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Atmospheric Occurrence and Deposition of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (PCDD/Fs) in the Open Mediterranean Sea

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The overall objective of this work is to provide the first evaluation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) occurrence and deposition to Mediterranean open seawater. $\Sigma 2,3,7,8$ -PCDD/F air (gas+aerosol) concentrations over the Mediterranean Sea ranged from 60 to 1040 fg m⁻³. The highest value (1555 fg m⁻³) was measured in a reference sample taken in the SW Black Sea. No consistent trend regarding the diel cycle of PCDD/Fs was observed. PCDD/Fs transported to the open sea waters from continental areas and across the Atlantic as well as ship emissions may be significant sources to the open Mediterranean. Seawater concentrations in the Mediterranean ranged from 42 to 64 fg L⁻¹. The $\Sigma 2,3,7,8$ -PCDD/F dry deposition fluxes in the Marmara and Black Seas (210 kg year⁻¹) are from 2 to 55 times higher than dry fluxes in the Mediterranean Sea (4–156 kg year⁻¹). Analysis of estimated diffusive air–water fluxes and air/water fugacity ratios show that a net volatilization of some PCDD congeners is feasible. However, evidence of a net absorption flux for the rest of PCDD/F is found. When both atmospheric deposition processes are considered together the open Mediterranean Sea is a net sink of PCDD/F, due to the importance of dry deposition fluxes of aerosol-bound PCDDFs.

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Introduction

The marine environment is subjected to contamination by a wide spectrum of persistent organic pollutants (POPs) due to anthropogenic pressures. These contaminants are bio-accumulative, persistent and prone to long-range transport occurring in all environmental compartments. POPs have been reported to exhibit a wide range of adverse health effects in biota and humans (1, 2). Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are a family of POPs consisting of 210 possible congeners. Seventeen of these congeners (2,3,7,8-substituted) have been described as the most toxic (3). PCDD/Fs occur as unintentional byproduct of chemical manufacturing and incineration processes (4). There is a global concern regarding the presence of PCDD/Fs in the marine environment given their accumulation/effects in shellfish, fish and marine top predators. Proof of that is that PCDD/Fs have been included in the main international programmes for pollution monitoring and impact assessment in the NE Atlantic, the Baltic, and the Mediterranean Seas (5–7). The loading of PCDD/Fs and other POPs to marine environments and possible toxic effects is driven by atmospheric deposition in the open waters (8, 9) and riverine inputs and runoff in coastal zones (10, 11). The atmospheric compartment acts as an important vector for transport of PCDD/Fs (as for other POPs families) to marine waters. Airborne organic contaminants participate in exchange or deposition processes that determine their inputs to the marine environment (5, 8, 9). Questions arising are what are the current ambient levels in the Mediterranean Sea airshed and waters. These data will be also valuable for the risk assessment and contaminant fate model development and validation.

The Mediterranean Sea, due to its nature as a semi-enclosed environment surrounded by highly populated areas, is a region of special ecological and commercial interest. Some data are available on ambient air, water column and sediment concentrations for some POPs families (OCs, PCBs, PAHs, and PBDEs) in the Mediterranean Sea (12–21). Regarding PCDD/Fs, the information is more limited due to the methodological complexity of their sampling and analysis and the high costs. Few data are available in some environmental compartments in the Mediterranean region. In addition, these data have been acquired from coastal areas and the spatial coverage is even more reduced than for the other POPs families (22–24, 11). No experimental data on PCDD/Fs ambient levels and behavior have been reported for the open Mediterranean Sea.

The overall objective of this work was to assess the current status of PCDD/Fs pollution in the open Mediterranean Sea: (a) to obtain current PCDD/Fs ambient air and water concentrations across the open Mediterranean Sea and reference PCDD/F air concentrations in the Black Sea; (b) to investigate the PCDD/Fs occurrence and congener patterns in the atmosphere over the open Mediterranean; (c) to estimate the atmospheric dry particle fluxes and air–water diffusive exchange of PCDD/F in the Mediterranean and Black Seas.

Materials and Methods

Study Area. The Mediterranean Sea is a semi-enclosed environment with limited water exchanges. It covers an area of about 2.5 million km² and has connection to the Atlantic Ocean through the strait of Gibraltar that is ~14 km wide. The rapid increase of human activities in the Mediterranean Sea area, particularly in the fields of industrialization,

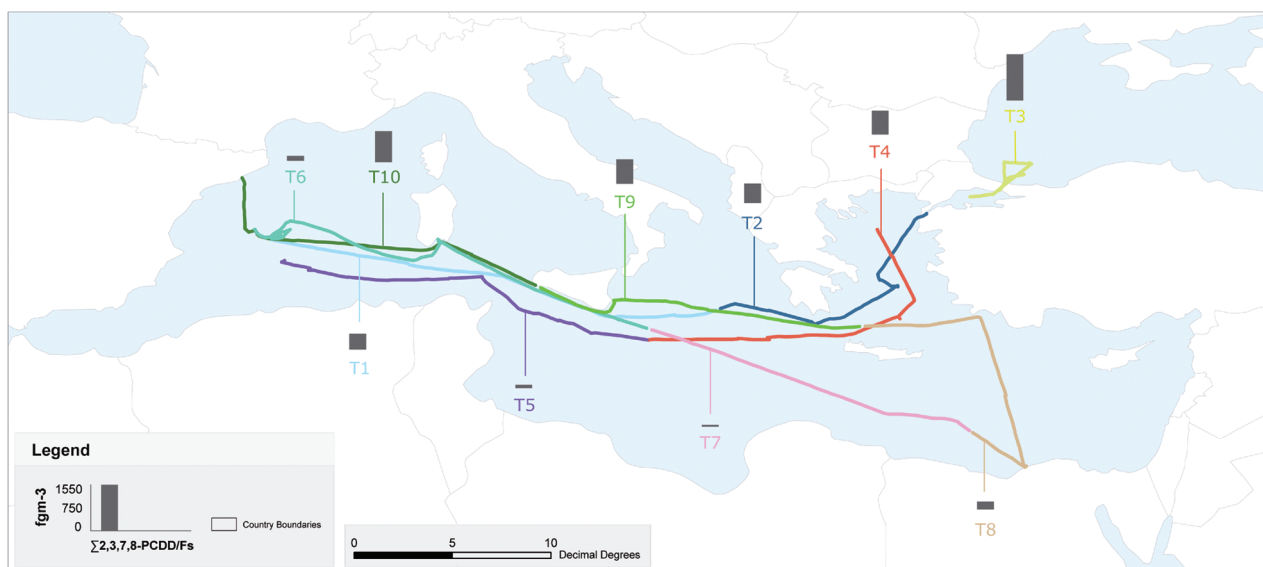


FIGURE 1. Transects sampled during both cruises across the Mediterranean Sea and in the SW Black Sea. Bars are air (gas + particulate phase) $\Sigma 2,3,7,8$ -PCDD/Fs concentrations measured for each of the transects.

urbanization and agriculture, and the seasonal increase in coastal tourism is a threat to the environment and biodiversity in the area (25). In addition, commercial activities in the Mediterranean Sea reflect intense maritime traffic (26) and a high potential for contamination.

Sampling. Samples were collected during two surveys performed in June 2006 and May 2007 on board of the oceanographic vessel B/O *García del Cid* (CSIC). In both campaigns, Barcelona was the initial and final port, with Istanbul and Alexandria being the intermediate stops, respectively. Transects covered an extensive area within a year of difference allowing a good spatial coverage of different regions (Figure 1). Air and water sampling details are presented in the Supporting Information (SI) (Text S1; Table S1 and Text S2; Table S7, respectively). Briefly, air samples were taken by using high volume samplers. Particulate phase collection was performed by quartz fiber filter (QFFs) whereas gas phase trapping was achieved by polyurethane foams (PUFs) according to the U.S. EPA TO-9A Method (27). Ten transects (Figure 1) were sampled during both cruises obtaining a total of 22 gas phase and 22 aerosol phase samples. Sampling volumes varied from 300 to 1600 m³, depending on the sampling strategy. Seawater was pumped on board into an overflow container and two different sampling systems were used (low and high-volume). Retention of the particulate water phase was performed by glass fiber filters (GFFs) or cartridge-type QFFs, whereas the dissolved water phase was sampled by using 50 or 250 g XAD columns depending of the sampling system employed. A total of 11 particulate and 11 dissolved water samples were collected. Sampling volumes varied from 250–350 L (low-volume sampler) and 900–1100 L (high-volume sampler).

Analysis. Details on the extraction and analytical procedures are presented in SI Text S3. Briefly, QFFs, GFFs, and PUFs were Soxhlet extracted with *n*-hexane/acetone (220:30 v/v) for 24 h. XAD columns (50 g) were directly loaded in an accelerated solvent extraction (ASE) apparatus and extracted with sequential cycles of methanol-*n*-hexane, whereas 250 g XAD columns and cartridge-type QFFs were Soxhlet extracted with toluene for 48 h. Samples were spiked with ¹³C-labeled internal standards before extraction in the case of the Soxhlet procedure and after the extraction (in order to avoid cross contaminations) in the case of the ASE. Extract purification was executed with an automated cleanup system (Power-Prep). This method has proven a high quality purification of PCDD/Fs and has been previously used in the JRC-IES

laboratories for dioxin analysis (11, 28). Purified extracts were concentrated to 30 μ L under gentle nitrogen flow. Prior to injection, syringe ¹³C-labeled standards were added to the extracts. Analysis of PCDD/Fs was performed by isotope dilution high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) following the 1613 U.S. EPA method (29).

Quality Assurance/Quality Control (QA/QC). The QA/QC procedures followed are detailed in SI Text S4. Summarizing, all material employed was precleaned and properly stored before the campaigns. Field and procedural blanks (sampling and analysis) were collected for air and water samples and were analyzed with the samples. Blank values were at the limit of detection (LOD) levels. Procedural blanks showed similar levels to field blanks so no contamination of samples during manipulation or processing occurred. A breakthrough test was also performed for air and water samples. Concentrations observed in the second half of the PUFs or the second XAD columns were at LOD levels. An air sampling reproducibility study was carried out by operating two samplers (A and B) contemporaneously during the 2007 cruise (T6–T9) with good agreement found between concentrations obtained from both samplers. Although some differences in absolute concentrations were found for some congeners, a significant correlation ($p < 0.001$) was obtained when comparing results from the two sampling devices by performing a linear regression (see SI Tables S2–S4 for details). Therefore, it was decided to average the concentrations for T6–T9 for further calculations and discussion.

Standards (natives + ¹³C-compounds) were introduced in the chromatographic sequence to evaluate possible variations during the time of analyses. Chromatographic peaks of target compounds were only considered when complying with the following QA/QC criteria: (a) the retention time of target compound were ± 3 s of those observed for the corresponding standards; (b) experimental isotopic ratio of natives compounds were within $\pm 20\%$ of the theoretical ratio and (c) peaks were at least 3 times higher than the noise. LODs were calculated on the basis of a signal-to-noise ratio of 3/1 in real samples (therefore taking into account the matrix effect and the influence of both processing and analytical steps). LODs ranged from 0.01 to 2.9 fg m⁻³ for air samples and from 0.03 to 3.6 fg L⁻¹ for water samples depending on the congener and the sample analyzed. Method recoveries (extraction-cleanup-analysis) ranged from 32–75% and from 31–60% for the air and water samples, respectively. Results

TABLE 1. PCDD/Fs (Gas+Particulate Phase) Ambient Air Concentrations (fg m⁻³) in the Mediterranean Open Sea, and Marmara and Black Seas (2006–2007)^a

2,3,7,8- PCDD/Fs	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	T-9	T-10
2,3,7,8-TCDD	0.43	≤0.2	0.35	0.08	0.14	0.99	0.41	≤0.23	≤0.66	≤0.51
1,2,3,7,8-PeCDD	0.63	≤0.5	0.92	0.28	≤0.2	1.15	1.14	0.61	3.26	2.52
1,2,3,4,7,8-HxCDD	0.65	1.16	1.76	0.82	0.35	1.04	0.52	0.47	3.96	5.78
1,2,3,6,7,8-HxCDD	3.36	4.04	10.04	3.54	1.14	1.50	0.75	1.83	12.87	10.35
1,2,3,7,8,9-HxCDD	2.09	2.53	5.78	1.94	0.50	1.59	0.59	0.93	9.18	11.21
1,2,3,4,6,7,8-HpCDD	109.34	140.85	339.59	166.27	21.50	15.60	5.20	54.95	114.49	179.87
OCDD	377.28	463.08	1082.41	598.39	64.12	45.98	12.48	183.31	280.23	762.96
2,3,7,8-TCDF	4.86	5.06	9.56	5.92	4.14	23.51	7.86	5.84	6.75	6.17
1,2,3,7,8-PeCDF	2.05	2.66	7.12	2.57	1.44	8.19	3.34	2.28	6.08	3.80
2,3,4,7,8-PeCDF	2.96	4.00	8.95	3.53	1.71	9.30	5.05	3.06	15.69	6.46
1,2,3,4,7,8-HxCDF	2.73	3.50	9.08	3.16	2.10	6.41	3.22	2.23	26.03	5.33
1,2,3,6,7,8-HxCDF	2.40	3.62	8.09	3.05	1.87	5.53	2.80	1.78	21.66	4.32
2,3,4,6,7,8-HxCDF	2.69	3.40	8.22	2.49	1.98	5.95	2.98	2.27	33.18	6.75
1,2,3,7,8,9-HxCDF	0.72	0.46	2.93	0.70	0.71	1.39	0.71	0.48	11.13	2.74
1,2,3,4,6,7,8-HpCDF	7.05	11.75	25.51	8.26	6.48	18.62	7.53	4.86	153.66	15.91
1,2,3,4,7,8,9-HpCDF	1.02	1.16	3.34	1.06	0.76	1.87	0.83	0.66	20.02	2.99
OCDF	8.57	15.01	31.83	11.10	4.88	12.39	4.96	4.26	109.51	13.20
Σ2,3,7,8-PCDDs	493.79	611.66	1440.84	771.32	87.75	67.85	21.09	242.34	424.66	973.20
Σ2,3,7,8-PCDFs	35.04	50.63	114.64	41.83	26.07	93.16	39.29	27.71	403.71	67.65
Σ2,3,7,8-PCDD/Fs	528.83	662.30	1555.48	813.15	113.81	161.01	60.38	270.05	828.36	1040.86
WHO-TEQ ₉₈ ^b	6.50	7.18	15.58	6.34	2.90	12.25	6.32	4.70	27.47	13.78
WHO-TEQ ₀₅ ^b	5.88	6.41	13.87	5.70	2.54	10.24	5.25	4.08	24.28	12.57
Cl₄₋₈-PCDD/Fs										
TCDD	10.57	14.74	32.97	7.37	9.16	29.33	11.77	11.69	105.23	22.78
PeCDD	10.14	11.88	46.68	12.34	6.31	24.42	10.53	8.22	149.52	43.93
HxCDD	36.78	24.45	92.01	28.85	11.27	28.34	10.79	15.72	206.27	113.61
HpCDD	194.77	269.10	599.18	282.96	39.01	38.57	10.17	98.33	223.17	345.05
OCDD	377.28	463.08	1082.41	598.39	64.12	45.64	12.34	182.30	279.91	762.96
TCDF	55.29	137.68	223.31	72.42	72.23	332.26	160.22	133.25	250.64	158.29
PeCDF	41.25	60.39	165.00	58.04	35.83	144.68	65.67	46.99	410.54	93.03
HxCDF	32.52	75.35	83.24	32.57	22.33	57.29	28.10	16.57	267.54	58.06
HpCDF	12.32	22.60	43.49	15.57	10.45	27.58	11.43	8.46	233.50	31.38
OCDF	8.57	15.01	31.83	11.10	4.88	12.30	4.81	4.14	109.35	13.20
ΣCl ₄₋₈ DDs	629.54	783.24	1853.24	929.91	129.87	150.75	55.58	316.04	916.21	1288.34
ΣCl ₄₋₈ DFs	149.95	311.03	546.86	189.70	145.71	574.12	270.23	209.41	1271.57	353.96
ΣCl ₄₋₈ DD/Fs	779.49	1094.27	2400.10	1119.61	275.58	724.86	325.81	525.45	2187.78	1642.30

^a Values (≤) are limits of detection and are considered in the totals. ^b TEQ values are upper bound concentrations.

were corrected by recoveries (isotopic dilution method). Blank values were at LOD levels (see above) so no blank correction of results was performed.

Results and Discussion

Ambient Levels.

Atmospheric Concentrations. PCDD/F ambient air concentrations (gas+particulate) measured in both campaigns are detailed in Table 1. Individual gas and particulate phase concentrations are reported in SI Tables S5 and S6, respectively. Among the 10 transects sampled, nine were collected in the Mediterranean Sea and just one in the Marmara and Black Seas (T-3). Σ2,3,7,8-PCDD/F (i.e., sum of 2,3,7,8 substituted PCDD and PCDF congeners) air concentrations (gas+particulate) over the Mediterranean Sea ranged from 60 to 1040 fg m⁻³ (3–27 WHO₉₈-TEQ fg m⁻³), whereas in Marmara and Black Seas a concentration of 1555 fg m⁻³ (16 WHO₉₈-TEQ fg m⁻³) was measured. ΣCl₄₋₈DD/Fs (i.e., sum of the tetra- to octa-chloro substituted PCDD and PCDF homologue series) ranged from 275 to 2187 fg m⁻³ in the Mediterranean Sea whereas a concentration of 2400 fg m⁻³ was observed in the Marmara and Black seas. Concentration in the gas phase for the Mediterranean transects ranged from 33 to 295 fg m⁻³ and from 222 to 822 fg m⁻³ for Σ2,3,7,8-PCDD/F and ΣCl₄₋₈DD/Fs, respectively. Particulate phase concentrations varied from 27 to 990 fg m⁻³ and from 39 to

1365 fg m⁻³ for Σ2,3,7,8-PCDD/F and ΣCl₄₋₈DD/Fs, respectively. The higher particulate phase concentration corresponded again to the Marmara-Black sea transect (1353 and 1600 fg m⁻³ for Σ2,3,7,8-PCDD/F and ΣCl₄₋₈DD/Fs, respectively). Back trajectories (BTs) analysis showed that for this sample, the air masses (especially at 50 and 100 m height) were circulating mainly over eastern Europe (see SI Figure S2). Similar average values were obtained from the western (T-1, T-5, T-6, and T-10) and eastern (T-2, T-4, T-7, T-8, T-9) Mediterranean basins pointing to a homogeneous distribution of PCDD/Fs atmospheric levels during late spring-early summer. This is suggesting that even if there are hot spots in the Mediterranean basin the levels found in open sea will be mostly driven for the atmospheric circulation patterns (see BTs discussion below).

No PCDD/F air concentrations in the open Mediterranean Sea were found in the literature for comparison. Concentrations measured were up to 10-fold higher than those reported for the Atlantic Ocean or remote coastal and inland areas in Australia or North America. Reported values from the Atlantic ocean ranged from 0.5 (close to the Antarctic) to 11 (close to the African Coast) WHO₉₈-TEQ fg m⁻³ (30). A mean value of 1 WHO₉₈-TEQ fg m⁻³ was reported for a coastal pristine site in Australia, where only air masses coming from the ocean were sampled (31). Values reported for remote areas in North America varied from 0.1 to 3 WHO₉₈-TEQ fg m⁻³

TABLE 2. PCDD/Fs Total (Particulate+Dissolved) Water Concentrations (fg L⁻¹) in the Mediterranean Open Waters (2006–2007). (Only Samples Where Quantification Was Possible)^a

2,3,7,8- PCDD/Fs	TW 8 L	TW 9 L	TW 10 L	TW 11 L
2,3,7,8-TCDD	≤0.53	≤0.71	≤1.12	≤0.42
1,2,3,7,8-PeCDD	≤0.62	≤0.91	≤1.65	≤0.60
1,2,3,4,7,8-HxCDD	≤0.72	≤0.52	≤0.83	≤0.58
1,2,3,6,7,8-HxCDD	5.09	6.14	3.80	3.30
1,2,3,7,8,9-HxCDD	2.62	4.03	2.71	2.07
1,2,3,4,6,7,8-HpCDD	15.47	8.13	4.74	5.83
OCDD	28.23	17.09	12.73	14.77
2,3,7,8-TCDF	1.83	2.14	3.72	2.32
1,2,3,7,8-PeCDF	≤0.63	≤0.79	≤1.96	≤0.77
2,3,4,7,8-PeCDF	≤0.84	≤1.07	≤2.03	≤0.95
1,2,3,4,7,8-HxCDF	≤1.51	≤0.60	≤0.94	0.93
1,2,3,6,7,8-HxCDF	≤0.54	≤0.59	≤0.79	1.07
2,3,4,6,7,8-HxCDF	0.38	1.05	0.79	1.51
1,2,3,7,8,9-HxCDF	≤0.38	≤0.29	≤0.73	≤0.20
1,2,3,4,6,7,8-HpCDF	1.53	1.28	2.85	2.83
1,2,3,4,7,8,9-HpCDF	≤0.34	≤0.22	≤0.36	≤0.41
OCDF	2.81	2.67	≤1.63	3.92
Σ2,3,7,8-PCDDs	53.28	37.55	27.58	27.58
Σ2,3,7,8-PCDFs	10.78	10.69	15.82	14.91
Σ2,3,7,8-PCDD/Fs	64.06	48.24	43.39	42.48
WHO-TEQ ₉₈ ^b	3.09	3.83	5.39	2.82
WHO-TEQ ₀₅ ^b	2.91	3.61	4.95	2.62
Cl₄₋₈-PCDD/Fs				
TCDD	0.70	13.64	5.95	5.06
PeCDD	22.07	17.54	18.40	20.89
HxCDD	35.72	45.12	34.01	33.07
HpCDD	24.69	15.20	7.38	11.35
OCDD	28.23	17.09	12.73	14.77
TCDF	27.26	23.69	31.28	35.68
PeCDF	0.00	0.00	0.00	5.25
HxCDF	4.90	5.45	6.04	11.23
HpCDF	2.31	1.77	4.62	5.88
OCDF	2.81	2.67	≤1.63	3.92
ΣCl ₄₋₈ DDs	111.41	108.60	78.46	85.14
ΣCl ₄₋₈ DFs	37.28	33.58	41.95	61.97
ΣCl ₄₋₈ DD/Fs	148.68	142.18	120.40	147.11

^a Values (≤) are limits of detection and are considered in the totals. ^b TEQ values are upper bound concentrations.

(32). The measured concentrations were however within the range of those reported for European remote sites (<10 WHO₉₈-TEQ fg m⁻³) (33), for remote sites in the Baltic Sea (~10 fg TEQ m⁻³, average) (34) and levels (186 to 1442 fg m⁻³) measured in a Mediterranean coastal lagoon (11).

Different atmospheric concentrations during the day and night have been reported for some POPs families in open seas (day/night cycling). For example, higher daytime gas phase concentrations than at night for PCBs in the open Atlantic Ocean have been observed (35), whereas a decrease of gas phase PCB concentrations during the day attributed to OH radical attack was observed in the Mediterranean (36). However, no information on diel cycle of PCDD/Fs is available over the open sea. Day and night samples were gathered during four transects (T1, T2, T4, T5) in the first cruise (2006).

SI Figure S1 presents the Σ2,3,7,8-PCDD/Fs and ΣCl₄₋₈DD/Fs concentrations obtained during the day and night for the mentioned transects. Overall, there was not a consistent trend, with higher day time concentrations for some transects and compounds, and the opposite trend in others. These trends may be the result of a complex interaction of different factors such as degradation with OH radical, water-column processes driving air–water exchange, proximity to sources or dominant air masses. Other authors studied the day night variability of PCDD/F in coastal NW Atlantic, also reaching inconclusive results (37).

Water Concentrations. Σ2,3,7,8-PCDD/F concentrations in open Mediterranean waters were very low and under LODs for all samples collected with the low-volume system. However, in four of the samples gathered with the high-volume system quantification was possible and values (particulate+ dissolved phase) ranged from 42 to 64 fg L⁻¹ (3–5 WHO₉₈-TEQ fg L⁻¹). ΣCl₄₋₈DD/Fs concentrations varied from 120 to 150 fg L⁻¹ (Table 2). Individual congener concentrations in the particulate and dissolved phases are presented in SI Tables S8 and S9, respectively. PCDD/Fs were generally enriched in the dissolved phase, even the higher chlorinated PCDDs exhibiting slightly higher concentrations in the dissolved phase than in the particulate phase. We attribute this to the oligotrophic character of open sea waters and low organic matter content. No PCDD/Fs levels in open seawaters were found in the literature for comparison. Concentrations were lower than those reported for a Mediterranean coastal site (163–476 fg L⁻¹) (11).

Congener Patterns and Occurrence. The composition of the PCDD/F mixture in the atmosphere provides useful information about possible sources and atmospheric transformation (“weathering”) processes. It has been reported that there is a consistent PCDD/F homologue pattern, except close to significant sources (33). Two types of PCDD/F patterns appeared in the Mediterranean Sea, pointing to substantial differences in the composition of the PCDD/F

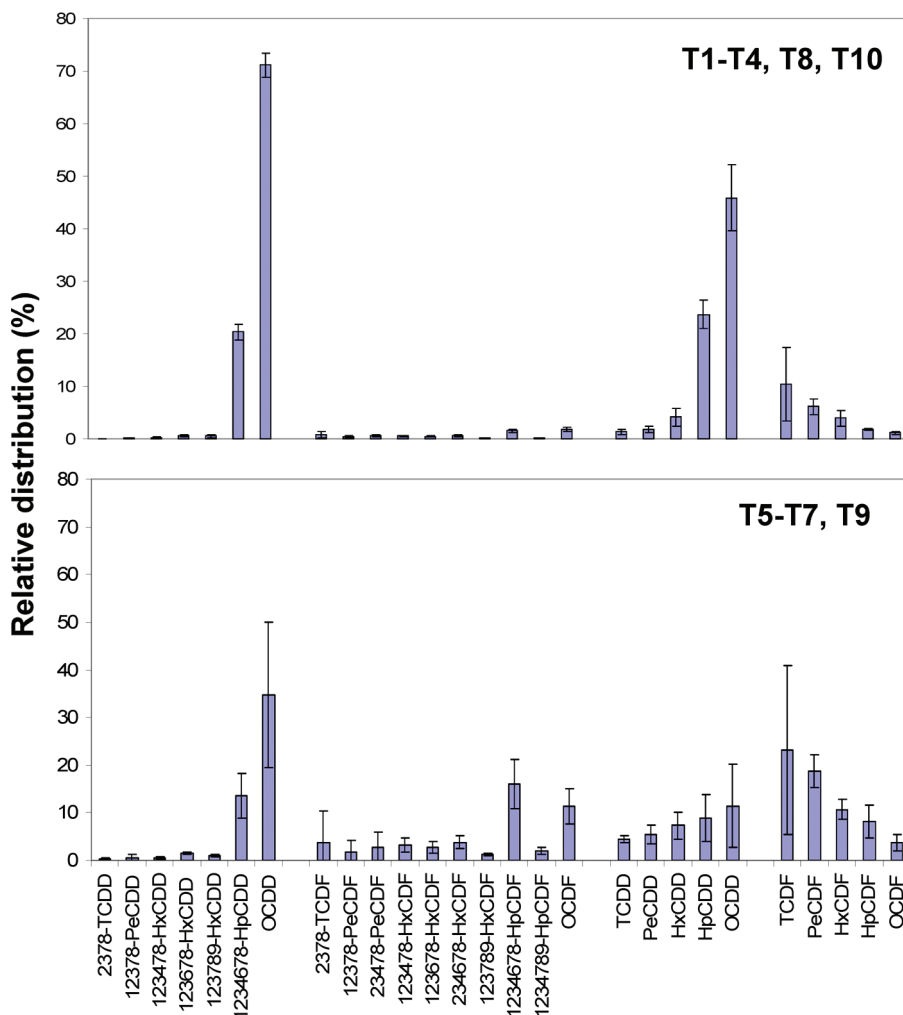


FIGURE 2. Averaged congener patterns observed in both cruises. The first group (T1–T4, T8, T10) resembles a typical “sink” pattern, whereas the second group (T5–T7, T9) resembles a typical “source” pattern.

mixture depending on the groups (Figure 2). One group of patterns (T1–T4, T8, and T10) was characterized by a significantly higher predominance of higher chlorinated PCDDs, OCDD accounting for the $71 \pm 2\%$ and $46 \pm 6\%$ of the $\Sigma_{2,3,7,8}$ -PCDD/Fs and Σ_{Cl_4-8} DD/Fs, respectively (*t*-test, $p < 0.001$). However, a significantly higher predominance of PCDFs was observed in the other group of pattern (T5–T7, T9) where 1,2,3,4,6,7,8-HpCDF and OCDF accounted for the $16 \pm 5\%$ and $11 \pm 4\%$ of the $\Sigma_{2,3,7,8}$ -PCDD/Fs, respectively and PeCDF accounted for the $19 \pm 3\%$ of the Σ_{Cl_4-8} DD/Fs (*t*-test, $p < 0.001$). In addition, higher $\Sigma_{2,3,7,8}$ -PCDD/F and Σ_{Cl_4-8} DD/F concentrations were measured in general in the first group of transects, whereas lower concentration were recorded in the second group (Figure 1, Table 1), although no statistically significant differences were found (*t*-test, $p = 0.28$).

A predominance of higher chlorinated PCDDs and little contribution of PCDFs is considered as a ‘sink’ signal where the lighter congeners were ‘weathered’ in their travel from the source to the sampling sites due to atmospheric processes (e.g., photodegradation). On the other hand, when higher contribution of PCDFs occurs the pattern represents a “fresh” emission (source) where lower chlorinated congeners in particular PCDFs have insufficient time to experience significant degradation/depletion processes (33, 38). Transects giving a source signal occurred both in the western and eastern Mediterranean so no regional effect seemed to be observed (as for the absolute concentrations).

Our hypothesis is therefore that the air masses giving rise to the source pattern are transported from areas with low

PCDD/Fs concentrations and become “contaminated” from local sources in opening transit. Whereas air masses giving rise to a sink pattern reflect a higher concentration from a nonsource environment. In order to examine this hypothesis the air mass origins were determined for the cruise samples using the HYSPLIT model. Since the sampling origin was different along each of the transects, GPS position records from the ship were used to determine the boat position every hour and a 120 h back trajectory was calculated computing from the current location every 6 h. Trajectories were calculated at 50, 100, 500, and 1000 m above the sea level. BT frequency plots are presented in SI Figure S2.

Air masses corresponding to a “source” pattern (T5–T7, T9) came from the Atlantic and arrived to the Mediterranean basin crossing western Europe (mainly Spain and France) or NW Africa at different latitudes. Air masses giving rise to a ‘sink’ pattern (T1–T4, T8, and T10) came (or were circulating) from N, NE Europe (except T10 where air masses were circulating in western Europe and an Atlantic contribution, more similar to the other group, was observed). Even if there are sources in N or central Europe, what the air masses are reflecting is more a weathered signal coming from these areas, after several years of abatement practices and PCDD/Fs emissions reduction from point sources. Therefore, a signal reflecting a higher continental background concentration but no particular source is observed in the open Mediterranean Sea. On the other hand, “clean” air (low/background pollutant concentration) arriving from the Atlantic becomes contaminated to different degrees in transport to the

Mediterranean basin given rise to a source pattern. T9 exhibited a higher concentration than expected if our hypothesis were true, but these air masses had crossed NW Africa until reaching the eastern Mediterranean Basin. That may explain a higher load of pollutants (in particular PCDFs, see Table 1, pointing in addition to a potential source character of this region) compared to the other transects (T5–T7) where air masses find their way to reach the Mediterranean mainly from the Gibraltar strait to northern France (SI Figure S2 B).

The higher predominance of low chlorinated PCDD/F in the source pattern might result from net volatilization from seawater acting as a source in a background concentration situation. In fact, a net volatilization of some PCDD is estimated (see fluxes discussion below) and taking into consideration the uncertainties in the flux estimations revolatilization cannot be excluded a priori and may contribute to the signal observed. