BEHAVIOR OF HIGH MOLECULAR WEIGHT PAHs IN THE NEW SEDIMENT LAYER OF THE BAIE DES HA!HA! (SAGUENAY FJORD)

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ABSTRACT

A series of four sediment cores was collected between 1998 and 2002 in the center of the Baie des Ha !Ha! with the objective to study the behavior of a number of high molecular weight polyaromatic hydrocarbons (PAHs) deposited immediately after the July 1996 flash flood in the Saguenay Fjord. Dry samples were extracted with dichloromethane (DCM) and then analysed by liquid chromatography (HPLC-Fluorescence). Benzo(a)pyrene (BaP) was selected as the best indicator of the mixing process with the underlying sediment layer. Results show a progressive burying of BaP and its homogenization in the top 0-12 cm layer during the four years of continuous observation. Considering the very low solubility of BaP, its low degradability by microorganisms, and its preferential binding to particulate organic carbon, we consider BaP as a good indicator for the estimation of the organic carbon burying rate in a sediment layer from a recent surface sedimentation.

RÉSUMÉ

Une série de quatre carottes de sédiment a été échantillonnée entre 1998 et 2002 au centre de la Baie des Ha !Ha ! afin de déterminer le comportement de quelques hydrocarbures aromatiques polycycliques (HAPs) de haut poids moléculaire déposés immédiatement après le déluge de juillet 1996. Les échantillons secs ont été extraits au dichloro-méthane (DCM) et ensuite analysés par chromatographie liquide (HPLC-Fluorescence). Le benzo(a)pyrène (BaP) a été retenu comme le meilleur marqueur du processus de mélange avec la couche sous-jacente. Les résultats montrent un enfouissement progressif du BaP et une homogénéisation de la couche entre 0-12 cm au cours des 4 années d'observation. Étant donné la très faible solubilité du BaP, sa faible biodégradabilité par les microorganismes et sa liaison préférentielle avec la matière organique, nous considérons que le BaP est un bon marqueur pour le calcul de l'enfouissement du carbone organique dans une couche sédimentaire à partir d'une récente sédimentation en surface.

1. INTRODUCTION

The catastrophic flood which occurred in Saguenay – Lac saint-Jean area in July 1996 offered an excellent opportunity to study the behaviour of the flood capping layer deposited on contaminated sediments of the Saguenay Fjord (Pelletier et al. 2003; Tremblay et al. 2003). Most chemical and geological studies were oriented toward the stability of the capping layer and its capacity to sequester the old contaminants (PAHs and trace metals) into the pre-flood layer. Very few studies paid attention to the mixing process of the new toxicants (brought to the Saguenay after the flood) within in the flood layer, and as a function of the recolonisation of the new layer by benthic organisms.

Preliminary work conducted a few weeks after the flood and one year later (Pelletier et al. 1999) indicated that the concentration of particulate suspended matter in the water column of the entire Saguenay Fjord, including the Baie des Ha!Ha!, was significantly higher than values previously recorded, indicating that a fairly large amount of very fine clay particles took a long time to settle down and to be incorporated to the surface sediment layer. As a result, the first few mm of sediment at the water/sediment interface were enriched with fine clay particles forming a very thin layer different from the underlying flood layer (grain size data not shown here). This thin layer was presumably also enriched with particulate organic matter as organic matter has a low specific gravity and will tend to stay a longer time in the water column than heavier mineral particles. As PAHs are highly hydrophobic molecules, they preferentially tend to bind to organic rich particles and fine clays (Onuska 1989, Kennish 1997). It is then assumed that this thin surface layer was also enriched by PAHs already present in old glacial epoch deposits (forest fires) leached to the Fjord during the flood or by more recent PAHs emitted by industrial and urban activities immediately after the flood.

