Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France)

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Abstract:

Atmospheric concentrations and deposition fluxes of PCDD/F and PCB have been evaluated over a 1-year period in a Mediterranean coastal lagoon (Etang de Thau, France). Indicative PBDE air concentrations in the hot season are also reported in this work. $\sum$2,3,7,8-PCDD/Fs and $\sum$18PCBs (gas + particulate) air concentrations ranged from 67 to 1700 fg m^{-3} and from 13 to 95 pg m^{-3}, respectively whereas $\sum$8PBDEs (gas + particulate) summer time levels varied from 158 to 230 pg m^{-3}. The PCDD/F and PCB atmospheric occurrence over Thau lagoon and subsequent inputs to the surface waters are determined by an assemble of factors, being the seasonality of atmospheric concentration, the air mass origin and meteorological conditions important drivers. Total (wet + dry) $\sum$2,3,7,8-PCDD/Fs and $\sum$18PCBs deposition fluxes to Thau Lagoon waters are 117 and 715 pg m^{-2} d^{-1}, respectively.

Highlights

► PCDD/F and PCB atmospheric concentrations in Thau lagoon are typical from rural/semi-rural areas. ► PBDE atmospheric concentrations in Thau lagoon are typical from urban/industrial sites. ► PCDD/F and PCB atmospheric concentrations over Thau lagoon and inputs to surface waters are very variable, even changing between the same week of the month in two consecutive years. ► Metallurgical industry may be a possible local source of PCDD/Fs in the Thau lagoon basin. ► Annual PCBs and PCDD/Fs atmospheric inputs are dominated by dry deposition

PCDD/F and PCB atmospheric concentrations over Thau lagoon and inputs to surface waters are very variable, even changing between the same week of the month in two consecutive years.

1. **Introduction**

Persistent organic pollutants (POPs) present in the atmosphere may participate in exchange or deposition mechanisms that will determine their inputs to open waters and coastal areas of the sea ([Agrell et al., 2002], [Jurado et al., 2004] and [Jurado et al., 2005]). In addition, physico-chemical properties of POPs may favor long range atmospheric transport to other areas, even reaching remote zones ([Wania and Mackay, 1996] and [Lohmann et al., 1999a]). After deposition these contaminants are distributed into various environmental compartments, bioaccumulate and are considered potent toxicants, capable of producing a wide spectrum of adverse health effects in biota and humans ([Safe, 1984], [Safe, 1990] and [Vreugdenhil et al., 2002]). POP airborne concentrations in a specific region will be driven by local emissions as well as inputs arriving from other areas. Local inputs are mainly derived from on-site industrial and agricultural activities, vehicles, residential heating facilities and POPs mobilization from environmental reservoirs (e.g. soils, vegetation or water bodies) present in the area

1 (Cousins and Jones, 1998, Lohmann et al., 2000; Br z et al., 2000; Kulkarni et al., 2008).

2 Airborne concentrations then will be determined by the pollutant amounts transported from

3 adjacent or more distant areas (Wania and McKay, 1996, Cleverly et al., 2007) and

4 governed by dominant air mass trajectories and winds.

5

6 Short-term surveys are usually performed in order to acquire punctual data on pollutant

7 ambient levels and in order to have a first estimation on the status of a given environment.

8 However, longer term campaigns are needed to better understand the system dynamics as

9 well as to provide comprehensive datasets. Data on POPs atmospheric concentrations and

10 deposition are also valuable for the environmental exposure assessment (as part of the risk

11 assessment) and for contaminant fate model development and validation. This work

12 presents and discusses a one year dataset on POPs atmospheric concentrations and

13 deposition (wet and dry) in a Mediterranean coastal location. The Thau lagoon (France) is

14 one of the largest Mediterranean lagoons with an intensive shell farming activity (oysters

15 and mussels), covering about 20% of the lagoon, and produces about 15000 tons of oysters

16 yearly (Gangnery et al., 2001). A detailed site description has been reported elsewhere

17 (Castro-Jiménez et al, 2008). The Thau lagoon is under intense anthropogenic pressure

18 (urban, industrial, port, agricultural and shell farming activities). POPs ambient levels have

19 been studied over the last decades in this system, being research mainly focused in the

20 aquatic compartment (i.e. sediment and mussels). Results from the French Monitoring

21 Network for Chemical Contamination (ROCCH) reported high contamination levels in

22 lagoon sediments of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated

23 biphenyls (PCBs) and to a lower extent of organochlorine pesticides (DDTs, DDEs, DDDs,

1 lindane) (ROCCH website; Tronczynski 1998; Léauté 2008). In addition, polychlorinated

2 dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polybrominated diphenylethers

3 (PBDEs) ambient levels have been reported in sediment and mussels (Johansson et al.,

4 2006, Castro-Jiménez et al., 2008; Munschy et al., 2008; Hong et al., 2009) and PCB and

5 PCDD/Fs in water (Castro-Jiménez et al., 2008). However, little information is available on

6 POPs atmospheric levels and potential inputs to the lagoon. Results from a 1-week

7 experimental campaign in this ecosystem (Castro-Jiménez et al, 2008) and preliminary

8 modeled PCDD/F deposition fluxes (Dueri et al., 2010) highlighted the important role of

9 the atmosphere in the accumulation of PCDD/Fs in the lagoon.

10 In this work, the sampling period has been expanded to 1 year and the target contaminants

11 now include dioxin-like (DL)-PCBs and polybrominated diphenylethers (PBDEs), in

12 addition to PCDD/Fs and indicator PCBs. These three POPs families enter the environment

13 as a result of anthropogenic activities although their sources are different. PCDD/Fs occur

14 as unintentional byproducts of chemical manufacturing and incineration processes (Harrad

15 and Jones, 1992; Bruzy and Hites, 1996) whereas, PCBs were mainly used by the power

16 industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants.

17 Current emissions to the environment are urban/industrial centers, landfills, open burning

18 of products containing PCBs, waste incinerations, accidental fires and re-volatilization from

19 environmental reservoirs (Cousins and Jones; 1998, Breivik et al., 2002). PBDEs constitute

20 an important group of brominated flame retardants and, unlike PCBs, are still being used as

21 additives in commercial products (especially in electrical equipment and textiles) to meet

22 fire safety regulations (Law et al., 2006).

1　The objectives of this work are: (1) to gather in-depth knowledge on the PCDD/Fs, PCBs,

2　and PBDE atmospheric occurrence and ambient levels over Thau lagoon; (2) to estimate

3　the wet and dry atmospheric deposition fluxes of these POP families to surface waters of

4　this ecosystem.

5

6　**2. Experimental**

7　*2.1 Air sampling and site description*

8　Sampling equipment details and materials are presented in supporting information.

9　Integrated air samples were collected during the period February 2007-2008 by using a

10　high volume air sampler. The sampler was set up at the Ifremer Institute, located on the

11　south shore of Thau lagoon (43°23 51 N, 3°39 34 E). Location of the lagoon and the

12　sampling station has been described elsewhere (Castro-Jiménez et al, 2008), see Figure S1.

13　The sampling head module integrated a quartz fibre filter (QFF) of 102 mm diameter for

14　the air particulate phase collection and a polyurethane foam (PUF) plug of 65 mm diameter,

15　75 mm length and 0.22 g cm^{-3} of density for the gas phase trapping, according to the U.S.

16　EPA TO-9A Method (US EPA, 1999a). The sampler was operated once a month for a

17　period of 7 days. A total of 13 samples was collected the average volume being ~ 1400 m^{3}.

18　Atmospheric temperature and pressure were recorded at the site. In addition, temperature,

19　precipitation, relative humidity and wind direction and speed for the sampling period were

20　obtained from the Météo-France meteorological station at Sète. Sampling details are

21　presented in Table S1.

22

23

1   2.2. *Analytical determinations*

2   Details on the extraction and analytical procedures are presented in supporting information

3   (Text S1). Briefly, QFFs and PUFs were Soxhlet extracted separately with n-

4   hexane/acetone (220:30 volume/volume) for 24 hours after being spiked with ^{13}C-labeled

5   PCDD/Fs, PCBs and PBDE internal standards. Extract purification was executed with an

6   automated clean-up system. This method, previously used in our laboratory, has proven a

7   high quality purification of the studied POPs (Vives et al., 2007). Two fractions were

8   collected: one containing mono-ortho PCBs, indicator PCBs and PBDEs and one

9   containing non-ortho PCBs and PCDD/Fs. Purified extracts were concentrated to near

10   dryness, ^{13}C-syringe standards were added and a final volume of 30 µl was adjusted.

11   Analyses of PCDD/Fs, PCBs and PBDEs were performed by isotopic dilution high

12   resolution gas chromatography ó high resolution mass spectrometry (HRGC-HRMS)

13   according to EPA1613, EPA 1668 and EPA 1614 methods (US EPA, 1994, 1999b, 2003).

14

15   *2.3. Quality assurance /Quality control (QA/QC)*

16   QFF were individually wrapped in aluminum foil, baked at 450 ºC for 8 h and then stored

17   at -18 ºC in a sealed plastic bag until used. PUFs were Soxhlet extracted with acetone

18   during at least 24 hours before use, dried in a dessicator under vacuum and individually

19   wrapped in n-hexane rinsed aluminum foil. Both cleaned QFF and PUF were placed in a

20   Teflon sealed metallic transport container. Field blanks, consisting on cleaned QFFs and

21   PUF mounted in the sampling head, transported to the sampling area, mounted in the

22   sampler, dismounted and transported back to the laboratory were also collected and then

23   processed together with the samples. Procedural blanks (sampling) consisting on clean

1   filters and PUFs (packed in the lab and untouched until analysis) were employed in order to

2   evaluate the potential contamination of samples due to handling and storage during the

3   sampling campaign. Procedural blanks (analysis) consisting on only extracting solvent

4   (Soxhlet extracted and cleaned-up as for the samples) were also processed for each batch of

5   fourteen samples. Procedural blanks showed similar levels to field blanks so no

6   contamination of samples during storage in the laboratory or transport occurred.

7   Breakthrough was tested in a previous campaign in the same place and similar conditions

8   and was found to be Öl0 % (Castro-Jiménez et al., 2008).

9   PCDD/F and PCB blank values were in general at limit of detection (LOD) levels except

10   for some congeners, for which the average concentrations estimated using the levels

11   measured in both PUF and filter blanks were Ö 8 % of the concentrations measured in the

12   samples (Tables 1 and 2). A quantification problem occurred for PCDD/Fs and PCBs in the

13   particulate phase samples corresponding to April and November 2007. Concentrations for

14   those samples are not reported. Since PCDD/Fs were predominant in the particulate phase,

15   April and November total concentrations were excluded for discussion (Table 1). In the

16   case of total PCB concentrations (driven by gas phase concentrations), only gas phase

17   concentrations were considered for discussion for the mentioned months (Table 2).

18   Gas phase PBDE blank values for all congeners measured were in general equal or higher

19   than the concentrations measured in the samples except for three of them (corresponding to

20   the months of May, July and August 2007). Samples presenting high blank levels were not

21   considered. Particulate phase blank levels were high only in four samples, which were

22   discharged. For the accepted samples, Û8PBDEs average blank values were Ö 4 and 15 %

23   of the gas and particulate phase Û8PBDE concentrations (18% in only one case),

1 respectively (Table S6). Discussion on PBDE occurrence and ambient levels only

2 considered the three months were both gas and particulate phase concentrations were

3 available, corresponding to the warm period of the year (May, July and August 2007).

4 POPs concentrations reported were not corrected for blank values.

5 Standards (natives + ^{13}C-compounds) were introduced in the chromatographic sequence to

6 evaluate possible variations during the time of analyses. Chromatographic peaks of target

7 compounds were only considered when complying with the following QA/QC criteria: (1)

8 the retention time of target compounds were ± 3s of those observed for the corresponding

9 standards; (2) experimental isotopic ratios of natives compounds were within ± 20% of the

10 theoretical ratio and (3) peaks were at least 3 times higher than the noise. LODs were

11 calculated on the basis of a signal to noise ratio of 3/1 in real samples (therefore taking into

12 account the matrix effect and the influence of both processing and analytical steps) and

13 ranged from 0.01 to 5 fg m^{-3} depending on the POPs family, congener and sample analyzed.

14 PCDD/F, PCB and PBDE average recoveries throughout the whole analytical method

15 (extraction-cleanup-analysis) ranged from 46 to 84 %, 34 to 97% (except for CBs-28 and

16 52: 21%) and 62 to 130% (except for BDE-28: 38%), respectively. Results were corrected

17 by recoveries (isotopic dilution method).

18

19 *2.4. Wet and dry deposition fluxes*

20 Atmospheric concentrations (gas and particle phase) of PCBs and PCDD/Fs were combined

21 with temperature and rainfall measured at the meteorological station in Sète in order to

22 estimate the wet and dry deposition fluxes as well as to study their seasonality in Thau

23 lagoon. Gaseous and particulate atmospheric concentrations were interpolated using a

1   polynomial fitting approach in order to have a continuous time series. The methodology

2   used to calculate dry and wet deposition is similar to the one described in Castro-Jiménez et

3   al. (2009) to estimate PCBs deposition in the Lago Maggiore area. Equations and approach

4   used are described in detail in the supplementary material (Text S2). The results from this

5   calculation only provide indicative estimation of fluxes that should be eventually validated

6   by experimental measurements.

7

8   *2.5. Statistics*

9   Principal component analysis (PCA) was performed using the software package SPSS. As

10   proposed by Zhu et al. (2008) data were normalize before PCA calculation in order to

11   reduce the effect of concentration differences among congeners. OCDD concentration

12   dominated the Thau samples and most of the emission source fingerprints, so the

13   mentioned congener could overwhelm the influence of less dominant congeners during

14   normalization by relative concentration. Therefore, the congener profiles for the 16 possible

15   2,3,7,8 substituted congeners without OCDD were normalized by dividing the

16   concentration of each congener by the sum of the concentration of these 16 congeners.

17   OCDD concentration was normalized by dividing its concentration by the sum of the

18   concentrations of all 17 possible 2,3,7,8 substituted congeners.

