

COMPARED TEMPORAL TRENDS OF SELECTED PERSISTENT ORGANIC CONTAMINANTS (PCDD/Fs, PCBs, PBDEs) IN MARINE MUSSELS FROM THE FRENCH COASTS

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Introduction

The temporal trends of the contamination levels of selected persistent organic contaminants have been studied in marine mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) at selected sites along the French coastlines. The archived mussel samples were used for this study and they were collected within the French Monitoring Network (RNO –Réseau National d’Observation). The samples from year 1981 to year 2005 were analysed for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) at different sites. The analyses of these compounds were performed on the same samples. The temporal variations during the past 24 years and the regional differences in the contamination of marine mussels were determined. This work extends a previous study on levels and temporal trends of PBDEs and PCBs¹ in mussels along French coast.

Materials and Methods

Sampling sites

The analysed samples were chosen from selected sites located in the English Channel, the Atlantic and the Mediterranean coasts. The locations of the studied sites are shown in Figure 1. To avoid possible differences of contaminant concentrations due to seasonal variations related to the physiological state of the mussel (i.e. spawning), all samples were collected in the same way and at the same period each year (from late November to early December).



Figure 1: Location of the studied sampling stations

Mussel analysis

The analyses were conducted using approximately five grams (dry weight) of the freeze-dried samples. The analytical protocols for extraction and cleanup have been described previously^{1,2,3}.

The quantification of seventeen congeners of PCDD/Fs was performed by High Resolution Gas Chromatography - High Resolution Mass Spectrometry (HRGC-HRMS) with an AutoSpec Ultima (Waters) by isotopic dilution method based on the US EPA method 1613. Two columns were used: a DB-5MS (J&W Scientific, CA) capillary column (60 m x 0.25 mm i.d. x 0.25 μm film thickness), and an RTX-Dioxin2 (Restek Corp.) capillary column (40 m x 0.18 mm x 0.18 μm film thickness)^{2,3}.

Analyses of PBDEs were performed by HRGC-MS in electron capture negative ionisation mode¹ with a DB-1 (J&W Scientific, CA) capillary column (15 m x 0.25 mm i.d. x 0.10 μm film thickness). PCBs were analysed by HRGC fitted with two electron capture detectors using two columns: a DB5 capillary column (60 m x 0.25 mm i.d. x 0.25 μm film thickness), and a HT8 capillary column (50 m x 0.22 mm i.d. x 0.25 μm film thickness).

Quality Assurance / Quality Control procedures (blanks, analysis of replicates and certified materials) were included within every batch of six to eight samples. The laboratory also routinely participates in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercomparison exercises.

Results and Discussion

The present contamination levels of PCDD/Fs ($\Sigma 17$ congeners) and PCBs ($\Sigma 7$ ICES congeners) determined in marine mussels from the studied sites are between 19 pg g^{-1} dry weight (Thau lagoon, Mediterranean Coast) and 184 pg g^{-1} dry weight (Toulon, Mediterranean Coast) and between 24 ng g^{-1} dry weight (Marennes, Atlantic Coast) and 1501 ng g^{-1} dry weight (Toulon, Mediterranean Coast) respectively. The local differences can be related to the anthropogenic inputs from urban and industrial activities.

Figure 2 shows time-series concentrations of PCDD/Fs and PCBs in mussels during the period 1981-2004 at two different sites on the Atlantic (Pen Bé) and Mediterranean coasts (Thau). The concentrations of PCDD/Fs show a significant decrease over the studied period of time, with a time required to decrease by a factor of two ($t_{1/2}$) being 13.6 years (Atlantic Coast) and 10 years (Mediterranean). The corresponding rates of decrease for PCBs (expressed as the sum of the seven ICES congeners) are $t_{1/2} = 10$ years and $t_{1/2} = 7$ years. The decrease observed for banned or restricted persistent organohalogen contaminants like PCBs and PCDD/Fs in mussels has been observed in previous studies, and is related to the general decrease in usage and emissions of these compounds⁴.

The decrease observed for PCDD/Fs and PCBs contrasts with the increase of PBDEs determined in the same set of samples¹. An example of the temporal variations of the concentrations of the sum of BDE-47, BDE-99 and BDE-100 is given in figure 3 for samples from the Thau lagoon. The results show an exponential increase with a doubling time of 7 years for the period between 1981 and 1993-1995, followed by a stabilization of the concentration levels.

