

# Geochronology for Polycyclic Aromatic Hydrocarbon Contamination in Sediments of the Saguenay Fjord

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■ The geochronology of polycyclic aromatic hydrocarbon (PAH) concentrations and fluxes to the sediments of the Saguenay Fjord, Quebec, and changes in the chemical assemblage are accounted for by concurrent developments in the region's aluminum industry. After a gradual increase in 1926 from the preindustrial background, PAH inputs increased dramatically in the 1940s after a major expansion in facilities and adoption of the Soderberg process. The assemblages of PAHs in the sediments indicate that their principal source until 1964 was atmospheric emissions, while direct discharges of scrubber effluents into the Saguenay River far exceeded the atmospheric inputs between 1964 and 1976, doubling the overall flux to the sediments. An input model based on a combined atmospheric/fluvial transport and deposition mechanism is derived from aluminum production data and compared with the observed fluxes. A linear relationship between the PAH and organic matter concentrations indicates that scavenging from the water column may be the dominant mechanism for the deposition of PAHs.

## Introduction

Of the wide range of organic contaminants in the environment, polycyclic aromatic hydrocarbons (PAHs) are of concern because of their potential or proven carcinogenicity. The main source of these substances is combustion of organic materials (1, 2), and after entering the environment, they are widely disseminated by fluvial and aeolian pathways and eventually accumulate in soils and sediments (1, 3-7). The present study examines the time-stratigraphic record of PAH accumulation at the head of the Saguenay Fjord, Quebec (Figure 1) and attempts to resolve the detailed geochronology for PAH transport through the region and to identify the mechanisms governing PAH uptake in the different environmental phases.

## Industrial and Sedimentological Setting

The hydroelectric resources of the Saguenay region with its ready accessibility to sea were recognized by the aluminum industry early in this century, and the first hydroelectric station and aluminum smelter began operation at Isle-Maligne and Arvida, respectively, in 1926. The Arvida smelter was converted from the prebake to the Soderberg process and underwent a major expansion between 1938 and 1945, and a smaller smelter began production in 1943 at Isle-Maligne. By 1960, the region had become one of the world's largest centers for aluminum production (8). Although emissions from aluminum smelting have been recognized as a major source of PAHs in both North America (9) and Europe (10), they are produced during the combustion of all organic materials and, consequently, their history extends beyond the era of the aluminum industry to the time of early settlement and to the more distant past, when natural forest and grass fires were their main source.

The Saguenay Fjord is a partially submerged glacial valley separated from the St. Lawrence Estuary by a shallow sill (Figure 1). More than 90% of the freshwater input to the fjord is from the Saguenay River, which is

regulated by a system of dams and hydroelectric installations. Elevated river discharges and hydrodynamic energies during the spring result in pronounced seasonal variability in sedimentation rates and sediment texture (11). While unusually high sediment accumulation rates occurred in 1924, 1928, 1942, 1947, and 1964 (12), the most dramatic sediment transport event in the Saguenay Fjord during the 20th century followed a massive landslide at Saint Jean-Vianney in May 1971. Subsequent resuspension of landslide material from the river channel and its transport to the fjord led to high sedimentation rates during 1972-1977. The influx of organic material from pulp and paper mills and sawmills (13) has resulted in an anoxic sediment regime that is almost totally devoid of bioturbation at the head of the fjord. Consequently, time-stratigraphic sequences can be resolved with a precision of  $\pm 1$  year in sediments deposited during the 20th century (12, 14).

## Sampling and Analytical Methods

Sediment core D-1 (227 cm) was collected at the head of the Saguenay Fjord in 1979 (Figure 1) and subdivided into 1-cm intervals. The sediment geochronology was established from the  $^{210}\text{Pb}$  distribution for all 227 segments of the core and a constant flux model (11, 12), and the content of organic matter was determined by a wet oxidation method (15). To extend the historical record, a second core (core 72) was collected nearby in 1982.

**Capillary Column Gas Chromatography.** Selected samples ( $\sim 1$  g) were weighed and Soxhlet extracted for 6 h with a mixture of benzene and hexane (20:80). The extract was concentrated to  $\sim 0.5$  mL, passed over activated copper to remove sulfur, and passed through a silica gel column to separate the aliphatic and aromatic fractions. The latter was reduced to  $\sim 200$   $\mu\text{L}$  for injection into the gas chromatograph (Hewlett-Packard 5880A). The analysis was carried out using a 15 m  $\times$  0.25 mm o.d. fused silica column with a 0.25- $\mu\text{m}$  coating of DB1 (J&W Scientific Inc.) and a temperature program of 4  $^{\circ}\text{C}/\text{min}$  from 60 to 265  $^{\circ}\text{C}$ . Chromatographic peaks were identified by comparing retention times with those from a mixture of common PAHs. In two cases, the fractions containing the saturated components were analyzed.

