A COMPLETE RE-ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SEDIMENTS OF THE SAGUENAY FJORD (QUEBEC).

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ABSTRACT
The objective of this work is to provide a new series of data on the spatio-temporal distribution of PAHs in sediments of the Saguenay Fjord and the Baie des Ha!Ha! about 15 years after the last exhaustive report on the topic. Five sediment cores have been sampled from various sectors of the Fjord in Spring 2002 and analysed for their content in PAHs by GC/MS. Total PAHs (selected 16 priority HAPs) are reported for the first 28 cm of each core. The mean concentration in the surface layer (0.0-0.5 cm) was 310 ng/g (dry weight) with a maximum value of 460 ng/g found at core 5 in the North Arm of the Fjord and a minimum value of 227 ng/g found in the Baie des Ha!Ha!. Surface values reported here are between 10 and 30 times lower than those previously reported for cores sampled in 1982 (Martel et a. 1987). All cores show maximum PAHs values in layers between 15 and 28 cm depth indicating a slow burying process of highly contaminated sediments brought to the fjord in 1960s and 1970s.

RÉSUMÉ
L'objectif de ce travail est de fournir une nouvelle série de données sur la distribution spatio-temporelle des HAPs dans les sediments du fjord du Saguenay et de la baie des Ha!Ha! environ 15 ans après la dernière publication détaillée sur le sujet. Cinq carottes de sédiment ont été échantillonnées dans différentes sections du fjord au printemps 2002 et analysées pour leur contenu en HAPs par GC/MS. Les HAPs totaux (une sélection de 16 HAPs prioritaires) sont présentés pour les 28 premiers cm de chaque carotte. La concentration moyenne dans la couche de surface (0.0-0.5 cm) était de 310 ng/g (poids sec)avec une valeur maximale de 460 ng/g trouvée pour la carotte 5 dans le bras nord du fjord et une valeur minimale de 227 ng/g dans la baie des Ha!Ha!. Les valeurs de surface rapportées ici sont entre 10 et 30 fois inférieures aux valeurs rapportées pour des carottes prélevées en 1982 (Martel et al. 1987). Toutes les carottes montrent des valeurs maximales en HAPs à des profondeurs variant entre 15 et 28 cm montrant le lent processus d'enfouissement des sédiments hautement contaminés apportés au fjord dans les années 1960 et 1970.

1. INTRODUCTION

Polyaromatic hydrocarbons (PAHs) are known to be persistent pollutants present in rivers, lakes and coastal zones close to industrial and urban activities (Suess 1976). These hydrophobic compounds are produced by the combustion of fossil fuels, such as oil and coal, and also wood, fabrics and plastics. Among PAHs, some molecules are known for their toxic effects on living organisms. Benzo(a)pyrene (BaP), a large 5-ring molecule, is the best known PAH and is considered as the first responsible for the lung cancer of cigarettes smokers (Harvey 1991). Presence of PAHs in sediments is associated to a number of fish diseases (Krahn et al. 1986) and other toxic effects on aquatic invertebrates (Uthe and Musial 1986).

The presence of high concentrations of PAHs in sediments of the Saguenay Fjord has been first reported in middle 1980s (Martel et al. 1986, 1987). Authors found that the concentration of total PAHs in top cm of cores ranged from about 2500 ng/g (d.w.)in the deepest basin of the Fjord to about 14000 ng/g (d.w.) in the North Arm of the Fjord near the mouth of the Saguenay River. A decrease in PAHs concentrations in superficial layer was already observed in most sampled stations except in the Baie des Ha!Ha! where the concentrations were still increasing with a maximum value of 3505 ng/g (d.w.). The flux of total PAHs to the North Arm in 1981 was estimated to about 1800-2000 ng cm^{-2} yr^{-1} whereas the flux to the Baie des Ha!Ha! was estimated to 278 ng cm^{-2} yr^{-1}. When calculated for the whole sediment surface of the Fjord, the flux of total PAHs to the Saguenay Fjord was estimated at 868 kg yr^{-1} in 1980 whereas the flux of benzo(a)pyrene was about 20 times lower with a value of 44 kg yr^{-1} in 1980.

