ASSESSMENT OF PCDD/F AND NONYLPHENOL CONTAMINATION IN A SEMI-ENCLOSED BAY (MASAN BAY, SOUTH KOREA) AND A MEDITERRANEAN LAGOON (THAU, FRANCE)

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Abstract
The contamination of mussel and sediment by PCDD/Fs and nonylphenols was studied in a semi-enclosed bay in Korea (Masan Bay) and in a Mediterranean lagoon in France (Thau lagoon). Both systems receive different inputs from urban and industrial activities. Thau lagoon is also surrounded by agriculture (vineyards) and is a centre of important fish and shellfish farming activities. The contamination levels of sediment are the highest in Masan Bay, showing a decreasing gradient from the inner part to the outer part of the bay. A point source is also identified in the middle of the bay, corresponding to a municipal sewage outlet. This point source is characterized by high concentrations of PCDD/Fs and a specific isomeric pattern. In Thau lagoon, the concentrations of PCDD/Fs are highest in the Eastern part of the lagoon where the main urban and industrial activities are concentrated, and decrease to a lower level in the Western part. Contamination levels and patterns in both systems are more homogeneous in mussels than in sediment.

Introduction
Under the 'Science and Technology Amicable Relationship (STAR)' program, KORDI (Korea Ocean Research and Development Institute) and IFREMER (Institut français de recherche pour l'exploitation de la mer) have been conducting joint research on the status of environmental pollution in both countries since 2005. Masan Bay in Korea and Thau lagoon in France have been selected for this study. To evaluate and compare the status and characteristics of organic contamination in these regions, surface sediment and mussel were studied. This paper highlights the outcome on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Nonylphenol (NP) as sewage/wastewater tracer were used to aid identification of PCDD/F origin in the study area. The results presented here correspond to the first part of the joint work done under the collaboration program.

Materials and methods
Sampling
Mussel (*Mytilus galloprovincialis*) and sediment samples were collected from Masan Bay, Korea, in May 2006, and from Thau lagoon, France, in May 2004 (Figure 1). Surface sediment samples were collected using a van Veen grab sampler or a sediment corer. Approximately 2 cm of top sediment was taken from each site for chemical analysis. Mussels were collected manually in both bays and depurated at room temperature for 24 hours before further analysis. This allowed a natural removal of gut content from the mussels, permitting the determination of true contaminant concentrations in the mussel soft tissues. Samples were freeze-dried and transported for analysis at respective laboratories in France and Korea. PCDD/Fs were analysed in France and NP in Korea.
Masan Bay is a semi-enclosed embayment located in the southern part of Korea (Figure 1a). This bay is surrounded by heavily populated cities and industrial complexes discharging significant amounts of organic pollutants into the bay. Discharges from municipal sewage treatment plant enter the bay at site S12. The semi-enclosed nature of the bay leads to accumulation of pollutants in the bay.
Thau lagoon is one of the largest Mediterranean lagoons, located in the South of France on the Mediterranean coast (Figure 1b). It covers a surface area of 75 km^2, with an average depth of 4-5 m and a maximum depth of

11 m. Its catchment area covers 250 km^2. The lagoon is isolated from the Mediterranean Sea by an offshore bar and is connected to the sea by two channels. It receives inputs from different human activities, i.e. urban activities, industries (cement, fertilizer and wine production plants), port activities and agriculture (crops and vineyards)[1]. The majority of urban, industrial and port activities are located near the city of Sète in the Eastern part of the lagoon. Fishing, fish farming and shellfish farming, the latter covering about 20% of the total area of the lagoon, are other important economic activities of the region.

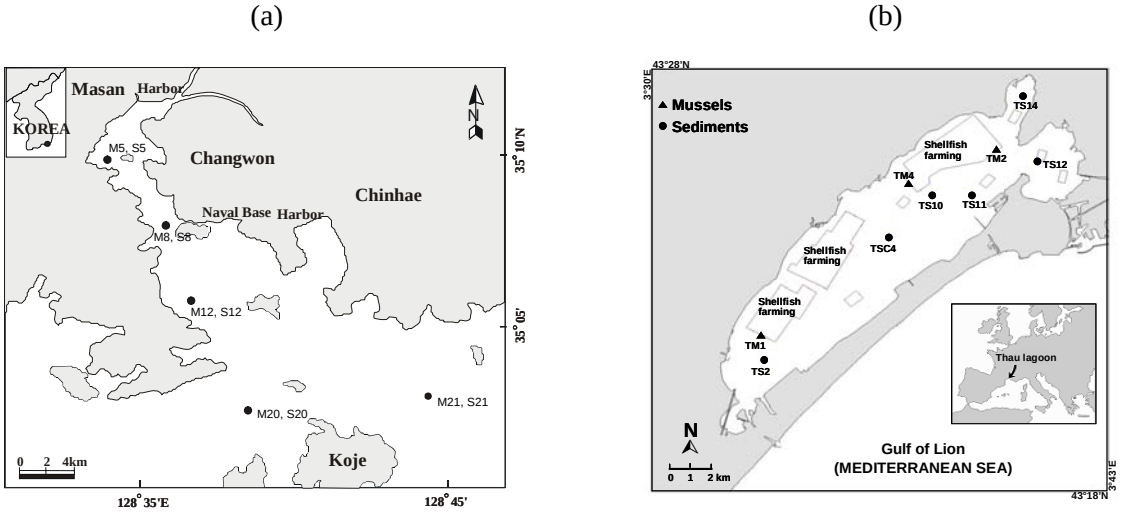

Figure 1. Sampling locations of surface sediments (S) and mussels (M) from (a) Masan Bay, Korea and (b) surface sediments (TS) and mussels (TM) in Thau lagoon, France.

Chemical analysis

PCDD/Fs analysis

The analytical protocols for extraction and cleanup of PCDD/Fs have been described elsewhere[2]. The quantification of seventeen congeners of PCDD/Fs was based on the isotopic dilution method stipulated in US EPA method 1613, and was performed by High Resolution Gas Chromatography - High Resolution Mass Spectrometry (HRGC-HRMS) with an AutoSpec Ultima (Waters), with an RTX-Dioxin2 (Restek Corp.) capillary column (40 m x 0.18 mm x 0.18 µm film thickness). Quality Assurance / Quality Control procedures (i.e. analysis of blanks and certified materials) were included within every batch of six to eight samples. The laboratory routinely participates in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercomparison exercises.

NP analysis

Nonylphenol analysis followed the procedure of Li *et al.*[3]. Briefly, sediment samples were treated with 0.1 M HCl, digested for 10 min, and then extracted three times with dichloromethane. Ten nanograms of internal standard (IS) (hepthylphenol) was added to the samples before extraction. The extract was concentrated and solvent-exchanged to acetone for silyl derivatization. After derivatization, the sample was eluted with hexane using 1 g of Florisil. The elute was analyzed by Gas Chromatography (Shimadzu GC-17A)–Mass Spectrometry (Shimadzu MS QP-5000) with selected ion monitoring mode as described in Li *et al.*[4],. Mussel samples were Soxhlet-extracted with dichloromethane for 16 h. The extract was concentrated, solvent-exchanged to hexane, and cleaned on Florisil column for lipid removal. An 18 ml fraction of hexane was discarded and 6 ml of dichloromethane fraction was subsequently collected for NP analysis. The dichloromethane fraction was solvent-exchanged to acetone. Stages such as silyl derivatization, cleanup and instrumental analysis that followed were similar to sediment sample analysis.

Results and discussion

Concentrations of PCDD/Fs and NP determined in sediments and mussels collected in Masan Bay and Thau lagoon are presented in Table 1.

PCDD/Fs concentrations in **sediments** are at least three times higher in Masan Bay than in Thau lagoon. The spatial distribution of PCDD/Fs in Masan Bay indicates that the inner part of the bay is more contaminated than the outer Bay except at site S12, a municipal sewage outlet area located in the middle of the Bay, where the highest levels for PCDD/Fs were determined (4,680 pg g^{-1} dry weight). In Thau lagoon, the concentrations of PCDD/Fs are highest at site TS12 (1,660 pg g^{-1} d.w.) in the Eastern part of the lagoon, and decrease to a lower level at site TS2, located in the Western part. This indicates that sources of contamination originate from the Eastern part of the lagoon, where the main urban and industrial activities are concentrated. In addition to this, at all sites in both Korea and France, the concentrations of PCDDs are higher than the concentrations of PCDFs. However, at site S12 in Masan Bay, the level of PCDFs is approximately two times more concentrated than the level of PCDDs. This implies that sewage outfall, which carries both domestic and industrial wastes and constitutes the point source at this particular location, is contributing to the inputs of PCDD/Fs into the Bay with a higher contribution of PCDFs giving a specific pattern, especially for congeners 1,2,3,4,6,7,8-HpCDF and OCDF. Nonylphenol, a sewage/wastewater tracer, was also ubiquitously observed in both systems, although the concentrations determined in Thau lagoon were much lower. Its distribution showed a good relationship with that of PCDD/Fs, particularly in Thau Lagoon (r^2=0.97, $p<0.001$). This indicates that sources of both classes of contaminants are located in the same area and distribute similarly into the lagoon, and that PCDD/F contamination may be related to domestic and industrial activities, as traced by NP.

PCDD/F concentrations in **mussels** originating from Masan Bay are in the same range as those determined in mussels from Thau lagoon. The highest concentration (21.4 pg g^{-1} d.w.) is found at site TM1 in the Western part of Thau lagoon, whereas for Masan Bay, the highest concentration (14.6 pg g^{-1} d.w.) is found at the inner part of the Bay. The spatial distribution of concentrations is quite homogeneous in Thau lagoon, indicating that the sources of the contamination of sediments in the Eastern part of the lagoon do not significantly contaminate the mussels. Concentrations of PCDDs are higher than PCDFs in samples from Thau lagoon, mainly because of OCDD contribution. However, when results are expressed in WHO-TEQ (Toxic Equivalent), PCDFs contribution to the total PCDD/F TEQ is higher in Thau lagoon. In samples from Masan Bay, the differences in the levels between PCDDs and PCDFs are low.

Table 1. Summary of the concentrations of PCDDs and NP in sediment and mussels collected from Masan Bay, Korea, and Thau lagoon, France.

(a) Sediment

Compounds	unit	Masan Bay					Thau Lagoon					
		S5	S8	S12	S20	S21	TS14	TS12	TS11	TS10	TSC4	TS2
PCDFs	pg/g dw	252	224	3,100	38	31	10	205	36	27	30	7
PCDDs	pg/g dw	506	496	1,590	279	229	89	1,450	190	126	137	27
PCDD/Fs	pg/g dw	758	720	4,680	317	260	100	1,660	226	153	166	34
NP	ng/g dw	504	206	471	37	24	8	70	20	9	8	ND

ND: not detected

(b) Mussel

Compounds	unit	Masan Bay					Thau Lagoon		
		M5	M8	M12	M20	M21	TM1	TM2	TM4
PCDFs	pg/g dw	7.7	3.9	5.2	2.5	3.6	6.7	6.0	5.6
PCDDs	pg/g dw	6. 9	2.5	4.7	3.6	6.1	14.7	8.4	7.2
PCDD/Fs	pg/g dw	14.6	6.3	9.9	6.0	9.7	21.4	14.4	12.8
PCDFs WHO-TEQ	pg/g dw	0.8	0.4	0.5	0.2	0.3	0.5	0.6	0.5
PCDDs WHO-TEQ	pg/g dw	0.8	0.3	0.6	0.2	0.3	0.4	0.1	0.1
PCDD/Fs WHO-TEQ	pg/g dw	1.6	0.7	1.1	0.4	0.6	0.9	0.7	0.6
NP	ng/g dw	289	170	111	77	51	40	32	42

Isomeric composition of PCDDs and PCDFs shows differences in matrices and regions. In **sediment**, the pattern is dominated by OCDD in most cases, followed by 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF.

Although the congener profiles in sediment could result from mixed sources, the observed patterns, dominated by hepta- and octa-CDDs, have been linked to pentachlorophenol-related inputs [5]. However, in the inner Masan Bay, including sites S5, S8, and S12, contribution from OCDD is lower. In particular, municipal sewage outlet site (S12) shows a big compositional difference, with furans and hepta-chlorinated dioxins more abundant than at other sites. A principle component analysis on the composition of individual PCDD/F congeners and NP was attempted (Figure 2). NP, HxCDFs, HpCDFs and OCDF are closely related, indicating sewage outfall as a point source. Similar observation was made by Kannan *et al.*[6] in Masan Bay. Conversely, Thau Lagoon sediment samples show a rather uniform congener pattern. **Mussels** differ from sediment in their isomeric composition as 2,3,7,8-TCDF and OCDD are the dominant congeners. The observed patterns in mussels are homogeneous within a given area, for both Masan Bay and Thau lagoon. The different chemical fingerprints of PCDD/Fs in mussels from the two bays may be related to different sources of contamination.

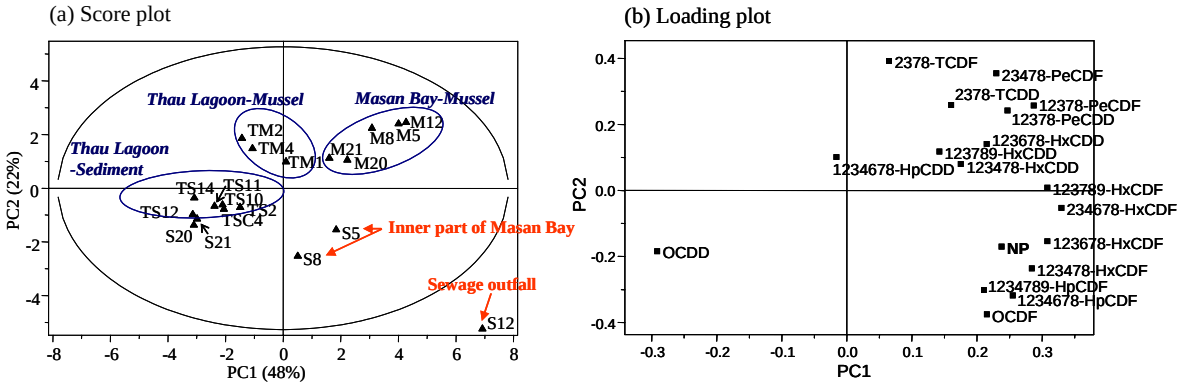

Figure 2. Principal component analysis (a) score plot and (b) loading plot of the PCDD/Fs congener patterns and NP in sediments and mussels from Masan Bay and Thau lagoon. Individual congener concentrations are normalized to total PCDD/Fs.

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Acknowledgments

KORDI and IFREMER wish to thank the ‘Science and Technology Amicable Relationship (STAR)’ program under which the joint work could be achieved. The authors gracefully acknowledge the crew and participants to the sampling cruises in Korea and France for valuable help during sampling.