SELECTIVE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM CONTAMINATED SEDIMENTS USING A HIGH MOLECULAR WEIGHT SURFACTANT.

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ABSTRACT
The objective of the project was to develop a selective extraction method for PAHs that could mimic the digestive action of microorganisms and benthic invertebrates and contribute to understand the influence of chemical sequestration on the bioavailability and the toxicity of organic molécules present in marine sediments. Preliminary tests to determine the selectivity and efficiency of a series of surfactants led us to the choice of the polyoxyethylene(100)stearyl ether (Brij® 700) with an optimum concentration of $5.25x10^{-3}$ M. Results obtained with Brij® 700 show that the development of a selective extraction method of PAHs using a high molecular weight synthetic surfactant presenting some similarities with natural surfactants produced by microbial communities can provide relevant data that can be related to sequestration mechanisms. Our protocol was tested with 17 samples from the Saguenay Fjord. In a general manner, the high-molecular weight PAH compounds were less extracted by Brij® 700 than the low-molecular weight PAH compounds.

RÉSUMÉ
L'objectif du projet était de développer une méthode d'extraction sélective des HAP pouvant mimer l'action digestive des microorganismes et des invertébrés benthiques et contribuer à comprendre l'influence de la séquestration chimique sur la biodisponibilité et la toxicité des composés organiques présents dans les sédiments marins. Des tests préliminaires pour déterminer la sélectivité et l'efficacité d'une série de tensioactifs nous ont conduits à choisir l'éther stéaryle de polyoxyéthylène(100) (Brij® 700) avec une concentration optimale de $5.25x10^{-3}$ M. Les résultats obtenus avec le Brij® 700 montrent que le développement d'une méthode d'extraction sélective des HAP utilisant un tensioactif synthétique de haut poids moléculaire présentant des similitudes avec les tensioactifs naturels produits par les communautés microbiennes peut procurer des données pertinentes pouvant être reliées à un mécanisme de séquestration. Notre protocole a été testé avec 17 échantillons provenant du fjord du Saguenay). De manière générale, les HAP de haut poids moléculaire étaient moins extraits par le Brij® 700 que ceux de faible poids moléculaire.

1. INTRODUCTION

Traditionally, solvant extraction techniques have been used for the determination of "total" organic contaminant concentrations in soils and sediments. Soils have usually been "exhaustively" extracted, for example, by Soxhlet and saponification procedures (Brilis and Marsden 1990, Eschenbach et al. 1994). However, in light of the increasing body of knowledge related to contaminant availability and aging, such methods are now considered to have little relevance in measuring the proportion of contaminant that may pose an ecological risk i.e., the "bioavailable" fraction (Bosma et al. 1997, Kelsey and Alexander 1997, Kelsey et al. 1997, White et al. 1997).

Less exhaustive techniques have therefore been the subject of more recent studies in the hope that they may access the "labile" or bioavailable pool (Alexander 1995, Kelsey and Alexander 1997, Kelsey et al. 1997, White et al. 1997, Ten Hulscher et al. 1999, Cuypers et al. 2000, Reid et al. 2000, Krauss and Wilcke, 2001). For example, Kelsey et al. (1997) correlated the extraction of phenanthrene using butan-1-ol (BuOH) against bacterial mineralization and earthworm uptake (extraction with and without agitation, respectively). This extraction technique did not however provide a good correlation for all of the pollutants tested. Other extractants were found to be more appropriate in other cases, e.g., a 1:1 methanol:water mixture for atrazine bioavailability evaluation to microbes and a 9:1 methanol:water mixture for atrazine bioavailability evaluation to earthworms (Kelsey et al. 1997).

While the use of less exhaustive techniques may be more appropriate than exhaustive extractions for contaminated soil risk assessments, they may still poorly mimic the processes inherent to bioavailability. Moreover, these techniques ignore the fact that bacteria are capable to secrete exoenzymes and biopolymers which have surfactant properties to help to partially dissolve particulate organic material and to allow the passage of dissolved molecules through the cell membrane (Falatko and Novak 1992).

The method described hereafter has been optimized and tested for the extraction of 13 polycyclic aromatic hydrocarbons (PAHs) in 17 samples from a contaminated marine environment (Saguenay Fjord, Qc) (Fig. 1) using a series of surfactants.