19

20   **3. Results and Discussion**

21

22   *3.1 Ambient concentrations*

23   *3.1.1. PCDD/Fs and PCBs*

1   Û2,3,7,8-PCDD/Fs and ÛCl$_{4-8}$DD/Fs (gas + particulate) air concentrations ranged from 67

2   to 1700 and from 175 to 4455 fg m^{-3}, respectively (Table 1). Higher levels were observed

3   during the winter months, in particular on December 2007 and February 2008. PCDD/F gas

4   and particulate phase concentrations are presented in Tables S2 and S3, respectively

5   (supplementary material). Û2,3,7,8-PCDD/F and ÛCl$_{4-8}$DD/F atmospheric concentrations

6   were driven by levels in the particulate phase ranging from 50 to 1500 and from 95 to 3300

7   fg m^{-3}, respectively. Gas phase concentrations were lower and less variable (5 ó 60 and 65 ó

8   475 fg m^{-3} for Û2,3,7,8-PCDD/Fs and ÛCl$_{4-8}$DD/Fs, respectively) during the whole year

9   except for November 2008 where values of 290 and 1730 fg m^{-3} were registered for

10 Û2,3,7,8-PCDD/Fs and ÛCl$_{4-8}$DD/Fs, respectively. Higher PCDD/Fs concentrations in

11 winter time have been reported in literature. These variations have been attributed to a

12 combined effect of several factors, such as the atmospheric mixing layer height seasonal

13 cycle (exhibiting considerably lower height in winter time and therefore less favoring

14 dispersion of local emissions) and the increase of diffuse domestic heating (combustion)

15 sources during colder conditions (Lohmann and Jones, 1998; Lee et al., 1999; Coutinho et

16 al., 2007).

17

18 Atmospheric concentrations of dioxin-like (CB-81, -77, -105, -114, -118, -123, -126, -156,

19 -157, -167, -169, -189) and indicator (CB-28, -52, -101, -153, -138, -180) PCBs are

20 reported in this work (Table 2). ÛDL-PCB ambient concentration (gas + particulate) varied

21 from 1 to 8 pg m^{-3}, whereas Ûindicator PCB levels ranged from 11 to 87 pg m^{-3}. Ambient

22 air concentrations over Thau lagoon are dominated by the PCB concentrations in the gas

23 phase, contrary to PCDD/Fs. PCB gas and particulate phase concentrations are presented in

1 Tables S4 and S5, respectively (supplementary material). Levels in the gas phase varied

2 from 1 to 7 and from 9 to 84 pg m^{-3} for ÛDL-PCB and Ûindicator PCB, respectively,

3 whereas values in the particulate phase ranged from 0.1 to 0.7 and 0.5 to 7 pg m^{-3} for ÛDL-

4 PCBs and Ûindicator PCBs, respectively. The highest concentration was measured on

5 February 2008 but not a clear seasonal trend was observed. Total WHO$_{98}$ TEQ levels

6 (PCDD/Fs + DL-PCB) ranged from 3 to 143 fg m^{-3} and were clearly dominated by the

7 PCDD/F contribution, in particular in winter months (Tables 1 and 2). PCDD/Fs and PCB

8 concentrations measured are in agreement with the values found in Thau lagoon in 2005

9 when Û2,3,7,8-PCDD/Fs and indicator PCB concentrations ranged from 186 to 1440 fg m^{-3}

10 and from 31 to 57 pg m^{-3}, respectively. In addition, results confirm the previous observation

11 that POPs levels in the lagoon airshed are in general typical of those reported for rural or

12 semi-rural areas in spite of the anthropogenic impact in this lagoon (Castro-Jiménez et al.,

13 2008 and references therein)

14

15 *3.1.2. PBDEs*

16 Ambient air concentrations of PBDE (BDE-28, -47, -100, -99, -154, -153, -183 and -209)

17 are reported in this work for three months. Û8PBDEs total air concentrations (gas +

18 particulate) varied from 158 to 230 pg m^{-3} (Table 3). PBDE atmospheric concentrations in

19 Thau lagoon during summer are driven by gas phase levels which ranged from 156 to 227

20 pg m^{-3}, whereas particulate phase levels ranged from 1 to 18 pg m^{-3} (Table S6). These

21 concentrations correspond only to the period May-August 2008 (see section 2.3.) when

22 temperatures between 19 and 22 °C were recorded (Table S1) and probably higher

23 volatilization occurred. Concentration for the same set of PBDE congeners (except BDE-

1   209) ranging from 0.5 to 250 pg m^{-3} over Europe has been reported in a continental study

2   conducted using passive samplers (Jaward et al., 2004). Concentrations measured in Thau

3   lagoon are on the higher end of this European range, being closer to values measured in

4   inland aquatic environments with more urban influence (Mariani et al., 2008; Bogdal et al.,

5   2010) and similar to those reported for urban or industrial sites (Cetin and Odabasi, 2007).

6

7   *3.2. Atmospheric occurrence*

8

9   *3.2.1. Congener patterns*

10 Contaminant congener patterns (gas + particulate) are presented in Figure 1.

11 *PCDD/Fs:* Two groups of patterns were identified. The first group (T1, T2, T7, T11 and

12 T12) was characterized by a significantly higher predominance (*t*-test, *p*<0.001) of higher

13 chlorinated dioxins compared to the second group (T4-6, T8, T9 and T13). OCDD

14 accounted in the first group for the 48 ± 3% and 19 ± 1% of the Û2,3,7,8-PCDD/Fs and

15 ÛCl$_{4-8}$DD/Fs, respectively (Figure 1A). The second group was characterized by greater

16 predominance of furans (*t*-test, *p*<0.009-0.018), congener 1,2,3,4,6,7,8-HpCDF accounting

17 for the 13 ± 4% of the Û2,3,7,8-PCDD/Fs, and TCDF accounted for the 22 ± 2% of the

18 ÛCl$_{4-8}$DD/Fs (Figure 1B). The existence of these two situations indicates that there is not a

19 net and uniform pattern arriving to the area and therefore different sources may be driving

20 the overall PCDD/F atmospheric pattern (and concentrations) over Thau lagoon and

21 subsequent loads to surface waters. Although some indications of sink/source profiles were

22 found for both groups of patters, not a clear evaluation on their distant (sink) / local

1   (source) characteristics could be made according to the classical approach based on

2   congener pattern differences (Brubaker and Hites 1997, Lohmann and Jones, 1998).

3

4   *PCBs and PBDEs:* DL-PCB pattern was characterized by a predominance of CB-118 (65 ±

5   1%) followed by CB-105 (20 ± 1 %). Similar patterns were observed both in the gas and

6   the particular phases. Regarding indicator PCBs, congeners -101 (25 ± 4%), -153 (20 ± 4%)

7   and -52 (23 ± 8%) were more abundant. Particulate phase pattern presented high variability

8   depending on the sampling, most probably due to the low particle phase indicator PCB

9   concentrations. Congeners BDE-47 (45 ± 0.5%) and -99 (39 ± 0.2%) predominated in the

10   total (gas + particle) and in the gas phase patterns, whereas an enrichment of BDE-209 was

11   observed in the particulate phase pattern, accounting for the 70 ± 17% of the pattern.

12

13   *3.2.2. Influence of air mass origin*

14   To further investigate the atmospheric occurrence of POPs (in particular PCDD/Fs) in the

15   Thau lagoon airshed, the air mass origins during the sampling events were studied. Five

16   days (120h) back trajectories (BT) were calculated using the HYSPLIT model. Trajectories

17   were generated from the sampling location every 6h at four different heights (50, 100, 500

18   and 1000 m) above the sea level. BT frequency plots are presented in Figure 2. The highest

19   PCDD/Fs concentrations (December 2007 and February 2008, Table 1) corresponded to a

20   European continental influence of air masses (Figure 2). However, the majority of the

21   trajectories came from the NW Atlantic or had an Atlantic/ marine influence (Figure 2).

