

The influence of PCBs and PCDFs in the sediments of Baie des Anglais on the Lower St. Lawrence Estuary

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1. Introduction

For more than ten years, Baie des Anglais has been known to be contaminated by polychlorinated biphenyls (PCBs)¹⁾. The source of these contaminants has been attributed to an aluminum refinery (Reynolds) located on the western shore of the bay²⁾. Although the sediments within the bay have been monitored regularly³⁾, PCBs have only been determined in terms of Aroclor equivalents, providing no information on specific congeners or the distribution pattern of PCB homologue groups. Furthermore, the assessment of this contamination has been limited to sediments within the bay, so that the extent of PCB contamination outside the bay is not known.

PCB contamination can be a source of polychlorinated dibenzofurans (PCDFs), since commercial PCB mixtures contain PCDFs as impurities⁴⁾. Recently, Brochu et al.⁵⁾ reported the first data of polychlorinated dibenzo-*p*-dioxins (PCDDs) and PCDFs in sediment samples collected at one site in Baie des Anglais. Based on the prevalence of the low chlorinated furans in these samples, they suggested that PCDFs likely originate from PCB contamination.

In this paper, we report concentrations of PCBs and PCDD/Fs in surface sediment samples collected within and outside Baie des Anglais in order to assess the extent and the influence of this organochlorine contamination on the receiving system, the Lower St. Lawrence Estuary.

2. Methods

Site. Baie des Anglais is a small industrial bay (11 km²) located on the north shore of the St. Lawrence Estuary near the town of Baie Comeau. The maximum water depth in the bay is about 85 m. Within 20 km from the bay, the water depth reaches 200 m and increases to more than 300 m within 50 km.

Sampling. Surface sediment samples were collected along a transect starting near the western shore of Baie des Anglais and extending up to 58 km south-east, towards the middle of the Estuary. Most of the samples (0-3 cm) were collected using a Shipek grab sampler but three sediment samples (0-10 cm), (SED-P-1, SED-P-2, SED-P-3) were collected using a Van Veen grab sampler. Aliquots of each

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homogenized samples were transferred to solvent-cleaned glass jars or polyethylene bottles and kept frozen at -20°C for later analysis.

Sediment analyses. PCB analyses were performed on approximately 10-20 g of sediments mixed with sodium sulfate, spiked with a mixture of nine [¹³C₁₂]-labelled congeners and soxhlet extracted overnight with a solution of acetone/hexane (50:50). The extraction solution was purified by elution through a 10% deactivated silica gel column followed by treatment with Cu powder to remove sulfur. The final extract was reduced in volume to receive a mixture of two [¹³C₁₂]-labelled congeners and completed to 2.0 ml. PCDD/Fs analyses were performed in a similar way with the following exceptions. The sediments were air-dried and ground, spiked with a surrogate mixture of nine [¹³C₁₂]-labelled dioxins and furans and extracted with toluene. After solvent exchange to hexane, Cu fillings or mercury was used to remove the sulfur. This solution was reduced in volume to 1 ml and cleaned by elution through a multi-layer column packed with sodium sulfate, acidic, neutral and basic silicas. The clean extract was reduced in volume 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 containing four [¹³C₁₂]-labelled dioxins and furans. All measurements of both PCBs and PCDD/Fs 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 [¹³C₁₂] surrogates.

3. Results and Discussion

A decreasing gradient of total PCB concentrations in surface sediments was found along a 58 km south-east transect from the bay to the Estuary (Table 1). The PCB levels were highest in the two samples collected within the bay (B-BA-10 and B-BA-6) and are in agreement with the values previously reported as total Aroclor at these stations⁶⁾. The most rapid decrease of total PCB concentrations is detected between stations B-BA-6 and B-BA-4 which represents the transition from inside to outside the bay. The narrow range of carbon contents in these sediments (1.24-1.85%) cannot explain the gradient observed in PCB concentrations. The PCB concentrations at the stations in the Estuary are equal or lower than the values reported in sediments collected upstream in the Lower Estuary⁷⁾.

Table 1. Total PCB concentrations in surface sediments (0-3 cm) collected along a 58 km south-east transect from a reference point* in Baie des Anglais to the Estuary.

Station	Distance from the reference point (km)	Carbon content (%)	Total PCB concentration** (ng/g)
B-BA-10	1.2	1.64	284
B-BA-6	3.1	1.85	217
B-BA-4	5.9	1.37	39
B-BA-2	11	1.25	27
B-BA-1	12	1.65	22
SS7-2	14	1.24	17
C2	58	1.85	22

* The reference point is located on the western shore of Baie des Anglais in front of the aluminum refinery

** Total PCB concentration defined as the sum of the PCB concentration of each homologue group (tri to deca)

Although the PCB levels are 10-fold higher in sediments from within the bay as opposed to outside, part of the PCBs accumulated in the Estuary may result from Baie des Anglais. One way to estimate the extent of the PCB contamination consists of examining the distribution patterns of PCB homologue groups in the sediments along a south-east transect from Baie des Anglais to the Estuary.