Surfactant molecules have amphiphilic properties, having two distinct structural moieties. The polar moiety of the molecule has an affinity for water and other polar substances, while the nonpolar moiety is hydrophobic by nature. As a result, a surfactant molecule may dissolve in water as a monomer, adsorb at an interface, or be

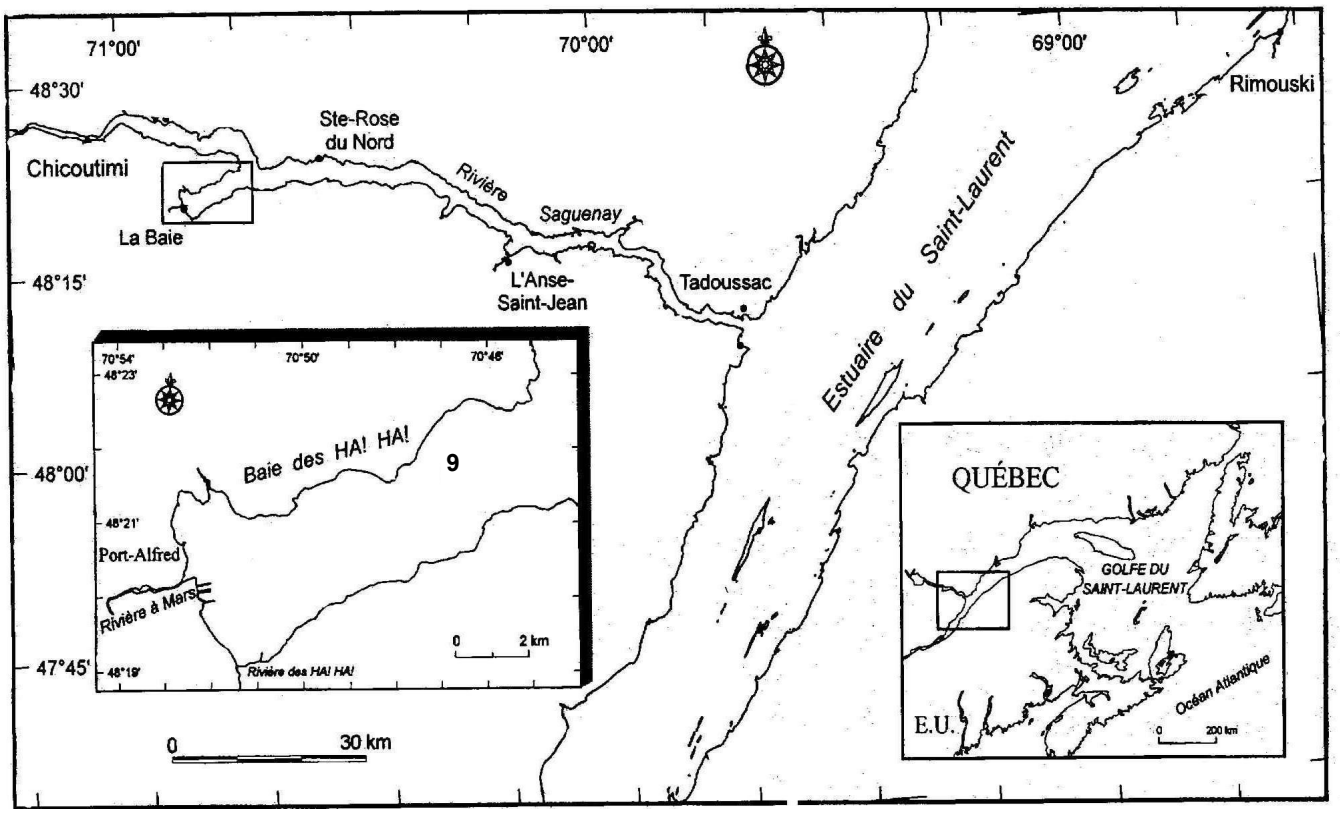

Figure 1. Saguenay Fjord, Qc (from Pelletier et al. 1999)..

incorporated with other surfactant molecules as part of a micelle (Shaw 1983, Edwards et al. 1991, Everett 1992, Yeom et al. 1995, Hiemenz and Rajagopalan 1997).

