Direct atmospheric deposition versus fluvial inputs of PCDD/Fs to the sediments of the Lower St. Lawrence Estuary

Michel Lebeuf, Charles Gobeil
Ministère des Pêches et des Océans, Institut Maurice-Lamontagne
C.P. 1000, Mont-Joli, Québec, G5H 3Z4, Canada
Charles Brochu and Serge Moore
Ministère de l'Environnement et de la Faune du Québec, Direction des laboratoires
850 boulevard Vanier, Laval, Québec, H7C 2M7, Canada

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are released directly into the atmosphere from various sources, such as industrial and municipal incinerators[1]. Vapor-phase and particle-bound PCDD/Fs can be transported over long distances in the atmosphere[2]. Following wet or dry deposition, PCDD/Fs may undergo further transport into aquatic systems before they eventually accumulate in bottom sediments.

In the marine system of St. Lawrence, the Lower St. Lawrence Estuary (LSLE) has been recognized as an important zone of accumulation of sediments and associated contaminants[3,4]. Recent studies have revealed that the majority of the highly toxic 2,3,7,8-PCDD/Fs occur in sediments of the LSLE[5,6]. The distribution patterns and historical sedimentary profiles have shown that inputs of PCDD/Fs to the LSLE are primarily from the atmosphere[6]. However, the relative contributions of PCDD/Fs via direct atmospheric deposition and atmospherically derived transport in fluvial waters has not yet been specifically investigated.

In this study, we attempt to determine the contributions of atmospheric versus fluvial inputs to the Estuary by comparing the inventories of PCDD/Fs and ^{210}Pb in three sediment cores collected in the LSLE and in one core from the Gulf of St. Lawrence. ^{210}Pb accumulated but not supported by the ^{226}Ra decay in the sediments is used as a tracer of direct atmospheric deposition and to correct PCDD/F inventories for lateral movement of sediments. The total burden of PCDD/Fs in the sediments of the LSLE was compared to the estimated load of PCDD/Fs in the LSLE that results from direct atmospheric deposition.

2. Methods

Study area. The St. Lawrence Estuary connects the upstream fluvial waters of the Great Lakes and the St. Lawrence River to the Gulf of St. Lawrence. The LSLE is approximately 200 km long, from Tadoussac to Pointe-des-Monts. A predominant feature is the starting point of the Laurentian Trough, a long undersea valley which extends the length of the LSLE into the Gulf of St. Lawrence.

Sampling. Sediments were collected at water depths greater than 300 m using a box corer along the longitudinal axis of the Laurentian Trough. Stations 24A, 23 and C2, are located in the LSLE at 55, 100 and 190 km downstream from Tadoussac, respectively. Station C1 is located in the Gulf of St. Lawrence at about 15 km from Pointe-des-Monts. Sediment cores were immediately sliced on board in 0.5 or 1 cm increments at the top, gradually increasing to 3 cm increments at 40 cm depth. Aliquots of each slice were transferred to solvent-cleaned glass jars and kept frozen at -20°C for later analysis.

Sediment analysis. Approximately 10-20 g of air dried and ground sediments were spiked with a surrogate mixture of nine [$^{13}C_{12}$]-labelled dioxins and furans and then soxhlet extracted overnight with toluene. The extraction solution was evaporated to about 1 ml, solvent exchanged to hexane and Cu fillings or Hg were added to the solution to remove sulfur. This solution was reduced in volume to 1 ml. The residue was eluted through a multi-layer column packed with sodium sulfate, acidic, neutral and basic silicas. The clean extract was evaporated to about 1 ml and fractionated on a freshly activated alumina column. The fraction containing the PCDD/Fs was evaporated to dryness and dissolved in a mixture of four [$^{13}C_{12}$]-labelled dioxins and furans. All measurements were made using a high resolution gas chromatography (HRGC)- high resolution mass spectrometry (HRMS) system operated at 10 000 resolution. All 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[7]. Radionuclide ^{210}Pb analysis was conducted on each sediment sample by measuring the activity of its grand-daughter ^{210}Po, as described by Eakins and Morisson[8].

3. Results and Discussion

Inventories. The inventory (I, in pg/cm^2) of individual PCDD/F homologue groups was calculated in each core according to the following equation:

$$I = \sum_{i=1}^{n} (1-\phi_i)\rho[\ ]_i Z_i$$

where ϕ_i represents the measured porosity, ρ, the sediment density (2.65 g.cm^{-3}), $[\ ]_i$, the concentration of the PCDD/F homologue group and Z_i the thickness of the layer i among the n slices in the core. The calculated inventories of individual homologue groups and their relative contributions in the cores are given in Table 1. O8CDD, H7CDD and H7CDF account for approximately 50, 15 and 10%, respectively, of the overall load of PCDD/Fs, while each one of the other homologue groups contributes less than 5%. This PCDD/F distribution pattern of homologue groups is typical to that resulting from chemical transformations of these compounds during long-range atmospheric transport[2]. This suggests that PCDD/Fs accumulated in the sediments of all stations in the Laurentian Trough originated mainly from the atmosphere, either by direct deposition over the LSLE or indirectly via fluvial transport.

Table 1. Inventories and relative contribution (%) of individual PCDD/F homologue groups in Laurentian Trough sediment cores.

