

UTILIZATION OF ARCHIVED SAMPLES TO ASSESS THE LEVELS AND TRENDS OF EMERGING CONTAMINANTS (HBCDS, PFCs) IN MARINE SHELLFISH FROM THE FRENCH COASTS

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Introduction

Marine shellfish, especially filter-feeder bivalves, have been widely used to monitor the chemical contamination of coastal areas by Persistent Organic Pollutants (POPs) because they exhibit broad geographical and temporal distributions, bioaccumulate contaminants and do not extensively degrade them. This monitoring, referred to as “Mussel Watch Programs”, has been followed in many countries worldwide^{1,2,3}. Environmental Specimen Banks (ESBs) have gained increasing interest over the past two decades, and have become a recognized approach for regular monitoring of the environment. In addition to the regular monitoring of historical contaminants, samples from ESBs can be used to monitor emerging compounds and also to undertake retrospective surveys^{4,5,6}.

The objectives of this work were to investigate the contamination levels and spatial distribution of selected emerging organohalogen contaminants in the French coastal marine environment, while also assessing their temporal trends over the last 30 years. The samples (the marine shellfish *Mytilus edulis*, *Mytilus galloprovincialis*, or *Crassostrea gigas*) were obtained from specimens collected within the French Monitoring Network (ROCCH –Réseau national d'Observation de la Contamination CHimique), i.e., the French Mussel Watch Program, operated by IFREMER since 1979. In this study, the target emerging contaminants were hexabromocyclododecanes (HBCDs) and perfluorinated compounds (PFCs). To our knowledge, data about the occurrence and trends of both classes of contaminant in France are very scarce, especially in the coastal environment. This work provides new results on the contamination of French coastal areas by these emerging contaminants, thus filling the gap of knowledge concerning past and present occurrences of these compounds on a national scale. This work represents a continuation of our previous work conducted on PCBs, PCDD/Fs and PBDEs in the French coastal environment and confirms archived samples as a valuable tool for the retrospective monitoring of contaminant levels and trends in the marine environment^{4,5}.

Materials and methods

The shellfish were collected and handled in accordance with international guidelines for the monitoring of contaminants in biota, as described in our previous studies (Johansson et al., 2006; Munschy et al., 2008). Either mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) or oysters (*Crassostrea gigas*) were used as biomonitors of the contamination. The analysed samples were chosen from selected sites located in the English Channel, the Atlantic and the Mediterranean coasts. The same sampling sites as those investigated in our previous study in 2008 and 2010⁷ were re-visited in 2011. For the temporal trend study, samples obtained from IFREMER's ESB between 1981 and 2011 were considered.

Analyses of HBCDs and PFCs were conducted at LABERCA's Laboratory. For HBCD analysis, samples were extracted by Accelerated Solvent Extraction (ASE) using toluene and acetone (70:30, v:v). Purification was performed on a column constituted with successive layers of anhydrous sodium sulfate, neutral silica gel, and concentrated sulphuric acid acidified silica. HBCD stereoisomers were analyzed using reverse-phase LC (Hypersil Gold column, 100 mm × 2.1 mm, 1.9 µm), and determined by LC-MS-MS (Agilent 6410) fitted with an electrospray ion source, operating in the negative ion mode.

For PFC analysis, the samples were extracted by liquid solid extraction using methanol. The extracts were purified using dispersive solid phase extraction with Envicarb stationary phase, according to a method described by Powley et al.⁸ followed by a hydrated silica column. The purified extracts were separated using liquid

chromatography (LC) equipped with a C18 reverse phase column (50 mm x 2.0 mm, 3 μ m) fitted with a guard column (10 mm x 2.0 mm, 3 μ m) by LC-MS-MS.

Results and discussion

Levels

Alpha-HBCD, the predominant of the three analysed stereoisomers, was detected in all samples, showing ubiquitous contamination of the French coastal environment by this brominated flame retardant. Its concentrations ranged from 0.02 ng g⁻¹ ww to 0.39 ng g⁻¹ ww and were in the same range as those determined in samples collected in 2008 and 2010⁷. The geographical distribution of the concentrations was similar to our previous findings and seems to fit to the most populated and/or industrialized areas in France. In the English Channel, the highest concentration was found at the Seine Estuary site, in relation with high inputs from human activities via the Seine River. Samples from the Mediterranean coast also exhibited high levels, while the median lower concentration was found on the Atlantic coast (Table 1).

	ng g ⁻¹ ww	English Channel	Atlantic	Mediterranean
α -HBCD	Median	0.06	0.03	0.10
	Max	0.16	0.39	0.20
	Min	0.05	0.02	0.05

Table 1: HBCD (alpha-isomer) concentrations (median, maximum, minimum in ng g⁻¹ ww) in shellfish collected in 2011 along the French coastlines

PFOS (perfluorooctane sulfonate) was found to be the dominant PFC in most of the samples from the English Channel and the Atlantic coast, while in the Mediterranean samples, PFCAs (perfluorocarboxylic acids) were identified at higher levels, suggesting different sources.