We hypothesized that an aqueous solution of surfactant can be used to extract labile soil-borne nonpolar organic contaminants while strongly bound or sequestered molecules will not be transferred to the aqueous phase and will therefore not be extracted. Thus, contaminant mass transfer mechanisms inherent to this extraction technique should closely mimic the processes involved in the microbial bioavailability of these molecules. It is proposed that this extraction may provide the microbial bioavailable fraction of soil-borne nonpolar organic contaminants and, once fully tested and understood, may provide a chemical extraction technique to reliably predict the bioavailable portion of toxic compounds in soils and sediments.

2. MATERIAL AND METHODS

The paper is subdivided as follows:

2.1 Experiment A

Optimization of the surfactant extraction procedure for the determination of (i) the optimal surfactant, and (ii) the optimal surfactant concentration.

2.2 Experiment B

Testing the optimized procedure on thirteen different PAHs on PAHs contaminated marine sediment (Saguenay Fjord, Qc (Fig. 1)).

3. EXPERIMENTAL SECTION

3.1 Sampling

Sediments were collected during the Alcide C. Horth cruise from May 24 to May 29, 2000 in the Saguenay Fjord, Qc (Fig. 1) with a multicorer (Maxicorer Mark V-400, Bowers & Connelly). The whole core was immediately sub-sampled with the help of a cutting-table (Edenborn et al. 1986). The sub-samples were then placed in glass flask pre-rinsed with dicholoromethane (DCM) and frozen in –20°C until their analysis in laboratory. For each sediment slice (from 0.5 cm to 2 cm), water content, grain size, total carbon and organic carbon contents, C_{org}/N and C/N elementary molar ratios and the concentration of individual and total PAHs were determined in laboratory.

3.2 Physical and chemical analysis

To determine the water content, the wet sediment samples were weighted and then placed in a freeze-dryer for 48h. The samples were again weighted and the difference

between the two masses gave the water content of the sample. The grain size distribution was determined by a Coulter LS100 apparatus on wet sediment. The total carbon content was determined on dry sediment. The sediment was crushed in a mortal and from 15 to 20 mg of the sediment was placed in a tin capsule before analysis by a Perkin Elmer PE 2400 CHN elemental analyzer which was calibrated with acetanilide. The organic carbon content was determined after reaction of sediment with HCl (10 %) at 60°C for 2h. The sediments were then crushed and analyzed. The concentration of individual and total PAHs was determined by an exhaustive extraction with DCM. Dried sediment (1 g) was solvent extracted with 10 ml of DCM by mechanic shaking for 16h into a 25 ml Teflon™ tube rinsed with DCM, centrifuged 20 min at 3000 rpm and the supernatant transferred in a conical flask. The sample was concentrated under nitrogen flow to 0.3-0.5 ml, diluted in 2 ml of pentane and concentrated to 1 ml. The sample was passed through the column for a liquid separation chromatography over octadecyl gel (Supelclean™ ENVI™ – 18 SPE 3 ml, SUPELCO) with 5 ml of 90:10 pentane:DCM. The sample was concentrated in acetonitrile to 1 ml into ice to minimize loss of lighter PAHs.

All liquid chromatographic analyses were carried out on a HPLC-Fluorescence. The apparatus consisted of a Rheodyne 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, SUPELCO; a SpectraSYSTEM FL3000 detector and a Waters 746 Data Module integrator, Millipore. All analyses were made at a constant flow of 0.8 mL/min. The solvents used for the mobile phase were water and acetonitrile. The ratio between these two solvents changed during the running time of the apparatus using the following pump program (Fig. 2).

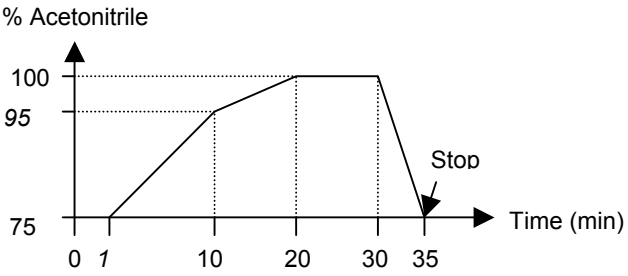

Figure 2. Solvent gradient program for PAHs separation.