PCDD/F homologue group	Inventory (pg/cm^2)			
	Station 24A	Station 23	Station C2	Station C1
T4CDD	109 (0.5)	60 (0.4)	47 (1.3)	42 (2.0)
P5CDD	165 (0.7)	109 (0.7)	49 (1.3)	26 (1.2)
H6CDD	1125 (4.7)	670 (4.1)	204 (5.4)	101 (4.7)
H7CDD	3945 (16.7)	2740 (16.9)	655 (17.4)	323 (15.1)
O8CDD	11594 (49.0)	8513 (52.5)	1734 (46.1)	987 (46.3)
T4CDF	758 (3.2)	479 (3.0)	211 (5.6)	170 (8.0)
P5CDF	595 (2.5)	356 (2.2)	133 (3.5)	115 (5.4)
H6CDF	1169 (4.9)	778 (4.8)	181 (4.8)	102 (4.8)
H7CDF	2776 (11.7)	1578 (9.7)	371 (9.9)	185 (8.7)
O8CDF	1432 (6.1)	925 (5.7)	173 (4.6)	81 (3.8)
Total	23668	16208	3758	2132

The total PCDD/F inventory in each core was calculated by summing the inventory of each individual PCDD/F homologue group. The PCDD/F inventories are highest at the stations located at the head of the Laurentian Trough, and decrease progressively downstream (Table 1), which could be the result of the fluvial inputs of PCDD/Fs and/or the lateral movement of fine sediments (sediment focusing) within the Estuary. It has been shown in lakes that some of the heterogeneity associated with uneven sediment deposition can be removed by correcting for focusing[9]. To investigate this possibility in the LSLE, sediment focusing factors (SFF) were calculated according to the following equation:

$$SFF = \frac{I_{core}}{I_{atm.}}$$

where I_{core} is the unsupported ^{210}Pb inventory determined at each station by subtracting the ^{210}Pb activity in the sediments produced by ^{226}Ra decay and obtained from the constant ^{210}Pb activities at depth in each core, from the measured ^{210}Pb values of each core slice. $I_{atm.}$ is the representative ^{210}Pb inventory (16.6 pCi/cm^2) from atmospheric sources in Canadian Atlantic provinces[10]. The PCDD/F focus-corrected inventories, obtained from the ratio of total PCDD/F inventory to the SFF for each of the four stations, are reported in Table 2. Since a PCDD/F focus-corrected inventory gradient is still obvious, correction for sediment focusing is clearly not the sole explanation for the different inventories recorded at these stations. These results suggest that PCDD/Fs accumulated in the LSLE sediments do not enter into the global atmosphere as it is the case for ^{210}Pb. The observed PCDD/F inventory gradient from stations 24A to C1 may be the result of upstream releases of atmospherically derived PCDD/Fs which are subsequently transported by fluvial waters to the LSLE.

Table 2. Unsupported ^{210}Pb inventories, sediment focusing factors and focus-corrected inventories of PCDD/Fs from the sample stations.

Station	Unsupported ^{210}Pb inventory (pCi/cm^2)	Sediment focusing factor (SFF)*	PCDD/F focus-corrected inventory (pg/cm^2)
24A	42.09	2.54	9334
23	40.92	2.47	6575
C2	29.65	1.79	2104
C1	18.13	1.09	1952

* Sediment focusing factor calculated from the value of 16.6 pCi/cm^2 reported by Urban et al.(1990)

Burden. The PCDD/F focus-corrected inventories were used to estimate the total burden of PCDD/Fs in the LSLE. The region has been divided into three zones covering a surface area of approximately 9675 km^2, with a representative sample station in each zone. A total sediment burden of 547 kg of PCDD/Fs was obtained by extrapolating the focus-corrected inventory at each station to its representative zone (Table 3). This estimate is considered to be conservative since it has been assumed that all the unsupported ^{210}Pb inventoried in these cores results from direct deposition over the LSLE. However, at least a portion of ^{210}Pb is deposited upstream in fluvial waters and transported to the Estuary. Consequently, the focusing factors at stations 24A and 23 are most probably smaller than the reported values, resulting in larger PCDD/F focus-corrected inventories and burdens in the two upstream zones (Table 3).

Table 3. Estimation of the total burden of PCDD/Fs accumulated in the sediments of the LSLE.

Zone	Representative sample station	Area (km^2)	PCDD/F focus-corrected inventory (g/km^2)	Total burden of PCDD/Fs (kg)
1	24A	2380	93.34	222.1
2	23	3802	65.75	250.0
3	C2	3493	21.52	75.2
	Total	9675		547.3

Direct vs indirect atmospheric contribution. To determine the contribution of direct atmospheric PCDD/F deposition versus fluvial inputs of atmospherically derived PCDD/Fs, the PCDD/F focus-corrected inventory at station C1 (19.52 g/km^2), located in the Gulf, was extrapolated to the LSLE area (9675 km^2). This approach was based on the assumption that PCDD/Fs carried to the Lower Estuary by fluvial transport are completely contained in the Estuary, and station C1 receives these compounds only via direct atmospheric deposition. The contribution of PCDD/Fs from direct atmospheric deposition is estimated at approximately 189 kg which represents less than 35% of the total PCDD/Fs sediment burden, thus illustrating the significance of fluvial inputs. As mentioned above, the estimate for the total PCDD/Fs burden is conservative, hence the contribution of PCDD/Fs from direct atmospheric deposition could be even less than 35%.

4. Conclusions

We have demonstrated that less than 35% of the 547 kg of PCDD/Fs accumulated in the LSLE sediments are due to direct atmospheric deposition. More importantly, the distribution pattern PCDD/F homologue groups indicates that these compounds are emitted into the atmosphere upstream of the LSLE and subsequently transported downstream by fluvial waters into the region.

5. Acknowledgements

We thank S. Trottier, R. Tremblay, S. Laliberté, M. Noël and G. Hamelin for their contribution to laboratory works, and D. Steel for critical comments on the manuscript.

6. References

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