Bull. Environ. Contam. Toxicol. (1986) 37:133–140
© 1986 Springer-Verlag New York Inc.

Bulletin of Environmental Contamination and Toxicology

Polycyclic Aromatic Hydrocarbons in Sediments from the Saguenay Fjord, Canada

Louis Martel,[1] Michel J. Gagnon,[2]* Robert Massé,[1] André Leclerc,[2] and Line Tremblay[1]

[1]INRS-Santé, 7401, boul. Hochelaga, Montréal (Québec) Canada H1N 3M5 and
[2]Dép. des Sciences fondamentales, Université du Québec à Chicoutimi, Chicoutimi, Québec, Canada G7H 2B1

Polynuclear aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants that pose a potential hazard not only to human life, but to the other forms of life as well. Some PAH's, namely benzo(a)pyrene (BAP) and dibenzo(a,h) anthracene, are highly potent carcinogens, which have been associated to the etiology of some human cancers (Conney 1982).

The purpose of this study is to determine the spatial distribution of PAH concentrations in the Saguenay Fjord surface sediments and to study the behavior of these compounds in this marine environment. This 100 km river is the major tributary to the St-Lawrence estuary. It is highly industrialized and aluminium smelting plants, which dominate the industrial sector, are apparently the major source of PAH to the river. Moreover, a study by Primeau and Goulet (1983) has shown high levels of PAH in the sediments of Baie des Ha! Ha! in the Saguenay Fjord. The bioavailability of PAH and particularly that of BAP in this marine environment was demonstrated in two studies with Mytilus edulis L. (Cossa et al. 1983; Picard-Bérubé et al. 1983).

MATERIALS AND METHODS

The samples were collected in August 1983. A sediment grab (0.2 square meter) was used to sample the surface sediments at stations along the Fjord (Fig. 1). The top layer (2-3 cm) of the sediments was collected using a metallic spoon. However, when horizontal stratifications were observed in the top sediments, each layer was carefully sampled. The sediments were collected in solvent-washed glass jars and stored in a dark room at -15°C until analysis.

30 g of each sample were used for the analysis of PAH. The sediment was fortified with two internal standards (B,B'-binaphthyl and n-tetraphenyl) and Soxhlet-extracted with dichloromethane for 15 h. The extracts were concentrated under reduced pressure and successively applied to copper, silica gel and alumina chromatography columns. Blank samples were run periodically and no significant level of coextracted contaminents was detected.

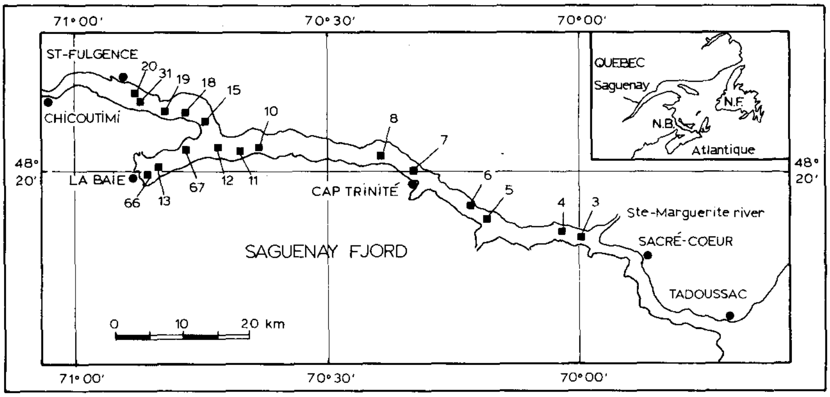

Figure 1. Location of the sampling stations in the Saguenay Fjord.

The extracts were silylated prior to analysis with a mixture of acetonitrile-BSTFA-TMCS (80:20:1, v/v). The PAH containing fractions were analysed by capillary column (DB-5) gas chromatography. PAH were identified by their relative retention times. The identity of each chromatographic peak was verified by gas chromatography-mass spectrometry analysis (table 1). Quantitation of the PAH of interest was performed using the internal standard method.

Table 1. PAH detected in surface sediment samples from the Saguenay Fjord.