PFOS concentrations were in the 0.20-0.68 ng g⁻¹ ww range, with a median value of 0.27 ng g⁻¹ ww. The highest concentration was found in one sample collected at the Loire Estuary site on the Atlantic coast. This result is unexpected, as the Loire Estuary drainage basin, in comparison to the Seine River drainage basin, is neither very much industrialized nor urbanized. However, the “Pays de la Loire” region, where the Loire Estuary is located, is the foremost region for wood transformation and paper industries, as well as metal surface treatment industries; both of which represent potential sources of PFOS.

Temporal trends

The temporal trends of HBCD and PFC concentrations were both investigated in the Seine Estuary from 1981 to 2011 in archived samples from the French Environmental Specimen Bank held by IFREMER. This site was chosen as the French reference of a highly contaminated estuary. Moreover, the data obtained in this study are complementary to our previous studies on other POPs (PCBS, PCDD/Fs, PBDEs) at this site^{4,5}.

The temporal trend of HBCD concentrations (alpha-isomer) determined over the 1981–2011 period is presented in Fig. 1, with concentrations in the 0.01-0.39 ng g⁻¹ ww range. The data obtained in the Seine Estuary samples from 1981 to 2011 reveal a significant exponential increase over the entire study period, with a doubling time of 7 years. Similar to our previous results on PCBs and PBDEs, a concentration higher than the one predicted by the exponential curve was observed in years 2000 and 2008, coinciding with a higher flooding of the Seine River^{4,5}.

HBCD time trend studies published in the literature bring diverging results, either showing an increasing trend, no significant trend or decreasing trends. For example, Johansson et al.⁹ showed a significant increase of 11% per year in HBCD concentrations in peregrine falcon in Sweden from the mid-1980's until 2005, with a possible levelling off or decline after 2000. In ringed seals from East Greenland, Vorkamp et al.¹⁰ found a statistically significant exponential time trend with an annual increase of 6.1%. Conversely, several studies showed recent decreasing trends, generally in relation with local drop in production or industrial emissions, for example in the UK or in Germany^{11,12}. The results obtained in the Seine Estuary did not suggest any recent reduction of point source emissions.

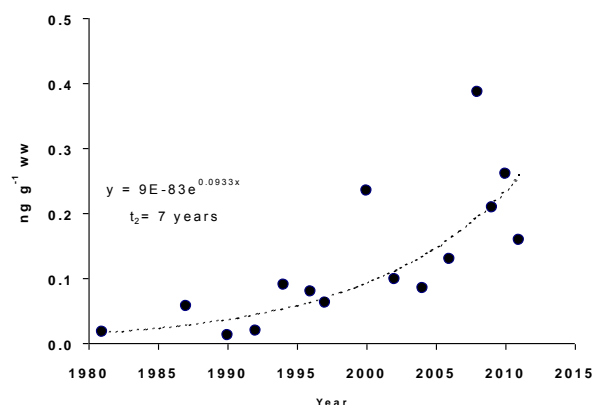


Figure 1: Temporal trends of HBCD concentrations (alpha-isomer, $\text{ng g}^{-1} \text{ ww}$) in mussel samples (*Mytilus edulis*) from the English Channel (Seine Estuary) from 1981 to 2011

The temporal variation of PFOS concentrations at the Seine Estuary site showed a significant linear decrease ($r = 0.88$, $\alpha = 0.05$) starting in 1990 until 2011 (Fig. 2). Although the observed trend was significant over this time period, the concentrations did not show a high variation range between 1990 and 2002 ($1.42\text{--}2.22 \text{ ng g}^{-1} \text{ ww}$ range), while lower concentrations were observed in the 2004–2011 period ($1.07\text{--}0.26 \text{ ng g}^{-1} \text{ ww}$ range). The observed trend seems consistent with other studies, which have shown that in many industrialized countries, PFOS levels were increasing until the mid-1990s, followed by a decline, although not always significant^{13,14,15,16}.

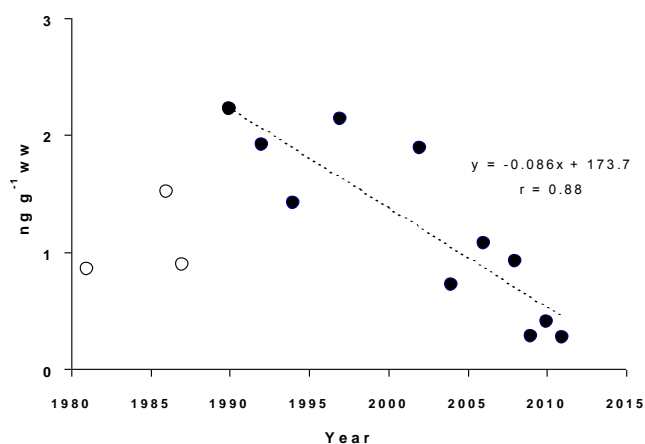


Figure 2: Temporal trends of PFOS concentrations ($\text{ng g}^{-1} \text{ ww}$) in mussel samples (*Mytilus edulis*) from the English Channel (Seine Estuary) from 1981 to 2011

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