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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)

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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). $\sum_{2,3,7,8}$ -PCDD/F and \sum_{7} ICES PCB air concentrations (0.2–1.4 and 31–57 $\mu\text{g m}^{-3}$, 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

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

3

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

15

16 Coastal lagoons represent less than 1% of the surface covered by oceans and seas, however
17 they are characterized by a high biodiversity and intense primary production leading to both
18 ecological and economical considerable importance (Nixon, 1982). Such is the case of
19 Thau lagoon, one of the largest Mediterranean lagoons. Located on the French
20 Mediterranean coast along the Gulf of Lion (Figure 1), it covers a surface of 75 km² with an
21 average depth of 4.5 m and is isolated from the Mediterranean Sea by an offshore bar. The
22 lagoon is connected to the sea North-East by the channel of Sète (90% of the exchanges)
23 and South-West by the channel de Pisse-Saumes (10% of exchanges). Winds are often

1 strong in the area with an average of 118.5 days per year above Beaufort force 5 (data from
2 Météo France), in particular when blowing from North-West (Tramontane). Wind has been
3 described as an important variable influencing the lagoon hydrodynamics (Lazure, 1992).
4 There is an intensive shell farming activity (oysters and mussels) that covers about 20% of
5 the whole lagoon area and yearly produces about 15000 tons of oysters. (Gangnery et al.,
6 2001).

7 Thau lagoon seems to be under intense anthropogenic pressure (urban, industrial,
8 agricultural and shell farming activities). The biggest town (Sète) and most of urban
9 activities are located in the Eastern part of the lagoon. A considerable increase of
10 population in the area during the summer months is contributing to the anthropogenic
11 impact. The results of the French Monitoring Network (RNO Réseau National
12 d'Observation) show high contamination of the lagoon sediments by hydrophobic organic
13 compounds compared to other Mediterranean lagoons, especially by polycyclic aromatic
14 hydrocarbons (PAHs) and to a lesser extent by PCBs (Tronczyński, 1998; Leauté et al.
15 2007). However, no information on PCDD/Fs ambient levels in Thau lagoon is available
16 yet. A better knowledge of the fate and dynamics of POPs in this semi-enclosed marine
17 ecosystem is needed in order to apprehend their long-term impacts. The main objectives of
18 this work were: (1) to obtain ambient concentrations, congener patterns and multi-media
19 distribution of PCBs and PCDD/Fs in air, water column, mussel and surface sediment from
20 Thau Lagoon; (2) to generate a data set on multi-media ambient concentrations that serves
21 as a first step for POPs fate modeling validation and future risk assessment in this
22 ecosystem. In addition, some specific aspects regarding the atmospheric input of the
23 pollutants studied will be discussed.

1 **Materials and methods**

2 Sampling

3 Locations of all sampling sites are detailed in Figure 1. Air samples were collected in
4 November 2005 by using high volume samplers at two sites: Ifremer Institute (IF) located
5 on the South shore and Bouzigues (BZ), a small village on the North shore of the lagoon.
6 Air particle phase was retained by using a 102 mm diameter quartz fibre filter (QFF)
7 whereas the gas phase was trapped with a polyurethane foam (PUF) plug of 65 mm
8 diameter, 50 mm length and a raw density of 30 kg m^{-3} . Volumes of $\sim 400 \text{ m}^3$ were
9 collected for each sample (5 samples at IF and 4 at BZ) except for the last one taken at IF
10 site where a volume of $\sim 200 \text{ m}^3$ was sampled.

11 Lagoon water was sampled from a boat also in November 2005 by using pre-equilibrated
12 Teflon tubing and a Teflon membrane pump (ASTI, France) operated with compressed
13 nitrogen. The sample was collected in stainless steel (StS) containers. Four samples (\sim
14 120L) were taken from the lagoon (T12, T11, C4 and T2) and an additional sample ($\sim 80\text{L}$)
15 was also collected at the riverine reference station (outlet of the river Véne, RV) (Figure 1).
16 Once in the laboratory samples were filtered (GFF). The filtrated water was collected in
17 clean StS containers and PCDD/F and PCB ^{13}C -labeled internal standard mixtures were
18 added. Filtrates were then passed through a pre-cleaned (MiliQ-UV and sequential soxhlet
19 extraction with methanol, acetonitrile and dichloromethane, 8h each) and pre-conditioned
20 (methanol) 50g AmberliteTM XAD-2 Teflon column at a flow $\leq 80 \text{ mL/min}$ (Tronczyński et
21 al., 2004, 2005a). The water sample was sucked using a peristaltic pump. Columns were
22 dried by passing air using a vacuum pump. Elution of XAD-2 columns was performed with

1 dichloromethane. Na₂SO₄ anhydrous (baked at 450 °C / 8h) was added, the samples were
2 placed in the freezer for transport and then stored until further processing at the laboratory.

3

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

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

14

15 Analytical determinations

16 PCDD/Fs considered in this work were the 2,3,7,8 congeners since they have been
17 described as the most toxic ones (Van den Berg et al., 1998), whereas PCBs were 28, 52,
18 101, 118, 153, 138 and 180 congeners also referred in the text as the 7 ICES (International
19 Council for the Exploration of the Sea). Air and water samples were analyzed at the Joint
20 Research Centre laboratories whereas sediment and mussels sample analyses were carried
21 out at Ifremer laboratories.

22

23

1 *Air and water samples*

2 QFFs and PUFs were Soxhlet extracted separately with n-hexane/acetone (220:30 v/v) for
3 48 h after being spiked with internal standards (16 ¹³C-labelled 2,3,7,8-chlorine-substituted
4 congeners with 400 pg each, except OCDD with 800 pg). Extract purification was executed
5 with an automated clean-up system (Power-Prep P6, from Fluid Management Systems,
6 Inc., Watertown, MA, USA). The purification method was previously described by Abad et
7 al. (2000). Prior to injection, syringe ¹³C-labelled standards were added to the extracts to
8 determine the recoveries of the internal standards.

9 Regarding water samples, dichloromethane extracts were filtered with pre-cleaned glass
10 wool, concentrated, treated with concentrated H₂SO₄ and cleaned up as indicated for air
11 samples. GFF were thawed, cut into small pieces and transferred into 33mL ASE®
12 (Dionex) cartridges. ¹³C-labelled PCDD/F and PCBs internal standard mixtures were
13 added. The filters were extracted using the Dionex ASE® 300 applying in a 1st extraction
14 methanol (3 cycles each with a static time of 5 min at 75 °C, heat-up time of 5 min, a flush
15 volume of 100%, a purging time of 60s and a pressure of 1500 psi) and in a 2nd extraction
16 hexane (same parameters as for methanol), respectively. The methanol and hexane phases
17 were combined in a separatory funnel. The methanol phase was extracted three more times
18 with ~ 20 mL of hexane and all hexane phases were combined and concentrated to 10 mL.
19 From this point on samples were treated as indicated above for the XAD extracts.
20 Quantification of PCDD/Fs and PCBs was based on isotope dilution using a high resolution
21 gas chromatography – high resolution mass spectrometry (HRGC-HRMS). The method has
22 been previously described (Castro-Jiménez et al., 2008).

23

1 *Mussels and sediment samples*

2 The analytical protocols for extraction, cleanup and analysis have been previously
3 described (Munsch et al., 2005a, 2005b; Tronczyński et al., 2005b; Johansson et al.,
4 2006). Briefly, approximately 5 g (dry weight, d.w.) of mussel sample or 7 g d.w. of
5 sediment were extracted by pressurised solvent extraction (ASE, Dionex Corp., CA) with
6 dichloromethane. For mussel samples, the separation of co-extracted lipids was performed
7 by gel permeation chromatography (GPC). The purified mussel and sediment extracts were
8 concentrated and then further purified and fractionated on a two layer silica/alumina
9 column. Quantification of PCDD/Fs was performed by isotopic dilution using HRGC-
10 HRMS whereas PCBs were analysed by HRGC fitted with two electron capture detectors
11 using two columns.

12

13 Quality assurance/Quality control

14 QFF were baked at 450 °C for 6 h whereas PUFs were soxhlet extracted during at least 24 h
15 with acetone and then dried in a dessicator under vacuum before use. Both cleaned QFF and
16 PUF were wrapped in n-hexane rinsed aluminum foil and placed in a Teflon sealed metallic
17 transport container. Transport (clean filters and PUFs), field, and procedural blanks were
18 collected and processed together with the samples. Field and transport blank values were
19 below the limits of detection (LODs) or at least three times lower than the analyte value for
20 all compound studied, except for PCB-118 that exceeded this QA/QC threshold in some of
21 the air samples. A breakthrough test was performed by placing a smaller PUF plug in series
22 separated ~1 cm from the main PUF in the sampling head. Breakthrough rates for PCDD/Fs
23 were not possible to be calculated due to the fact that the concentrations found in the gas

1 phase (PUFs) both for the sample and the breakthrough PUFs were under the LOD (1 fg m^{-3})
2 ³) whereas the breakthrough rate for ΣPCB in the condition of the sampling period was
3 estimated to be less than 10%. Extraction blanks (QFF and PUFs) were processed for each
4 batch of samples.

5 Regarding water samples, extraction and clean-up analytical blanks were carried out to
6 check background levels. PCDD/F and PCB recoveries for the air gas and particulate phases
7 (PUFs and QFF) and for the water particulate phase (GFF) were in compliance with the
8 specifications of EPA 1613 and EPA 1668 methods, respectively (U.S. EPA., 1994, 1999).

9 However, PCDD/Fs recoveries in the water dissolved phase (XAD) were very low not
10 allowing quality congener quantifications except for the river water sample (RV) where
11 recoveries were sufficient to calculate a LOD. Therefore, PCDD/Fs dissolved water phase
12 concentrations were not taken into account in the present work except for the RV sample.
13 LOD for PCDD/Fs in water samples varied from $1\text{-}5 \text{ fg l}^{-1}$.

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

21 In order to calculate PCB recoveries in mussel and sediment samples, recovery surrogates
22 (CB 30, CB 198, CB 209, TCN) were added to each sample before extraction and were
23 used to control the recovery efficiency of the overall process. However, results were not

1 corrected for recoveries (Johansson et al., 2006). In our laboratory, the average recoveries
2 of internal standards in biota are: CB30 78%, TCN 80%, CB198 97% and CB209 98%
3 (n=65) and in sediments are: CB30 81%, TCN 84%, CB198 80% and CB209 78% (n=25).
4 For PCDD/Fs, ¹³C labelled congeners were added before extraction and calculations were
5 made by isotopic dilution method (Munschy et al., 2005b). Blanks and certified material
6 analyses were included within every batch of six to eight samples. The laboratory routinely
7 participates in the QUASIMEME (Quality Assurance of Information for Marine
8 Environmental Monitoring in Europe) intercomparison exercises for all analysed
9 contaminants.

10

11 Materials

12 TE-1000BL PUF high volume samplers were employed (Tisch Environmental, Inc. USA).
13 PUF plugs were obtained from Klaus Ziemer GmbH (Langerwehe, Germany), QFF (QMA-
14 4 type) and GFF were from Whatman International Ltd (Brentford, Middlesex, UK).
15 Amberlite™ XAD-2 was from Supelco (Bellefonte, Pennsylvania, USA). Teflon columns
16 used for water sampling were SeaStar Ltd type (37 cm length x 19 mm i.d.). All organic
17 solvents were dioxin analysis grade from Sigma-Aldrich (Buchs SG, Switzerland). All
18 gases (Alpha gaz, Italy) used were ultra pure grade suitable for PCDD/Fs analysis. Pre-
19 packed multi-layer silica, basic alumina, and carbon columns were obtained from Fluid
20 Management Systems (FMS) Inc. (Watertown, MA, USA). The standard mixture of native
21 7 ICES PCB used was PCB mix3 (Dr. Ehrenstorfer GmgH, Augsburg, Germany) and for
22 ¹³C-labelled congeners, 68-LCS from Wellington Laboratories (Guelph, Ontario, Canada).
23 EPA-1613CVS, EPA1613LCS+MDF-12346789 and EPA-1613ISS were native, ¹³C-

1 labelled internal and recovery standards, respectively for 17 PCDD/Fs also obtained from
2 Wellington Laboratories.

3

4 **Results and discussion**

5

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

9

10 Ambient concentrations

11 *Air*

12 2,3,7,8-PCDD/Fs air concentrations (particle + gas phase) at IF site ranged from 0.3 to 1.4
13 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
14 23 WHO-TEQ fg m^{-3}). PCDD/Fs were almost exclusively found to be associated to the air
15 particulate phase. Concentrations observed at both locations were low, typical of those
16 reported for rural areas in Europe, and North America (Lohmann and Jones, 1998; Cleverly
17 et al., 2007). Values found in other aquatic environments such as the Lake Maggiore
18 (located in a semi-rural area) in Northern Italy and from rural areas in Catalonia (Spain) are
19 also within the same range (Abad et al., 2004; Castro-Jiménez et al., 2005, 2008) (Table S1,
20 supporting information).

21

22 Σ PCBs air concentrations reported in this study does not include the congener 118 (see
23 QA/QC section). Σ PCB air concentrations (particulate + gas phase) found at IF site ranged

1 from 31 to 48 pg m^{-3} whereas in site BZ varied from 31 to 57 pg m^{-3} (Table 2). PCBs were
2 predominately in the gas phase. This fact has been previously reported (Mandalakis et al.,
3 2002; Totten et al., 2004; Hornbuckle et al., 2006). Concentrations within the same order of
4 magnitude were found in Venice lagoon, in air masses coming from the sea, in Lake
5 Maggiore and in a background/rural site in Crete, Greece (Mandalakis et al., 2001;
6 Gambaro et al., 2004; Manodori et al., 2006; Vives et al., 2007) (Table S2 supporting
7 information).

8

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

14

15 *Meteorological variables influence*

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

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

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

21

22

23

1 *Water*

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

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

18

19 $\sum 7$ ICES PCBs (dissolved + particulate phase) concentrations determined in the water
20 column from Thau Lagoon ranged from 138 to 708 pg l^{-1} , whereas a value of 390 pg l^{-1} was
21 found in the RV sample (Table 2). PCBs were found predominantly associated to the
22 dissolved water phase, especially the lower congeners (80 – 95%). This fact has already

1 been described in the literature for other aquatic systems (Zeng et al., 2002; Maldonado and
2 Bayona, 2002).
3 Concentrations within the same order of magnitude were found for a larger set of PCB
4 congeners in the waters of San Diego Bay, California (Zeng et al., 2002) and in Lake
5 Michigan, in USA (Pearson et al., 1996). Much higher concentrations were found for the 7
6 ICES PCBs in the Daya Bay, a semi-enclosed and anthropogenic impacted bay located in
7 Southern China, (Zhou et al., 2001). Lower PCB concentrations have been reported for
8 other coastal areas or open seas such as, the Black and Baltic seas (Bruhn and McLachlan,
9 2002; Maldonado and Bayona, 2002; Wodarg et al., 2004) (Table S2, supporting
10 information).

11

12 *Sediments*

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

18

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

1 PCDD/F levels were reported for an impacted estuarine system (Houston ship Channel,
2 USA) or for sediments from industrially influenced coastal areas in Southern and Easter
3 Spain (Eljarrat et al., 2005; Suarez et al., 2006). Comparing to another coastal lagoon,
4 levels at T12 were slightly higher than PCDD/F concentrations found in sediments from
5 different parts of Venice Lagoon, except for the industrial channels where a much higher
6 concentration was reported (Dalla Valle et al., 2003) (Table S1, supporting information).
7 Σ PCB concentrations in sediments from the lagoon ranged from 2.5 to 33 ng g⁻¹ d.w.
8 (Table 2). Lower values were measured at the western (T3) and middle (T10) part of the
9 lagoon (Figure 1) whereas the highest concentration was found at the eastern part (T12) as
10 occurred with PCDD/Fs. Again, the spatial variability observed for the contaminant
11 concentrations could not be solely attributed to different sediment OC contents (9.2, 5.1,
12 and 4.2 % at T3, T10 and T12, respectively).

13 PCB concentrations in Thau were comparable with values reported in the literature for
14 various fresh and coastal water ecosystems (Table S2, supporting information) such as,
15 various Mediterranean coastal lagoons, the Lake Maggiore, the Daya Bay, the Lake Taihu
16 (China) and the Qingdao coastal sea also located in China (Moret et al., 2001; Zhou et al.,
17 2001; Zhang and Jiang, 2005; Gómez-Gutiérrez et al., 2007; Pan et al., 2007; Vives et al.,
18 2007).

19

20 *Mussels*

21 2,3,7,8-PCDD/F concentrations ranging from 13 to 21 pg g⁻¹ d.w. (0.7 to 1 WHO-TEQ pg
22 g⁻¹ d.w.) were found for the analyzed mussels in the lagoon. The highest value was
23 observed in the western part of the lagoon (M1) although only a slight difference in the
24 concentrations along the lagoon was found (Table 1). PCDD/Fs concentrations in mussels

1 reported for the English Channel and the Atlantic French coast (Vilaine river bay) are in the
2 same range (Munsch et al., 2005b). The observed values in Thau lagoon were below the
3 threshold of 4 WHO-TEQ pg g⁻¹ w.w. (wet weight) set by the European Commission for
4 fishery products for human consumption (European Commission, 2006).

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

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

21

22

23

1 Congener patterns

2

3 *PCDD/Fs*

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

15

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

19 OCDD and 2,3,7,8-TCDF dominated the distribution patterns of PCDD/Fs in mussel
20 samples and these two congeners accounted for more than 70% of the Σ 2,3,7,8-PCDD/Fs.

21 This profile is similar to results previously published for mussels from other marine and
22 lake waters where the clear predominance of the two mentioned congeners was also

1 observed (Petreas et al., 1992; Abad et al. 2003; Munschy et al., 2005b; Zhang and Jiang,
2 2005; Danis et al., 2006).

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

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

1 water phase in the Baltic Sea but very few data are available in the literature on PCDD/Fs
2 in the dissolved water phase.

3

4 *PCBs*

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

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

1 found predominant in sediments from Taihu Lake in China and anthropogenic impacted site
2 (Zhang and Jiang, 2005).

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

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

14

15 **Conclusions**

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

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

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

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

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1 **References**

2

3 Abad E., Pérez F., Llerena J.J., Saulo J., Caixach J., Rivera J., 2002. Study on
4 PCDDs/PCDFs and co-PCBs content in food samples from Catalonia (Spain).
5 Chemosphere, 46, 1435-1441.

6

7 Abad E, Pérez F, Llerena J J, Caixach J, Rivera J. 2003. Evidence for a specific pattern of
8 polychlorinated dibenzo-*p* dioxins and dibenzofurans in bivalves. Environmental Science
9 and Technology 37, 5090-5096.

10

11 Abad E., Caixach J., Rivera J., gustems L., Massagué G., Puig O. 2004. Temporal trends of
12 PCDDs/PCDFs in ambient air in Catalonia (Spain). Science of the Total Environment 334-
13 335, 279-285.

14

15 Abad E., Saulo J., Caixach J. and Rivera J., 2000. Evaluation of a new automated cleanup
16 system for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in
17 environmental samples. J. Chromatography A 893, 383-391.

18

19 Bayarri S., Baldassarri L.T., Iacovella N., Ferrara F., di Domenico A., 2001. PCDDs,
20 PCDFs, PCBs and DDE in edible marine species from the Adriatic Sea. Chemosphere, 43,
21 601-610.

22

1 Breivik, K., Sweetman, A., Pacyna, J.M., and Jones, K.C., 2002. Towards a global
2 historical emission inventory for selected PCB congeners-a mass balance approach 2.
3 Emissions. *The Science of the Total Environment* 290, 199-224.
4
5 Broman D., Näf c., Rolff C., Zebühr Y., 1991. Occurrence and dynamics of polychlorinated
6 dibenzo-p-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed
7 surface layer of remote coastal and offshore waters of the Baltic. *Environmental Science*
8 *and Technology* 25, 1850-1864.
9
10 Brubaker W.W. JR. and Hites R.A., 1997. Polychlorinated dibenzo-p-dioxins and
11 dibenzofurans: gas-phase hydroxyl radical reactions and related atmospheric removal.
12 *Environmental Science and Technology* 31, 1805-1810.
13
14 Bruzy L.P. and Hites, R.A.,1996. Global mass balance for polychlorinated dibenzo-p-
15 dioxins and dibenzofurans. *Environmental Science and Technology* 30, 1797-1804.
16
17 Bruhn R., and McLachlan M.S., 2002. Seasonal variation of polychlorinated biphenyl
18 concentrations in the souther part of the Baltic Sea. *Marine Pollution Bulletin* 44, 156-163.
19
20 Castro-Jiménez, J., Canuti, E., Christoph, E.H., Eisenreich, S.J., Hanke, G., Mariani, G.,
21 Skejo, H., Umlauf, G., 2005. Tracing atmospheric deposition of PCDD/Fs in Lake
22 Maggiore (Italy): Preliminary results on settling material and sediments. *Organohalogen*
23 *Compounds* 67, 1209-1215.

1 Castro-Jiménez, J., Mariani, G. , Eisenreich, S.J., Christoph, E.H., Hanke, G., Canuti, E.,
2 Skejo, H. and Umlauf, G. 2008. Atmospheric input of POPs into Lake Maggiore (Northern
3 Italy): PCDD/Fs and dioxin-like PCBs profiles and fluxes in the atmosphere and aquatic
4 system. *Chemosphere* 73, S122–S130.

5

6 Cleverly D., Ferrario J., Byrne C., Riggs K., Joseph D., Hartford P. 2007. A general
7 indication of the contemporary background levels of PCDDs, PCDFs and coplanar PCBs in
8 the ambient air over rural and remote areas of the United States. *Environmental Science
9 and Technology* 41, 1537-1544.

10

11 Cousins, I.T., and Jones K.C., 1998. Air-soil exchange of semi-volatile organic compounds
12 (SOCs) in the UK. *Environmental Pollution* 102, 105-118.

13

14 Currado G.M. and Harrad S. 2000. Factors influencing atmospheric concentrations of
15 polychlorinated biphenyls in Birmingham, U.K. *Environmental Science and Technology*
16 34, 78-82

17

18 Dalla Valle M, Marcomini A, Sfriso A, Sweetman A J, and Jones K C. 2003. Estimation of
19 PCDD/F distribution and fluxes in the Venice Lagoon, Italy: combining measurement and
20 modeling approaches. *Chemosphere* 51, 603-616.

21

22 Danis B., Debacker V., Trujilo Miranda C., Dubois Ph. 2006. Levels and effects of
23 PCDD/Fs and co-PCBs in sediments, mussels, and sea stars of the intertidal zone in the

1 southern North Sea and the English Channel. *Ecotoxicology and Environmental Safety* 65,
2 188-200.

3

4 Eisenreich S.J., and Looney B.B., 1981. Evidence for the atmospheric flux of
5 polychlorinated biphenyls to Lake Superior. In: D. Mackay, S. Peterson, S.J. Eisenreich and
6 M.S. Simmons (Eds), *Physical behavior of PCBs in the Great Lakes*. Ann Arbor science
7 Publishers, Ann Arbor, MI, pp 141-153.

8

9 Eljarrat E., De La Cal A., Larrazabal D., Fabrellas B., Fernandez-Alba A.R., Borrull F.,
10 Marce R.M., Barcelo D., 2005. Occurrence of polybrominated diphenylethers,
11 polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in coastal sediments from
12 Spain. *Environmental Pollution* 136, 493-501.

13

14 European Commission, 2006. Commission Regulation (EC) No. 199/ 2006 of 3 February
15 2006 amending Regulation (EC) No. 466/2001 setting maximum levels for certain
16 contaminants in foodstuffs as regards dioxins and dioxin-like PCBs, *Official Journal of the*
17 *European Communities* L 32/34–38.

18

19 Gangnery A., Bacher C., Buestel D. 2001. Assessing the production and the impact of
20 cultivated oysters in the Thau lagoon (Mediterranee, France) with a population dynamics
21 model. *Canadian Journal of Fisheries and Aquatic Sciences* 58, 1012-1020.

22

1 Gossiaux D.C., Landrum P.F., Fisher S.W. 1998. The assimilation of contaminants from
2 suspended sediment and algae by the Zebra Mussel, *Dreissena polymorpha*. 1998.
3 *Chemosphere* 36, 3181-3197.
4
5 Gambaro A., Manodori L., Moret I., Capodoglio G., Cescon P. 2004. Determination of
6 polychlorobiphenyls and polycyclic aromatic hydrocarbons in the atmospheric aerosol of
7 the Venice Lagoon. *Analytical and Bioanalytical Chemistry* 378, 1806-1814.
8
9 Gómez-Gutiérrez A., Garnacho E., Bayona J.M., Albaigés J. 2007. Assessment of the
10 Mediterranean sediments contamination by persistent organic pollutants. *Environmental*
11 *Pollution* 148, 396-408.
12
13 Harrad S.J. and Jones K.C., 1992. A source inventory and budget for chlorinated dioxins
14 and furans in the United Kingdom environment. *The Science of the Total Environment*
15 126, 89-107.
16
17 Harrad S. and Mao H. 2004. Atmospheric PCBs and organochlorine pesticides in
18 Birmingham, UK: concentrations, sources, temporal and seasonal trends. *Atmospheric*
19 *Environment* 38, 1437-1445.
20
21 Hashimoto S., Matsuda M., Wakimoto T., and Tatsukawa R., 1995. Simple sampling and
22 analysis of PCDDs and PCDFs in Japanese coastal seawater. *Chemosphere* 30, 1979-1986.
23

1 Hornbuckle, K.C., Carlson, D.; Swackhamer, D.; Baker, J. and Eisenreich, S.J., 2006.
2 Polychlorinated Biphenyls in the Great Lakes. In: Persistent Organic Pollutants in the Great
3 Lakes (ed. Hites, R. A.), Handbook in environmental Chemistry Series, Springer-Verlag,
4 Heidelberg.

5

6 Johansson I, Moisan K, Guiot N, Truquet I, Munsch C, Tronczyński J. 2006.
7 Polybrominated diphenyl ethers (PBDEs) in mussels from selected French coastal sites:
8 1981-2003. Chemosphere 64, 296-305.

9

10 Knutzen J., Bjerkeng B., Naes K., Schlabach M., 2003. Polychlorinated
11 dibenzofurans/dibenzo-p-dioxins (PCDF/PCDDs) and other dioxin-like substances in
12 marine organisms from the Grenland fjords, S. Norway, 1975–2001: present contamination
13 levels, trends and species specific accumulation of PCDF/PCDD congeners. Chemosphere,
14 52, 745-760.

15

16 Lazure P.,1992. Etude de la dynamique de l'étang de Thau par modèle numérique
17 tridimensionnel. Vieet Milieu 42,137–145.

18

19 Léauté F., Tixier C., Munsch C., Tronczyński J. (2007) Present-day distributions and
20 background concentrations of persistent organic contaminants (PAHs and PCBs) in the
21 sediments of the Mediterranean lagoon (Thau) (to be submitted to Marine Pollution
22 Bulletin).

23

1 Lee K.M., Kruse H., Wassermann O., 1996. The pattern of organochlorines in Mussels
2 *Mytilus edulis* L. from the South West Baltic Sea. Archives of Environmental
3 Contamination and Toxicology 31, 68-76.
4
5 Legendre, Pierre & Louis Legendre. 1998. Numerical ecology. 2nd English Edition. [Elsevier](#)
6 [Science](#) BV, Amsterdam. xv + 853 pages.
7
8 Lohmann R., Brunciak P., Dachs J., Giglioti C.L., Nelson E., Van Ry D., Glenn T.,
9 Eisenreich S.J., Jones J.L. and Jones K.C., 2003. Processes controlling diurnal variations of
10 PCDD/Fs in the New Jersey coastal atmosphere. Atmospheric Environment 37, 959-969.
11
12 Lohmann R.; Green L.J.N., and Jones K.C., 1999. Detailed studies of the factors
13 controlling atmospheric PCDD/F concentrations. Environmental Science and Technology
14 33, 4440 – 4447.
15
16 Lohmann R. and Jones K.C., 1998. Dioxins and furans in air and deposition: a review of
17 levels, behavior and processes. The Science of the Total Environment 219, 53-81.
18
19 Lohmann R., Nelson E., Eisenreich S.J. and Jones K.C., 2000. Evidence of dynamic air-
20 water exchange of PCDD/Fs: a study in the Raritan Bay/Hudson River Estuary.
21 Environmental Science and Technology 34, 3086-3093.
22

1 Mandalakis M., Tsapakis M., and Stephanou E.G., 2001. Optimization and application of
2 high-resolution gas chromatography with ion trap tandem mass spectrometry to the
3 determination of polychlorinated biphenyls in atmospheric aerosols. *Journal of*
4 *Chromatography* 925, 183-196.
5
6 Mandalakis M., Tsapakis M., Tsoga A., and Stephanou E.G., 2002. Gas-particle
7 concentrations and distributions of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in
8 the Atmosphere of Athens (Greece). *Atmospheric Environment* 36, 4023-4035.
9
10 Manodori L., Gambaro A., Moret I., Capodoglio G., Cairns W.R.L., Cescon P. 2006.
11 Seasonal evolution of gas-phase PCB concentrations in Venice Lagoon Area. *Chemosphere*
12 62, 449-458.
13
14 Maldonado C., and Bayona J.M., 2002. Organochlorine compounds in the north-western
15 Black Sea water: distribution and water column process. *Estuarine, Coastal and Shelf*
16 *Science* 54, 527-540.
17
18 Moret I., Piazza R., Benedetti M., Gambaro A., Barbante C., Cescon P. 2001.
19 Determination of polychlorobiphenyls in Venice Lagoon sediments. *Chemosphere* 43: 559-
20 565.
21
22 Munsch C., Tronczyński J., Héas-Moisan K., Guiot N., Truquet I., 2005a. Analyse de
23 contaminants organiques (PCB, OCP, HAP) dans les organismes marins. Ed. ISBN 2-
24 84433-144-0, Méthodes d'analyse en milieu marin, 44p.
25
26 Munsch C, Johansson I, Guiot N, Héas-Moisan K, Tronczyński J. 2005b. Retrospective
27 monitoring of the contamination of marine mussels from the French Coasts by PCDD/Fs

1 (1981-2004). *Organohalogen Compounds* 67, 1243-1246.

2

3 Nixon S.W., 1982. Nutrients, primary production, and fisheries yields in coastal lagoons.

4 *Oceanol.Acta* 5, 357-371.

5

6 Pan J., Yang Y-L., Xu Q., Chen D-Z., Xi D-L. 2007. PCBs, PCNs and PBDEs in sediments

7 and mussels from Qingdao coastal sea in the frame of current circulations and influence of

8 sewage sludge. *Chemosphere* 66, 1971-1982.

9

10 Pearson R.F., Hornbuckle C., Eisenreich S.J., and Swackhamer D.L., 1996. PCBs in Lake

11 Michigan water revisited. *Environmental Science and Technology* 30, 1429-1436.

12

13 Petreas M.X., Wiesmüller T., Palmer F.H., Winkler J.J. and Stephens R.D. 1992. Aquatic life

14 as bimonitors of dioxins/furan and coplanar polychlorinated biphenyl contamination in the

15 Sacramento-San Joaquin river delta. *Chemosphere* 25, 621-631.

16

17 Piersanti A., Scrucca L., Galarini R., Tavolini T., 2006. Polychlorobiphenyls (18 congeners) in

18 mussels from middle Adriatic Sea. *Organohalogen Compounds* 68, 1951-1954.

19

20 Porte C., and Albaigés J. 1993. Bioaccumulation patterns of hydrocarbons and polychlorinated

21 biphenyls in bivalves, crustaceans, and fishes. *Archives of Environmental Contamination and*

22 *Toxicology* 26, 273-281.

23

1 Réseau National d'Observation de la qualité du milieu marin littoral (RNO)
2 (<http://www.ifremer.fr/envlit/surveillance/rno.htm>)
3
4 Rose C.L., McKay W.A., 1996. PCDDs (dioxins) and PCDFs (furans) in selected UK lake
5 and reservoir sites-concentrations and TEQs in sediments and fish samples. The Science of
6 the Total Environment 177, 43-56.
7
8 Safe S., 1984. Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs):
9 Biochemistry, toxicology and mechanism of action. Critical Reviews in Toxicology 13,
10 319-395.
11
12 Safe S., 1990. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs),
13 dibenzofurans (PCDFs) and related compounds: Environmental and mechanistic
14 considerations which support the development of toxic equivalency factors (TEFs). Critical
15 Reviews in Toxicology 21, 51-88.
16
17 Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., 2003, Environmental Organic
18 Chemistry, 2nd Edition, Wiley Interscience, New York.
19
20 Simcik M.F., Basu I., Sweet C.W., Hites R.A. 1999. Temperature dependence and temporal
21 trends of polychlorinated biphenyl congeners in the Great Lakes atmosphere.
22 Environmental Science and Technology 33, 1991-1995.
23

1 Suarez M.P., Rifai H.S., Palachek R. Dean, K., and Koenig L., 2006. Distribution of
2 polychlorinated dibenzo-p-dioxins and dibenzofurans in suspended sediments, dissolved
3 phase and bottom sediment in the Houston ship Channel. *Chemosphere* 62, 417-429.
4

5 Swackhamer D.L., McVeety B.D., and Hites R.A., 1988. Deposition and evaporation of
6 polychlorinated biphenyls to and from Siskewit Lake, Isle Royale, Lake Superior.
7 *Environmental Science and Technology* 22, 664-672.
8

9 Totten L.A., Gigliotti C.L., Vanry D.A., Offenber J.H., Nelson E.D., Dachs J., Reinfelder
10 J.R. and Eisenreich S.J., 2004. Atmospheric concentrations and deposition of
11 polychlorinated biphenyls to the Hudson River estuary. *Environmental Science and*
12 *Technology* 38, 2568-2573.
13

14 Tronczyński 1998 in *Surveillance du milieu marin. Travaux du Réseau National*
15 *d’Observation du milieu marin. Edition 1998.*
16

17 Tronczyński J., Catherine Munsch, Karine Moisan, Nadège Guiot, Isabelle Truquet,
18 Nathalie Olivier, Sophie Men and Audrey Furaut. 2004. Contamination of the Bay of
19 Biscay by polycyclic aromatic hydrocarbons (PAHs) following the T/V «*Erika*» oil spill.
20 *Aquatic Living Resources* 17, 243-259.
21

22 Tronczyński J., Munsch C., Héas-Moisan K., Guiot N., Truquet I., 2005a. Analyse de
23 contaminants organiques (herbicides, PCB, OCP, HAP) dans les eaux estuariennes et
24 marines côtières. Ed. ISBN 2-84422-148-3, *Méthodes d’analyse en milieu marin*, 52p.
25

1 Tronczyński J., Munsch C., Héas-Moisan K., Guiot N., Truquet I., 2005b. Analyse de
2 contaminants organiques (PCB, OCP, HAP) dans les sédiments marins. Ed. ISBN 2-84433-
3 145-9, Méthodes d'analyse en milieu marin, 44p.
4

5 Tysklind M., Fangmark I., Marklund S., Lindskog A., Thaning L., and Rappe C., 1993.
6 Atmospheric transport and transformation of polychlorinated dibenzo-p-dioxins and
7 dibenzofurans. *Environmental Science and Technology* 27, 2190-2197.
8

9 U.S. EPA., 1994. Method 1613: Tetra-through Octa-Chlorinated Dioxins and Furans by
10 Isotope Dilution HRGC/HRMS. U.S. EPA., 1999. Method 1668, revision A: Chlorinated
11 Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS.
12

13 U.S. EPA., 1999. Method 1668, revision A: Chlorinated Biphenyl Congeners in Water,
14 Soil, Sediment and Tissue by HRGC/HRMS.
15

16 Van den Berg, M., Birnbaum L., Bosveld A.T.C., Brunström B., Cook P, Feeley M., Giesy
17 J.P., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J. C., van Leeuwen
18 R.F.X., Djen Liem A.K., Nolt C., Peterson R.E., Poellinger L., Safe S., Schrenk D., Tillitt
19 D., Tysklind M., Younes M., Wærn F., and Zacharewski T., 1998. Toxic Equivalency
20 Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. *Environmental Health*
21 *Perspectives* 106, 775-792.
22

23 Vives I., Canuti E., Castro-Jiménez J., Christoph E.H., Eisenreich S.J., Hanke G., Huber T.,
24 Mariani G., Mueller A., Skejo H. Umlauf G., Wollgast J. 2007. Occurrence of

1 polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated
2 biphenyls (PCBs) and polybrominated diphenyls ethers (PBDEs) in Lake Maggiore (Italy
3 and Switzerland). *Journal of Environmental Monitoring* 9, 589-598.

4

5 Wania F., Haugen J-E., Lei Y.D., Mackay D. 1998. Temperature dependence of
6 atmospheric concentrations of semivolatile organic compounds. *Environmental Science and*
7 *Technology* 32, 1013-1021.

8

9 Wodarg, D., Kömp P., McLachlan M.S., 2004. A baseline study of polychlorinated
10 biphenyl and hexachlorobenzene concentrations in the western Baltic Sea and Baltic
11 Proper. *Marine Chemistry* 87, 23-36.

12

13 Zeng E.Y., Peng, J., Tsukada D., and Ku T-L., 2002. In situ measurements of
14 polychlorinated biphenyls in the waters of San Diego Bay, California. *Environmental*
15 *Science and Technology* 36, 4975-4980.

16

17 Zhang Q., Jiang G. 2005. Polychlorinated dibenzo-p-dioxins/furans and polychlorinated
18 biphenyls in sediments and aquatic organisms from the Taihu Lake, China. *Chemosphere*
19 61, 314-322.

20

21 Zhou J.L., Maskaoui K., Qiu Y.W., Hong H.S., and Wang Z.D. 2001. Polychlorinated
22 biphenyl congeners and organochlorine insecticides in the water column and sediments of
23 Daya Bay, China. *Environmental Pollution* 113, 373-384.

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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 concentrations 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

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Table 2. Concentrations of the 7 ICES PCBs in air (pg m⁻³), water column (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

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3 **FIGURE LEGENDS**

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

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

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

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

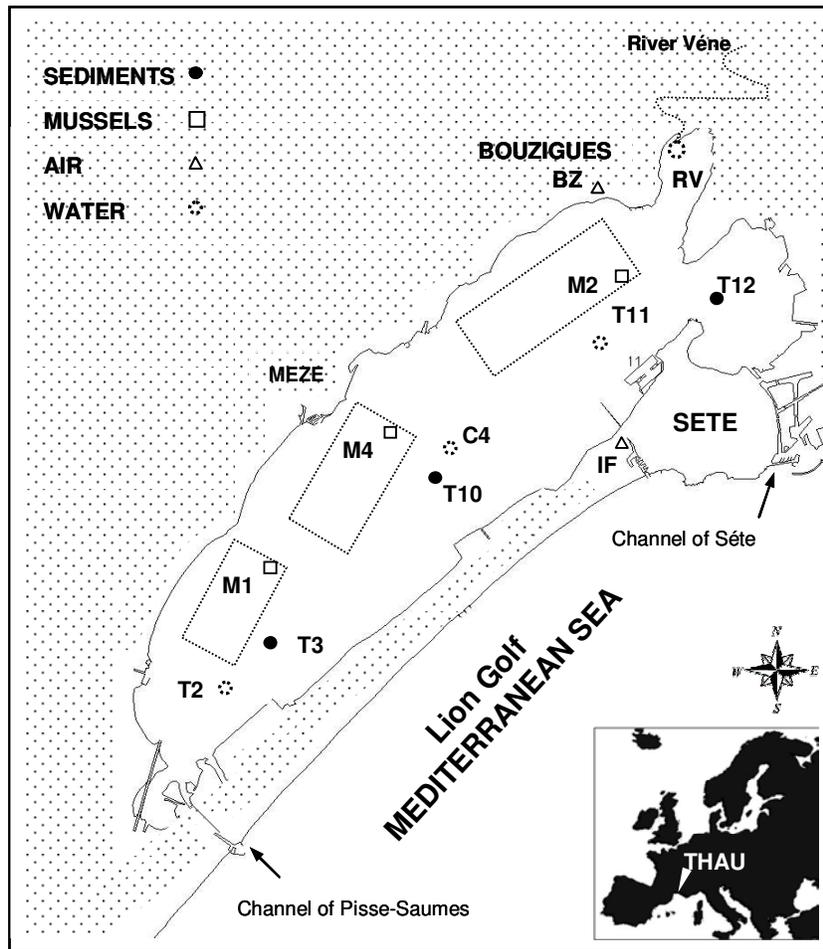
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26 **Figure 5.** Distribution pattern of PCB congeners in air gas phase (G), particulate phase (P),
27 and total (G+P) in both air sampling sites, water dissolved phase (D), particulate phase
28 (SPM) and whole water (D+SPM), sediment and mussels samples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

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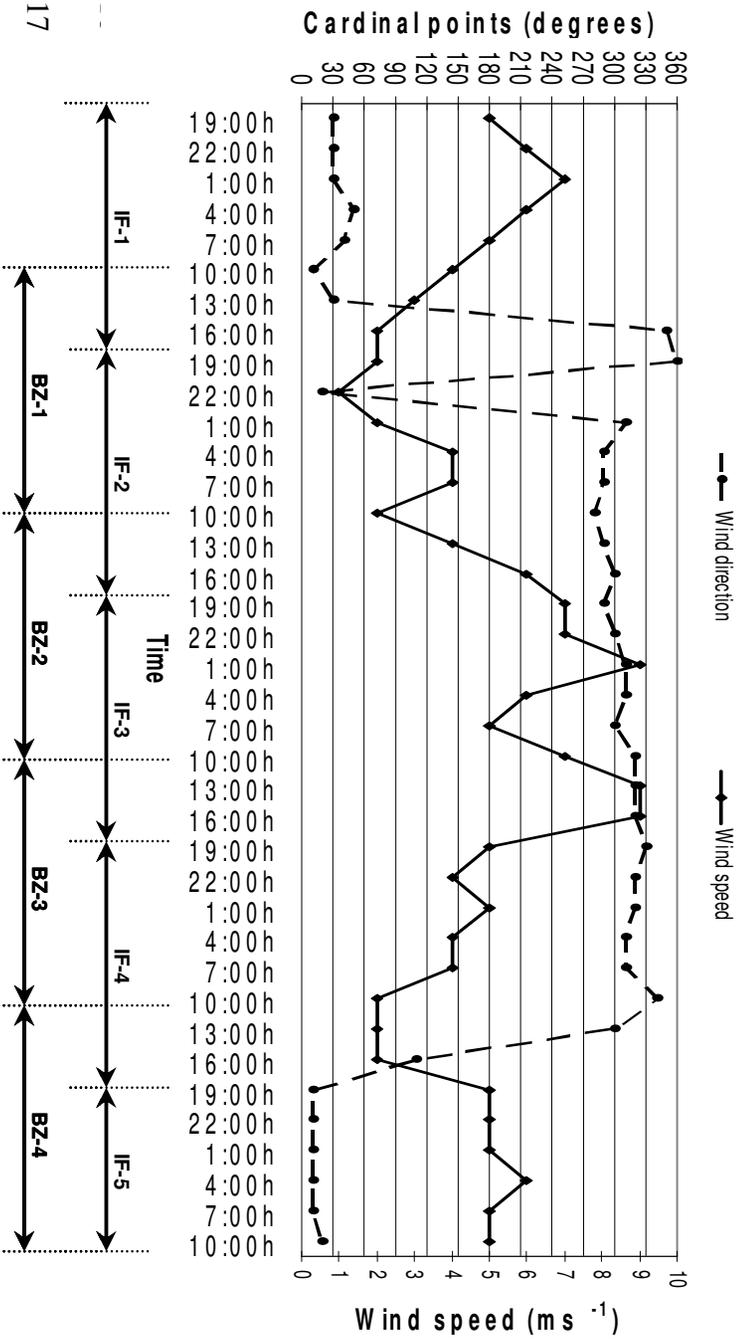
Figure 1



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

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Figure 2

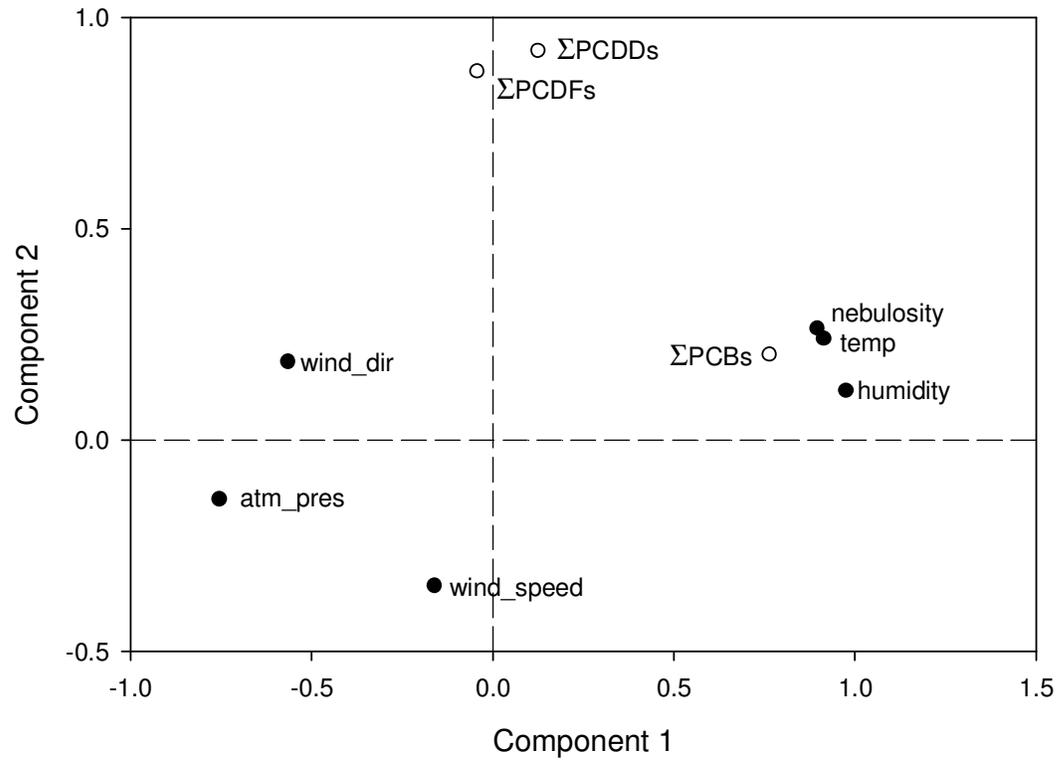


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Figure 3

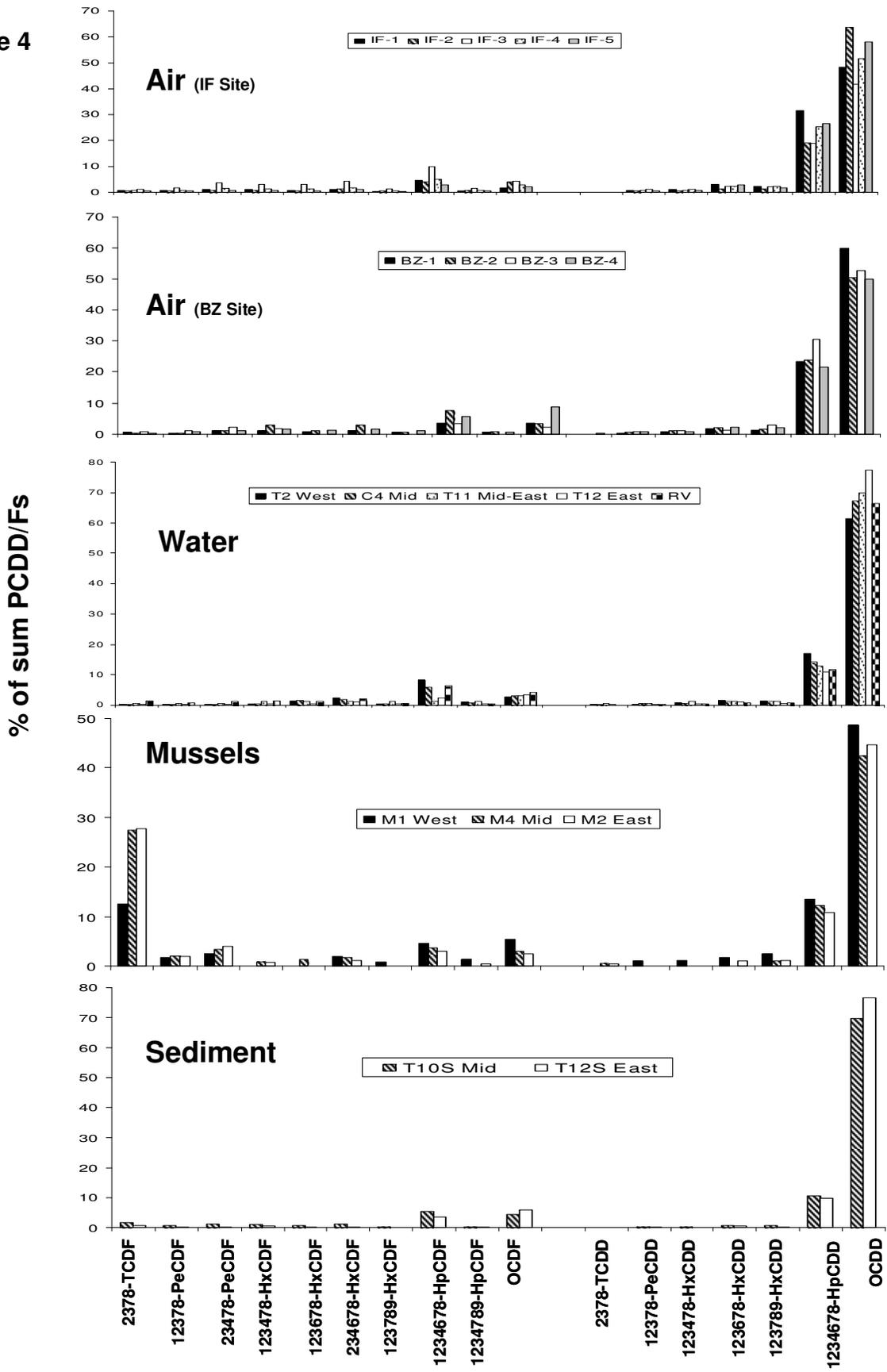


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	Temperature	Nebulosity	Humidity	Atm.Press	Wind direction	Wind Speed	ΣPCDDs	ΣPCBs
Nebulosity	0.9*							
Humidity	0.9*	0.9*						
Atm.Press	-0.9*	-0.6*	-0.8*					
Wind direction	-0.3	-0.6*	-0.5*	0.1				
Wind Speed	-0.1	-0.1	-0.3	-0.1	0			
ΣPCDDs	0.2	0.4	0.2	-0.1	0	-0.3		
ΣPCBs	0.6*	0.8*	0.7*	-0.4	-0.3	-0.5	0.4	
ΣPCDFs	0.3	0.2	0.1	-0.2	0.1	0	0.7*	-0.1

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Figure 4



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Figure 5