Table 1. Detector program for fluorescence detector.

Time (min)	λEx (nm)	λEm (nm)
0	280	340
5.5	280	410
25	280	410

PAHs were analyzed at an excitation wavelength (λEx) of 280 nm. The emission wavelength (λEm) was different for the low-molecular weight PAH compounds (340 nm) and for the high-molecular weight PAH compounds (410 nm). For this reason a change of λEm during the running time was necessary. The detector program is shown on Table 1.

3.3 Experiment A

3.3.1 Experiment A1: determination of the optimal surfactant

For our study, we needed surfactants easily water-soluble with a high HLB. Nine surfactants were first selected. Surfactant solutions were prepared using deionized water to provide a concentration of 10 g/L. Triplicate of tested wet sediment (1.0 g) were weighed accurately into a 25 ml Teflon™ tube, and surfactant solution (10 ml) was added to each. The tubes were sealed and placed on a mechanic shaker for 16h. The tubes were centrifuged at 3000 rpm for 10 min. The supernatants were then transferred in a separatory funnel, and 10 ml DCM added to transfer the extracted PAHs into the organic phase. The organic phase was removed and the extraction was repeated one more time. The two organic fractions were put together into a glass tube. The sample was then prepared as described in section 3.2. Results obtained by the surfactant extraction allowed us to calculate the surfactant extraction percentage (% XTRAC) for a specific sediment. The % XTRAC was defined as the ratio between the surfactant extracted fraction ($Q_{SURFACTANT}$) and the DCM extracted fraction (Q_{DCM}) (eq. 1).

$$\% \text{ XTRAC} = \frac{Q_{SURFACTANT} \times 100}{Q_{DCM}} \quad [1]$$

With the surfactant extraction percentage, it becomes possible to determine the sequestration percentage (% SEQ) of the sediment considered (eq. 2).

$$\% \text{ SEQ} = 100 - \% \text{ XTRAC} \quad [2]$$

3.3.2 Experiment A2: determination of the optimal surfactant concentration

To optimize the concentration of the best surfactant, a molarity gradient from 2.1 x 10^{-4} to 2.1 x 10^{-2} M was performed. Sediment was then extracted as described earlier.

3.4 Experiment B

The optimized procedure was tested on 17 samples from a contaminated marine sediment. We studied 13 PAHs listed on Table 2. The samples were DCM and surfactant extracted in triplicate as described above and the % XTRAC for each PAH was then calculated.

Table 2. The studied PAHs.

Acenaphtene	Chrysene
Fluorene	Benzo[b]fluoranthene
Phenanthrene	Benzo[k]fluoranthene
Anthracene	Benzo[a]pyrene
Fluoranthene	Dibenzo[a,h]anthracene
Pyrene	Benzo[g,h,i]perylene
Benzo[a]anthracene	

4. RESULTS AND DISCUSSION

4.1 Experiment A

4.1.1 Experiment A1: determination of the optimal surfactant

With these extractions, the polyoxyethylene(100) stearyl ether or Brij® 700 (molecular weight 4670) has been selected for its efficiency (% XTRAC) of 6.99 ± 0,36 % and the good reproducibility of the method.

4.1.2 Experiment A2: determination of the optimal surfactant concentration

As shown in Fig. 3, the concentration of total PAHs extracted was increasing with the increase of the concentration of the surfactant up to an optimum value (~ 5.25 x 10^{-3} mol.L^{-1}) and then reached a plateau. This phenomenon is known for surfactant extraction (Laha et al. 1995) and corresponds to the critical micelle concentration (CMC), the concentration above which micelle formation becomes appreciable with a maximum hydrophobic effect (Shaw, 1983).

