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PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France)

J. Castro-Jiménez[a, *], G. Deviller[a], M. Ghiani[a], R. Loos[a], G. Mariani[a], H. Skejo[a], G. Umlauf[a], J. Wollgast[a], T. Laugier[b], K. Héas-Moisan[c], F. Léauté[c], C. Munschy[c], C. Tixier[c] and J. Tronczyński[c]

[a] European Commission-DG Joint Research Centre, Institute for Environment and Sustainability(IES), TP 290, Via Enrico Fermi, 1. 21020 Ispra (VA), Italy
[b] Ifremer, Laboratory of Environmental Resources, Bd Jean Monnet, BP 171, 34203 Sète Cedex, France
[c] Ifremer, Laboratory of Biogeochemistry of Organic Contaminants, BP 21105, 44311 Nantes Cedex 3, France

*: Corresponding author : J. Castro-Jiménez, Tel.: +39 0332 786070; fax: +39 0332 786351, email address : javier.castro-jimenez@jrc.it

Abstract:

Ambient concentrations, congener patterns and multi-media distribution of PCDD/Fs and PCBs were determined in air, water, sediment and mussels in a semi-enclosed marine ecosystem (Thau lagoon, France). ∑2,3,7,8-PCDD/F and ∑7ICES PCB air concentrations (0.2–1.4 and 31–57 pg m^{-3}, respectively) were typical of rural areas. Concentrations in the water column were very low for PCDD/Fs (163–476 fg L^{-1}) and low for PCBs (138–708 pg L^{-1}). PCDD/F and PCB concentrations found in surface sediment (0.15–1.6 and 2.5–33 ng g^{-1} d.w., respectively) and mussel (13–21 pg g^{-1} d.w. and 10–39 ng g^{-1} d.w., respectively) were medium levels. PCDD/F congener patterns observed in air, water particulate phase and sediments were similar suggesting direct coupling among these compartments and atmospheric inputs of PCDD/Fs into the lagoon. Conversely, for the same set of samples, similar patterns were not observed for PCBs in the mentioned compartments.

Multi-media ambient concentrations and distribution of PCDD/Fs and PCBs in Thau Lagoon provide insight into the POPs behavior in semi-enclosed marine ecosystems.

Keywords: POPs; Air; Sediment; Mussel; Water column

1. Introduction

Persistent organic pollutants (POPs) enter the environment primarily or exclusively as a result of anthropogenic activities. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are two important families of POPs. These chemicals bioaccumulate and are considered as potent toxicants capable of producing a wide spectrum of adverse health effects in biota and humans ([Safe, 1984] and [Safe, 1990]). PCDD/Fs occur as unintentional byproducts of chemical manufacturing and incineration processes ([Harrad and Jones, 1992] and [Bruzy and Hites, 1996]) whereas current sources of PCBs are landfills, open burning of products containing PCBs, waste incineration, accidental fires and revolatilization from formerly exposed soils (Cousins and

Jones, 1998; Breivik et al., 2002). PCBs were mainly used by the power industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants.

PCDD/Fs and PCBs enter the aquatic systems by atmospheric deposition, direct and indirect discharges, and riverine inputs. A low aqueous solubility and vapor pressure, and resistance to extensive chemical and biological transformation characterize these compounds. Their general hydrophobic nature results in high partition coefficients to abiotic and especially biotic particles. PCDD/Fs and PCBs exist in the atmosphere as gases and bound to particles, being temperature an important variable affecting this partition (Schwarzenbach et al. 2003). Once delivered to the water column, the primary removal processes are sedimentation of atmospheric particles and partitioning of the gaseous/dissolved phase contaminants into organic carbon (OC)-rich particles with subsequent settling and accumulation in surface sediments, where contaminant and particle burial is slowed by resuspension and mixing of surface sediments by aquatic organisms.

Coastal lagoons represent less than 1% of the surface covered by oceans and seas, however they are characterized by a high biodiversity and intense primary production leading to both ecological and economical considerable importance (Nixon, 1982). Such is the case of Thau lagoon, 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 is connected to the sea North-East by the channel of Sète (90% of the exchanges) and South-West by the channel de Pisse-Saumes (10% of exchanges). Winds are often strong in the area with an average of 118.5 days per year above Beaufort force 5 (data from Météo France), in particular when blowing from North-West (Tramontane). Wind has been described as an important variable influencing the lagoon hydrodynamics (Lazure, 1992). There is an intensive shell farming activity (oysters and mussels) that covers about 20% of the whole lagoon area and yearly produces about 15000 tons of oysters. (Gangnery et al., 2001).

Thau lagoon seems to be under intense anthropogenic pressure (urban, industrial, agricultural and shell farming activities). The biggest town (Sète) and most of urban activities are located in the Eastern part of the lagoon. A considerable increase of population in the area during the summer months is contributing to the anthropogenic impact. The results of the French Monitoring Network (RNO Réseau National d'Observation) show high contamination of the lagoon sediments by hydrophobic organic compounds compared to other Mediterranean lagoons, especially by polycyclic aromatic hydrocarbons (PAHs) and to a lesser extent by PCBs (Tronczyński, 1998; Leauté et al. 2007). However, no information on PCDD/Fs ambient levels in Thau lagoon is available yet. A better knowledge of the fate and dynamics of POPs in this semi-enclosed marine ecosystem is needed in order to apprehend their long-term impacts. The main objectives of this work were: (1) to obtain ambient concentrations, congener patterns and multi-media distribution of PCBs and PCDD/Fs in air, water column, mussel and surface sediment from Thau Lagoon; (2) to generate a data set on multi-media ambient concentrations that serves as a first step for POPs fate modeling validation and future risk assessment in this ecosystem. In addition, some specific aspects regarding the atmospheric input of the pollutants studied will be discussed.

Materials and methods

Sampling

Locations of all sampling sites are detailed in Figure 1. Air samples were collected in November 2005 by using high volume samplers at two sites: Ifremer Institute (IF) located on the South shore and Bouzigues (BZ), a small village on the North shore of the lagoon. Air particle phase was retained by using a 102 mm diameter 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}. Volumes of ~ 400 m^3 were collected for each sample (5 samples at IF and 4 at BZ) except for the last one taken at IF site where a volume of ~ 200 m^3 was sampled.

Lagoon water was sampled from a boat also in November 2005 by using pre-equilibrated Teflon tubing and a Teflon membrane pump (ASTI, France) operated with compressed nitrogen. The sample was collected in stainless steal (StS) containers. Four samples (~ 120L) were taken from the lagoon (T12, T11, C4 and T2) and an additional sample (~ 80L) was also collected at the riverine reference station (outlet of the river Véne, RV) (Figure 1). Once in the laboratory samples were filtered (GFF). The filtrated water was collected in clean StS containers and PCDD/F and PCB ^{13}C-labeled internal standard mixtures were added. Filtrates were then passed through a pre-cleaned (MiliQ-UV and sequential soxhlet extraction with methanol, acetonitrile and dichloromethane, 8h each) and pre-conditioned (methanol) 50g Amberlite^{TM} XAD-2 Teflon column at a flow ≤ 80 mL/min (Tronczyński et al., 2004, 2005a). The water sample was sucked using a peristaltic pump. Columns were dried by passing air using a vacuum pump. Elution of XAD-2 columns was performed with dichloromethane. Na_2SO_4 anhydrous (baked at 450 °C / 8h) was added, the samples were placed in the freezer for transport and then stored until further processing at the laboratory.

Both surface sediments and mussels were collected in May 2004. Surface sediment samples were collected by divers at three sites along the lagoon (West, medium and East areas of the lagoon) using Teflon sediment corers. The results presented in this study were obtained from the analysis of the first centimeter of the sediment core. Before analysis, sediments were homogenized, freeze-dried and sieved (<2mm) (Tronczyński et al., 2005b).