Levels in biota

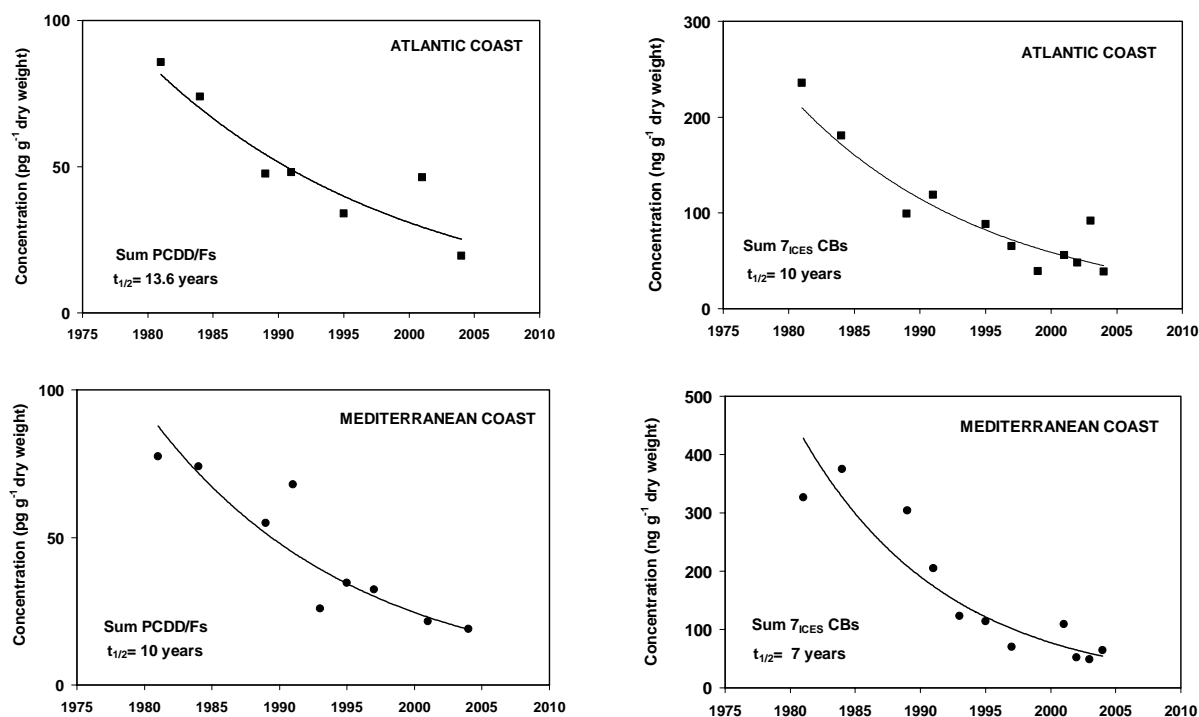


Figure 2: Temporal trends and rates of decrease of PCDD/Fs and PCBs in mussel samples from the Atlantic Coast (Pen Bê) and Mediterranean Coast (Thau lagoon) over the period 1981-2004.

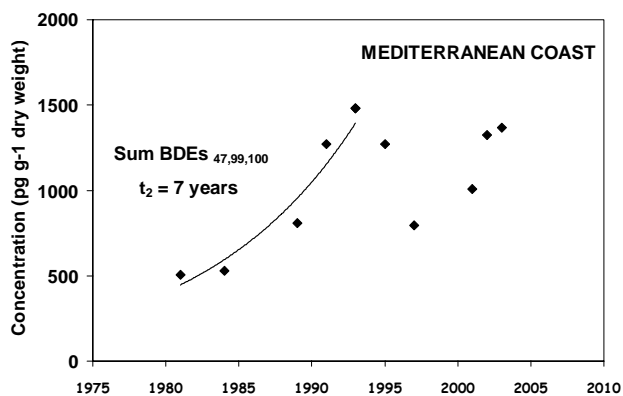


Figure 3: Temporal trends and rates of decrease of PBDEs in mussel samples from the Mediterranean Coast (Thau lagoon) over the period 1981-2004.

This study demonstrates that the French monitoring network bank of archived samples is a valuable tool for the retrospective monitoring of contaminants in the marine environment. The archived samples can be analysed for novel contaminants introduced into the environment, and for analytes for which more reliable analytical methods are

now available. Such long-time series on persistent organic contaminants levels provide information on the effectiveness of the measures aiming in reduction of the production, uses, and emissions of these compounds and in decreasing the contamination of the marine environment.

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