**Capillary Column Gas Chromatography/Mass Spectrometry.** Aromatic extract (1.9  $\mu\text{L}$ ) was injected splitless onto a 30-m SE-30 FSOT column (programmed at 4  $^{\circ}\text{C}/\text{min}$  from 65 to 265  $^{\circ}\text{C}$ ), and the mass spectrometer (Finnigan Model 4000 GC-MS coupled to an INCOS data system) was operated in the EI mode (70 eV). The major constituents were identified by matching their mass spectra with those in the mass spectral library with further confirmation by comparison with spectra obtained from the pure substances.

**Fluorescence Spectrophotometry.** Approximately 0.2 g of dried and pulverized sediment from the core segments was extracted by shaking with 20 mL of hexane. The suspension was centrifuged, and the "total" concentration of PAH in the supernatant was quantified in terms of chrysene equivalents by comparing the intensity of the fluorescence emission at 360 nm (excitation at 310 nm)

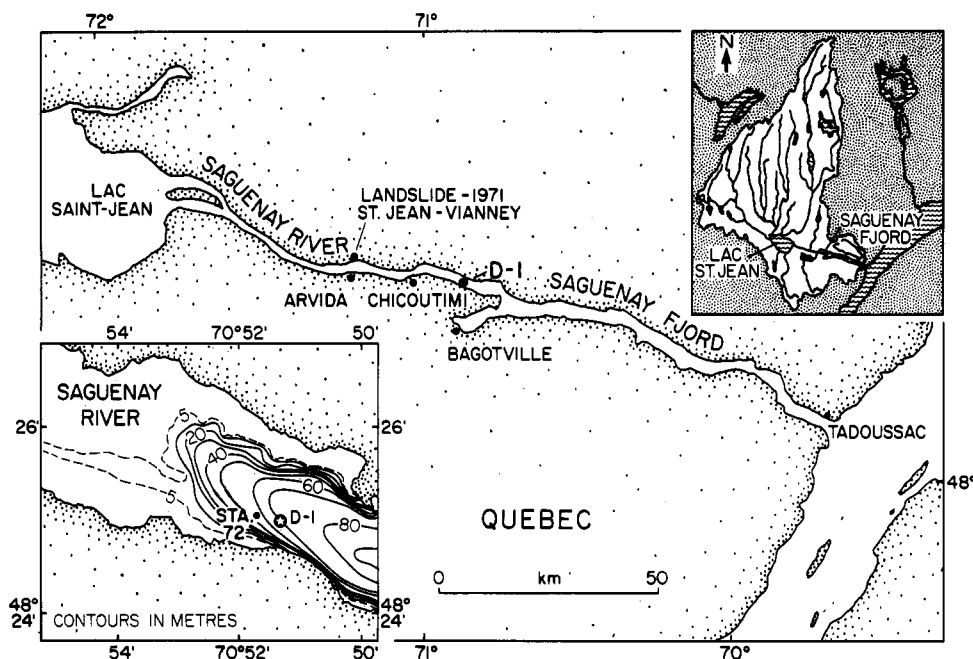


Figure 1. Map of the Saguenay River and Fjord.

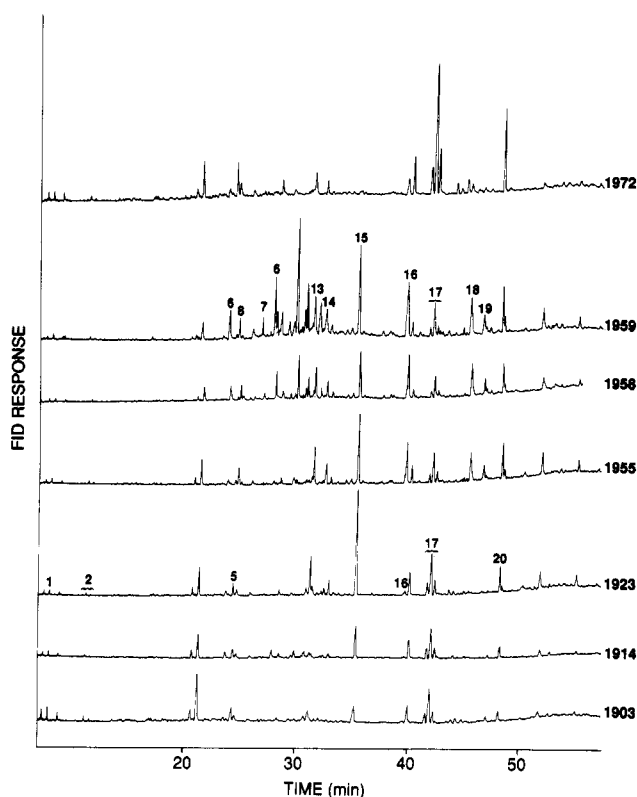


Figure 2. Capillary gas chromatograms of the aromatic fractions extracted from sediments deposited in the Saguenay Fjord between 1903 and 1972. 1, naphthalene; 2, methylnaphthalene; 3, biphenyl; 4, methylbiphenyl; 5, substituted benzene; 6, substituted indene; 7, substituted aromatic; 8, phenanthrene; 9, substituted aromatic; 10, substituted indene; 11, sulfur; 12, unidentified aromatic compound; 13, fluoranthene; 14, pyrene; 15, tetramethylphenanthrene; 16, chrysene; 17, substituted benzene; 18, benzofluoranthene; 19, benzopyrene; 20, squalene.

with that from a series of solutions of known concentrations of pure chrysene.

