depleted relative to O8CDD in either core. This supports previous observations that 2,3,7,8-substituted PCDD/Fs are not diffusive, because they all exhibit low water solubility, and are nondegradable in sediments[10-11]. It also suggests that an unique source of these specific congeners has been active since the beginning of the contamination by PCDD/Fs. This observation is valid for the most recent (above 12 cm) and the initial (below 30 cm) accumulation of O8CDF and 1,2,3,4,6,7,8-HpCDF in the Trough sediments. However, these two highly chlorinated furans also show net enrichment in both cores, over a certain depth interval. These enrichment profiles are likely attributable to a historical change in sources of at least a few PCDD/F congeners[12] and suggest that for a limited period of time, O8CDF and 1,2,3,4,6,7,8-HpCDF were being provided to the St.Lawrence Estuary from two distinct sources.

Distribution of PCDD/F homolog groups. The normalized distribution of PCDD/F homolog groups that characterizes the main source of O8CDD and most of the other congeners in both cores have been calculated (Figure 3). This distribution pattern, obtained from the upper part of the cores (above 12 cm), is very similar to the distribution pattern of atmospheric sources[2,13].

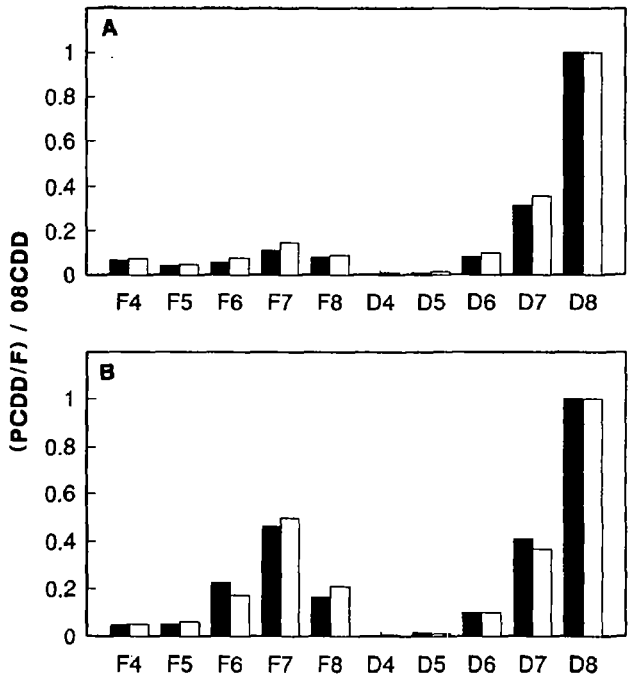

Figure 3..Normalized distribution of PCDD/F for the upper zone (A) and the enrichment maxima zone (B) in the sediment cores 23 (dark bars) and 24A (light bars).

However, the distribution pattern from the zone of enrichment maxima clearly shows an enhancement of the highly chlorinated furans in comparison to the distribution pattern of PCDD/F homolog groups from the more recent inputs. This zone of the cores is believed to combine the distribution patterns from two distinct sources. The first source, based upon characterization of the upper zone of the cores, is most likely the atmosphere, either directly or indirectly, due to long range transport. The distribution pattern that characterizes the second source is obtained by subtracting out the distribution pattern of the first source (upper zone) from the combined pattern in the zone of enrichment maxima. The resulting distribution pattern of PCDD/F homolog groups is comparable to the one reported for Lake Ontario sediments[14-15]. The possibility that Lake Ontario sediments are responsible for the enrichment of highly chlorinated furans in the Laurentian Trough appears to be reasonable since it has been shown, in the case of mirex[16], that hydrophobic organic contaminants can be transported from Lake Ontario to sediments of the St.Lawrence Estuary.