No.[a]	NAME	No	NAME
1	Fluoranthene (12,5)[b]	SI1	B,B'-binaphthyl (internal std)
2	Pyrene (12,9)	SI2	M-tetraphenyle (internal std)
3	Benzo(a)anthracene (7,8)	A	Benzo(b)naphto(2,1-d)furane
4	Chrysene+triphenylene (7,6)	B	Benzo(b)naphto(2,3-d)furane
5	Benzo(b)fluoranthene (7,8)	C	Benzofluorenes
6	Benzo(j)fluoranthene+ Benzo(k)fluoranthene (6,9)	D	Methylpyrenes
		E	Benzonaphtothiophenes
7	Benzo(e)pyrene (8,2)	F	Methylbenzoanthracenes or Methylbenzophenanthrenes
8	Benzo(a)pyrene (7,2)		
9	Perylene (7,8)	G	Phenylanthracenes
10	Indeno(1,2,3-c,d)pyrene (10,4)	H	Methylbenzoaceanthrylenes
11	Dibenzo(a,h)anthracene (14,0)		
12	Benzo(g,h,i)perylene (11,1)		
13	Dibenzo(a,e)pyrene (23,6)		

[a] PAH 1-13 were quantitated by gas chromatography. PAH A-H were identified by GC/MS analysis.

[b] experimental error (%).

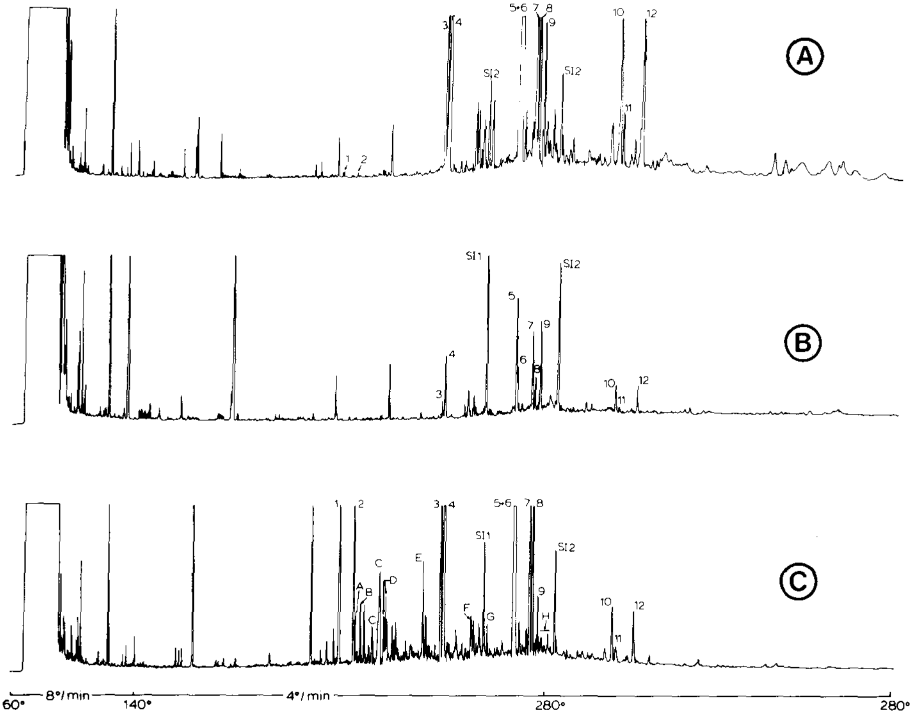

Figure 2. Chromatograms obtained from organic extracts of the Saguenay Fjord surface sediments; a, station 31; b, station 4 and c, station 12. The numbered and lettered peaks correspond to PAH listed in Table 1.

RESULTS AND DISCUSSION

The chromatographic data shown in Figure 2 indicate that the levels of alkylated homologs of PAH are relatively low as opposed to that of unsubstituted PAH. The ratios of alkylated/non alkylated PAH are relatively constant throughout the sediment samples collected in the Saguenay Fjord. This suggests that the dominant source for sedimentary PAH in the river is anthropogenic.

Gas chromatographic profiles obtained from sediment samples collected at station 31, 4 and 12 respectively are shown in Figure 2. These profiles, which are highly representative of the spatial distribution of PAH in the Saguenay Fjord, showed that the concentrations of PAH are maximum near the aluminium smelting plants located in the Chicoutimi area (Fig. 2a) and decrease with distance from this industrial zone (Fig. 2b). Qualitatively, the PAH profiles are very similar from one sediment sample to another.