#### Results

**Aliphatic Fraction.** The saturated fractions of extracts from sediments deposited during 1923 and 1959 were almost identical and comprised predominantly homologous

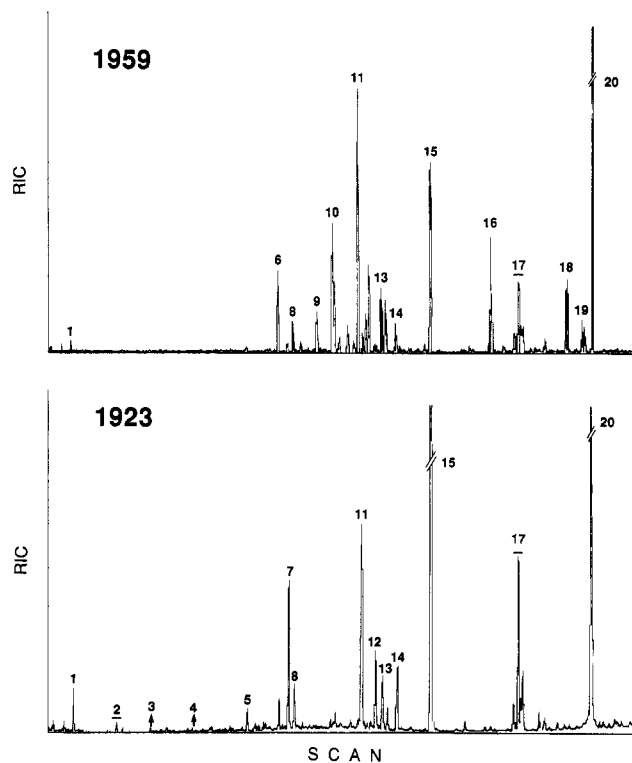


Figure 3. Reconstructed ion chromatograms of aromatic fractions extracted from sediments deposited in the Saguenay Fjord in 1923 and 1959. (Identity of peaks as given in Figure 2.)

series of *n*-alkanes ranging from *n*-C<sub>14</sub> to *n*-C<sub>33</sub>. A strong odd/even carbon preference in the *n*-C<sub>20</sub>-*n*-C<sub>31</sub> range and the pristane/phytane ratios (1.52 and 1.41) inferred a biological origin, and the prominence of *n*-C<sub>27</sub> and *n*-C<sub>29</sub> suggested that the main source of these compounds was plant material from the forested region and debris from pulp mills and sawmills. Since three decades of aluminum production had no detectable impact on these compounds, they were not studied further.

**Aromatic Fraction.** Both capillary gas chromatography (Figure 2) and capillary gas chromatography/mass spectrometry (Figure 3) demonstrated that the composition of the aromatic substances deposited in the Saguenay

Fjord underwent substantial changes during the past century. Before the advent of aluminum production in 1926, the aromatic fraction was a relatively uncomplicated mixture of hydrocarbons, all at very low concentrations (Figure 2). Naphthalene and methyl-substituted naphthalenes were only barely detectable, while phenanthrene, fluoranthene, pyrene, chrysene, and several substituted aromatics (not further identified) were present at only slightly higher concentrations. Tetramethylphenanthrene was the most abundant PAH at that time, and squalene ( $C_{30}H_{50}$ ), an isoprenoid hydrocarbon of biological origin, was a major constituent. In addition to confirming the identities of these constituents, the GC/MS analyses revealed trace amounts of biphenyl and methylbiphenyl. Since assemblages of PAHs with limited alkylation and little or no naphthalene or other two-ring components are generally accepted as characteristic of high-temperature pyrolysis, it is likely that the bulk of the PAHs deposited during this preindustrial period were from forest fires, local combustion of wood, etc. The gradual increase in concentration during this period presumably reflects an increase in combustion accompanying the growth in population.