The link between PAHs in sediment and the activities of two aluminum plants located a few km upstream to the Fjord was established by comparing PAH fingerprints from particles collected near the plants and the surface sediment from the Fjord (Martel et al. 1987).

The first objective of this work is to re-assess the presence of PAHs in sediments of the Fjord and to estimate the temporal changes in the input of PAHs in the last 20 years. To reach that goal, a series of five sediment cores were collected in Spring 2002 and analysed for their content in PAHs.

2. MATERIAL AND METHODS

2.1 Location of samples

The sampling was conducted onboard of the research vessel *Alcide C. Horth* in may 2002 using a multicorer Macicorer Mark V-400 specially designed to take multi-sediment cores while preserving intact the water/sediment interface and allowing precise sub-sampling of top few mm. Location of sampled stations appears in Fig. 1. Station 5 is located in North Arm of the Fjord and is close to the mouth of the Saguenay River considered as the main source of particulate PAHs in the past. Station 9 is located in the middle of the Baie des Ha!Ha! where the 1996 flood brought a tick layer of new sediment capping old contaminated sediments (Pelletier et al. 1999, Pelletier et al. 2003). Station 13 is located in the main axis of the Fjord at about 18 km downstream to the mouth of the Saguenay River. This station received only a thin layer of flood sediment. Stations 16 and 30 are located in the deep basin of the Fjord (>280 m) with a low sedimentation rate.

2.2 Analytical methods

Upon their recovery on the deck of the vessel, cores were protected from possible contamination and sub-sampled in thin slices from 0.5 cm in surface to 3 cm tick in the bottom. Samples were preserved in glass vials and frozen at –20 °C until laboratory analysis. Sediment samples were freeze-dried for 48h and finely crushed in a mortar. Sediment (1.00 g) was extracted in 10 ml dichloromethane (DCM) on a mechanical shaker over 16h and finally sonicated for 30 min at 20 °C. After centrifugation, extracts were transferred in conical tubes and evaporated to 0.5 ml in an ice bath to minimize losses of light PAHs. Extracts were cleaned on Supelclean ENVI-18 SPE® 3 ml min-columns by elution with hexane:DCM (90:10). Extracts were evaporated to 0.5 ml, deterated standards added, and transferred to an injection vial. PAHs were identified and quantified by GC/MS using a ThermoFinnigan Trace GC coupled to a Polaris Q® with automatic injection. Each PAH was identified and quantified by its molecular ion and its retention time determined from the «Quebec Ministry of Environment PAH Mix».

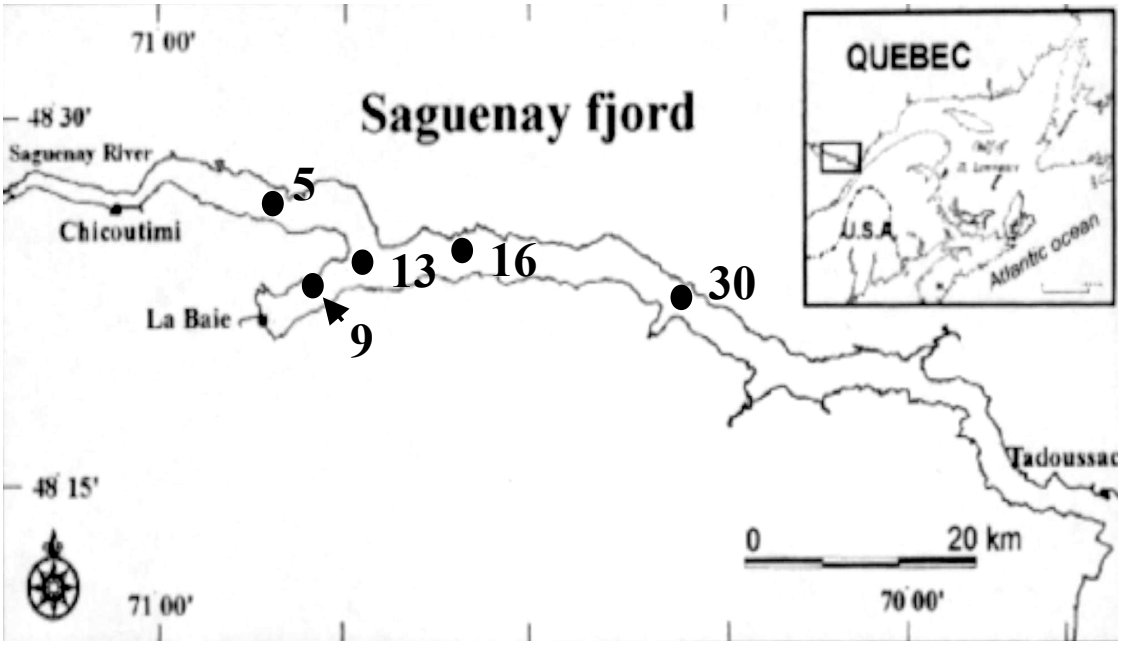

Figure 1: Location of stations sampled in May 2002 in the Saguenay Fjord.

3. RESULTS AND DISCUSSION

A total of 90 analyses have been performed and 25 PAHs have been identified and quantified by GC/MS for each sample. Among these compounds 16 PAHs have been selected following the priority list of the USAEPA and are designated as total PAHs hereafter. The most striking feature for all the cores is the low concentration of PAHs found in the first 10-12 cm in all cores. The mean concentration in the surface layer (0.0-0.5 cm) was 310 ng/g (dry weight) with a maximum value of 460 ng/g found at core 5 in the North Arm (Fig. 2) and a minimum value of 227 ng/g observed in the Baie des Ha!Ha! (Fig. 3).

The profile of core 5 shows low PAH values (about 400 ng/g) from the surface to about 15 cm and then a rapid increase up to 3310 ng/g in the deepest layer analysed at 26-29 cm. Assuming the sedimentation rate did not change since early 1980s (about 2.2 cm/yr following

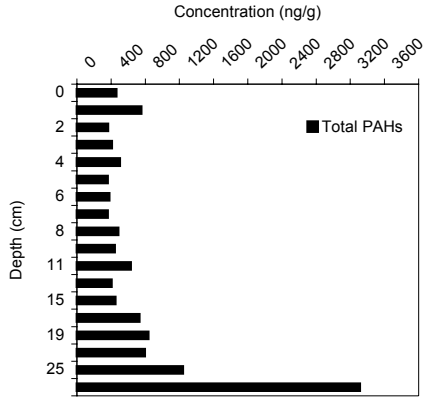

Figure 2. Profile of total PAHs in core 5 collected in the North Arm of the Sagueany Fjord.

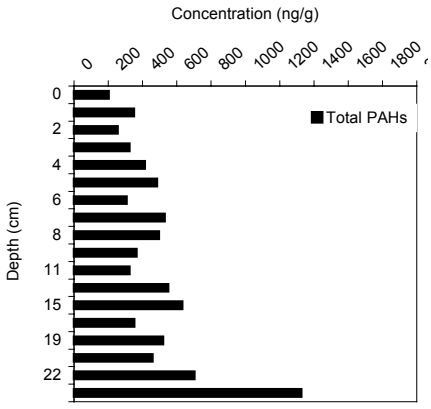

Figure 3: Profile of total PAHs in core 9 collected in the Baie des Ha!Ha!

Leclerc et al. 1986) and the 1996 flood did not bring an important contribution to sediment of the North Arm, it is suggested that the top 22 cm of the core 5 are representative of the contribution of the Saguenay River in the last 10-15 years.

The core 9 (Fig. 3) shows a rather similar profile to core 5 with values ranging between 200 and 700 ng/g in the first 22 cm and a higher value observed in the last 26-29 cm layer. However the chronology of sedimentation events in the Baie des Ha!Ha! is totally different from core 5. Grain size distribution and other geological and chemical results (Pelletier et al. 2003) indicated the presence of a flood capping layer of about 20-25 cm at the station 9 deposited over the old contaminated layer. PAHs in the flood layer of

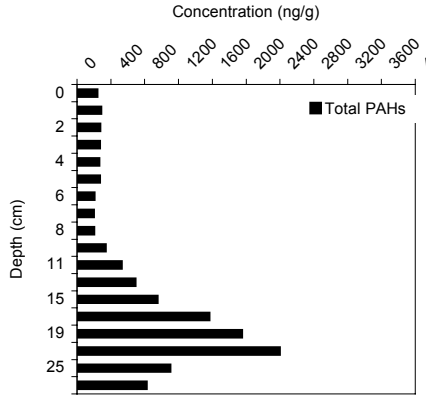

Figure 4. Profile of total PAHs in core 13 collected at the jonction between the North Arm and the Baie des Ha!Ha!.

core 9 are mainly from natural sources (forest fires) and from particles recently settled after the flood. The sedimentation rate at this station is about 0.1-0.2 cm/yr.

Core 13 shows a very nicely characterized profile where concentrations are below 400 ng/g over the first of 10 cm followed by a regular increase up to 2400 ng/g and a final decrease. The sedimentation rate at this location is currently estimated to about 0.5 cm/yr. This profile is a clear indication of the decrease of PAHs inputs in the fjord in the last 20-25 years.

Cores 16 and 30 (Fig. 5 & 6 below) show quite similar profiles with surface concentrations around 300 ng/g followed by a large peak at depth of 15-17 cm corresponding most probably to sedimentation events of mid-1960s (Martel et al. 1987). The sedimentation rate in the deep basin is estimated to about 0.2-0.3 cm/yr. The low sedimentation rate allowed the benthic organisms to intensively mix the sediment and flatten the peak of contaminated sediments.

4. CONCLUSION

These results are presented as the first complete re-assessment of the distribution of PAHs in sediment of the Saguenay Fjord since the publication of 1982 results by Martel et al. (1987). Our 2002 results show a drastic decrease of PAHs in all sectors of the Fjord and profiles confirm the burying of old contaminated sediments (Ouellet, 1990) by new sediments containing about 200 to 400 ng/g of PAHs which is well below the lowest effect threshold of 4000 ng/g proposed by the Ontario Minister of the Environment for aquatic sediments (OME, 1993).

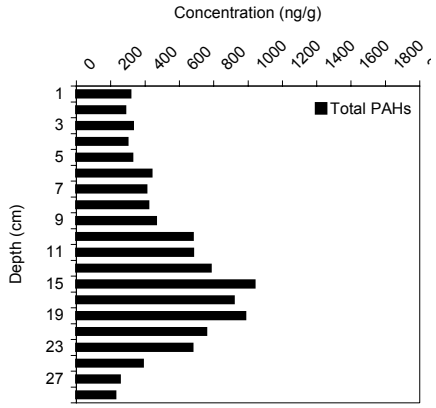

Figure 5. Profile of total PAHs in core 16 collected in the upper part of the deep basin of the Saguenay Fjord.

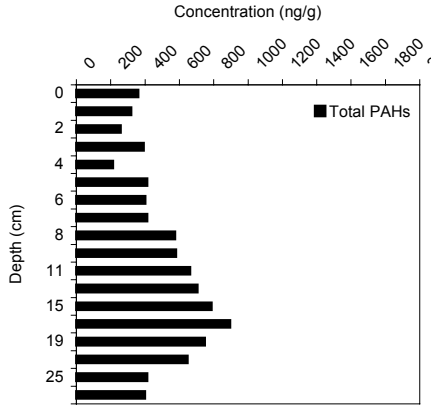

Figure 6. Profile of total PAHs in core 30 collected in the central part of the deep basin of the Saguenay Fjord.

5. ACKNOWLEDGMENTS

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