

Retrospective monitoring of the contamination of marine mussels from the French Coasts by PCDD/Fs (1981-2004)

Catherine MUNSCHY¹, Inger JOHANSSON¹, Nadège GUIOT¹, Karine HEAS-MOISAN¹, Jacek TRONCZYNSKI¹

¹Ifremer

1. Introduction

The contamination of marine mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) by organohalogen compounds has been studied at different sites along the French coastlines. Archived mussel samples were collected over the past 23 years within the French national mussel watch network (RNO –Réseau National d'Observation). These samples were analysed for PCDD/Fs. The studied sites represent areas characterized by different environmental contamination levels receiving various inputs from human activities, over the English Channel, the Atlantic Ocean and the Mediterranean Sea.

The results presented here focus on the contamination levels and temporal trends of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and are in line with a previous study which presented levels and temporal trends of PBDEs, PCBs and organochlorine pesticides in the same samples.^{1,2}

2. Materials and methods

Sampling sites

The locations of the studied sites are shown in Figure 1. Villerville is located in the English Channel, and under the direct influence of the Seine river basin, which is a highly industrialized and urbanized zone, characterized by high levels of contamination by PCBs. On the Atlantic Coast, the studied site (PenBé) is located in the Bay of the Vilaine river, whereas the Mediterranean site is located in the Thau lagoon. The selected mussel samples were collected in the same way and at the same period each year (from late November to early December). This sampling scheme avoids possible differences of contaminant concentrations due to seasonal variations related to the reproduction and spawning periods.

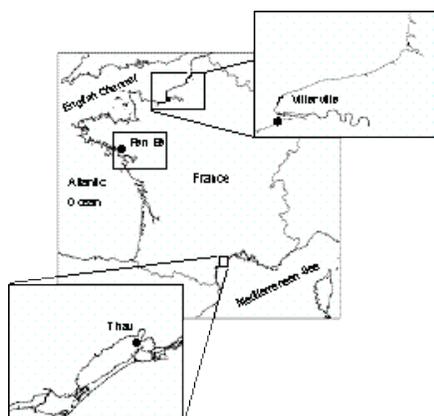


Figure 1: Location of the studied sampling stations

Mussel analysis

The analyses were conducted using approximately 5 grams (dry weight) of the archived samples. Detailed extraction and cleanup methods have been described elsewhere.^{1,2,3} Analyses of PCDD/Fs were performed by High

Resolution Gas Chromatography - High Resolution Mass Spectrometry with an AutoSpec Ultima (Waters) operated in Electronic Impact ionisation mode at a resolution of 10000 in the Selected Ion Monitoring mode, and equipped with a Hewlett-Packard (Palo Alto, CA, USA) 6890 GC and a Combi-Pal autosampler (ATAS). Two columns were used: a DB-5MS (J&W Scientific, CA) capillary column (60 m x 0.25 mm i.d., 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) used as a confirmation column. Seventeen congeners of PCDD/Fs were quantified by isotopic dilution method based on the US EPA 1613 method. Recoveries of individual labelled congeners were between 76% +/-15% and 94% +/- 12% for each compound (mean value +/- rsd, n= 33). Quality Assurance / Quality Control procedures (blank determinations covering the whole analytical procedure, 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 concentrations of PCDDs and PCDFs determined in the mussels collected in the English Channel (Villerville), Atlantic Ocean (Pen Bé) and Mediterranean Sea (Thau) are presented in Table 1. The highest concentrations are found in the samples collected at Villerville, presumably due to the influence of the Seine river. High levels of contamination of mussels by PCBs and PBDEs have also been reported in this area^{1,2} which receives higher inputs from human activities through the Seine river. The mussels collected at Pen Bé and Thau both show the same levels of contamination, which are 3 to 8 times lower than those determined in the mussels from Villerville.

When expressed as 2,3,7,8-TCDD equivalents (TEQs) using the WHO-TEFs for humans/mammals⁴, the levels are in the 0.43-2.01 pg TEQ.g⁻¹ wet weight (w.w.) range for the samples from the Atlantic and Mediterranean Coasts. The results obtained for the mussels collected at Villerville are in the 3.46-5.84 pg TEQ.g⁻¹w.w. range, thus exceeding the recommended limit set by the European Community for sea products intended for human consumption.⁵ The TEQ values calculated for planar PCBs (IUPAC nos. 77, 126 and 169) in the same samples from Villerville are in the 6.34-18.55 pg TEQ.g⁻¹w.w. range, whereas the contribution of mono-ortho congeners (IUPAC nos.123, 118, 105, 167, 156, 189) is between 3.87 pg TEQ.g⁻¹w.w. and 10.61 pg TEQ.g⁻¹w.w. Compared with the results previously reported in the literature⁶, the PCDD/F contamination levels determined in the mussels collected at Villerville are higher throughout the whole studied period.