A minimum of 50 mussels (Mytilus galloprovincialis) of homogeneous size were collected by hand from each of the three shellfish areas along the lagoon (Figure 1) and depurated in decanted water from the site for 24 h. The mussels were further shucked, homogenized and stored at –20°C before freeze-drying. Both freeze-dried sediment and mussel samples were stored in the dark at room temperature until analysis (Munschy et al., 2005a).

Analytical determinations

PCDD/Fs considered in this work were the 2,3,7,8 congeners since they have been described as the most toxic ones (Van den Berg et al., 1998), whereas PCBs were 28, 52, 101, 118, 153, 138 and 180 congeners also referred in the text as the 7 ICES (International Council for the Exploration of the Sea). Air and water samples were analyzed at the Joint Research Centre laboratories whereas sediment and mussels sample analyses were carried out at Ifremer laboratories.

Air and water samples

QFFs and PUFs were Soxhlet extracted separately with n-hexane/acetone (220:30 v/v) for 48 h after being spiked with internal standards (16 ^{13}C-labelled 2,3,7,8-chlorine-substituted 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). The purification method was previously described by Abad et al. (2000). Prior to injection, syringe ^{13}C-labelled standards were added to the extracts to determine the recoveries of the internal standards.

Regarding water samples, dichloromethane extracts were filtered with pre-cleaned glass wool, concentrated, treated with concentrated H_2SO_4 and cleaned up as indicated for air samples. GFF were thawed, cut into small pieces and transferred into 33mL ASE® (Dionex) cartridges. ^{13}C-labelled PCDD/F and PCBs internal standard mixtures were added. The filters were extracted using the Dionex ASE® 300 applying in a 1st extraction methanol (3 cycles each with a static time of 5 min at 75 °C, heat-up time of 5 min, a flush volume of 100%, a purging time of 60s and a pressure of 1500 psi) and in a 2nd extraction hexane (same parameters as for methanol), respectively. The methanol and hexane phases were combined in a separatory funnel. The methanol phase was extracted three more times with ~ 20 mL of hexane and all hexane phases were combined and concentrated to 10 mL. From this point on samples were treated as indicated above for the XAD extracts. Quantification of PCDD/Fs and PCBs was based on isotope dilution using a high resolution gas chromatography – high resolution mass spectrometry (HRGC-HRMS). The method has been previously described (Castro-Jiménez et al., 2008).

Mussels and sediment samples

The analytical protocols for extraction, cleanup and analysis have been previously described (Munschy et al., 2005a, 2005b; Tronczyński et al., 2005b; Johansson et al., 2006). Briefly, approximately 5 g (dry weight, d.w.) of mussel sample or 7 g d.w. of sediment were extracted by pressurised solvent extraction (ASE, Dionex Corp., CA) with dichloromethane. For mussel samples, the separation of co-extracted lipids was performed by gel permeation chromatography (GPC). The purified mussel and sediment extracts were concentrated and then further purified and fractionated on a two layer silica/alumina column. Quantification of PCDD/Fs was performed by isotopic dilution using HRGC-HRMS whereas PCBs were analysed by HRGC fitted with two electron capture detectors using two columns.

Quality assurance/Quality control

QFF were baked at 450 ºC for 6 h whereas PUFs were soxhlet extracted during at least 24 h with acetone and then dried in a dissicator under vacuum before use. Both cleaned QFF and PUF were wrapped in n-hexane rinsed aluminum foil and placed in a Teflon sealed metallic transport container. Transport (clean filters and PUFs), field, and procedural blanks were collected and processed together with the samples. Field and transport blank values were below the limits of detection (LODs) or at least three times lower than the analyte value for all compound studied, except for PCB-118 that exceeded this QA/QC threshold in some of the air samples. A breakthrough test was performed by placing a smaller PUF plug in series separated ~1 cm from the main PUF in the sampling head. Breakthrough rates for PCDD/Fs were not possible to be calculated due to the fact that the concentrations found in the gas phase (PUFs) both for the sample and the breakthrough PUFs were under the LOD (1 fg m^{-3}) whereas the breakthrough rate for ∑PCB in the condition of the sampling period was estimated to be less than 10%. Extraction blanks (QFF and PUFs) were processed for each batch of samples.

Regarding water samples, extraction and clean-up analytical blanks were carried out to check background levels. PCDD/F and PCB recoveries for the air gas and particular phases (PUFs and QFF) and for the water particulate phase (GFF) were in compliance with the specifications of EPA 1613 and EPA 1668 methods, respectively (U.S. EPA., 1994, 1999). However, PCDD/Fs recoveries in the water dissolved phase (XAD) were very low not allowing quality congener quantifications except for the river water sample (RV) where recoveries were sufficient to calculate a LOD. Therefore, PCDD/Fs dissolved water phase concentrations were not taken into account in the present work except for the RV sample. LOD for PCDD/Fs in water samples varied from 1-5 fg l^{-1}.

PCB recoveries in the dissolved phase were also low ranging from 16 – 53% except in only one sample (T2) where HxCB and HpCB internal standards were less than 10%. Even if the signal to noise ratio and the low blank levels found in all samples were enough to allow quality quantification of the studied PCB congeners, a limited used of those data was decided being mainly relegated to generation of congener fingerprints (relative composition) in the dissolved water phase and subsequent discussion. Total concentrations (dissolved + particulate phase) were only considered to compare levels with literature.

In order to calculate PCB recoveries in mussel and sediment samples, recovery surrogates (CB 30, CB 198, CB 209, TCN) were added to each sample before extraction and were used to control the recovery efficiency of the overall process. However, results were not corrected for recoveries (Johansson et al., 2006). In our laboratory, the average recoveries of internal standards in biota are: CB30 78%, TCN 80%, CB198 97% and CB209 98% (n=65) and in sediments are: CB30 81%, TCN 84%, CB198 80% and CB209 78% (n=25). For PCDD/Fs, ^{13}C labelled congeners were added before extraction and calculations were made by isotopic dilution method (Munschy et al., 2005b). Blanks and certified material analyses 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 for all analysed contaminants.

Materials

TE-1000BL PUF high volume samplers were employed (Tisch Environmental, Inc. USA). PUF plugs were obtained from Klaus Ziemer GmbH (Langerwehe, Germany), QFF (QMA-4 type) and GFF were from Whatman International Ltd (Brentford, Middlesex, UK). Amberlite^{TM} XAD-2 was from Supelco (Bellefonte, Pennsylvania, USA). Teflon columns used for water sampling were SeaStar Ltd type (37 cm length x 19 mm i.d.). All organic solvents were dioxin analysis grade from Sigma-Aldrich (Buchs SG, Switzerland). All gases (Alpha gaz, Italy) used were ultra pure grade suitable for PCDD/Fs analysis. Pre-packed multi-layer silica, basic alumina, and carbon columns were obtained from Fluid Management Systems (FMS) Inc. (Watertown, MA, USA). The standard mixture of native 7 ICES PCB used was PCB mix3 (Dr. Ehrenstorfer GmgH, Augsburg, Germany) and for ^{13}C-labelled congeners, 68-LCS from Wellington Laboratories (Guelph, Ontario, Canada). EPA-1613CVS, EPA1613LCS+MDF-12346789 and EPA-1613ISS were native, ^{13}C-labelled internal and recovery standards, respectively for 17 PCDD/Fs also obtained from Wellington Laboratories.

Results and discussion

Results on PCDD/Fs and PCBs in the studied matrixes from Thau lagoon are presented in Tables 1 and 2, respectively whereas values extracted from the literature for comparison are compiled in TS1 and TS2 in supporting information.