4. *Conclusions*

The majority of 2,3,7,8-PCDD/Fs were found in the sediments of the Laurentian Trough. Depth distribution profiles for most of these compounds were very similar to O8CDD profiles with the exception of two highly chlorinated furans, O8CDF and 1,2,3,4,6,7,8-HpCDF. Enrichment maxima displayed by these compounds suggest that a change in sources of at least a few PCDD/F congeners has occurred in the St.Lawrence Estuary. It is clear that a specific source of PCDD/Fs, enriched with highly chlorinated furans, has been active in the past. However, based on the distribution pattern of PCDD/F homolog groups in the upper zone of the cores, the recent contributions of PCDD/Fs to the St.Lawrence Estuary are likely due to atmospheric inputs.

5. References

1) Rappe C., R. Andersson, P.A. Bergqvist, C. Brohede, M Hansson, L.O. Kjeller, G. Lindström, S. Marklund, M. Nygren, S.E. Swanson, M. Tysklind and K. Wiberg (1987): Overview on environmental fate of chlorinated dioxins and dibenzofurans. Sources, levels and isomeric pattern in various matrices. Chemosphere 16, 1603-1618
2) Czuczwa J.M. and R.A. Hites (1984): Environmental fate of combustion-generated polychlorinated dioxins and furans. Environ. Sci. Technol. 18, 444-450
3) Eltzer B.D. (1993): Comparison of point and nonpoint sources of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans to sediments of the Housatonic River. Environ. Sci. Technol. 27, 1632-1637
4) Macdonald, R.W., W.J. Cretney, N. Crewe and D. Paton (1992): A history of octachlorodibenzo-p-dioxin, 2,3,7,8-tetrachlorodibenzofuran, and 3,3',4,4'-tetrachlorobiphenyl contamination in Howe Sound, British Columbia. Environ. Sci. Technol. 26, 1544-1550
5) Evers, E.H.G., H.J.C. Klamer, R.W.P.M. Laane, H.A.J. Govers (1993): Polychlorinated dibenzo-p-dioxin and dibenzofuran residues in estuarine and coastal North Sea sediments: sources and distribution. Environ. Toxicol. Chem. 12, 1583-1598
6) Loring D.H. and D.J.G. Nota (1973): Morphology and sediments of the Gulf of St. Lawrence. Bull. Fish. Res. Board Can. 182, 147 pp.
7) Gobeil C., W.K. Johnson, R.W. Macdonald and C.S. Wong (1995): Sources and burden of lead in St. Lawrence Estuary sediments: isotopic evidence. Environ. Sci. Technol. 28, 193-201

8) Keith L.H., A.W. Nichols, R.F. Moseman, T.P. Heil, J.C. Bradley and D.L. Bolt (1992): PCDD/PCDF soil standards from an international QA/QC program. Chemosphere 25, 1333-1341
9) Eisenreich S.J., P.D. Capel, J.A. Robbins, and R. Bourbonniere (1989): Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. Environ. Sci. Technol. 23, 1116-1126
10) Orazio C.E., S. Kapila, R.K. Puri and A.F. Yanders (1992): Persistence of chlorinated dioxins and furans in the soil environment. Chemosphere 25, 1469-1474
11) Broman D., C. Näf, C. Rolff and Y. Zebühr (1991): Occurrence and dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans and polycyclic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. Environ. Sci. Technol. 25, 1850-1864
12) Kjeller L.O. and C. Rappe (1995): Time trends in levels, patterns and profiles for polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in a sediment core from the Baltic Proper. Environ. Sci. Technol. 29, 346-355
13) Eltzer B.D. and R.A. Hites (1989): Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins, dibenzofurans. Environ. Sci. Technol. 23, 1396-1401
14) Czuczwa J.M. and R.A. Hites (1986): Airborne dioxins and dibenzofurans: sources and fates. Environ. Sci. Technol. 20, 195-200
15) Endicott D.D. and P.M. Cook (1994): Modeling the partitioning and bioaccumulation of TCDD and other hydrophobic organic chemicals in Lake Ontario. Chemosphere 28, 75-87
16) Comba M.E., R.J. Norstrom, C.R. Macdonald and L.E. Kaiser (1993). A Lake Ontario-Gulf of St. Lawrence dynamic mass budget for mirex. Environ. Sci. Technol. 27, 2198-2206