The objective of this work was to test the hypothesis that the heavier and highly persistent PAHs, such as benzo(a)pyrene (BaP), can be used as markers in an attempt to estimate the burial rate of particulate organic matter in a new sediment layer being submitted to an intensive recolonisation process by benthic organims. As the concentration of these high molecular weight PAHs was expected to be low in the flood layer (no or little anthropogenic inputs), it was decided to use HPLC coupled to a fluorescence detector which is usually one order of magnitude more sensitive than classical GC/FID or GC/MS for compounds with 4-5 aromatic rings.

2. MATERIAL AND METHODS

The sampling was conducted in May or June of year 1998 to 2002 in the Baie des Ha! Ha! (Fig. 1) onboard the Université du Québec à Rimouski research boat (Alcide C. Horth). Sediment cores (0-29cm) were sampled with a multicorer (Maxicorer Mark V400). Cores were immediately sub-sampled by slice of 0.5 cm (surface), 1 cm (1-8 cm), 2

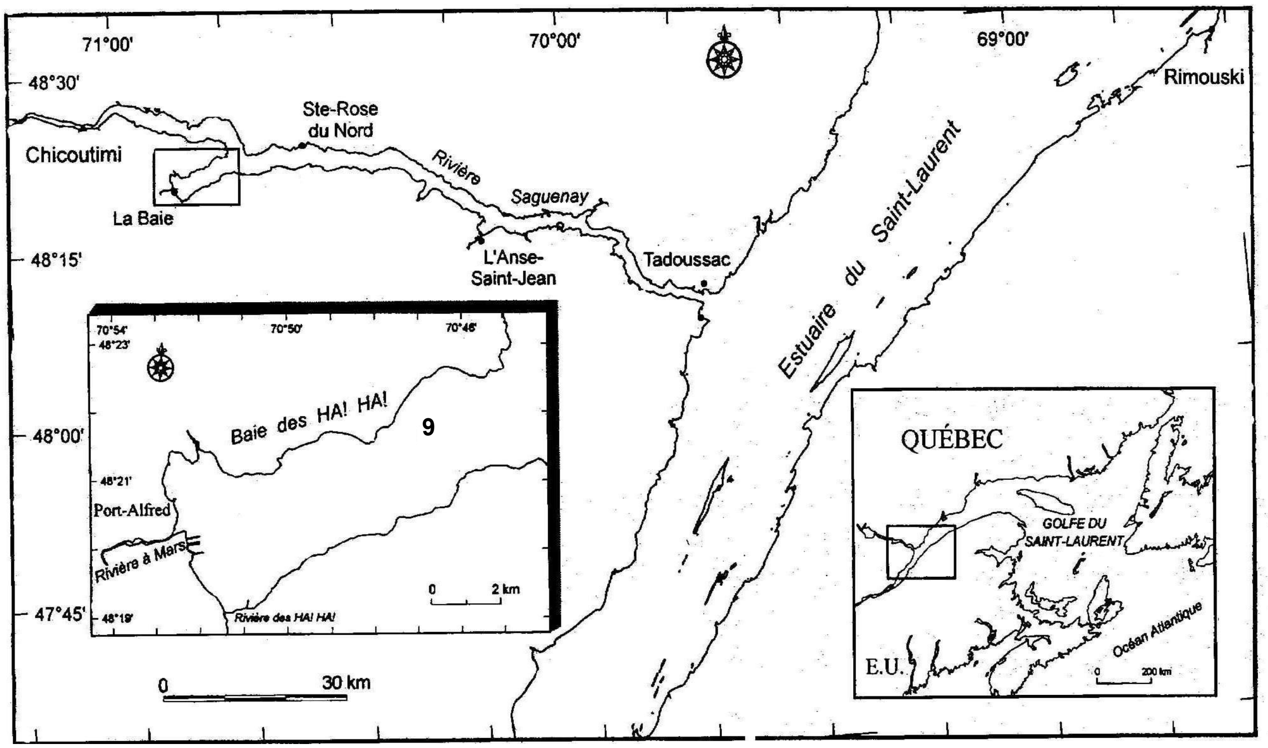

Figure 1. Localisation of station 9 in Baie des Ha! Ha! (from Pelletier et al. 1999).

cm (8-20 cm) and 3 cm (20-29 cm) with the help of a cutting-table (Edenborn et al. 1986) and frozen at –20°C until their analysis in laboratory. Carefully homogenized samples were used for the determination of water content and grain size analysis using a Coulter LS100 apparatus. An other portion of the sediment was freeze-dried for 48 h for the determination of total carbon content and for the extraction of hydrocarbon compounds (PAHs). Dry sediment was finely crushed in a mortal for CHN analysis (15-20 mg) using a Perkin Elmer PE 2400 elemental analyzer.

Dried sediment (1.0 g) from different layers was solvent extracted in a Teflon® tube with 25 ml of dichloromethane (DCM) by ultrasonic bath for 15 min, mechanic shaking for 18 h and a final 15 min in the ultrasonic bath. The extract was centrifuged for 10 min at 3000 rpm and the overlying solution transferred in a 125 ml flask. A second portion of 25ml DCM was added to the tube, shacked vigorously and sonicated for 15 min. After centrifugation, the supernatant was combined to the first extract, and the volume reduced between 3-6 ml with a rotational evaporating (Rotavapor R-114, Büchi). The extract was transferred in a graded conical tube. After evaporation of most of DCM, the extract was re-dissolved and concentrated in about 1 ml of hexane under a nitrogen flow, and eluted through an octadecyl gel column (Supelclean™ ENVI™ – 18 SPE of 3 ml, SUPELCO) with hexane:DCM (75:25) to remove fulvic and humic material. The sample was then evaporated to near dryness in ice bath to minimize loss of PAHs and finally re-dissolved in acetonitrile.

The HPLC-Fluorescence system consisted of an injector 7725i with a 20 µL injection loop; a Shimadzu LC-10AD pump; a SUPELCOSIL™ LC-PAH column (25 cm x 3 mm, 5 µm), a SpectraSYSTEM FL3000 detector and a Waters 746 Data Module integrator. The excitation wavelength was settled at 280 nm and the emission signal was recovered at 410 nm. All analyses were made at constant flow rate of 0.8 ml/min. Solvents used for the mobile phase are water and acetonitrile. The gradient between these two solvents changed during the elution through in the column. The gradient program is shown at Fig. 2. The identification of compounds was done by comparison of the retention time of each PAH with corresponding standards.

A preliminary examination of chromatograms indicated that some 5-ring aromatics were easily separated and quantified, e.g. benzo(a)anthracene (BaA), benzo(k) fluoranthene (BkFl) and benzo(a)pyrene (BaP). Among then, BaP was clearly the compound giving the best signal/noise ratio and easily identified from others. For these practical reasons and also because BaP is highly persistent in sediment (turnover time > 3500 days) and very slightly soluble in seawater (0.005 mg/L at 22 °C), BaP was chosen as the best marker we can find under the Saguenay Fjord conditions to estimate the PAHs behavior in the surface flood layer.

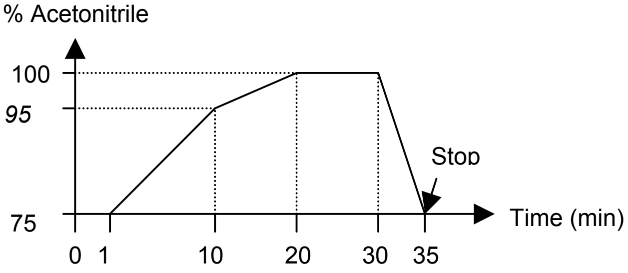

Figure 2. HPLC gradient program for the elution of PAHs.

3. RESULTS AND DISCUSSION

The profile obtained with the grain size analysis as a function of the depth (Fig. 3) allowed the determination of the thickness of the sediment layer brought by the 1996 flash flood. The maximum of sand contribution (over 40%) in the layer 26-30 cm is a clear indication of the boundary between the old sediment (below 30 cm) and the flood layer (above 30 cm). This transition sandy layer was brought during the catastrophic event as a turbidite flowing on the bottom of the Baie des Ha!Ha! (Tremblay et al. 2003). The relative proportion of silt is very constant at about 75% in the flood layer whereas changes in the surface layer (0-3 cm) are indicative of the contribution of the sedimentation process after the flood.

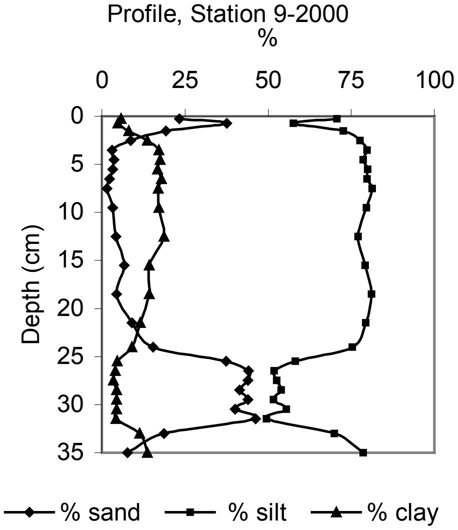

Figure 3. Grain size distribution at station 9 in 2000.

The profile of BaP concentrations (Fig. 4) shows that levels are very low and usually below 0.05 µg/g (dry weight). In an attempt to detect the influence of the clay on the BaP vertical distribution, concentrations of BaP were normalized for the clay content of samples following the equation 1 below.

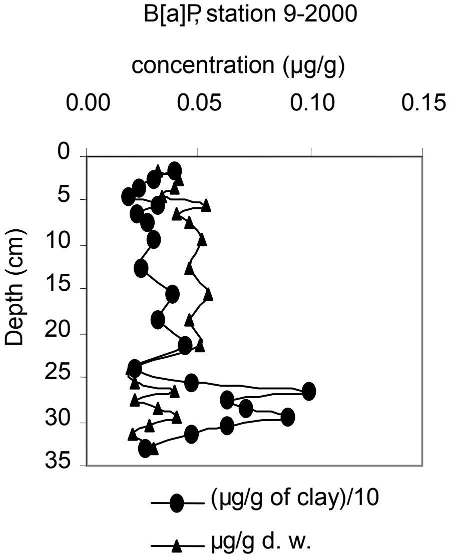

Figure 4. Vertical distribution of BaP concentrations in µg/g (dry weight) in station 9 in 2000. Also shown are BaP concentrations normalized towards clay content in sediment (µg/g of clay/10).

$$\left[\frac{B[a]P}{g\ of\ clay}\right] = \frac{\left[\dfrac{\mu g}{g\ dry\ sediment}\right]}{\%\ clay} \times 10 \qquad [1]$$

As expected from the grain size distribution (Fig. 3), the normalized profile shows higher values in the layer 26-30 where the reduction of BaP concentrations was not proportional to the reduction of the clay content. Again this sandy layer abnormally rich in BaP is a relict of the old layer and the result of strong physical mixing which occurred during the flood event. The top 10-15 layer seems to show some fine variations that need to be closely examined. The sedimentation rate at the location of station 9 was estimated to about 0.3 cm/year before the flood (Leclerc et al. 1986).

The detailed profile of BaP in 1998 (Fig. 5) shows a very characteristic distribution of our marker less than 2 years after the flood. BaP deposited after the flood was present only in the first 3 cm showing only the beginning of the mixing induced by benthic organisms. BaP was barely present in the following 4-10 cm layer. The situation has drastically changed in the core collected in 1999 where BaP was evenly distributed on the entire profile, except with the expected lower level near the surface as the new settling sediment was containing less clay and less BaP. The profile observed in the 2001 core seems to be a normal continuation of the burrowing process with again a lower value near the surface and a maximum value at about 5-6 cm. The last profile obtained in 2002 seems to indicate the end of the borrowing process where BaP concentrations have reached an average value of about 0.25 µg/g in the first 12 cm of sediment, corresponding to the maximum

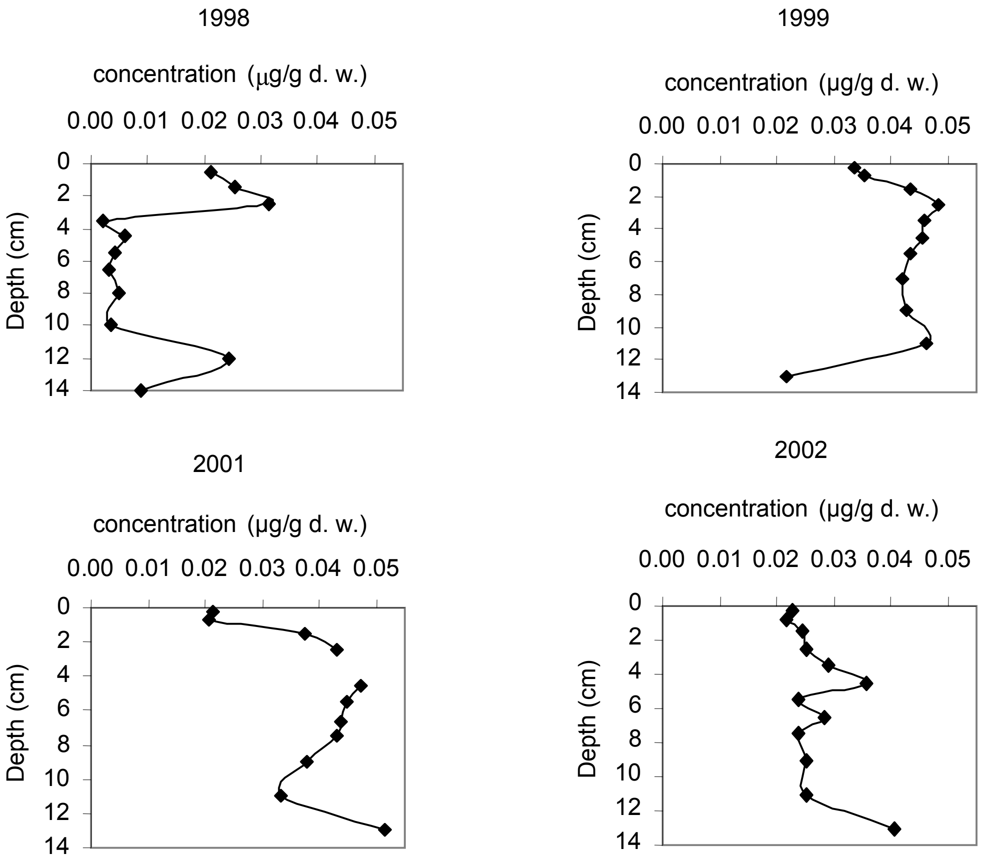

Figure 5. Vertical distribution of BaP concentrations from 0 to 14 cm in 4 cores sampled at station 9 from 1998 to 2002.

activity of the benthic organisms (Michaud et al. 2002). The concentration of BaP in the layer (0-0.5 cm) is now stable at 0.02 µg/g and is a good indication that we now have reached at steady state process almost 6 years after the flood.

4. CONCLUSION

This work provides an interesting method to trace the burying process of particulate organic matter settled at the sediment/water interface over a relatively short period of time (a few months). Using already developed transport and mixing models, it will be possible to calculate the burying rate of particulate organic carbon in a northern cold oxic marine environment.

5. ACKNOWLEDGMENTS

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