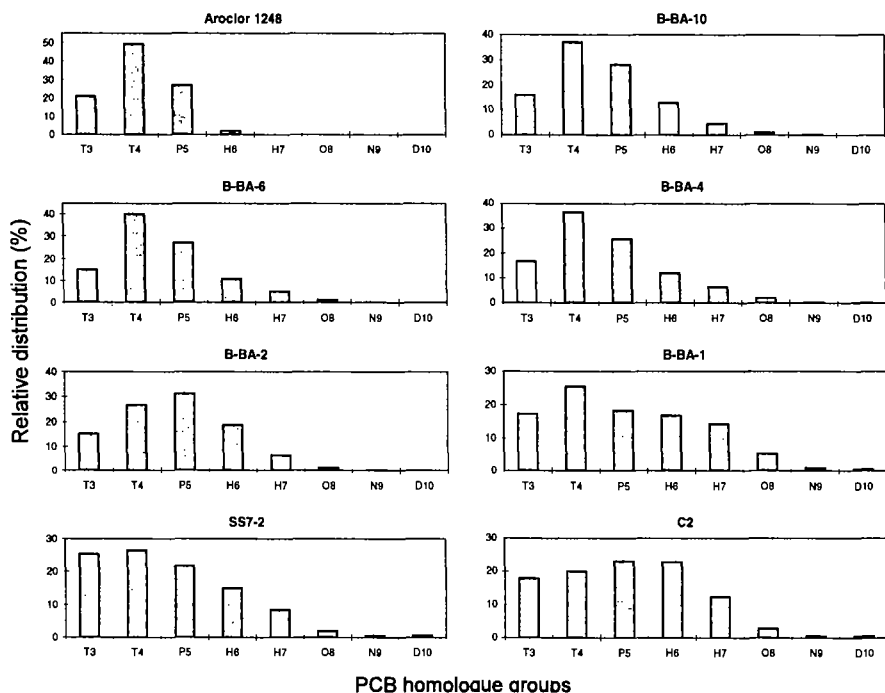


Figure 1. Relative distribution patterns of PCB homologue groups in Aroclor mixture 1248 (Erickson 1992)⁹, and in surface sediments (0-3 cm) collected along a south-east transect from Baie des Anglais to the Lower St. Lawrence Estuary. PCB levels and distances of sampling stations from the reference point in the bay are reported in Table 1.

The distribution pattern of PCB homologue groups in the commercial PCB mixture Aroclor 1248⁹ is similar to the patterns reported in sediments from the bay (B-BA-10 and B-BA-6) (Figure 1). The sediment sample collected at 5.9 km from the reference point in the bay also show PCB distribution patterns similar to those from inside the bay, suggesting that the adjacent area of the bay may be contaminated by PCB originating from the bay. However, the PCB distributions in the sediments collected at more than 10 km from the bay to the middle of the Estuary revealed elevated levels of highly chlorinated homologue groups, but these PCB distribution patterns are not different enough to totally exclude a possible contribution of PCBs from the bay. Therefore, the comparison of PCB distribution patterns in these sediments does not permit an accurate assessment of the extent of the PCB contamination in the Estuary resulting from Baie des Anglais.

PCDD/F distribution patterns are potentially more appropriate to assess the influence of the PCB contamination from Baie des Anglais to the Estuary since the PCDD/F pattern reported in sediments from Baie des Anglais by Brochu et al. (1995)⁹ has been linked to the PCB contamination and is very different than the PCDD/F pattern reported by Lebeuf et al. (1995)⁹ in sediments from the Lower St. Lawrence Estuary. In Baie des Anglais sediments, low chlorinated furan homologue groups prevail,

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whereas sediments collected upstream in the Lower St. Lawrence Estuary show a PCDD/F distribution pattern characteristic of long range atmospheric sources where highly chlorinated dioxins dominate.

The distribution patterns of PCDD/F homologue groups in the sediments collected along a south-east transect from the bay to the Estuary indicate a transition from high levels of less chlorinated furans to predominately highly chlorinated dioxins (Figure 2). The typical PCDD/F distribution pattern in Aroclor mixture 1248⁹ is easily recognized in the sediment sample (SED-P-1) located 0.7 km from the reference point in the bay. On the contrary, the sediment sample collected in the middle of the Estuary (C2) show a PCDD/F distribution pattern characteristic of long range atmospheric sources⁹. Hence, these two different distribution patterns of PCDD/F homologue groups can be used as end members to evaluate the influence of Baie des Anglais on the contamination of the Estuary by these compounds. The PCDD/F patterns show that within only 10 km from the reference point in the bay, the contribution of these compounds from the bay is hidden by the contribution of PCDD/Fs from atmospheric sources. Hence, the bay has only a small influence on the total levels of PCDD/Fs in sediments of the Estuary adjacent to the bay. However, part of the low chlorinated PCDF levels accumulated in the sediments of the Estuary may result from the bay.

4. Conclusions

The levels of both PCBs and PCDFs in sediments are 10-fold higher within Baie des Anglais when compared to the St. Lawrence Estuary. Concentrations of these contaminants decrease rapidly within a few kilometers of the bay to reach levels found elsewhere in the sediments of the Estuary. This indicates that the influence of the PCB and PCDF contamination in the sediments of Baie des Anglais on the Estuary is low. However, one cannot eliminate the possibility that Baie des Anglais has provided some of the PCBs and the low chlorinated PCDFs which have accumulated in the sediments of the Estuary adjacent to the bay.

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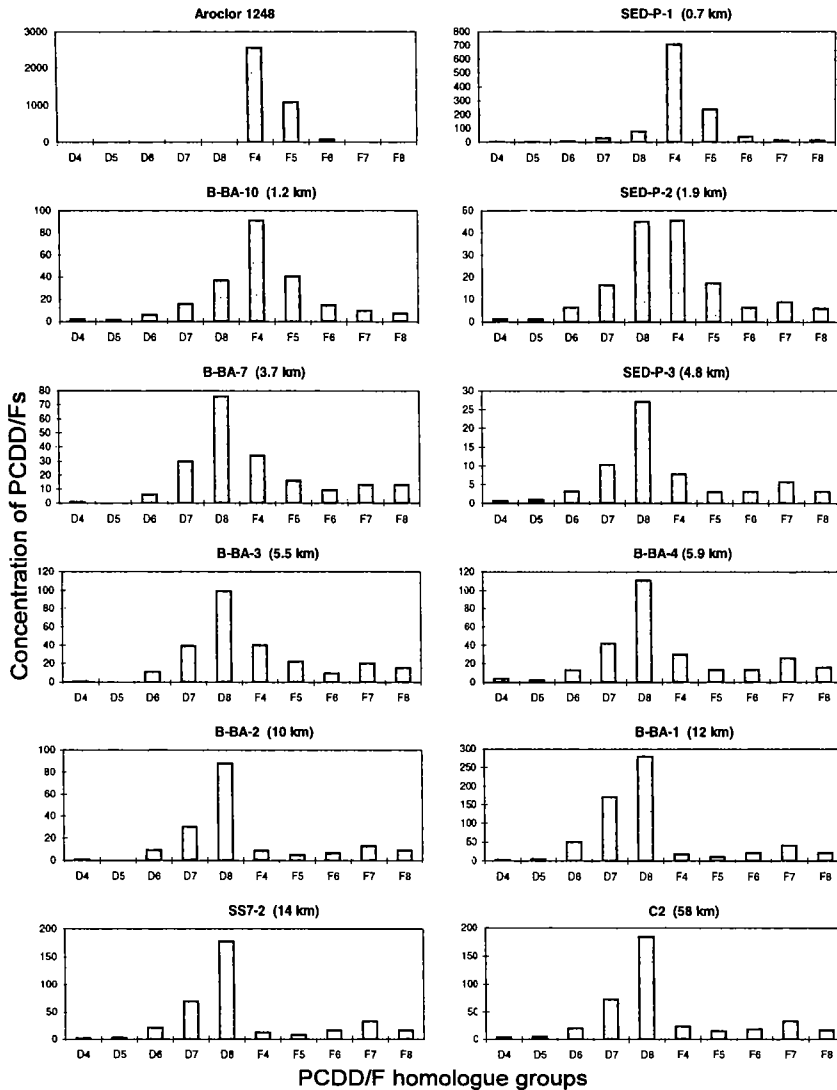


Figure 2. Distribution patterns of PCDD/F homologous groups in an Aroclor mixture 1248 (ng/g) (Wakimoto et al. 1988)⁴⁾ and in surface sediments (pg/g) collected along a south-east transect from Baie des Anglais to the St. Lawrence Estuary. Distances of sampling stations from the reference point in the bay are reported in parentheses.

6. References

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