Ambient concentrations

Air

2,3,7,8-PCDD/Fs air concentrations (particle + gas phase) at IF site ranged from 0.3 to 1.4 pg m^{-3} (16 to 26 WHO-TEQ fg m^{-3}) whereas for BZ site varied from 0.2 to 0.8 pg m^{-3} (7 to 23 WHO-TEQ fg m^{-3}). PCDD/Fs were almost exclusively found to be associated to the air particulate phase. Concentrations observed at both locations were low, typical of those reported for rural areas in Europe, and North America (Lohmann and Jones, 1998; Cleverly et al., 2007). Values found in other aquatic environments such as the Lake Maggiore (located in a semi-rural area) in Northern Italy and from rural areas in Catalonia (Spain) are also within the same range (Abad et al., 2004; Castro-Jiménez et al., 2005, 2008) (Table S1, supporting information).

∑PCBs air concentrations reported in this study does not include the congener 118 (see QA/QC section). ∑PCB air concentrations (particulate + gas phase) found at IF site ranged from 31 to 48 pg m^{-3} whereas in site BZ varied from 31 to 57 pg m^{-3} (Table 2). PCBs were predominately in the gas phase. This fact has been previously reported (Mandalakis et al., 2002; Totten et al., 2004; Hornbuckle et al., 2006). Concentrations within the same order of magnitude were found in Venice lagoon, in air masses coming from the sea, in Lake Maggiore and in a background/rural site in Crete, Greece (Mandalakis et al., 2001; Gambaro et al., 2004; Manodori et al., 2006; Vives et al., 2007) (Table S2 supporting information).

PCDD/Fs and PCBs concentrations at both sampling sites were within the same order of magnitude, indicating a homogeneous situation at both shores of the lagoon along the North-South axis. Indeed a Student's t test (α=0.05) confirmed that there were no significant differences between the two sites for the air concentrations of PCDD/Fs (P=0.33) and PCBs (P=0.79).

Meteorological variables influence

The weather conditions during the sampling week, where precipitation (on 14th and 15th November) and wind peaks up to 9 m s^{-1} were registered (Météo France, station from Sète), might have favored the low concentrations found in the area, specifically for some days. Higher wind speeds are associated with greater height of the mixed boundary layer (more turbulent sampling conditions) and therefore an effect of pollutant dilution may occur under these conditions (Lohmann et al., 1999; 2003). Wind blew predominantly from North/West (NW) during the sampling period except for a short gap (in the beginning and the end of the period) where it blew from North-North/East (N-NE) (Figure 2).

Principal components analysis (PCA) was applied to identify the main relationships among meteorological variables and ∑PCDD/Fs and ∑PCBs air concentrations. As measurement units of the different variables studied were not homogeneous, the principal components were extracted from the correlation matrix (Legendre and Legendre, 1998). The first two principal components explained 67 % of the total variance (PC1=49%; PC2=18%). The main relationships among variables are shown in the factor loading plot (Figure 3). PCDD/Fs air concentrations were not correlated with local atmospheric conditions whereas PCBs air concentrations during the sampling week were clearly linked to air temperature, humidity and nebulosity (Figure 3). This observation is in agreement to other results reported in the literature where air temperature has been identified as an important variable affecting PCB atmospheric concentrations (Wania et al., 1998; Simcik et al., 1999; Currado and Harrad, 2000).

Although not statistically relevant, the wind speed seemed to have an influence on the pollutant concentrations in air. Thus, the lowest PCDD/Fs and PCBs concentration at IF and BZ sites were found in general during the intervals of higher wind speeds, especially for IF site (Figure 2 and Table 1). However, in spite of some wind peaks observed the average wind speed during the sampling period was ~ 5 m s^{-1}. Harrad and Mao (2004) reported that PCB air concentrations were negatively correlated to wind speed only when wind speeds were higher than 4.4 m s^{-1}. This value is very close to the one observed in Thau lagoon and the phenomenon described may explain our observations.

Water

Concentrations were reported only for the particulate phase except for the RV sample (see QA/QC section) where total concentration (dissolved + particulate) is reported. 2,3,7,8-PCDD/Fs concentrations in the water column from Thau Lagoon (Table 1) varied from 163 to 476 fg l^{-1} (4 to 9 WHO-TEQ fg l^{-1}). PCDD/Fs measured in RV were predominantly found in the particulate phase and exhibited a concentration of 2770 fg l^{-1} (53 WHO-TEQ fg l^{-1}). The higher concentration observed in RV can be explained by the higher suspended particulate mater (SPM) load in the waters from the river than in the lagoon waters. In fact, when normalizing the PCDD/F concentration by the SPM content, concentrations of 247 and 223 pg g^{-1} d.w. were obtained for RV and T12, respectively. Lower values were obtained in the central and western parts of the lagoon (89, 82 and 52 pg g^{-1} d.w. at T11, C4 and T2, respectively).

Few data are available in the literature on PCDD/Fs measurements in water. For instance, levels found in Thau lagoon were lower than those reported for various aquatic systems such as, non anthropogenic impacted Japanese coastal areas, the central part of Venice Lagoon, Italy or the Raritan Bay/Hudson River Estuary, USA (Hashimoto et al., 1995; Lohmann et al., 2000; Dalla Valle et al., 2003) (Table S1, supporting information).

$\sum$7 ICES PCBs (dissolved + particulate phase) concentrations determined in the water column from Thau Lagoon ranged from 138 to 708 pg l^{-1}, whereas a value of 390 pg l^{-1} was found in the RV sample (Table 2). PCBs were found predominantly associated to the dissolved water phase, especially the lower congeners (80 – 95%). This fact has already been described in the literature for other aquatic systems (Zeng et al., 2002; Maldonado and Bayona, 2002).

Concentrations within the same order of magnitude were found for a larger set of PCB congeners in the waters of San Diego Bay, California (Zeng et al., 2002) and in Lake Michigan, in USA (Pearson et al., 1996). Much higher concentrations were found for the 7 ICES PCBs in the Daya Bay, a semi-enclosed and anthropogenic impacted bay located in Southern China, (Zhou et al., 2001). Lower PCB concentrations have been reported for other coastal areas or open seas such as, the Black and Baltic seas (Bruhn and McLachlan, 2002; Maldonado and Bayona, 2002; Wodarg et al., 2004) (Table S2, supporting information).

Sediments

Results on PCDD/Fs were available for sediments at sampling sites T10 and T12 where concentrations of 150 pg g^{-1}d.w. (3 WHO-TEQ pg g^{-1} d.w.) and 1660 pg g^{-1}d.w. (14 WHO-TEQ pg g^{-1} d.w.) for the sum of the 17 congeners were found, respectively. This higher concentration observed at the Eastern part can not be attributed to a higher sediment organic carbon (OC) content at T12, since values were 4.2% at T12 site, and 5.1% at T10.

PCDD/F sediment concentrations within the same order of magnitude were measured in fresh water locations in the UK, where the main sources of PCDD/Fs were thought to be atmospheric (Rose and McKay, 1996). Levels reported for Lake Maggiore sediments where atmospheric inputs have also been identified as major source of PCDD/Fs to the lake were as well within the same order of magnitude (Castro-Jiménez et al., 2005, 2008). Higher

PCDD/F levels were reported for an impacted estuarine system (Houston ship Channel, USA) or for sediments from industrially influenced coastal areas in Southern and Easter Spain (Eljarrat et al., 2005; Suarez et al., 2006). Comparing to another coastal lagoon, levels at T12 were slightly higher than PCDD/F concentrations found in sediments from different parts of Venice Lagoon, except for the industrial channels where a much higher concentration was reported (Dalla Valle et al., 2003) (Table S1, supporting information).

∑PCB concentrations in sediments from the lagoon ranged from 2.5 to 33 ng g^{-1} d.w. (Table 2). Lower values were measured at the western (T3) and middle (T10) part of the lagoon (Figure 1) whereas the highest concentration was found at the eastern part (T12) as occurred with PCDD/Fs. Again, the spatial variability observed for the contaminant concentrations could not be solely attributed to different sediment OC contents (9.2, 5.1, and 4.2 % at T3, T10 and T12, respectively).

PCB concentrations in Thau were comparable with values reported in the literature for various fresh and coastal water ecosystems (Table S2, supporting information) such as, various Mediterranean coastal lagoons, the Lake Maggiore, the Daya Bay, the Lake Taihu (China) and the Quingdao coastal sea also located in China (Moret et al., 2001; Zhou et al., 2001; Zhang and Jiang, 2005; Gómez-Gutiérrez et al., 2007; Pan et al., 2007; Vives et al., 2007).

Mussels

2,3,7,8-PCDD/F concentrations ranging from 13 to 21 pg g^{-1} d.w. (0.7 to 1 WHO-TEQ pg g^{-1} d.w.) were found for the analyzed mussels in the lagoon. The highest value was observed in the western part of the lagoon (M1) although only a slight difference in the concentrations along the lagoon was found (Table 1). PCDD/Fs concentrations in mussels reported for the English Channel and the Atlantic French coast (Vilaine river bay) are in the same range (Munschy et al., 2005b). The observed values in Thau lagoon were below the threshold of 4 WHO-TEQ pg g^{-1} w.w. (wet weight) set by the European Commission for fishery products for human consumption (European Commission, 2006).

Data on PCDD/Fs in shellfish are quite numerous. However, different ways of data reporting and different studied species make data comparison difficult. Moreover, results are rarely associated with the sampling period, despite a significant influence of shellfish sexual maturity (spawning season and lipid content) on the contamination levels. Therefore, the ranges reported for mussels are usually broad. PCDD/Fs concentration in various types of mussel reported for different aquatic systems are slightly higher than those found in Thau lagoon (Petreas et al., 1992; Bayarri et al., 2001; Abad et al., 2002, 2003; Knutzen et al., 2003) (Table S1, supporting information).

∑PCB exhibited concentrations in mussels ranged from 10 to 39 ng g^{-1} d.w. Lower values were observed at the western (M1) and middle (M4) part of the lagoon and the highest at the eastern part (M2). This distribution was also observed in sediments. On the other hand, the PCB concentration distribution appears to be the opposite than the one observed for PCDD/Fs in mussels where the highest concentration was found in the western part of the lagoon as indicated above. Concentrations within the same order of magnitude were found in mussels from various spots in different marine locations (Porte and Albaigés 1993; Lee et al., 1996; Bayarri et al., 2001; Piersanti et al., 2006) (Table S2, supporting information).

Congener patterns

PCDD/Fs

PCDD/F congener patterns in the environmental compartments studied are presented in Figure 4. Air samples for the different days of the studied period at both sites exhibited very similar PCDD/F congener patterns indicating a homogeneous situation in both shores of the lagoon. OCDD and HpCDD predominated in the pattern, followed at a lower percentage, by HpCDF and OCDF. This congener distribution ("sink" profile) has been described in the literature as the resultant patter from combustion sources after preferential removal of lower chlorinated dioxins and furans by atmospheric processes (Brubaker and Hites, 1997). Air patterns found in Thau lagoon were in agreement with those reported for various rural areas influenced by deposition of these pollutants after long range transport (Tysklind et al., 1993; Lohmann and Jones., 1998; Castro-Jiménez et al., 2005, 2008; Cleverly et al., 2007).

Particulate water phase and surface sediment patterns were also dominated by HpCDD and OCDD and were similar in all sampling sites suggesting a homogeneous situation in the lagoon and a direct coupling between these compartments.

OCDD and 2,3,7,8-TCDF dominated the distribution patterns of PCDD/Fs in mussel samples and these two congeners accounted for more than 70% of the ∑2,3,7,8-PCDD/Fs. This profile is similar to results previously published for mussels from other marine and lake waters where the clear predominance of the two mentioned congeners was also observed (Petreas et al., 1992; Abad et al. 2003; Munschy et al., 2005b; Zhang and Jiang, 2005; Danis et al., 2006).

A very similar signal was observed when comparing the patterns from air (dominated almost exclusive by the particulate phase), particle water phase and sediment. A similar behavior has been observed in the sub-alpine Lake Maggiore where no local sources are present and the PCDD/Fs and PCBs inputs to the water column and the sediments could be attributed to long range transport and subsequence scavenging of atmospheric particulates (Castro-Jiménez et al., 2005, 2008). The similar finding in Thau lagoon suggests a predominant role of the atmosphere in the accumulation of PCDD/Fs in surface sediments from this system.

The signal observed in mussels was different to the one exhibited by the other compartments. Thus, whereas the signal observed for HpCDD, OCDD, HpCDF and OCDF in the mussels was very similar to the one in the water and sediment (and also air), the predominance of the low chlorinated PCDFs (specially the 2,3,7,8-TCDF) in mussels was not observed in any of the other compartments (Figure 4). This fact could be interpreted as a combined PCDD/Fs signal in mussels arriving in part from the water SPM but also from the dissolved water phase, since mussels have been described to accumulate contaminants both from the dissolved and particulate phases (Gossiaux et al., 1998). However, no confirmation on the contribution from the dissolved water phase to this fingerprint could be made with the available data, since it was only possible to determine the PCDD/Fs dissolved water phase concentrations in one sample (RV) and most of the congeners were below the LOD. Broman et al. (1991) reported a predominance of TCDFs in dissolved water phase in the Baltic Sea but very few data are available in the literature on PCDD/Fs in the dissolved water phase.

PCBs

Results on PCBs patterns are presented in Figure 5. As observed for PCDD/Fs, PCB air patterns at both sites of the lagoon were very similar suggesting also a homogeneous situation at both shores for this chemical group. When examining the patterns of the air gas and particulate phases, low chlorinated congeners were predominant in the air gas phase pattern, whereas higher chlorinated PCB were more abundant in the particulate air phase pattern. Regarding PCB-118, although not reported (see QA/QC section) no predominance for the samples in which this congener was measured was observed in the congener pattern. The PCB pattern found in water showed a predominance of PCB-101 followed by PCB-52 in the dissolved water phase, whereas in the SPM phase, PCB-153 followed by PCB-138 were found predominant. Regarding surface sediment and mussel patterns, both matrixes exhibited a predominance of PCB-153 followed by PCB-138. The fact that the pattern found in all sampling location for each compartment (water, mussels and sediments) was very similar suggests a homogeneous situation throughout the lagoon.

The predominance of hexachlorinated PCBs in mussels, especially PCB-153 and PCB-138, has been reported in the literature for different coastal locations along the western Mediterranean (Porte and Albaigés, 1993) and the Adriatic Sea (Bayarri et al., 2001; Piersanti et al., 2006). Predominance of PCB-153 was reported from industrial and urban impacted site sediments from Venice lagoon whereas for the less contaminated areas of the lagoon, PCB-28 seemed to be predominant (Moret et al., 2001). Conversely, PCB-28 was found predominant in sediments from Taihu Lake in China and anthropogenic impacted site (Zhang and Jiang, 2005).

Interestingly, when comparing the PCB pattern in the dissolved and particulate water phases with the pattern exhibited in mussel and sediment, a similarity was observed only with the particulate water phase (Figure 5). It seems that although the PCBs were predominately found in the dissolved water phase, the resultant pattern in mussels reflected better the one found in the SPM or sediments.

When comparing the patterns from air particulate phase, water SPM and sediments no similarity was observed as occurred for PCDD/Fs. The predominance of PCB-153 observed in SPM and sediment was not observed in air, where PCB-180 predominated. However, in the case of PCBs, air-water exchange has been described as an important mechanism of incorporation of these chemical to water bodies (Eisenreich and Looney, 1981; Swackhamer et al., 1988) and this input way has not been evaluated in the present work.

