PCDD/Fs OCCURRENCE IN A MEDITERRANEAN COASTAL LAGOON (ETANG DE THAU, FRANCE): CONCENTRATIONS AND PATTERNS IN DIFFERENT ENVIRONMENTAL COMPARTMENTS

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Introduction

Thau lagoon is one of the largest Mediterranean lagoons. Located on the French Mediterranean coast along the Gulf of Lion (Figure 1), it covers a surface of 75 km^2 with an average depth of 4.5 m and is isolated from the Mediterranean Sea by an offshore bar. The lagoon receives inputs from different human activities: urban activities, industries, agriculture and shell farming. The biggest town (Sète) and most of urban activities, like incineration, are located in the Eastern part of the lagoon. Thus, Thau lagoon appears to be under an intense anthropogenic pressure. For instance, the results of the French Monitoring Network (RNO Réseau National d'Observation) shows high contamination of the Thau lagoon sediments by hydrophobic organic compounds such as, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [1]. However, only few data in relevant environmental compartments from Thau lagoon on other important groups of persistent organic pollutants (POPs), like polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), have been reported to date. Moreover, the dynamics, long term impacts and ultimate fate of the contamination induced by these chemicals in the lagoon is not well known.

The aim of this work was to investigate the PCDD/Fs concentrations and patterns in air (where no data are available yet), sediments and mussels from Thau Lagoon. The influence of the atmosphere in the accumulation of these POPs in the aquatic system was studied. Two land air sampling sites were set up in the lagoon and sediments and mussels samples were collected from selected stations.

Materials and methods

Sampling

Air samples were collected with two High Volume Samplers (TE-1000BL PUF sampler, Tisch Environmental, inc. USA) operating in a 24h basis at two locations (Ifremer Institute and at the other side of the shore of the lagoon close to a small village, Bouzigues, (Figure 1). Sampling started on 14 Nov 05 at IF site, on 15 Nov at BZ site and finished on 19 Nov 05 in both sites. Thus, 5 samples were collected for IF site whereas 4 were obtained for BZ site. Air particle phase was retained by using a 102 mm diameter Whatman QMA grade quartz fibre filter (QFF) whereas the gas phase was trapped with a polyurethane foam (PUF) plug of 65 mm diameter, 50 mm length and a raw density of 30 kg m^{-3}. An average volume of 400 m^3 was collected.

Divers using PTFE sediment corers collected the surface sediment samples. The results presented in this study were obtained from the analysis of the first centimeter of the sediment core. Mussels (*Mytilus galloprovincialis*) were collected by hand and depurated during 24 hours before further treatment. The mussels were shucked, homogenized, stored at –20°C before freeze-drying, and stored in the dark at room temperature until analysis. Surface sediments and mussels were collected in May 2004. The locations of the studied sites are shown in Figure 1.

Analytical determinations

Air samples

Samples were Soxhlet extracted with n-hexane/acetone (220/30) for 48 h after being spiked with internal standards (16 ^{13}C-labelled 2,3,7,8-chlorine-substituited congeners with 400 pg each, except OCDD with 800 pg). Extract

purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems, Inc., Watertown, MA, USA). Analysis and quantification of PCDD/Fs was based on isotope dilution using HRGC-HRMS following the U.S. EPA Method 1613 [2]. The HRMS was operating in EI-mode at 34 eV with a resolution of >10000. The samples were analyzed on a 60 m long, 0.25 mm i.d. and 0.25 µm film BP-DXN capillary column (SGE, Victoria, Australia).

Mussels and sediment samples

The analytical protocols for extraction and cleanup have been described previously [3,4]. Briefly, approximately five grams (dry weight) of mussel sample and seven grams of dry sediments samples were extracted by pressurised solvent extraction (ASE, Dionex Corp., CA) using 22 ml extraction cells. Each extraction consisted of five static cycles, two minutes long, at a temperature of 100°C and 138 bars of pressure. The extracts were concentrated by rotary evaporation and subsequently under gentle nitrogen stream. The separation of co-extracted lipids of mussel samples was performed by gel permeation chromatography (GPC) on a laboratory prepared column (Bio Beads SX-3 200-400 Mesh, 460 mm x 26 mm column). The purified mussel extracts and sediments extracts were concentrated and further purified and fractionated on a two layer silica/alumina column (H_2O 5% deactivated silica gel and alumina) using hexane and hexane/dichloromethane (9:1) as an eluent. The analyses and quantification were performed as indicated above for air samples. 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) [4].

Quality Assurance / Quality Control procedures (blanks, analysis of replicates 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.

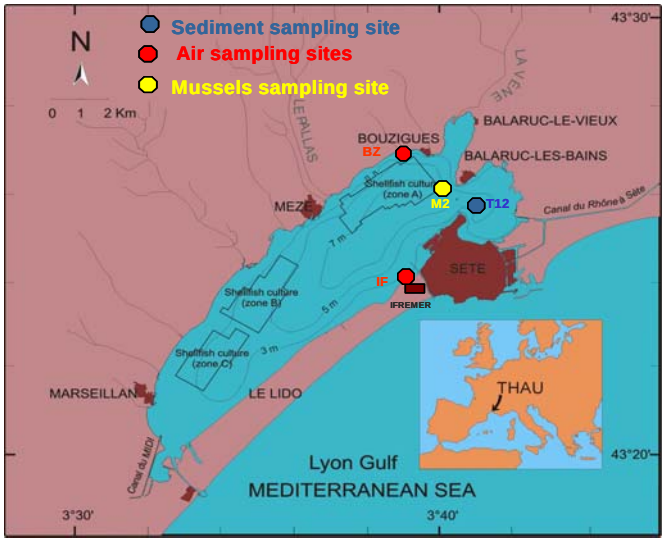

Figure 1. Location of Thau Lagoon (France) and air, sediments and mussels sampling sites. Surface sediments and mussels were collected in May 2004 whereas air samples were collected in November 2005.

Results and discussion

Concentration levels

Air

Total PCDD/Fs air concentrations (particle + gas phase) measured in both sampling sites are compiled in Table 1. PCDD/Fs WHO-TEQ concentrations found in IF site ranged from 15.8 to 25.7 WHO-TEQ fg m^{-3} whereas for BZ site varied from 6.9 to 22.6 WHO-TEQ fg m^{-3}. Concentrations observed in both locations were low, typical of those from rural areas [5-7].

Table 1. Concentrations of PCDD/Fs in air (fg m^{-3}), surface sediments, and mussels (pg g^{-1} dry weight) found in Thau lagoon.

Compounds	Air (gas+particle phase)									Sediment	Mussel
	Site IF (14-19 Nov 05)					Site BZ (15-19 Nov 05)				(May 04)	(May 04)
	IF-1	IF-2	IF-3	IF-4	IF-5	BZ-1	BZ-2	BZ-3	BZ-4	T12	M2
2,3,7,8-TCDD	<1.0*	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.4	1.15	n.d.
1,2,3,7,8-PeCDD	6.0	5.7	2.3	5.7	5.4	1.6	3.5	1.3	5.5	2.27	n.d.
1,2,3,4,7,8-HxCDD	8.5	8.3	2.8	4.9	6.8	3.5	6.1	1.7	6.8	2.08	n.d.
1,2,3,6,7,8-HxCDD	24.8	19.1	7.2	12.3	28.0	9.1	14.5	2.1	18.9	7.46	0.16
1,2,3,7,8,9-HxCDD	17.7	16.6	6.1	11.8	16.7	6.7	10.9	5.2	17.2	5.54	0.17
1,2,3,4,6,7,8-HpCDD	247.7	276.4	59.2	132.5	262.3	121.1	162.5	55.3	175.2	162.19	1.57
OCDD	379.2	917.9	132.0	273.2	576.7	310.2	340.8	95.4	406.1	1270.05	6.44
2,3,7,8-TCDF	6.7	7.1	2.4	4.9	6.0	2.5	1.6	1.2	2.3	12.61	4.00
1,2,3,7,8-PeCDF	5.7	6.5	5.9	4.5	4.5	1.5	1.7	1.6	6.1	5.05	0.27
2,3,4,7,8-PeCDF	7.0	11.1	10.9	8.0	7.7	4.6	7.1	4.1	8.5	6.21	0.58
1,2,3,4,7,8-HxCDF	8.9	11.1	10.0	6.9	7.9	5.3	18.2	3.2	11.8	6.57	0.11
1,2,3,6,7,8-HxCDF	5.5	6.6	9.9	6.3	4.8	4.0	7.6	n.d.	10.5	4.51	n.d.
2,3,4,6,7,8-HxCDF	8.9	19.6	13.6	9.5	9.1	5.9	18.9	n.d.	13.2	6.16	0.18
1,2,3,7,8,9-HxCDF	2.8	6.5	4.2	2.4	3.4	2.1	4.2	n.d.	7.9	1.35	n.d.
1,2,3,4,6,7,8-HpCDF	36.4	59.5	31.2	26.6	28.4	18.1	52.4	6.0	45.9	60.04	0.43
1,2,3,4,7,8,9-HpCDF	4.7	12.3	4.5	3.4	5.0	3.0	5.1	n.d.	4.8	3.99	n.d.
OCDF	14.9	57.0	14.0	15.0	20.9	18.5	21.6	4.0	70.7	98.88	0.36
∑PCDDs	*683.9*	*1244.1*	*209.6*	*440.5*	*895.9*	*452.1*	*538.4*	*161.1*	*631.1*	1450.73	8.34
∑PCDFs	*101.5*	*197.2*	*106.5*	*87.3*	*97.7*	*65.6*	*138.5*	*20.2*	*181.7*	205.37	5.92
∑PCDD/Fs	**785.4**	**1441.4**	**316.1**	**527.8**	**993.6**	**517.7**	**676.8**	**181.4**	**812.8**	**1656.1**	**14.3**
WHO-TEQ	***22.1***	***25.7***	***15.8***	***18.4***	***20.7***	***10.4***	***18.6***	***6.9***	***22.6***	***13.8***	***0.8***

* Limits of detection are (<) values and were calcultated on the bases of a signal to noise ratio of 3/1

The weather conditions during the sampling week, where precipitation (14th and 15th Nov) and winds up to 9 m/s were registered (Meteo France, station from Sete), might have favored the low concentrations levels found some days. Wind blew predominantly from NW during the sampling period except for a short gap (in the beginning and the end of the period) where it blew from N-NE (Figure 2). The lowest concentration in IF site (IF-3) was found when the highest wind speeds were registered, and the maximum value (IF-2) when the lowest wind speeds were registered (Figure 2). Regarding BZ site, located at the other shore of the lagoon, the lowest PCDD/Fs concentrations were observed in BZ-3 corresponding with some wind speed peaks. The highest value was obtained in BZ-4 when N winds were predominant. However, although wind speed seems to affect the PCDD/Fs concentrations observed in different days, only some preliminary indications can be presented so far regarding dynamics of PCDD/Fs in air over the Thau Lagoon. An atypical situation in the sampling week occurred, probably due to the meteorological local conditions, in which some important phenomena affecting the burden of POPs in the air masses were minimized such as, the sea breeze. The sea breeze has been described as an important vector in modulating the transport of pollutants between terrestrial and marine ecosystems [8].

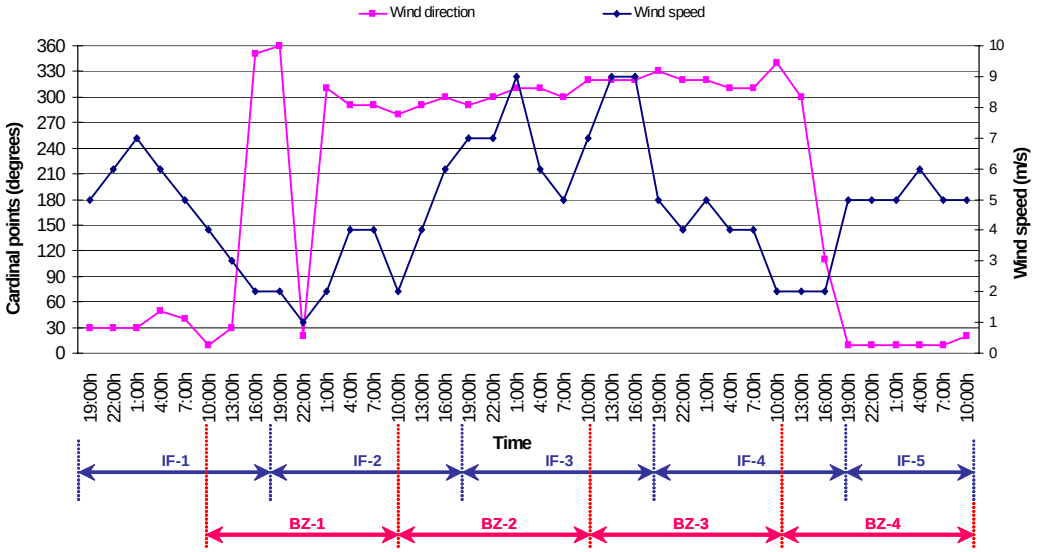

Figure 2. Wind directions and wind speeds registered during the sampling period (14-19 November 2005) together with the daily sampled intervals for both sites. Temperature varied from 5 to 16 ^{0}C during that period. Precipitation was registered on 14th and 15th Nov. Data are from Meteo France, station from Sete.

Sediments and mussels

A concentration of 13.8 WHO-TEQ pg g^{-1} was found for PCDD/Fs in surface sediment. Concentrations within the same range have been reported in the literature for surface sediments from several aquatic environments. PCDD/Fs concentrations in sediments from industrially influenced coastal areas in Southern and Easter Spain [9] ranged from 0.1 to 48 WHO-TEQ pg g^{-1}. PCDD/Fs concentrations in sediments from an impacted estuarine system in Texas (USA)[10] varied from 17.5 to 32.6 WHO-TEQ pg g^{-1}. Levels found in sediments from the Venice Lagoon [11] varied from 2.2 to 6.2 WHO-TEQ pg g^{-1}. In the latter study values from 20 to 11000 WHO-TEQ pg g^{-1} were also reported for the industrial canals of the lagoon. PCDD/Fs concentrations in lake sediments (located in a semi-rural area) in Northern Italy [6,7] varied from 0.13 to 16.9 WHO-TEQ pg g^{-1}.

A value of 0.8 WHO-TEQ pg g^{-1} was found for the analyzed mussels in the lagoon. Similar PCDD/Fs concentrations in mussels have been reported for the English Channel and the Atlantic French coast (Vilaine river bay) [4]. The observed value in Thau lagoon does not exceed the maximum level set by the European Community for marine products intended for human consumption[12].

Congener patterns

PCDD/Fs congener patterns observed in air samples for the different days of the sampled period in both sites were very similar suggesting a homogeneous situation during the sampled week in both shores of the lagoon (Figure 2). Air and surface sediments patterns were dominated by HpCDD and OCDD (Figure 3) and were in agreement with those usually reported in available literature [5-7, 13], although a predominance of OCDF in sediments from Venice Lagoon has been reported [11].

The distribution pattern of PCDD/Fs in mussel samples are dominated by 2,3,7,8-TCDF and OCDD, these two congeners accounting for more than 70% of the quantified congeners (Figure 3) . This profile is similar to results previously described for mussels from other marine areas [4,14].

When comparing the patterns from air, sediments and mussels (Figure 3), a very similar signal was observed in air and sediments. This finding suggests an influence of the atmosphere in the accumulation of PCDD/Fs in surface

sediments. The signal observed in mussels was different to the one exhibited by the other two studied compartments suggesting a selective mechanism of accumulation. Thus, whereas the signal observed for HpCDD, OCDD, HpCDF and OCDF in the mussels it was very similar to the one in the sediment, the predominance of the low chlorinated PCDFs was not observed in any of the other compartments. This observation suggests a combined PCDD/Fs signal in mussels arriving in part from the sediment but also most probably from the water column.

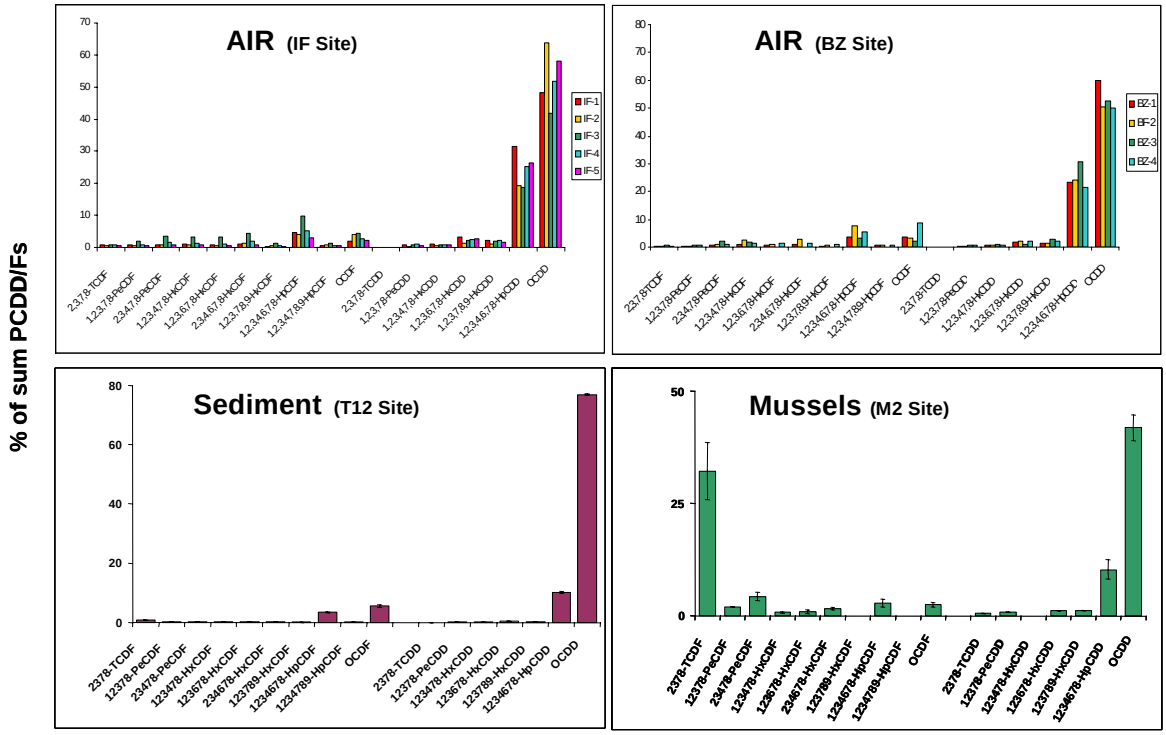

Figure 3. Distribution pattern of PCDD/F congeners in air (both air sampling sites), sediment (mean values and standard deviations, n=2) and mussels samples (mean values and standard deviations, n=3) from Thau lagoon.

In spite of some clear indications presented in this work, further research is needed in order to determine whether the atmosphere has a significant role in the accumulation of PCDD/Fs in surface sediments. Moreover, more data are needed to clarify the source of PCDD/Fs in mussels from Thau lagoon. Thus, a wider spatial distribution of sediment sampling together with measurements of PCDD/Fs concentrations in the water columns is ongoing. Analyses of other relevant POPs such as, PCBs in air of Thau Lagoon is taking place in order to verify the presented hypotheses. Back trajectories of air masses arriving to the area will also be evaluated in order to better understand the occurrence of these pollutants in this coastal lagoon.

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