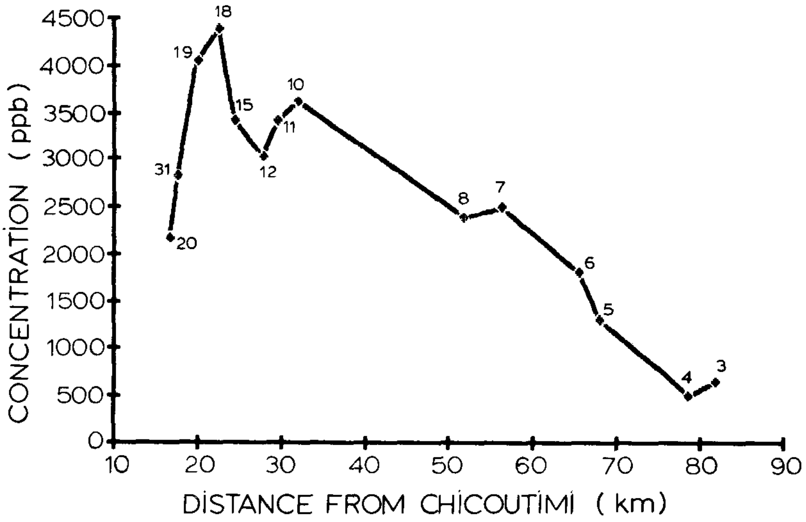

Figure 3. Spatial distribution of the total PAH concentrations through the Saguenay Fjord. The numbers on the curve correspond to the sampling stations.

The spatial distribution of PAH levels in the Fjord sediments is presented in Figure 3. This distribution pattern is different from the one reported by Windsor and Hites (1979) in the sediments of Massachussetts Bay, U.S.A., where a logarithmic decrease of the PAH concentrations, as a function of the distance from the emission source, was observed. There was a strong hydrodynamic element to the distribution of PAH concentrations in Saguenay Fjord. In the upper section of the Fjord, PAH levels increase strongly from sampling station 20 which is located at about 16 km from Chicoutimi to station 18, 7 km down stream. Previous studies by Smith and Walton (1980) have shown that the sedimentation rate is very high in that section of the Fjord (approximately 7 cm/year).

The high rate of sedimentation in the upper section of the Fjord was rationalized by the introduction of large particles (free of any PAH) originating from various sources such as soil, domestic and industrial wastes and wood products. A largely reduced flow and the presence of a salinity gradient in this section of the Fjord also contribute to the high sedimentation rate. Consequently, such an increased sedimentation of solid matter in the upper section of the Fjord dilutes the sedimentary PAH in a larger volume of surface sediments, thus decreasing their relative concentrations. Down stream however, the sedimentation rate decreases and PAH levels increase accordingly up to sampling station 18 (Fig. 3). Surprisingly, a similar dilution of the surface sediments occurs between sampling stations 18 to 10 where a slight decrease in the PAH levels was observed (Fig. 3). This phenomenon was attributed to supplementary input of sedimentary particules from Baie des Ha! Ha! (Fig. 1) where a paper mill is located.

Finally, down stream from sampling station 10, in the lower section of the Fjord, the PAH concentrations decrease linearly as a function of the distance from sampling station ($r = 0.983$). Comparison between the spatial distribution of PAH concentrations in the surface sediments and the corresponding sedimentary profiles observed over the whole extent of the Saguenay Fjord clearly indicates that major sources of PAH are located up stream, in the Chicoutimi vicinity.

A study of the spatial distribution of individual PAH concentrations was performed and the data are presented in Figure 4. Two low molecular weight PAH (fluoranthene and pyrene) and one high molecular weight PAH (dibenzo(a,e) pyrene) exhibit distribution patterns which are very different to those of the other PAH. Fluoranthene and pyrene are among the most volatile PAH in the aquatic environment (Southworth 1979). In addition, losses from evaporation may have occurred during the extraction and purification procedures. On the other hand, the distribution pattern of dibenzo(a,e) pyrene might not be accurately representative of its actual concentrations in the marine sediments, since its gas chromatographic quantitation was impaired by excessive peak broadening. The distribution profiles of the other individual PAH was similar to that of the total PAH concentrations with the exception of perylene concentration profile. Correlations between the levels of individual PAH and that of the total PAH concentration were calculated. As expected, four PAH (fluoranthene, pyrene, dibenzo (a,e) pyrene and perylene) did not show a significant correlation factor ($\alpha = 0.01$). However, these data can be rationalized on the basis of their physico-chemical and gas chromatographic properties as described above, with the exception of perylene. The latter has a molecular weight similar to that of benzofluoranthene and dibenzopyrene which distribution profile shows a positive correlation ($r = 0.97$) with the total PAH concentration pattern. As shown in Figure 4, the distribution pattern of perylene is much more constant than those of the other sedimentary PAH. This indicates that perylene is uniformly and regularly released throughout the Saguenay Fjord and that its concentration in surface sediments is not dependent on a localized anthropogenic source as, for example, is benzo(a) pyrene. A source for perylene distinct from that of other PAH is clearly indicated by the profiles shown in Figure 4. The concentrations of PAH in sediments samples collected in Baie des Ha! Ha! are summarized in Table 2.

The PAH levels increase from the head toward the mouth of the bay (Fig. 1). An inverse relationship was found between the organic matter and the PAH concentrations in the surface sediments. The high levels of organic matter found at station 66 and 13 and the corresponding PAH levels indicates that sedimentary PAH were diluted in these samples. This large input of organic matter in Baie des Ha! Ha! may account for the specific distribution of PAH levels in its vicinity. The organic matter which probably originates from the paper mill located alongside the bay can be transported up to the mouth of the bay, where it induces a noticeable

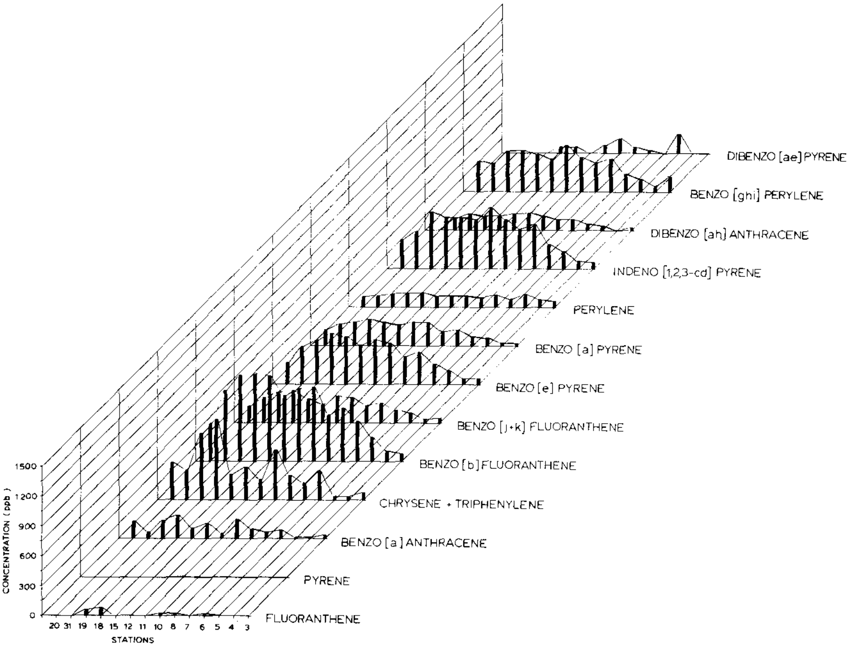

Figure 4. Spatial variation of the individual PAH concentrations in the surface sediments through the Saguenay Fjord.

Table 2. Spatial variation of PAH in the Baie des Ha! Ha! sediments.

Stations	Distance from Ville de la Baie (km)	% organic carbon	Total PAH concentration (ppb)
66	1,5	4,26	2046
13	2,5	3,90	2140
67	8,0	2,01	3783

decrease in the PAH concentrations namely at stations 11, 12 and 15 (Fig. 3). Our results are in accordance with those previously reported by Primeau and Goulet (1983).

In selected sediment samples, horizontal stratifications were present and the results of the corresponding PAH analysis are presented in Figure 5. The data show that for the stations located up stream to the mouth of the bay (stations 15, 19, 31 and 20), the PAH levels increase as a function of the sediment depth. Slight variations were observed in the sediment layer from samples collected within the bay (stations 13 and 66). On the contrary in the sediments collected at the mouth of the bay (station 67) and

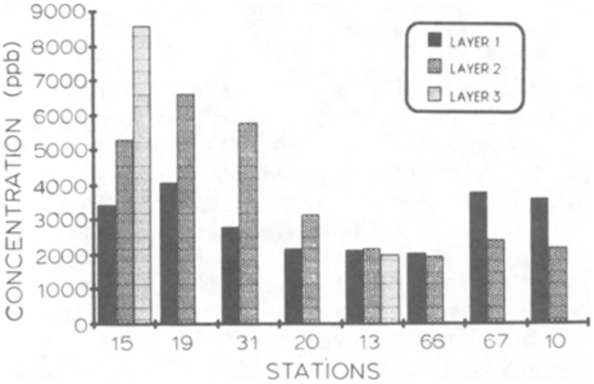

Figure 5. Fluctuation of the total PAH concentrations in the surface sediment layers.

down stream the Saguenay Fjord (station 10), the concentrations of PAH decrease with depth. These data can be rationalized if one considers the relative sedimentation rates characteristic to each sector of the Saguenay Fjord and Baie des Ha! Ha!. Thus, upstream to the Baie des Ha! Ha!, where the sedimentation rates are relatively high (4 to 7 cm/year), the PAH levels measured as a function of depth reflect their accumulation for about the last 10-15 years (Fig. 5, stations 15 to 20). These data indicates a definite recent decreasing trend for PAH input in the Saguenay Fjord. In fact, this trend appears to coincide with the stopping in 1976 of effluent discharges from the aluminium smelting plants to the Saguenay Fjord, upstream the sampling stations (Alcan, personal communication). On the other hand, downstream to Baie des Ha! Ha!, where the sedimentation rates are as low as 0.1 to 0.2 cm/year, the PAH levels in the surface sediments correspond to PAH accumulation for about the last 30 to 60 years. Consequently, the decreasing trend in PAH yearly input observed upstream in recent sediments cannot be detected in these older sediments. On the contrary, in sample 10 and 67 (Fig. 5), an increase of PAH levels from deep (> 100 years old) to top sediments was observed. These data also indicates that PAH accumulation in the Saguenay Fjord sediments is directly related to the establishment of aluminium smelting plants in the vicinity of Chicoutimi (Fig. 1) in the late 1930.

In a study by Laflamme and Hites (1978), it was reported that the background level of total PAH in «uncontaminated sediments» is about 55 ppb. In comparison, the PAH concentrations found in the Saguenay Fjord sediments are 9 to 80 times higher than normal PAH background level. In the Saguenay Fjord, it appears that the river is not the main route of entry of PAH. On the basis of the partial data presented herein and data to be published shortly, it seems that a large proportion of PAH are atmospherically transported to the river. In addition, the highly active hydrology observed in the Fjord and the spreading of a fresh water layer on top of the water column are likely to favor the widespread distribution of PAH in the sediments throughout the Fjord.

In conclusion, the nature of the PAH found in the sediments of the Saguenay Fjord is strongly suggestive of localized and anthropogenic inputs. A source for perylene distinct from that of other PAH is clearly indicated by its distribution pattern through the Fjord. Although PAH are diluted by excessive organic matter inputs in some sediment samples, the mean level of contamination is relatively high in this marine environment. A decreased PAH input was observed in recent surface sediments. It is not certain, however, whether this decrease in sedimentary PAH levels is sufficient to protect marine life from the adverse effects of these toxic pollutants. Complementary studies on the temporal variations and fluxes of PAH in the Saguenay Fjord sediments are in progress.

Acknowledgments. This project was made possible through an NSERC operating grant (A-2629) to M.J. Gagnon.

REFERENCES

Conney AH (1982) Induction of microsomal enzymes by foreign chemical and carcinogenesis by polycyclic aromatic hydrocarbons: GHA Clowes Memorial Lecture. Cancer Research 42:4875-4917

Cossa D, Picard-Bérubé M, Gouygou JP (1983) PAH in mussels from the Estuary and northwestern Gulf of St-Lawrence, Canada. Bull Environ Contam Toxicol 31:41-47

Laflamme RE, Hites RA (1978) The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochim Cosmochim Acta 42:289-303

Picard-Bérubé M, Cossa D, Piuze J (1983) Teneurs en benzo 3,4 pyrene chez Mytilus edulis L. de l'estuaire et du golfe du St-Laurent. Mar Environ Res 10:63-71

Primeau S, Goulet M (1983) Résultats d'échantillonnage de l'eau et des sédiments de la Baie des Ha! Ha!. Service de la Qualité des Eaux, ministère de l'Environnement, No. 83-19, p 56

Smith JN, Walton A (1980) Sediment accumulation rates and geochronologies measured in the Saguenay fjord using the Pb-210 dating method. Geochim Cosmochim Acta 44:225-240

Southworth (1979) The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull Environ Contam Toxicol 21:507-514

Windsor JG Jr, Hites RA (1979) Polycyclic aromatic hydrocarbons in Gulf of Maine sediments and Nova Scotia soils. Geochim Cosmochim Acta 43:27-33

Received August 28, 1985; accepted September 10, 1985.