Conclusions

PCDD/F and PCB air concentrations in Thau lagoon are typical of those reported for rural or semi-rural sites in spite of this area has been described as an anthropogenic impacted zone. Most probably the local meteorological conditions such as the strong wind regimes affecting the lagoon area during the whole year (except summer months) favor these low air concentrations. PCDD/F and PCB concentrations in the lagoon waters are low, especially those for dioxins. PCDD/F and PCB sediment concentrations are in the range of those from moderate urban/anthropogenic impacted areas, especially at the Eastern part of the lagoon. Concentrations of PCDD/F, in all cases below the threshold set by the European

Commission for fishery products for human consumption, and PCB in mussels point again to a medium/moderate level situation.

The congener patterns of the studied POPs in the different environmental compartments provide insight into the multi-media contamination distribution in a marine lagoon. The patterns of PCDD/F congeners in air, water particulate phase and sediments are very similar suggesting direct coupling between these compartments. Therefore, PCDD/F atmospheric inputs mainly associated to the air particle phase are expected to contribute to the total load of PCDD/Fs in this aquatic system. However, for the same set of samples and available data, no similarity is found for PCB congener patterns in air particulate phase relative to those obtained in water phase (particulate and dissolved) and sediment. Further investigation of other input mechanisms such as air-water exchange is needed to elucidate the role of the atmosphere in the input of PCBs in this aquatic system.

The similarity of patterns observed in all sampling sites for each compartment (spatial distribution) indicates a homogeneous situation in the lagoon and same type of source (s) can be expected to affect the whole aquatic system. A complete year of air sampling, including summer months and back trajectories analyses of air masses arriving to the area are undergoing and will allow to more precisely evaluate the occurrence of airborne PCDD/Fs and PCBs in this coastal lagoon.

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

Compounds	Air (gas+particle phase) fg m^{-3}									Mussel (pg g^{-1} d.w.)			Sediment (pg g^{-1} d.w.)		Surface Water (fg l^{-1})**				
	Site IF (14-18 Nov 05)					Site BZ (15-18 Nov 05)				May 04			May 04		Nov 05				
	IF-1	IF-2	IF-3	IF-4	IF-5	BZ-1	BZ-2	BZ-3	BZ-4	M1	M4	M2	T10	T12	T2	C4	T11	T12	RV
2,3,7,8-TCDD	≤ 1.0*	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	1.4	nd	0.1	n.d.	0.1	1.1	≤ 1.0	≤0.7	≤ 1.0	≤ 1.0	≤ 2.0
1,2,3,7,8-PeCDD	6.0	5.7	2.3	5.7	5.4	1.6	3.5	1.3	5.5	0.24	nd	n.d.	0.5	2.3	≤ 1.0	2.8	≤ 1.0	≤ 1.0	4.0
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	0.26	<0.07	n.d.	0.4	2.1	3.5	2.8	≤ 2.0	≤ 2.0	9.6
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	0.37	<0.06	0.2	1.1	7.5	7.3	6.0	≤ 2.0	4.3	24.1
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	0.53	0.1	0.2	1.1	5.5	5.8	5.6	≤ 2.0	2.8	21.6
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	2.91	1.6	1.6	16.2	162.2	74.4	67.6	21.2	49.7	321.7
OCDD	379.2	917.9	132.0	273.2	576.7	310.2	340.8	95.4	406.1	10.44	5.4	6.4	107.0	1270.1	266.6	320.1	114.1	350.4	1841.7
2,3,7,8-TCDF	6.7	7.1	2.4	4.9	6.0	2.5	1.6	1.2	2.3	2.7	3.5	4.0	2.9	12.6	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	40.0
1,2,3,7,8-PeCDF	5.7	6.5	5.9	4.5	4.5	1.5	1.7	1.6	6.1	0.4	0.3	0.3	1.3	5.1	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	25.4
2,3,4,7,8-PeCDF	7.0	11.1	10.9	8.0	7.7	4.6	7.1	4.1	8.5	0.6	0.4	0.6	1.8	6.2	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	33.9
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	nd	0.1	0.1	1.5	6.6	≤ 2.0	≤ 2.0	≤ 2.0	≤ 2.0	41.7
1,2,3,6,7,8-HxCDF	5.5	6.6	9.9	6.3	4.8	4.0	7.6	≤ 1.0	10.5	nd	0.2	n.d.	1.3	4.5	6.2	8.2	≤ 2.0	≤ 2.0	32.2
2,3,4,6,7,8-HxCDF	8.9	19.6	13.6	9.5	9.1	5.9	18.9	≤ 1.0	13.2	0.4	0.2	0.2	2.0	6.2	10.9	8.3	≤ 2.0	4.3	55.1
1,2,3,7,8,9-HxCDF	2.8	6.5	4.2	2.4	3.4	2.1	4.2	≤ 1.0	7.9	0.2	<0.06	n.d.	0.3	1.4	≤ 2.0	≤ 2.0	≤ 2.0	≤ 2.0	14.3
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	1.0	0.5	0.4	8.4	60.0	35.6	28.3	≤ 2.0	*10.9*	175.0
1,2,3,4,7,8,9-HpCDF	4.7	12.3	4.5	3.4	5.0	3.0	5.1	≤ 1.0	4.8	0.3	<0.07	n.d.	0.5	4.0	4.5	3.7	≤ 2.0	≤ 2.0	12.3
OCDF	14.9	57.0	14.0	15.0	20.9	18.5	21.6	4.0	70.7	1.2	0.4	0.4	6.9	98.9	11.4	14.9	≤ 5.0	*15.4*	118.9
∑2,3,7,8-PCDDs	*684.9*	*1245.1*	*210.6*	*441.1*	*896.9*	*453.1*	*539.4*	*162.1*	*631.1*	*14.7*	*7.2*	*8.3*	*26.9*	*1450.7*	*359.6*	*405.7*	*143.3*	*411.2*	*2224.7*
∑2,3,7,8-PCDFs	*101.5*	*197.2*	*106.5*	*87.3*	*97.7*	*65.6*	*138.5*	*24.2*	*181.7*	*6.7*	*5.6*	*5.9*	*126.4*	*205.4*	75.6	*70.4*	*20.0*	*41.6*	*548.8*
∑2,3,7,8-PCDD/Fs	**786.4**	**1442.4**	**317.1**	**528.8**	**994.6**	**518.7**	**677.8**	**186.4**	**812.8**	**21.4**	**12.8**	**14.3**	**153.3**	**1656.1**	**435.2**	**476.1**	**163.3**	**452.8**	**2773.5**
WHO$_{98}$-TEQ*	***22.1***	***25.7***	***15.8***	***18.4***	***21.7***	***10.4***	***18.6***	***6.9***	***22.6***	***1.0***	***0.7***	***0.8***	***2.89***	***13.8***	**7.6**	***8.7***	***4.3***	***5.3***	***53.4***

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

*** TEQ concentations were calculated as upperbound

** Values are particle phase concentrations except for RV sample that is total (dissolved+particle phase)

nd= not detected due to a bad isotopic ratio

Table 2. Concentrations of the 7 ICES PCBs in air (pg m^{-3}), water colum (pg l^{-1}), surface sediments and mussels (pg g^{-1} dry weight) found in Thau lagoon.

Compounds	Air (gas+particle phase) pg m^{-3}									Mussel (pg g^{-1} d.w.)			Sediment (pg g^{-1} d.w.)			Surface Water (pg l^{-1})**				
	Site IF (14-18 Nov 05)					Site BZ (15-18 Nov 05)				May 04			May 04			Nov 05				
	IF-1	IF-2	IF-3	IF-4	IF-5	BZ-1	BZ-2	BZ-3	BZ-4	M1	M4	M2	T3	T10	T12	T2	C4	T11	T12	RV
TrCB28	8.4	6.4	4.4	4.9	4.5	11.3	7.5	6.5	3.9	118	146	173	158	158	647	0.9	1.2	3.0	3.4	1.7
TeCB-52	8.9	7.8	5.0	5.3	4.9	11.2	6.0	5.3	4.1	92	209	254	n.rs	434	855	1.0	53.6	90.6	155.7	55.3
PeCB-101	8.3	7.7	5.6	5.1	6.9	10.3	5.9	5.3	4.5	955	1972	3543	252	299	5580	78.6	550.9	230.1	389.5	236.7
PeCB-118	n.rp.	n.rp.	n.rp.	n.rp.	n.rp.	n.rp.	n.rp.	n.rp.	n.rp.	802	1554	3327	347	479	5103	15.9	21.7	14.4	14.0	19.9
HxCB-153	10.0	10.3	7.2	6.5	11.1	11.8	7.7	6.3	5.8	5242	11107	18670	1115	1848	11346	18.8	36.6	30.7	37.3	31.1
HxCB-138	7.1	7.3	4.9	5.0	8.5	7.2	5.6	4.7	4.0	2305	6261	12229	441*	908*	7724*	15.8	24.8	20.1	22.0	28.2
HpCB-180	5.3	5.3	4.2	4.2	8.0	5.2	4.9	3.2	3.1	322	388	503	215	317	2064	6.6	19.8	13.1	13.8	16.8
∑ PCBs	**48.1**	**45.0**	**31.2**	**31.0**	**43.9**	**56.9**	**37.6**	**31.3**	**25.4**	**9836**	**21637**	**38699**	**2528**	**4443**	**33319**	**137.6**	**708.5**	**402.2**	**635.6**	**389.7**

n.rp.= not reported; n.rs = not well resolved; *CB138 quantified on DB5 column is not resolved with CB163/164

** Values are the sum of particulate and dissolved phase concentrations

FIGURE LEGENDS

Figure 1. Location of Thau Lagoon (France) and air, water, sediments and mussels sampling sites. Surface sediments and mussels were collected in May 2004 whereas air and water samples were collected in November 2005. Locations in the map are approximated (see coordinates for exact location).

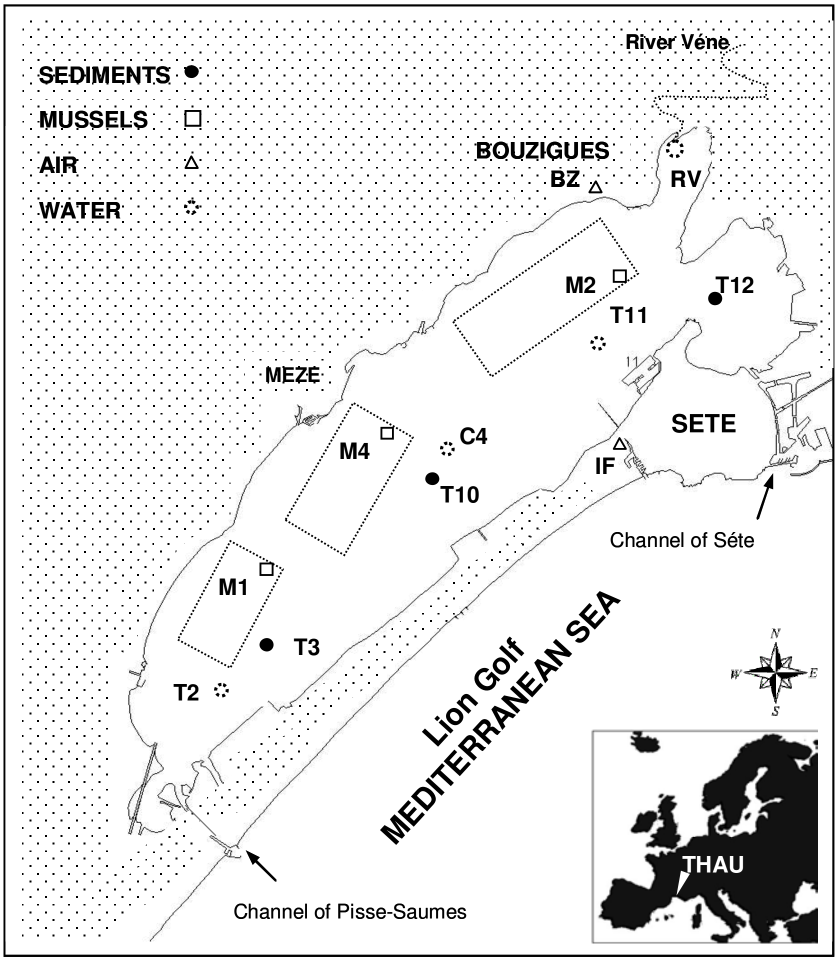
Figure 2. Wind directions and wind speeds registered during the sampling period (14th -19th November 2005) together with the daily sampled intervals for both sites. Temperature varied from 5 to 16 ^{0}C during that period. Precipitation was registered on days 14th and 15th. Data are from Météo France,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

Figure 3. Principal components loading plot and correlation matrix among atmospheric variables and ∑PCBs and ∑PCDD/Fs air concentrations during the sampling week. Values were expressed as mean over the 24h period. Numbers are Pearson R^2 (* $p<0.05$).

Figure 4. Distribution pattern of PCDD/F congeners in air (sum of particuale + gas phases) in both sampling sites, particulate water phase (East, middle, mid-East and West sites), sediment (middle and East sites) and mussels samples (East, middle and West sites) from Thau lagoon.

Figure 5. Distribution pattern of PCB congeners in air gas phase (G), particuale phase (P), and total (G+P) in both air sampling sites, water dissolved phase (D), particulte phase (SPM) and whole water (D+SPM), sediment and mussels samples (East, middle and West sites) from Thau lagoon. G and P patters presented correspond to a selection of IF and BZ samples.

Figure 1



Code	Sample type	Latitude (N)	Longitude (E)	Depth (m)
IF	Air	43°23 51	3°39 34	Sea level
BZ	Air	43°26 26	3°39 01	Sea level
RV	River water (outlet)	43°27 28	3°40 17	Surface
T12	Lagoon water	43°25 79	3°41 02	7.5
T11	Lagoon water	43°25 01	3°39 15	8.5
C4	Lagoon water	43°24 03	3°36 70	9
T2	Lagoon water	43°21 10	3°33 20	4.5
M2	Mussel	43°26 10	3°39 90	1.5
M4	Mussel	43°25 26	3°37 38	1.5
M1	Mussel	43°21 72	3°33 13	1.5
T12	Sediment	43°25 79	3°41 02	7.5
T10	Sediment	43°25 00	3°38 01	9
T3	Sediment	43°21 68	3°33 20	4