	Villerville (n=12)		Pen Bé (n=6)		Thau (n=8)	
	(English Channel)		(Atlantic Coast)		(Mediterranean Sea)	
	Min	Max	Min	Max	Min	Max
PCDFs pg.g ⁻¹ dry weight (d.w.)	72.06	129.51	16.50	46.66	13.90	49.65
PCDDs pg.g ⁻¹ d.w.	23.26	173.51	17.46	39.13	7.66	42.76
PCDFs pg.g ⁻¹ wet weight (w.w.)	18.97	32.43	3.63	10.26	2.92	11.32
PCDDs pg.g ⁻¹ w.w.	6.75	41.64	2.49	9.64	1.61	9.41
PCDFs pg WHO-TEQ.g ⁻¹ w.w	3.02	5.07	0.55	1.67	0.42	1.73
PCDDs pg WHO-TEQ.g ⁻¹ w.w.	0.30	1.01	0.15	0.37	0.01	0.17

Table 1: Concentrations of PCDFs (Sum of 10 congeners) and PCDDs (Sum of 7 congeners) expressed in pg.g⁻¹ on a d.w. or w.w. basis, and in WHO-TEQ.g⁻¹w.w. in mussel samples collected at selected sites of the French Coasts, 1981-2004.

The temporal trends of the levels of PCDD/Fs determined in the archived samples over the 1981-2004 period are shown in Figure 2. The results show a general decrease in the contamination over the past 23 years at all sites. At Villerville, the levels determined in 1999, and to a lesser extent in 2001, show a significant increase, followed by a drop to the lowest concentrations in 2004. The same relative increase has been reported previously for PCBs and PBDEs, in relation to significant flooding of the River Seine during these years.^{1,2}

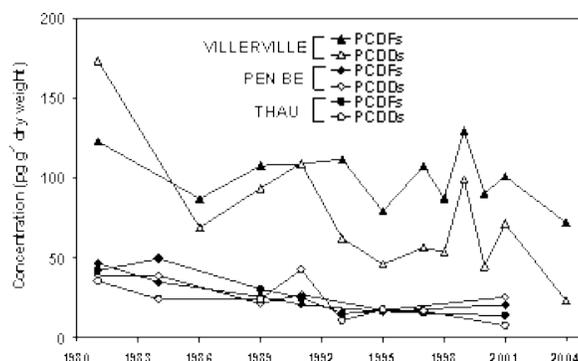


Figure 2: PCDD/F concentrations (pg.g^{-1} d.w.) in mussels from different sites over the years 1981-2004.

The contamination patterns in mussel samples are dominated by 2,3,7,8-TCDF and OCDD, these two compounds representing more than 60% of the sum of the seventeen 2,3,7,8-PCDD/F congeners (Figure 3). Moreover, the tetra-chlorinated furans' profile is characterized by a complex mixture of different congeners. This pattern is different from the one observed previously in dab in the Seine estuary³, and from the PCDD/F profiles reported in the literature for different marine species⁷. However, this profile seems to be typical for mussels and is similar to observations already reported for mussels from other marine areas.⁶ The patterns are similar for all samples among the different sites, suggesting that no distinct source could be identified on a local scale. Combustion and metallurgic processes are important sources of the dominant congeners identified in mussels.^{8,9,10} However, the contamination of mussels is also related to assimilation preferences and metabolism.

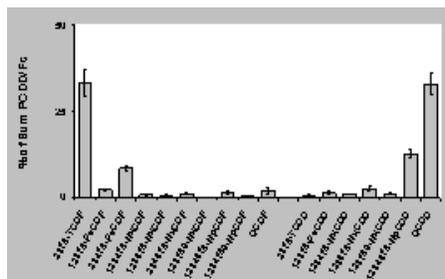


Figure 3: Normalized distribution pattern of PCDD/F congeners in mussel samples from Pen Bé (mean values, expressed as a percentage of the sum of 17 PCDD/F congeners, $n=6$). Error bars are for standard deviations.

This study provides new information with respect to contaminant levels and temporal trends of PCDD/Fs in the French coastal marine environment. A general decrease in levels of PCDD/Fs was observed at all studied sites, with still high levels remaining in the Seine Bay.

3. Acknowledgements

Funding for this work is from the French « Ministère de l'Ecologie et du Développement Durable » also supporting the RNO (Réseau National d'Observation) from which samples were available. I. Johansson received a grant from Ifremer for her post-doctoral studies.

4. References

- Johansson I., Moisan K., Guiot N., Truquet I., Munsch C., and Tronczynski J., (2004) *Organohalogen Compounds* 66: 1844-1852.
- Johansson I., Moisan K., Guiot N., Truquet I., Munsch C., and Tronczynski J., (2005) *Chemosphere*, accepted.
- Munsch C., Moisan K., and Tronczynski J., (2004) *Organohalogen Compounds* 66: 1672-1680.

4. van Leeuwen F.W.R., Feeley M., Schrenk D., Larsen J.C., Farland W., Younes M., (2000) *Chemosphere* 40: 1095-1101.
5. 2002/201/CE, (2002) Journal officiel des communautés européennes, C(2002) 836.
6. Abad E., Pérez F., Llerena J.J., Caixach J., Rivera J., (2003) *Environ. Sci. Technol.* 37: 22, 5090-5096.
7. Knutsen J., Bjerkeng B., Naes K., Schlabach M., (2003) *Chemosphere* 52: 745-760.
8. Hellou J. and Payne J.F., (1993) *Mar. Environ. Res.* 36: 117-128.
9. Fernandez M.P., Ikonomou M.G., Courtenay S.C., and Wirgin I.I., (2004) *Environ. Sci. Technol.* 38: 976-983
10. Umlauf G., Christoph E.H., and Bidoglio G., (2004) *Organohalogen Compounds* 66: 1333-1339.