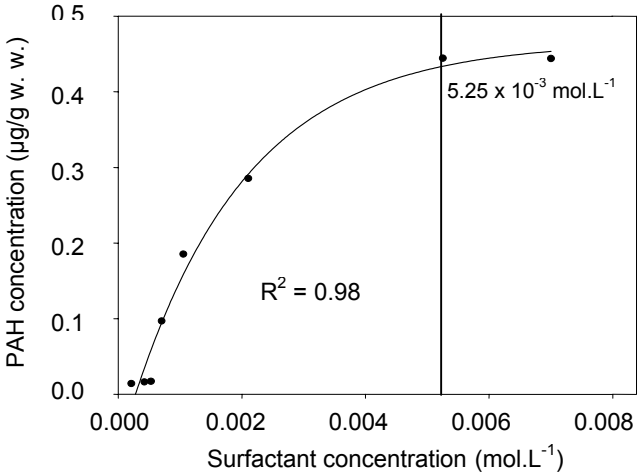

Figure 3. Extraction efficiency with a Brij® 700 molarity gradient.

4.2 Experiment B

The surfactant extraction procedure was tested on 17 sediment samples from station 9 Saguenay Fjord (Fig 1) by analyzing PAHs listed in Table 2. The samples were DCM and surfactant extracted in triplicate as described above and the % XTRAC for each PAH was then calculated on a dry weight basis. The results for ΣPAHs are given in Table 3. It is first observed that the total of 13 extracted PAHs by DCM is relatively low on the whole core, ranging from a 0.429 µg/g in the near surface layer to a maximum of 1.679 µg/g in the deep layer deposited before the 1996 flash flood (Pelletier et al. 1999). Surfactant Brij 700 extracted between 6.4 and 60.0 % of the ΣPAHs extracted by DCM. It resulted that the % SEQ ranged from a low 40 % near de surface to a maximum of 93.6 % in the 14-18 cm layer.

Very interestingly, these results bring a strong support to the sequestration hypothesis, and to the surfactant extraction procedure that seems efficient to discriminate between various PAHs chemical behaviors in the whole sequestration process. In first instance, three layers can be recognized in the whole core: a near surface layer (0-3 cm) with a relatively low % SEQ, an intermediate layer with high % SEQ (often above 90 %), and a deep layer (below 22 cm) where % SEQ is usually below 90 %. The top layer corresponds to freshly deposited particles bio-mixed with the underlying layer after the 1996 flood. The intermediate layer corresponds roughly to the sediment layer deposited during the flood, while the deeper layer corresponds to sediment already in place before 1996 and containing PAHs brought to the Baie des Ha!Ha! in 1970s and 80s. The apparent reduction of % SEQ in the deeper layer may be the result of a slow desorption process already reported in the literature (Aochi and Farmer 1997, Nam and Alexander 1998, Ten Hulsher et al. 1999).

Table 3. Results of extraction by DCM and Brij® 700 and calculation of % XTRAC of studied sediments. Saguenay Fjord, station 9.

Depth (cm)	ΣPAHs concentration (µg/g d. w.) DCM	Σ PAHs concentration (µg/g d. w.) Brij® 700	% XTRAC	% SEQ
00-0.5	0.794	0.476	60.0	40.0
01-02	0.539	0.222	41.2	58.8
02-03	0.429	0.141	32.8	67.2
03-04	0.856	0.076	8.9	91.1
04-05	1.031	0.106	10.3	89.7
05-06	0.999	0.089	8.9	91.0
06-10	0.783	0.155	19.8	80.2
10-14	0.844	0.054	6.4	93.6
14-18	1.146	0.085	7.4	92.6
18-22	1.192	0.078	6.6	93.4
22-24	0.770	0.110	14.3	85.7
24-26	0.695	0.063	9.1	90.9
26-28	0.957	0.165	17.2	82.8
28-30	1.679	0.264	15.7	84.3
30-32	0.799	0.100	12.5	87.5
32-34	0.480	0.115	23.9	76.1
34-36	0.963	0.183	19.0	81.0

The difference between the % XTRAC values of the layer deposited during the flood and the other layers can be explained in part by differences in the elementary composition of the layers but also by the age of layers as the sequestration seems to increase with the age of the sediment, the flood layer being the oldest sediment brought from the last glacial deposits by rivers.

Table 4 shows that % XTRAC of PAHs was generally poorly correlated to physical and chemical characteristics of extracted sediment. Only fluorene and pyrene % XTRAC are reasonably correlated to total extraction with DCM. Unexpectedly, % XTRAC data are not correlated to % C_{org}.

Table 4. Linear correlation (r^2) between % XTRAC of principal PAHs and the physical and chemical characteristics of studied sediments. Saguenay Fjord, station 9.