22   During the corresponding sampling events lower concentrations were measured in

1   particular for the months of June, July, and August 2007 when trajectories exhibited a clear

2   and predominant Atlantic influence.

3   The studied area is frequently under influence of strong ─Tramontaneø wind events, blowing

4   from NW direction. Higher wind speeds are associated with a contaminant dilution effect

5   due to a greater height of the mixed boundary layer, the dispersion of local emissions and

6   the introduction of ─cleanerø air in the local environment (Lohmann et al., 1999b, 2003).

7   There will be a combined effect between air masses coming from the Atlantic (low

8   pollutant loads) and local strong winds events. Under these conditions, PCDD/Fs ambient

9   levels and inputs to the aquatic system will decrease. On the contrary, when air masses are

10   coming from continental Europe and no local winds occur, a higher atmospheric load of

11   pollutants can be expected therefore increasing atmospheric inputs to the lagoon (see also

12   fluxes discussion below). In addition, the PCDD/Fs seasonality (higher concentrations in

13   winter time, section 3.1.1.) may certainty play an important role on the final PCDD/Fs

14   atmospheric levels over Thau lagoon and deposition into the system.

15

16   Interestingly, PCDD/F and PCB concentrations measured February 2008 were more than 3-

17   fold times higher than the levels measured in the same week of February 2007 (Table1).

18   We hypothesize that these differences can be attributed to a combined effect of a different

19   air mass origin and meteorological conditions during the sampling events. Trajectories

20   corresponding to the sample taken in February 08 came from continental Europe (Figure 2),

21   potentially transporting a higher load of pollutants (see above) whereas air masses

22   trajectories corresponding to the sample February 07 had an Atlantic influence. That could

23   also explain the different congener patterns observed (Figure S2) for both samples. In

1   addition, precipitation events were registered in the sampled week of February 07

2   (44.6mm) whereas almost no precipitation was recorded in February 08 (0.2mm) (Table

3   S1). This may contribute as well to the decreasing of ambient levels measured in February

4   2007 since airborne contaminants were most probably washout from the atmosphere.

5   Indeed, wet deposition fluxes supported this hypothesis. PCDD/F and PCB fluxes in

6   February 07 are considerably higher than those calculated for February 08 (see fluxes

7   discussion below). This observation highlights the fact that the atmospheric occurrence and

8   final deposition of POPs in Thau lagoon may be very variable, even changing between the

9   same week of the month in two consecutive years.

10

11   *3.2.3. Possible sources of PCDD/Fs in Thau Lagoon*

12   Several industry types operate in the Languedoc-Roussillon region, where the Thau lagoon

13   is located, being urban waste incinerator, chemical and metallurgic industries the most

14   abundant (RFEP website). The urban waste incineration industry has been historically

15   reported as the most likely emission source of PCDD/Fs in the Languedoc-Roussillon

16   region. The second largest facility in the area is located in Sète, gathering residues from all

17   Thau lagoon basin and processing more than 60000 ton/year (PRQA, 1999). PCA was

18   carried out in order to investigate the most likely PCDD/Fs source in the area based in our

19   experimental measurements. The statistical analysis included the PCDD/Fs atmospheric

20   concentrations generated in Thau lagoon and most common PCDD/F emission source

21   fingerprints (including the above mentioned among others) as reported in Buekens et al.

22   (2000), Carroll et al. (2001), Zhu et al. (2008), Tysclind et al. (1993), Hagenmaier et al.

23   (1994), and Lin et al. (2007) (Figure 3). The PCA provided a single three-dimensional

1   model that accounted for more than 80% of the variance (Figure 3). The first principal

2   component is highly and positively correlated with pentaCDD, hexaCDD and hexa CDF.

3   The second principal component is inversely correlated with OCDD. The two types of

4   congener pattern found in the Thau lagoon presented in this test relatively similar

5   fingerprints in comparison to the well defined emission fingerprints tested. The Thau

6   samples were differentiated from air profiles of sites with no direct PCDD/F emission

7   impact (background) and presented a relative influence of metallurgical industry.

8   It has been reported that the main PCDD/F emission source (municipal solid waste

9   incinerators, MSWI) in Europe has been replaced by metallurgic industry related sources in

10   the last two decades (Quaß et al., 2004; Martinez et al., 2010). That seems to be the

11   situation for Thau Lagoon area. This fact highlights the necessity of updating PCDD/Fs

12   emission inventories in the area in order to evaluate the relative influence of PCDD/F

13   sources in the region. In addition, dedicated sampling campaigns to be carried out closer to

14   main suspected sources are needed to confirm this first observation and in order to gather a

15   deeper insight on the PCDD/Fs source apportionment in the area.

16

17   *3.3. Atmospheric deposition*

18   Daily wet and dry deposition fluxes of 2,3,7,8-PCDD/Fs and 18PCBs were calculated

19   for the period covered by the sampling campaign (February 2007-2008). PBDE fluxes are

20   not reported since no year round-data was available. Averaged daily fluxes are in the lower

21   end of those reported in literature for other coastal and inland urban/suburban sites (Tables

22   S7-S8 and reference therein). PCDD/Fs dry deposition fluxes (5 - 170 pg m^{-2} d^{-1}) have

23   been reported for the Mediterranean open waters (Castro-Jiménez et al., 2010), whereas

1   Û54 PCB dry deposition fluxes (0.1-1.1 ng m^{-2} d^{-1}) were calculated for a marine

2   background sampling station in the Eastern Mediterranean (Mandalakis et al., 2005).

3   Calculated dry deposition fluxes in Thau lagoon for PCDD/Fs (64 pg m^{-2} d^{-1}) and Σ18PCBs

4   (0.4 ng m^{-2}d^{-1}) are within this range.

5

6   The yearly dry, wet and total atmospheric deposition fluxes as mass and toxic equivalents

7   (WHO$_{98}$-TEF, for PCDD/Fs and DL-PCBs) are presented in Table 4. On a yearly basis,

8   atmospheric inputs of PCBs and PCDD/Fs are dominated by dry deposition. TEQ fluxes

9   are dominated by PCDD/Fs (97-98% of total TEQ flux) while DL-PCB play a minor role,

10   even though the mass flux of PCBs is higher than the one for PCDD/Fs. The averaged daily

11   TEQ flux (PCB + PCDD/Fs) was estimated to be 4.3 pg TEQ m^{-2}d^{-1}. Total (wet + dry)

12   Σ2,3,7,8-PCDD/Fs and Σ18PCBs mass inputs to Thau Lagoon waters (70 km^2 surface) are

13   3 and 18 g y^{-1}, respectively.

14   The monthly dry fluxes of DL-PCBs and PCDD/Fs show a seasonal pattern with generally

15   higher dry deposition fluxes during the cold season and lower input during summer (Figure

16   4). The seasonal trend is less pronounced for the indicator PCBs, partly because the more

17   volatile PCBs (28, 52 and 101) show higher dry deposition fluxes during summer. The

18   overall dry deposition is still more important in winter. For all the measured compounds,

19   the wet deposition pattern depends on the occurrence of rainfall and peaks during the month

20   of May 2007.

21   The dominance of dry deposition compared to wet deposition on a yearly basis for the Thau

22   Lagoon system is likely to be a regional attribute of the relatively dry climate. In other

23   systems characterized by higher rainfall a dominance of wet deposition has been reported

1   for PCDD/Fs such as for the Bayreuth Region and the Great Lakes (Kaupp and McLachlan

2   1999; Zhang et al., 2009).

3

4   *3.4. Conclusions*

5   A 1-year dataset of PCDD/Fs and PCBs atmospheric concentrations and indicative PBDE

6   summer concentrations in Thau lagoon has been generated. These data are now available

7   for contaminant fate modeling development and validation. In addition, they provide

8   exposure data for risk assessment in Mediterranean coastal lagoons. PCDD/Fs and PCBs

9   ambient levels over Thau lagoon are typical from rural/semi-rural areas whereas PBDE

10   levels (in summer time) are typical from urban/industrial sites. The PCDD/F and PCB

11   atmospheric occurrence over Thau lagoon and subsequent inputs to the surface waters are

12   determined by an assemble of factors, being the seasonality of atmospheric concentration,

13   the air mass origin and meteorological conditions important drivers. Different sources may

14   be responsible for the PCDD/Fs atmospheric concentrations over Thau lagoon, metallurgic

15   industry probably being an important source in the region. PCDD/F and PCB yearly inputs

16   (mass and toxic equivalent) to the lagoon waters showed the importance of wet deposition

17   during rainy events although on a yearly basis dry deposition is dominant. A seasonal

18   pattern of atmospheric fluxes emerged from our calculations showing higher fluxes during

19   the cold season. These facts highlight the ‑dynamicø character of POPs atmospheric

20   concentrations and subsequent deposition in a Mediterranean coastal location, even

21   changing between the same week of the month in two consecutive years. In order to

22   properly evaluate the environmental/human exposure to these pollutants in this ecosystem

23   and in general in semi-enclosed coastal lagoons, an assessment of the POP-airshed is

1 required. Since the experimental results point to high environmental variability, model

2 simulations are useful to evaluate the load of POPs into coastal lagoons and to complement

3 experimental data.

4

5

1 **Acknowledgments**

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22

1 **FIGURES**

Figure 1
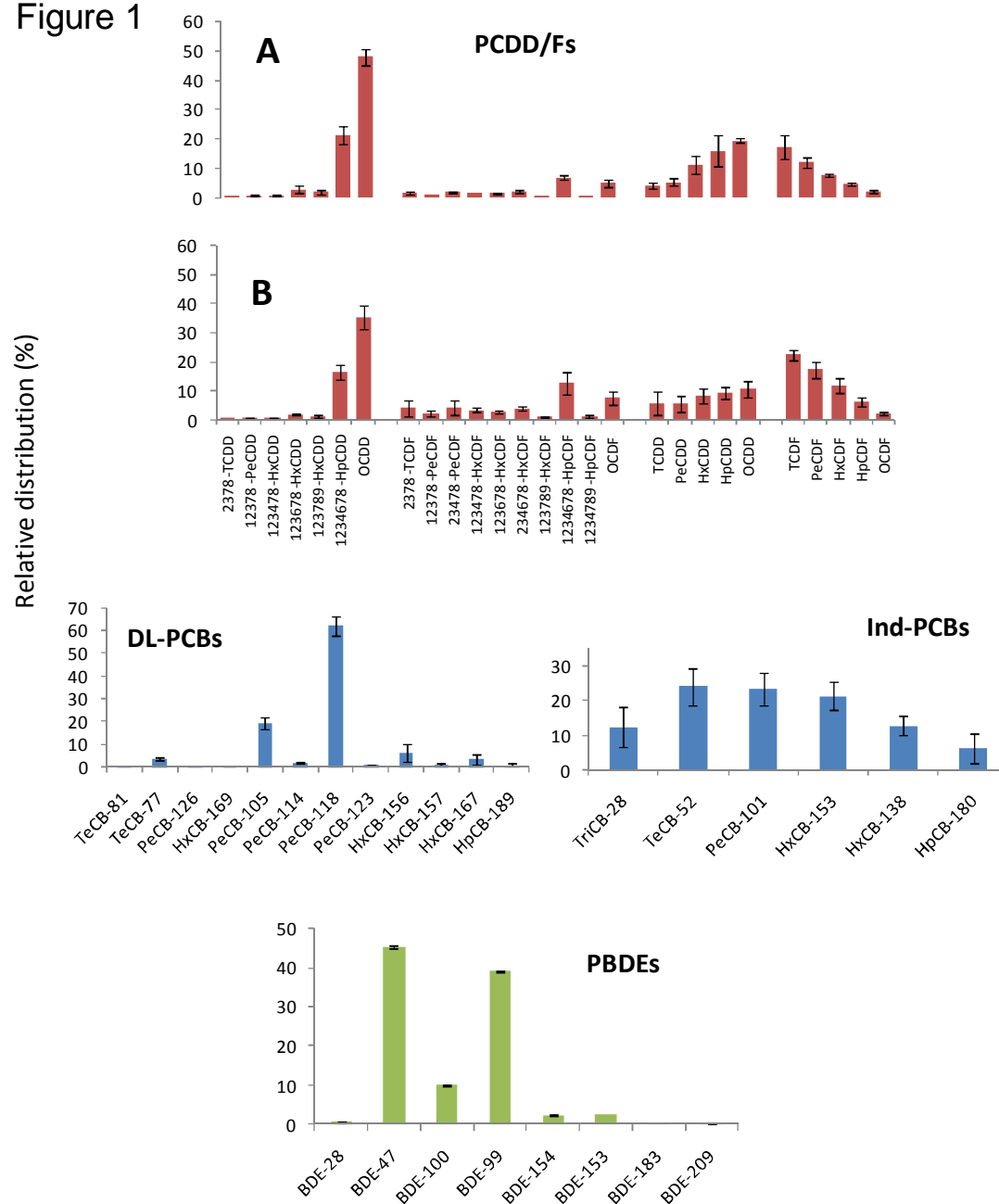
2

3 **Figure 1**. PCDD/F, PCB and PBDE congener pattern observed in Thau lagoon airshed from February 2007 to

4 2008.

Feb 07 (T-1)

Mar 07 (T-2)

May 07 (T-4)

Jun 07 (T-5)

Jul 07 (T-6)

Aug 07 (T-7)

Sep 07 (T-8)

Oct 07 (T-9)

Dec 07 (T-11)

Jan 08 (T-12)

Feb 08 (T-13)

1
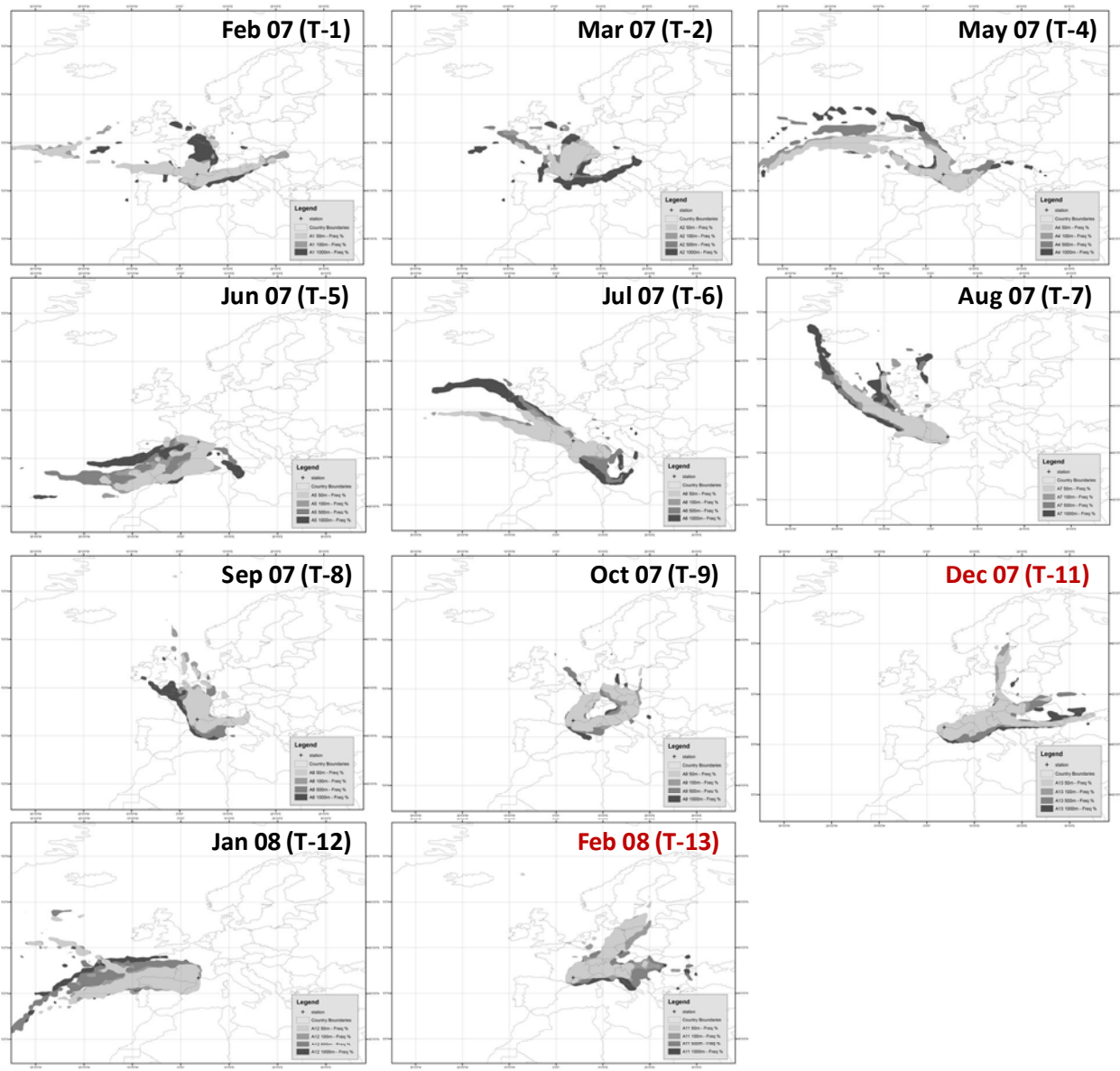
1   **Figure 2**. Overlay of back trajectories (120h) frequency plots at 50, 100, 500 and 1000m (not considering BTs frequency < 10 %). Trajectories were

2   calculated from the sampling location (cross in the map) every 6 hours during the sampling week. Black labels are trajectories presenting a NW

3   Atlantic/marine influence (T1-9, T12) and red labels are trajectories presenting a continental influence (T11 and T13).

Figure 3

X-exp: 54%, 16%

- ◆ copper smelter
- ■ aluminium plant
- ▲ PVC combustion
- ✕ waste incineration
- ✳ Diesel fuel vehicles
- ✶ Pb fuel
- ● No-Pb fuel
- + Utilities and industrial boilers
- ▬ Coal Power Plant
- ▬ Background Air sample
- ◆ MWI Gas
- ■ Metal processing
- ▲ Thau A
- ✕ Thau B

1

2
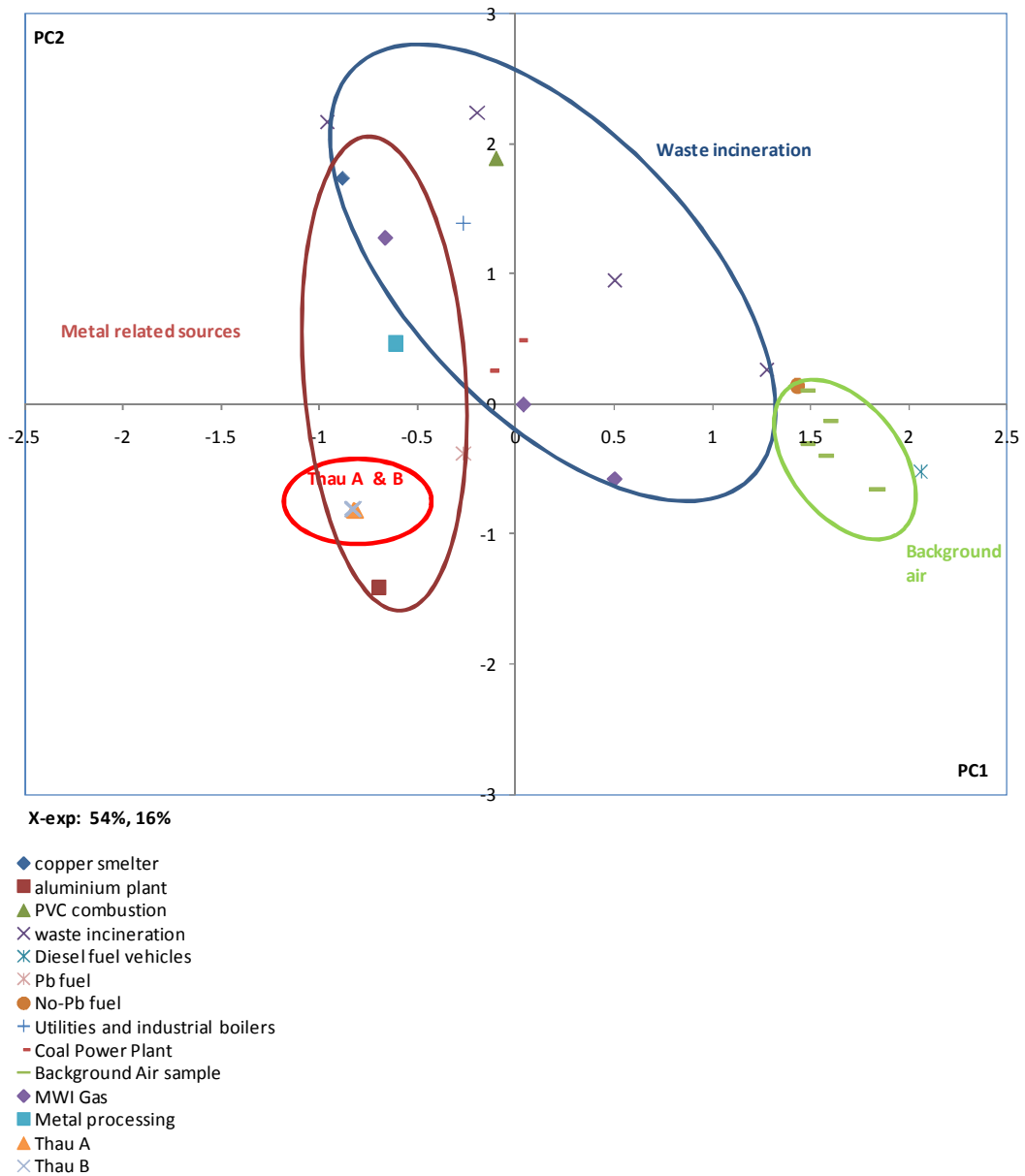
3   **Figure 3**. Principal component analysis (PCA) score plot of PCDD/F air samples collected in Thau lagoon

4   and samples related to PCDD/F emission sources and background sites from literature.

5

PCDD/Fs

DL-PCBs

Ind-PCBs

Dry, pg month^{-1} m^{-2}

Wet, pg month^{-1} m^{-2}

1

2
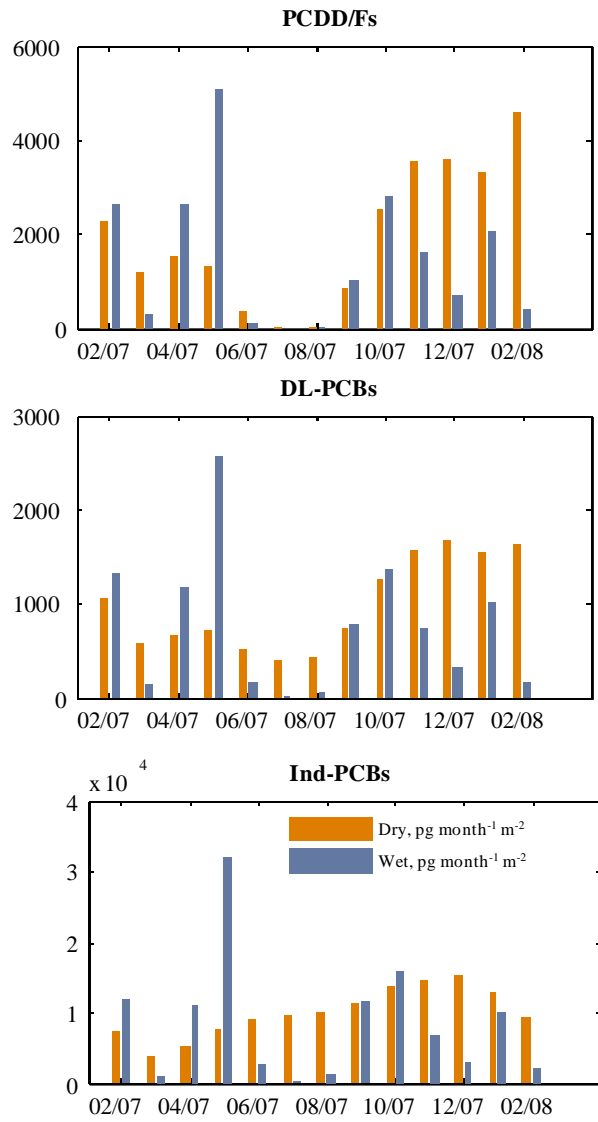
3 **Figure 4**. PCDD/F and PCB deposition fluxes (dry and wet) to Thau lagoon waters during the period

4 February 2007-2008

5

Table 1. PCDD/F atmospheric concentrations (gas + particulate) in the airshed of Thau lagoon (2007-2008). Concentrations are fg m^{-3}

Table 1. PCDD/Fs atmospheric concentrations (gas + particulate) in the airshed of Thau Lagoon (2007-2008). Concentrations are fg m^{-3}											
Sample month/code	Feb-07	Mar-07	May-07	Jun-07	Jul-07	Aug-07	Sep-07	Oct-07	Dec-07	Jan-08	Feb-08
2,3,7,8-PCDD/Fs	T-1	T-2	T-4	T-5	T-6	T-7	T-8	T-9	T-11	T-12	T-13
2,3,7,8-TCDD	0.46	0.90	0.25	0.23	0.19	0.06	0.11	0.32	2.59	0.58	2.12
1,2,3,7,8-PeCDD	3.06	5.42	1.43	0.48	0.36	0.44	0.67	0.94	18.00	1.77	7.67
1,2,3,4,7,8-HxCDD	3.88	3.93	1.26	0.56	0.25	0.30	0.74	1.72	15.03	2.68	9.48
1,2,3,6,7,8-HxCDD	12.70	19.95	4.94	1.44	1.18	1.13	3.04	5.79	57.00	8.25	25.82
1,2,3,7,8,9-HxCDD	9.29	12.98	3.28	0.82	0.58	0.88	1.86	4.25	35.00	6.20	17.68
1,2,3,4,6,7,8-HpCDD	119.78	95.19	35.72	11.22	13.23	11.20	16.43	55.40	380.90	74.91	262.78
OCDD	264.53	199.81	65.92	24.28	32.07	34.74	37.42	110.11	699.87	161.55	599.63
2,3,7,8-TCDF	8.27	6.94	3.92	2.85	2.63	1.64	4.01	5.78	27.56	5.52	166.95
1,2,3,7,8-PeCDF	5.82	5.90	2.35	1.29	1.58	0.75	2.97	4.37	15.71	3.72	71.78
2,3,4,7,8-PeCDF	10.99	9.73	4.95	2.89	1.99	1.05	6.03	8.25	36.95	6.97	153.04
1,2,3,4,7,8-HxCDF	8.71	7.60	4.41	2.26	1.23	3.01	5.83	7.44	24.60	5.48	67.93
1,2,3,6,7,8-HxCDF	8.32	7.99	4.79	2.04	2.18	1.02	5.15	7.42	20.91	5.24	51.59
2,3,4,6,7,8-HxCDF	10.53	9.63	8.13	2.83	2.70	1.77	7.51	9.72	30.37	8.69	56.71
1,2,3,7,8,9-HxCDF	3.41	3.04	2.27	0.72	0.47	0.43	1.79	2.80	8.62	2.50	18.17
1,2,3,4,6,7,8-HpCDF	35.29	32.44	24.21	9.71	11.62	5.23	23.94	33.94	86.10	25.91	103.04
1,2,3,4,7,8,9-HpCDF	4.70	4.08	3.27	0.92	0.58	0.65	3.07	3.89	12.82	3.06	15.79
OCDF	23.40	23.56	13.96	4.60	8.17	4.78	14.10	21.02	57.20	15.04	69.39
Û2,3,7,8-PCDDs	413.70	338.19	112.80	39.03	47.86	48.75	60.27	178.53	1208.39	255.95	925.18
Û2,3,7,8-PCDFs	119.43	110.91	72.26	30.11	34.93	18.55	74.40	104.63	320.84	82.14	774.40
Û2,3,7,8-PCDD/Fs	**533.14**	**449.10**	**185.05**	**69.14**	**82.80**	**67.30**	**134.67**	**283.16**	**1529.23**	**338.09**	**1699.58**
WHO-TEQ$_{98}$ [a]	17.44	20.03	8.21	3.79	3.19	2.08	7.37	11.05	66.64	11.54	135.21
WHO-TEQ$_{05}$ [a]	15.18	18.01	7.19	3.19	2.77	1.87	6.12	9.34	59.09	10.11	103.30
Cl$_{4-8}$-PCDD/Fs											
TCDD	45.40	45.25	35.34	45.63	9.00	6.72	27.39	35.85	139.13	52.11	100.14
PeCDD	56.09	63.68	37.71	37.15	7.73	7.13	31.39	36.27	233.78	54.57	130.21
HxCDD	123.30	139.89	60.76	43.37	14.68	12.99	35.28	68.86	552.87	97.05	301.69
HpCDD	282.91	163.48	65.88	23.67	22.81	20.44	33.41	99.62	776.23	86.91	477.11
OCDD	264.53	199.81	65.92	24.28	32.07	34.74	37.42	110.11	699.87	161.55	599.63
TCDF	210.25	180.78	122.59	69.38	62.10	39.48	113.02	197.45	433.50	157.76	1066.13
PeCDF	134.55	128.24	92.85	48.98	44.93	26.00	96.76	132.83	399.79	103.89	988.42
HxCDF	94.69	84.72	64.91	30.08	33.94	13.35	80.79	93.89	257.96	70.22	550.07
HpCDF	57.95	52.81	40.83	16.65	19.44	8.77	39.26	55.48	148.96	41.99	172.15
OCDF	23.40	23.56	13.96	4.60	8.17	4.78	14.10	21.02	57.20	15.04	69.39
ÛCl$_{4-8}$-PCDDs	772.23	612.12	265.62	174.10	86.29	82.01	164.89	350.71	2401.88	452.19	1608.78
ÛCl$_{4-8}$-PCDFs	520.84	470.11	335.13	169.68	168.58	92.38	343.92	500.66	1297.41	388.90	2846.15
ÛCl$_{4-8}$-PCDD/Fs	**1293.07**	**1082.23**	**600.75**	**343.78**	**254.87**	**174.39**	**508.81**	**851.38**	**3699.30**	**841.10**	**4454.94**

[a] TEQ values are upper bound concentrations

Table 2. PCB atmospheric concentrations (gas + particulate) in the airshed of Thau lagoon (2007-2008). Concentrations are pg m^{-3}

Sample month/code	Feb-07	Mar-07	Apr-07	May-07	Jun-07	Jul-07	Aug-07	Sep-07	Oct-07	Nov-07	Dec-07	Jan-08	Feb-08
Congeners	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	T-9	T-10	T-11	T-12	T-13
Non-ortho PCBs													
TeCB-81	0.007	0.006	0.006	0.008	0.008	0.009	0.003	0.009	0.007	0.003	0.008	0.004	0.013
TeCB-77	0.096	0.089	0.132	0.155	0.190	0.246	0.089	0.190	0.134	0.040	0.086	0.052	0.139
PeCB-126	0.012	0.012	0.013	0.015	0.019	0.022	0.010	0.019	0.016	0.005	0.020	0.008	0.059
HxCB-169	0.002	0.002	0.001	Ö0.001	0.001	0.001	0.001	0.001	0.002	Ö0.001	0.005	0.001	0.012
Mono-ortho PCBs													
PeCB-105	0.664	0.480	0.671	0.670	0.859	1.122	0.446	0.914	0.697	0.234	0.674	0.363	0.931
PeCB-114	0.061	0.054	0.067	0.061	0.085	0.103	0.040	0.091	0.074	0.024	0.050	0.036	0.126
PeCB-118	1.929	1.511	2.184	2.187	2.768	3.592	1.416	3.005	2.240	0.799	2.002	1.209	3.856
PeCB-123	0.030	0.020	0.032	0.045	0.041	0.063	0.030	0.042	0.030	0.011	0.022	0.019	0.047
HxCB-156	0.196	0.141	0.155	0.204	0.192	0.249	0.099	0.200	0.166	0.046	0.256	0.104	1.455
HxCB-157	0.034	0.024	0.025	0.102	0.031	0.065	0.020	0.031	0.028	0.008	0.051	0.016	0.165
HxCB-167	0.100	0.076	0.092	0.086	0.114	0.142	0.060	0.120	0.094	0.027	0.112	0.059	0.779
HpCB-189	0.017	0.014	0.013	0.011	0.011	0.012	0.005	0.013	0.013	0.002	0.032	0.011	0.283
WHO-TEQ$_{98}$^{a} (fg m^{-3})	*1.689*	*1.511*	*1.738*	*2.040*	*2.481*	*2.904*	*1.238*	*2.489*	*2.023*	*0.615*	*2.508*	*1.083*	*7.391*
WHO-TEQ$_{05}$^{a} (fg m^{-3})	*1.409*	*1.301*	*1.443*	*1.685*	*2.098*	*2.399*	*1.043*	*2.090*	*1.728*	*0.510*	*2.244*	*0.918*	*6.466*
Indicator PCBs													
TriCB-28	5.31	2.58	5.38	4.54	2.88	2.33	2.58	1.98	1.04	2.87	1.34	3.25	6.63
TeCB-52	5.89	4.85	7.97	7.32	8.07	8.92	4.52	5.66	6.10	3.73	4.54	4.21	7.34
PeCB-101	5.04	4.29	6.95	6.54	7.98	9.85	3.77	8.69	6.60	2.30	3.66	3.37	10.47
HxCB-153	4.71	3.68	5.51	5.09	6.98	8.16	3.09	7.19	5.41	1.48	3.10	2.92	27.87
HxCB-138	2.87	2.15	3.16	2.92	3.95	4.78	1.81	4.13	3.21	0.83	2.39	1.64	17.27
HpCB-180	1.53	1.08	1.34	1.11	1.63	1.74	0.66	1.55	1.24	0.25	1.18	0.82	16.99
Û DL-PCBs	**3.15**	**2.43**	**3.39**	**3.54**	**4.32**	**5.62**	**2.22**	**4.64**	**3.50**	**1.20**	**3.32**	**1.88**	**7.64**
Û indicator PCBs	**25.36**	**18.62**	**30.31**	**27.53**	**31.48**	**35.78**	**16.43**	**29.21**	**23.60**	**11.46**	**16.20**	**16.20**	**86.58**
Û 18PCBs	**28.50**	**21.05**	**33.71**	**31.07**	**35.80**	**41.41**	**18.65**	**33.84**	**27.10**	**12.65**	**19.52**	**18.08**	**94.44**

Values (Ö) are limits of detection and are considered in the totals, ^{a} TEQ values are upper bound concentrations;

Results from non-ortho PCB in April and all congeners in Nov-07 are only gas phase concentrations

1 **Table 3**. Indicative hot season PBDE atmospheric concentrations (gas + particulate) in the

2 airshed of Thau lagoon (May-August 2007). Concentrations are pg m^{-3}

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Sample month/code	May-07	Jul-07	Aug-07
Congeners	T-4	T-6	T-7
BDE-28	1.28	1.05	0.81
BDE-47	103.49	93.24	70.89
BDE-100	23.14	19.94	16.02
BDE-99	89.67	79.00	61.96
BDE-154	5.49	4.77	3.81
BDE-153	5.70	5.03	4.02
BDE-183	0.20	0.11	0.09
BDE-209	1.38	1.35	0.77
$\sum$ 8 PBDEs	**230.35**	**204.48**	**158.38**

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6

1 **Table 4.** Annual atmospheric inputs of POPs into Thau lagoon (dry and wet deposition as
2 mass and TEQ fluxes)
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	Total Flux (ng m^{-2} y^{-1})		TEQ ^{a} (pg m^{-2} y^{-1})		
	Û2,3,7,8-PCDD/Fs	Û18PCBs	Û2,3,7,8-PCDD/Fs	ÛDL-PCBs	Total
Dry	23.4	136.1	876	18	894
Wet	19.4	124.8	669	15	684
Total	42.8	260.9	1545	33	1578

5 ^{a} TEQ values are calculated using WHO TEF 98