Following the start-up of the first aluminum smelter, several changes in the composition of the aromatic substances began to manifest themselves (Figure 2), and by the late 1950s, a marked increase had occurred in both the complexity and the concentrations of the PAHs in the sediments. Components, not present previously, were identified by GC/MS (Figure 3) as substituted indenenes, benzofluoranthene and benzopyrene, while unidentified aromatic compounds eluting at 30.1 min and at times greater than 42 min were also present. This greatly increased complexity was particularly evident in 1959 (Figure 2), although it is noteworthy that naphthalene and substituted naphthalenes were virtually absent. During this period there was also a marked change in the relative abundances of the PAHs, the most pronounced being the change in the concentration of chrysene relative to phenanthrene and pyrene. These changes coincided with developments in the aluminum industry. The first smelter in the region used the "prebake" process, and PAHs volatilized during the fabrication of the electrodes or produced by the reaction of the electrodes with oxygen liberated by the electrolysis of molten alumina were emitted into the atmosphere. Until the early 1940s, the dominant pathway for the input of PAHs to the Fjord was by atmospheric dispersion and deposition in the drainage basin followed by riverine processes that resulted in their subsequent transport and deposition in the fjord.

To meet a rapidly increasing demand for aluminum, a new smelter with 15 Soderberg potlines was constructed at Arvida between 1938 and 1943, and another constructed at Isle-Maligne brought an additional 4 potlines into production in 1943, 1951, 1952, and 1956. The Soderberg process generates ~1000 times more PAHs than the prebake process for the same aluminum production (16). To control atmospheric pollution, scrubbers were installed at the Arvida smelter with the scrubber liquor being processed to destroy PAHs. No attempt was made, however, to control atmospheric emissions from the Isle-Maligne smelter until 1956, when the first scrubber was installed. A second was installed in 1960, and the remaining two potlines were equipped in 1961. Between 1964 and 1976, the scrubber liquors from this plant were discharged directly into the Saguenay River (17).

These developments resulted in a substantial increase in the input function of PAHs to the Saguenay Fjord and

were accompanied by a marked change in the composition of the PAHs (Figures 2 and 3). The assemblage of PAHs in sediments deposited in the late 1950s was very similar to that reported (17) for the potline effluents which, in turn, was similar to those associated with particulate emissions from an aluminum reduction plant (18) and in air and soil samples near an aluminum smelter in Norway (10). The enhanced complexity and, particularly, the observed increase in chrysene concentration are considered typical of contamination from aluminum plants (10). The aromatic content of the sediments underwent an especially dramatic change in 1971 following a massive landslide at St. Jean-Vianney. Since the landslide material had been isolated from atmospheric fallout, the assemblage of PAHs in these sediments was reminiscent of those of the preindustrial era. A striking difference, however, was the virtual absence from the landslide-displaced sediments of tetramethylphenanthrene (previously the most abundant PAH) and of the low-boiling substituted benzenes and indenenes, which were abundant during the industrial period.

**PAH Geochronology.** A second diagnostic for changes in PAH inputs to the sediments over the period of industrialization is provided by the "total" concentration (chrysene equivalents) of PAHs and their flux (concentration times sediment accumulation rate) to the sediments (Figure 4). During the 19th century, the PAH concentration and flux were 2–3  $\mu\text{g/g}$  and 5–8  $\mu\text{g cm}^{-2} \text{ year}^{-1}$  respectively, representing the "base-line" conditions that existed before industrialization. The first sustained increase in concentration occurred in 1926, simultaneous with the first smelter entering production, and the doubling of the PAH concentrations and fluxes during the 1930s was probably a consequence of the operation of this smelter. Much greater increases occurred following the introduction of the Soderberg process and the accompanying expansion in aluminum production, attaining a maximum in the 1960s and then decreasing during the 1970s. The extremely low concentrations in sediments deposited during the 1970s were a consequence of the "dilution" caused by the influx of uncontaminated sediments displaced by the landslide. During this period, the PAH flux geochronology (Figure 4) is considered to be more representative of the source function and clearly demonstrates that PAH inputs underwent a pronounced increase in 1964 followed by an abrupt decrease in 1976.

## Discussion

**PAH Emissions and an Input Model.** PAHs produced during combustion condense from the vapor phase onto particulate matter and become subject to atmospheric transport and deposition processes. According to estimates of residence times for particles in the atmosphere (1), all but the very smallest of the PAH-bearing particles emitted from the aluminum smelters return to the earth's surface within the Saguenay watershed. Those falling onto water surfaces are transported downstream with other suspended material and accumulate in the fjord on a relatively short time scale (19, 20), whereas those deposited onto land are detained and transported at the very much slower rates associated with soil erosion (11, 14). PAHs in scrubber liquors discharged into the river are deposited in the fjord by the same mechanisms and on the same time scale as those falling from the atmosphere onto water surfaces.

Accepting that the overall mechanism is a composite of these atmospheric and riverine pathways, the input function,  $I_{\text{PAH}}$ , (ton/year) for the PAH inputs to the Saguenay Fjord can be expressed as

$$I_{\text{PAH}}(t) = A + BI_{\text{atm}}(t) + I_{\text{liq}}(t) + C(t)I_{\text{atm}}(t) \quad (1)$$

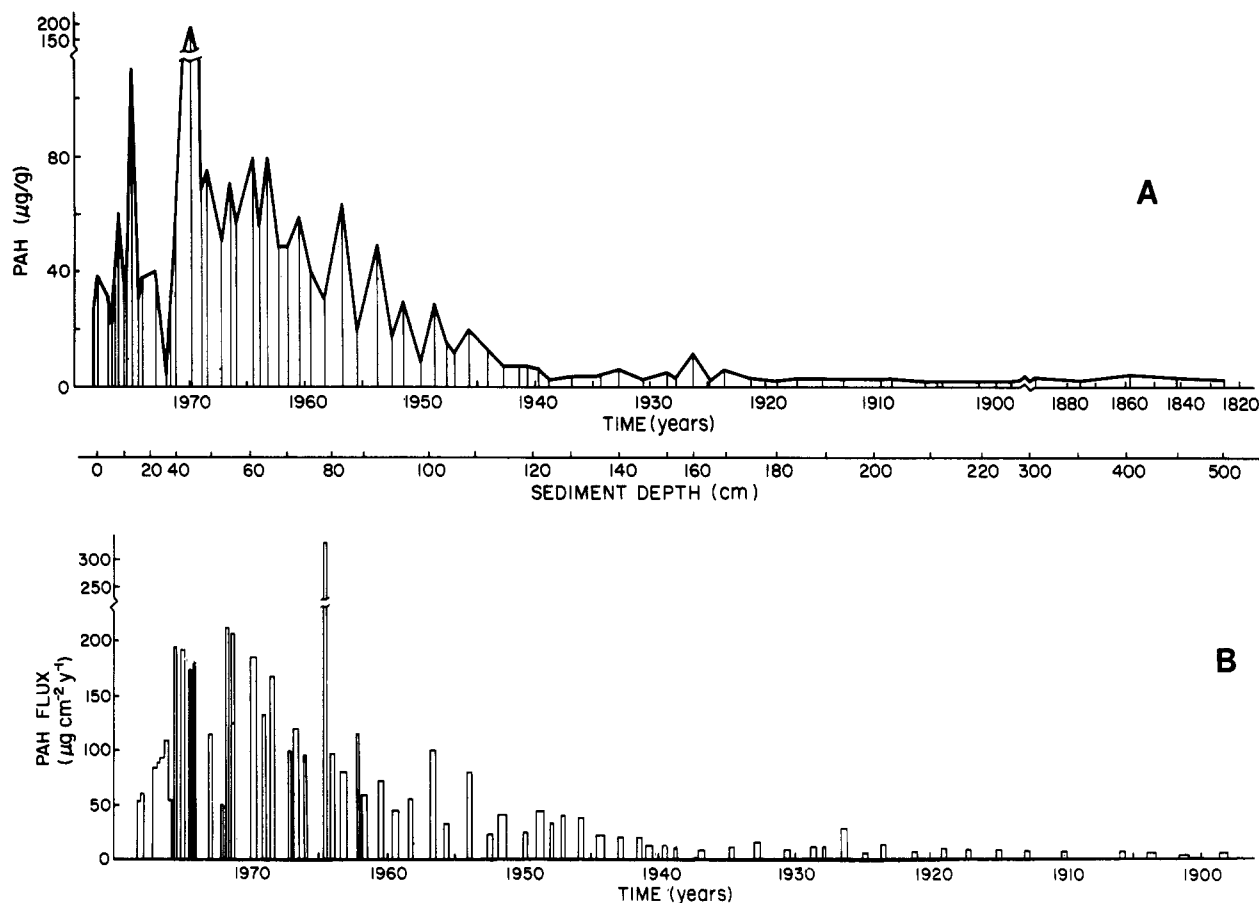


Figure 4. PAH concentration (A) and PAH flux (B) as a function of sediment deposition date (core D-1).

where  $I_{\text{atm}}(t)$  and  $I_{\text{liq}}(t)$  are the time-dependent rates (ton/year) of release of PAHs in gaseous and liquid states,  $A$  is the existing rate of input from other potential sources,  $B$  is a constant representing the fraction of the atmospheric releases that are deposited onto the surfaces of the river and fjord, and  $C(t)$  is a time-dependent parameter defining the fraction of the gaseous releases that are deposited on soils and other solid surfaces in the drainage basin but subsequently reach the river-fjord system via soil erosion/transport processes.

If the transport of PAHs in the water column is independent of the pathway by which they entered, the flux of PAHs to the sediments,  $F_{\text{PAH}}$ , ( $\mu\text{g cm}^{-2} \text{year}^{-1}$ ) is directly proportional to the input function

$$F_{\text{PAH}}(t) = kI_{\text{PAH}}(t) \quad (2)$$

where  $k$  is a constant ( $\mu\text{g ton}^{-1} \text{cm}^{-2}$ ). Provided a steady-state PAH concentration is established in which fluctuations are small relative to the input function and the input from soil erosion is negligible compared to other sources [i.e.,  $C(t) \approx 0$ ], eq 2 becomes

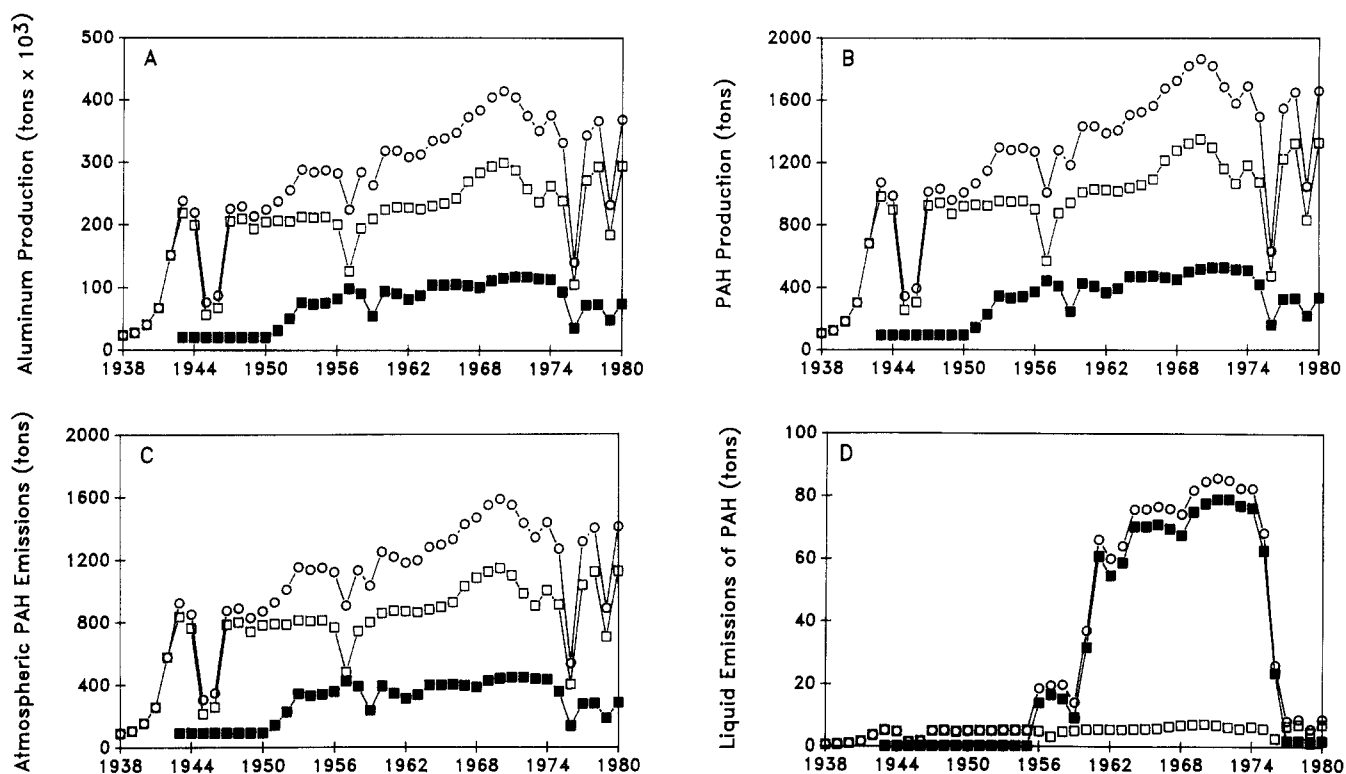
$$F_{\text{PAH}}(t) = k[A + BI_{\text{atm}}(t) + I_{\text{liq}}(t)] \quad (3)$$

where  $k$ ,  $A$ , and  $B$  are constants that can be derived by multiple linear regression analysis of the experimentally measured fluxes and estimates of the annual atmospheric and liquid emissions from the smelters.

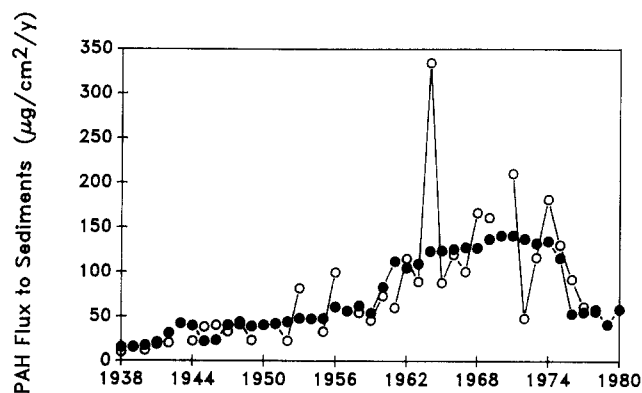
ALCAN (16) indicated that 4–5 kg of PAHs was generated per ton of aluminum produced by the Soderberg process and that the scrubbers had an efficiency of 10–20% for the removal of PAHs, the remainder being released to the atmosphere. From the outset, PAHs in scrubber liquor from the Arvida smelter were destroyed, although 3–4% of the liquid was spilled and entered the river. At the Isle-Maligne smelter, PAHs produced during the first

decade of operation were released to the atmosphere. With the installation of a scrubber on one of the four potlines in 1956, presumably 75% of the PAHs was emitted to the atmosphere, while the remaining 25% was scrubbed and the liquor was discharged into the river. The portions scrubbed increased to 50% in 1960 and to 100% in 1961 with the installation of scrubbers on the remaining potlines, and the effluent entering the river increased correspondingly. In 1976, discharges of scrubber liquors ceased.

The annual production of PAHs, the amount emitted to the atmosphere, and the amount discharged as liquid effluents from both smelters between 1938 and 1980 are readily estimated (Figure 5A–D) from ALCAN data (16) for the annual production of aluminum and the midpoints of the ranges given above. After reaching full capacity in 1943, the production of aluminum at the Arvida smelter was maintained at 200 000–300 000 tons/year except during operational problems in 1945–1946 and labor strikes in 1957, 1975, and 1977. The amounts of PAH produced and the rates of atmospheric and liquid emissions from this smelter paralleled the production of aluminum. At Isle-Maligne, however, aluminum production from the single potline was 20 000 tons/year until 1951 and then increased to 100 000 tons/year as the three additional potlines went into production. Until 1956, all PAHs from this smelter were released to the atmosphere, albeit the amounts were considerably less than the atmospheric emissions from the Arvida smelter. On installing the first scrubber, the liquid component of the PAH discharges quadrupled and then underwent a still more dramatic increase in 1960 and 1961 as additional scrubbers were installed. These discharges resulted in an input to the river-fjord system of as much as 80 tons of PAH annually, and by 1976 more than 1100 tons of PAH had entered the river-fjord system. In total,  $43.9 \times 10^3$  tons of PAHs were emitted to the atmosphere



**Figure 5.** Annual aluminum production (A) and estimates of PAH production (B), atmospheric emissions (C), and liquid discharges (D). O, total; ■, Isle-Maligne; □, Arvida.



**Figure 6.** Comparison measured (O) fluxes of PAH and those calculated (●) from the input model.

and  $1.37 \times 10^3$  tons were discharged in liquors between 1937 and 1980.

With these estimates of the yearly atmospheric and liquid emissions and the measured fluxes of PAHs to the sediments, the constants  $K$ ,  $A$ , and  $B$  were derived by multiple linear regression analysis, and eq 3 becomes

$$F_{\text{PAH}}(t) = 1.03[12.0 + 0.0253I_{\text{atm}}(t) + I_{\text{liq}}(t)]$$

$$R^2 = 0.772 \quad (4)$$

This simple model accounts for  $\sim 77\%$  of the variation in the flux of PAH to the sediment and provides a reasonably good representation of the observed fluxes (Figure 6) except for 1964, when a high concentration of PAH accompanied an abnormally high sedimentation rate, and during the aftermath of the 1971 landslide, when the deluge of sediment overwhelmed all other processes. The model suggests that sources other than emissions from the smelters account for input into the Saguenay Fjord of 12 tons/year PAHs and represents the level that existed during the period between 1926 and 1938 when emissions from the prebake process were the major supplement to the preindustrial background. As such, it provides a base

line against which the impact of the Soderberg process can be assessed.

The coefficient  $B$  indicates that  $\sim 2.5\%$  of the PAHs emitted to the atmosphere entered the water column and were available for immediate transport and deposition in the fjord sediments while the remaining  $97.5\%$  was deposited onto land surfaces within the drainage basin. The subsequent erosion and fluvial transport of this material represents an additional delayed input of PAHs to the sediments in the fjord. Previous studies in the Saguenay indicated  $\sim 0.05\%$  of the inventory of fallout radionuclides is eroded from the drainage basin each year (14) and the rate of erosional transport of PAHs, which are similarly strongly retained by the soil phase, is expected to be similar. That is,  $\sim 20$  tons of PAH are eroded from the reservoir of more than 40 000 tons that accumulated in the watershed between 1938 and 1980 and are transported through the river-fjord system each year. This represents a source for PAHs that will persist for many years to come even if emissions from the smelters are reduced or eliminated. The present reservoir of PAHs, if uniformly distributed over the entire land surface of the watershed, represents an accumulation of  $\sim 0.5$  kg/km<sup>2</sup>. However, since the prevailing winds are along the axis of the river valley, the concentrations of PAH in this zone would be much higher, possibly by several orders of magnitude. Since benzo[a]pyrene, a highly potent carcinogen, is 3% of the total PAH generated by the smelters (16), this reservoir and the continuing erosion from it present a serious, long-term hazard both to the environment and to human health in the region.