Compound	DCM	Depth (cm)	% C_{total}	% C_{org}	% Clay	%Clay+%Silt
Fluorene	r^2 = 0.447*	r^2 = 0.183	r^2 = 0.076	r^2 = 0.198	r^2 = 0.542*	r^2 = 0.507*
	n = 11	n = 11	n = 11	n = 11	n = 11	n = 11
Phenanthrene	r^2 = 0.416*	r^2 = 0.099	r^2 = 0.069	r^2 = 0.074	r^2 = 0.073	r^2 = 0.063
	n = 11	n = 11	n = 11	n = 11	n = 11	n = 11
Fluoranthene	r^2 = 0.308	r^2 = 0.180	r^2 = 0.234	r^2 = 0.411*	r^2 = 0.304	r^2 = 0.314
	n = 16	n = 16	n = 16	n = 16	n = 16	n = 16
Pyrene	r^2 = 0.527*	r^2 = 0.025	r^2 = 0.108	r^2 = 0.107	r^2 = 0.090	r^2 = 0.175
	n = 16	n = 16	n = 16	n = 16	n = 16	n = 16
Chrysene	r^2 = 0.182	r^2 = 0.037	$r^2 = 3 \times 10^{-4}$	$r^2 = 2 \times 10^{-6}$	r^2 = 0.182	r^2 = 0.137
	n = 13	n = 13	n = 13	n = 13	n = 13	n = 13
Benzo[b,k]fluoranthene	r^2 = 0.001	r^2 = 0.139	r^2 = 0.161	r^2 = 0.332	r^2 = 0.091	r^2 = 0.058
	n = 17	n = 17	n = 17	n = 16	n = 17	n = 17
Benzo[a]pyrene	r^2 = 0.037	r^2 = 0.004	r^2 = 0.214	r^2 = 0.359	r^2 = 0.024	r^2 = 0.013
	n = 17	n = 17	n = 17	n = 16	n = 17	n = 17
Total	r^2 = 0.170	r^2 = 0.056	$r^2 = 6 \times 10^{-5}$	r^2 = 0.003	r^2 = 0.007	r^2 = 0.003
	n = 101	n = 101	n = 101	n = 99	n = 101	n = 101

*chosen as significant.

or % clay, except fluorene and fluorenthene which seem to have a different behavior. These results are in contrast with the accepted model where PAHs are binding preferentially with organic matter (Onuska 1989, Kennish 1997). Indeed several studies showed that PAHs sequestration is more important in soil or sediment with high organic carbon percentage (Chung and Alexander 1998, Nam et al. 1998). Again the age of the organic matter might be a determining factor.

These observations support the hypothesis of the presence of one or more compartments not accessible for the high molecular weight surfactant but accessible for DCM (Steinberg et al. 1987, Scribner et al. 1992). DCM molecule being 100 to 1000 time smaller than Brij® 700's, it can access more easily to smallest size pores were PAHs are trapped and not available. The non-accessibility for Brij® 700 to small diameter pores seems to mimic well the nature because, as shown by Mayer (1999a, 1999b), these nanopores are too small to permit extra-cellular enzymes penetration.

The Brij® 700 extraction described in this study is proposed as a new approach to extract soil-associated nonpolar organic contaminants from soil and sediment, a practice recently criticized (Alexander and Alexander 1999). The Brij® 700 extraction technique seems to more closely mimic the mass transfer mechanisms that govern the availability of nonpolar organic contaminants (i.e., transfer to the aqueous phase). It should provide a more relevant, process-based extraction method for the determination of soil-associated nonpolar organic contaminant microbial bioavailability. Once fully tested and understood, the aqueous Brij® 700 extraction technique should be a reliable means to determine the bioavailability fraction of a range of soil- and sediment-associated organic contaminants and may be applicable in the risk assessment and to contaminated land bioremediation potential. Indeed, these preliminary results are encouraging and serve as the basis of further work on the comparison of this extraction technique with other techniques such as *in vitro* digestive fluid extraction (Weston and Mayer 1998a, 1998b), and cyclodextrine-based extraction (Reid et al. 2000).

5. ACKNOWLEDGMENTS

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