Figure 2

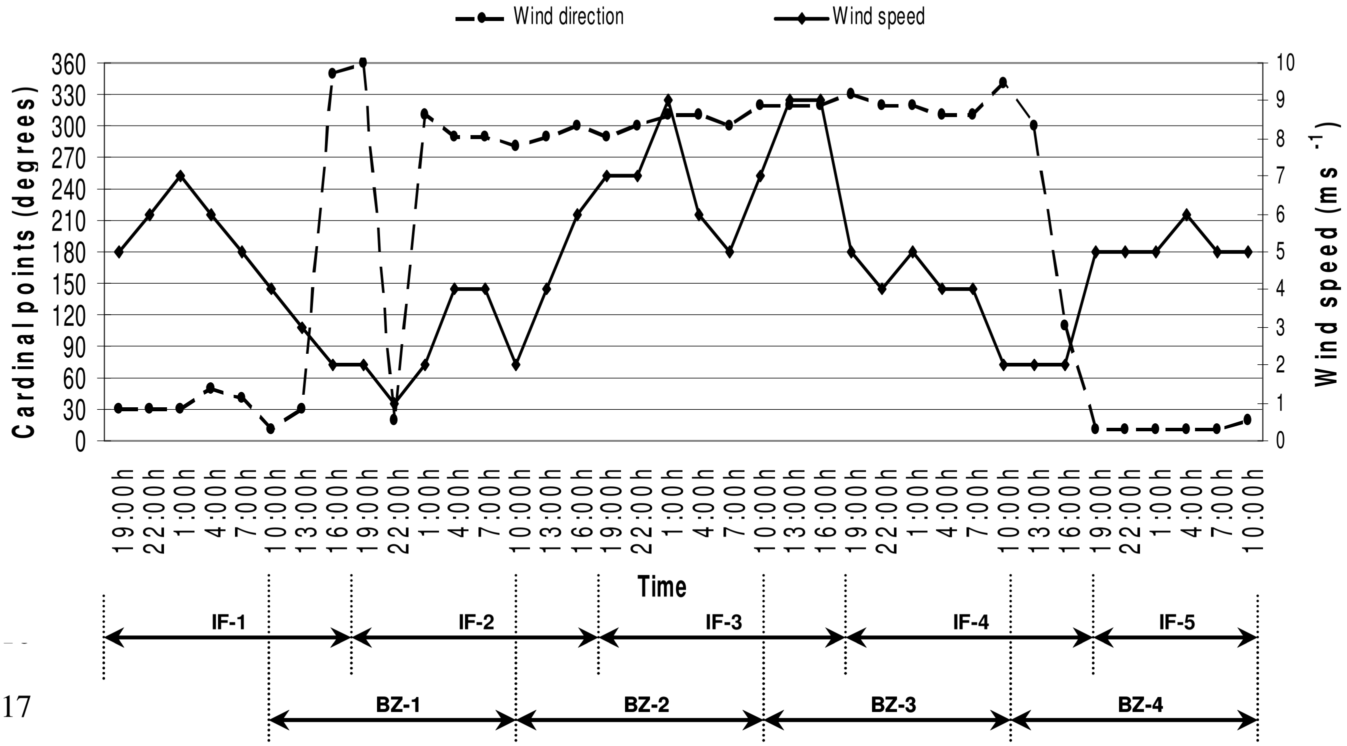
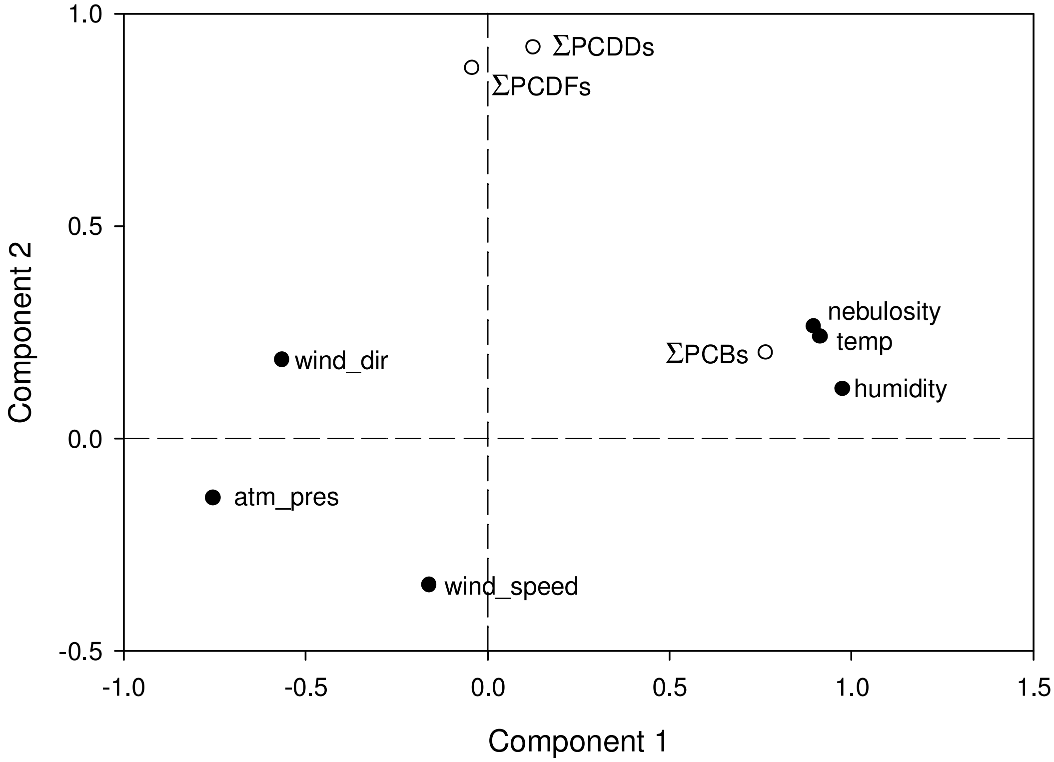
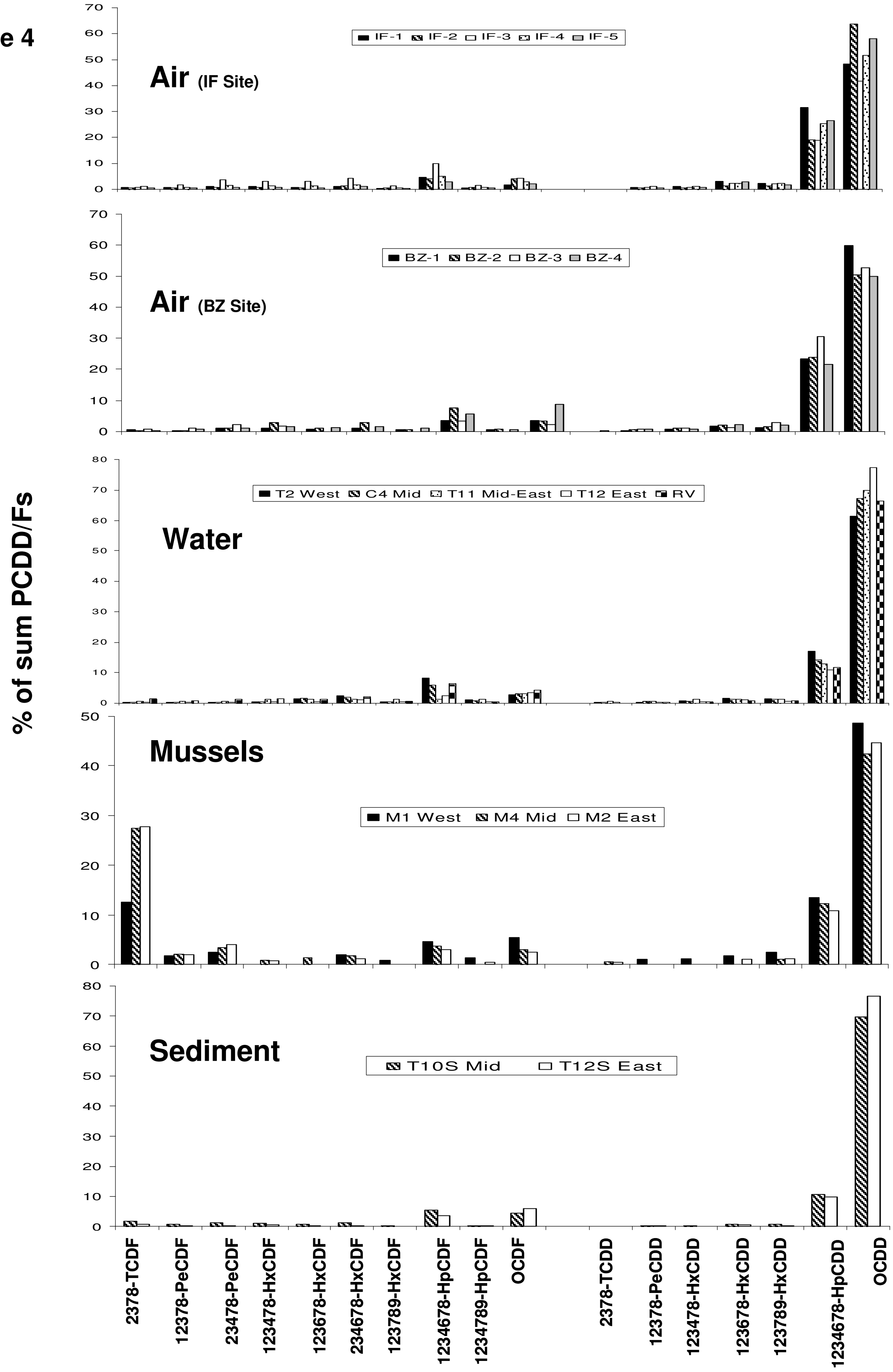