**PAH Association with Organic Matter.** All the data indicate that the mechanism for PAH transport changed from a predominantly airborne pathway prior to the 1960s to an overwhelmingly aqueous pathway between 1964 and 1976, followed by a return to a mainly airborne pathway. These changes are further reflected in a relationship between the concentration of PAHs and organic matter in the sediments. When the data are sorted according to

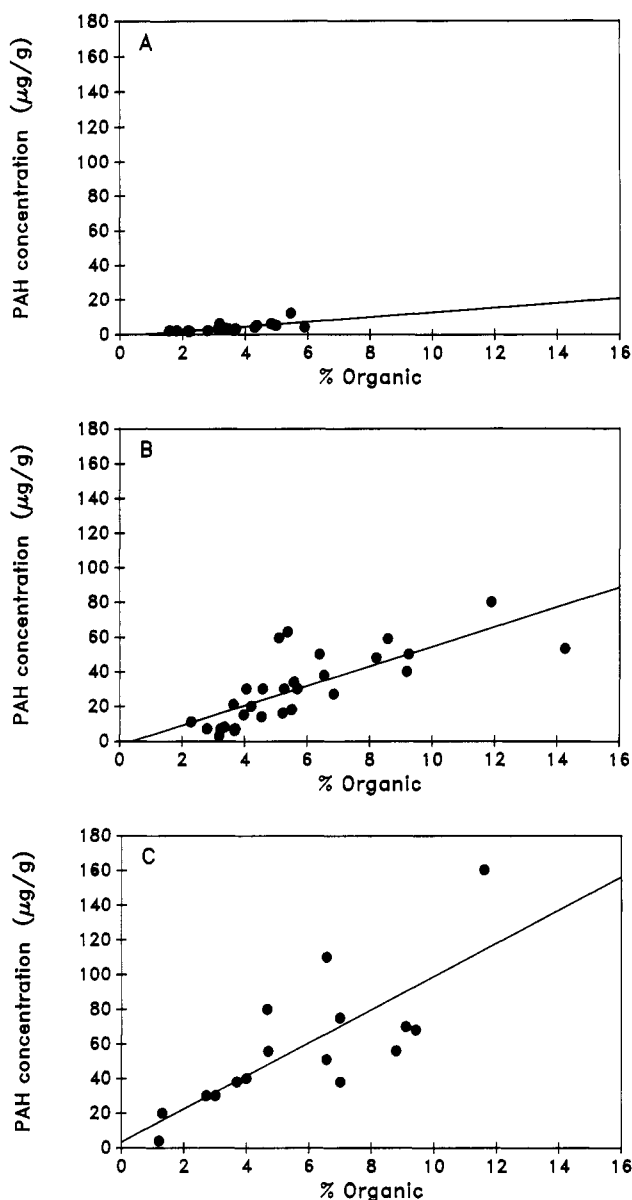


Figure 7. PAH versus percent organic matter distributions for core D-1. A, pre-1938; B, 1938–1963 and 1976–1978; C, 1964–1976.

pre-1938, 1938–1964 and 1976–1979, and 1964–1976, all three sets imply a linear relationship between the concentration of PAHs and that of organic matter (Figure 7A–C). The time dependence of the PAH concentration,  $[PAH]$ , ( $\mu\text{g/g}$ ) with respect to the percent organic matter concentration  $[OM]$  can be represented as

$$[PAH] = a + b(t)[OM] \quad (5)$$

where  $a = -1.09$ ,  $b = 1.37$  for  $t = \text{pre-1938}$  ( $n = 19$ ,  $r = 0.68$ );  $a = -2.33$ ,  $b = 5.68$  for  $t = 1938\text{--}1963$  and  $1976\text{--}1978$  ( $n = 29$ ,  $r = 0.76$ );  $a = 3.37$ ,  $b = 9.55$  for  $t = 1964\text{--}1975$  ( $n = 16$ ,  $r = 0.77$ ).

The effect of atmospheric emissions of PAH from the Soderberg process is given by subtracting the pre-1938 base-line component of  $[PAH]$  from that associated with the atmospheric releases between 1938–1963 and 1976–1978; i.e.

$$[PAH]_{\text{atm}} = -1.24 + 4.31[OM] \quad (6)$$

The additional effect of the discharge of scrubber liquors is given by

$$[PAH]_{(\text{atm}+\text{liq})} = -4.46 + 8.18[OM] \quad (7)$$

That is, the releases of scrubber effluents from the Isle-Maligne smelter during 1964–1977 essentially doubled the slope for the linear regression between the PAH and organic matter concentrations. This is consistent with a process in which the PAHs in the water column are scavenged and transported to the sediments in association with suspended organic material.

**Registry No.** Naphthalene, 91-20-3; methylnaphthalene, 1321-94-4; biphenyl, 92-52-4; methylbiphenyl, 28652-72-4; phenanthrene, 85-01-8; fluoranthene, 206-44-0; pyrene, 129-00-0; tetramethylphenanthrene, 71607-70-0; chrysene, 218-01-9; benzo[fluoranthene], 56832-73-6; benzopyrene, 73467-76-2; squalene, 111-02-4; aluminum, 7429-90-5.

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