Wind direction
Wind speed
Cardinal points (degrees)
0
30
60
90
120
150
180
210
240
270
300
330
360
Wind speed (m s -1)
0
1
2
3
4
5
6
7
8
9
10
19:00h
22:00h
1:00h
4:00h
7:00h
10:00h
13:00h
16:00h
19:00h
22:00h
1:00h
4:00h
7:00h
10:00h
13:00h
16:00h
19:00h
22:00h
1:00h
4:00h
7:00h
10:00h
13:00h
16:00h
19:00h
22:00h
1:00h
4:00h
7:00h
10:00h
13:00h
16:00h
19:00h
22:00h
1:00h
4:00h
7:00h
10:00h
Time
IF-1
IF-2
IF-3
IF-4
IF-5
BZ-1
BZ-2
BZ-3
BZ-4

Figure 3



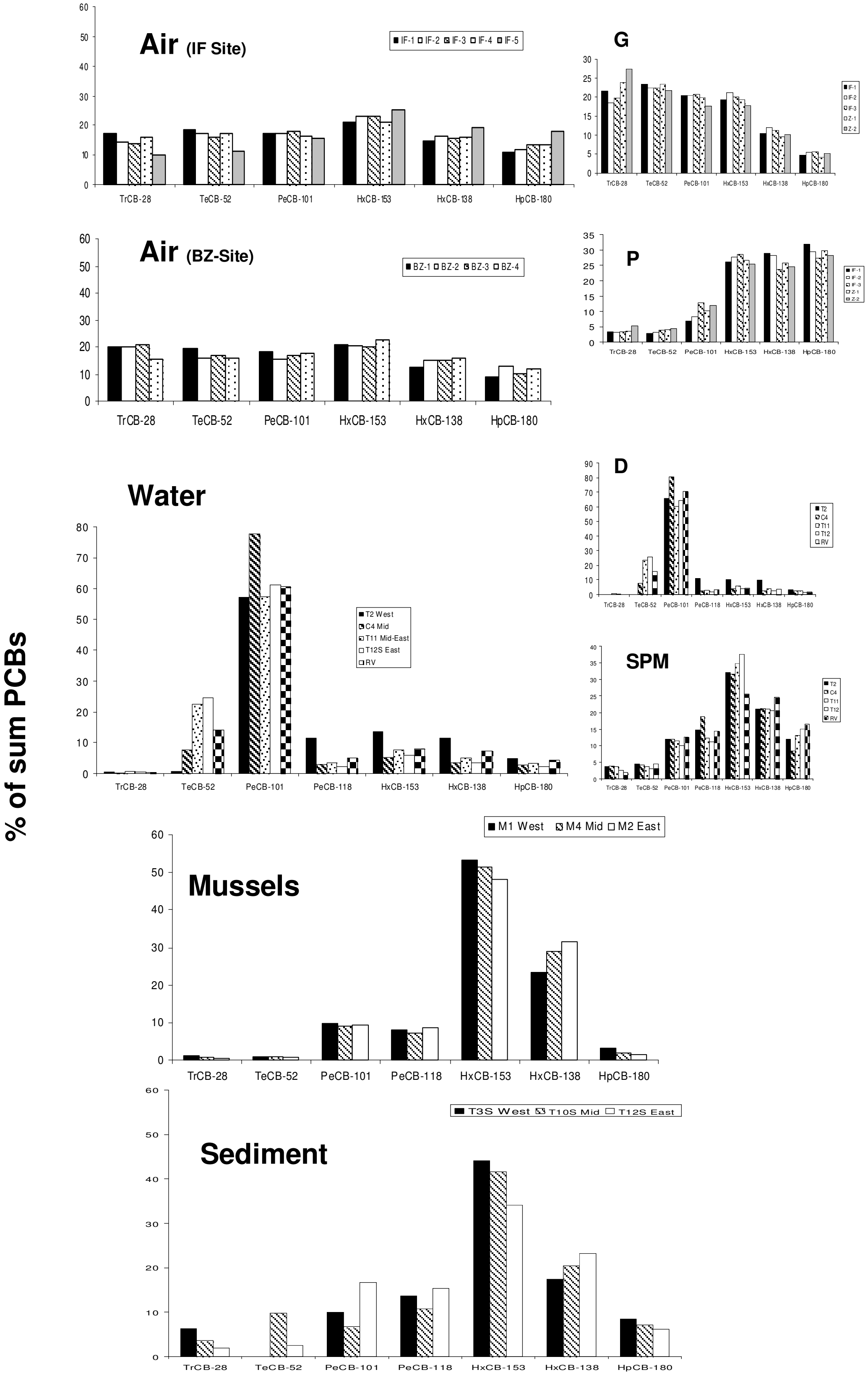
	Temperature	Nebulosity	Humidity	Atm.Press	Wind direction	Wind Speed	∑PCDDs	∑PCBs
Nebulosity	0.9*							
Humidity	0.9*	0.9*						
Atm.Press	-0.9*	-0.6*	-0.8*					
Wind direction	-0.3	-0.6*	-0.5*	0.1				
Wind Speed	-0.1	-0.1	-0.3	-0.1	0			
∑PCDDs	0.2	0.4	0.2	-0.1	0	-0.3		
∑PCBs	0.6*	0.8*	0.7*	-0.4	-0.3	-0.5	0.4	
∑PCDFs	0.3	0.2	0.1	-0.2	0.1	0	0.7*	-0.1

Figure 4



% of sum PCDD/Fs
Air (IF Site)
IF-1
IF-2
IF-3
IF-4
IF-5
Air (BZ Site)
BZ-1
BZ-2
BZ-3
BZ-4
Water
T2 West
C4 Mid
T11 Mid-East
T12 East
RV
Mussels
M1 West
M4 Mid
M2 East
Sediment
T10S Mid
T12S East
0
10
20
30
40
50
60
70
80
2378-TCDF
12378-PeCDF
23478-PeCDF
123478-HxCDF
123678-HxCDF
234678-HxCDF
123789-HxCDF
1234678-HpCDF
1234789-HpCDF
OCDF
2378-TCDD
12378-PeCDD
123478-HxCDD
123678-HxCDD
123789-HxCDD
1234678-HpCDD
OCDD

Figure 5


% of sum PCBs
Air (IF Site)
IF-1 IF-2 IF-3 IF-4 IF-5
Air (BZ-Site)
BZ-1 BZ-2 BZ-3 BZ-4
G
IF-1 IF-2 IF-3 Z-1 Z-2
P
IF-1 IF-2 IF-3 Z-1 Z-2
Water
T2 West
C4 Mid
T11 Mid-East
T12S East
RV
D
T2 C4 T11 T12 RV
SPM
T2 C4 T11 T12 RV
Mussels
M1 West M4 Mid M2 East
Sediment
T3S West T10S Mid T12S East
TrCB-28
TeCB-52
PeCB-101
PeCB-118
HxCB-153
HxCB-138
HpCB-180
0 10 20 30 40 50 60 70 80 90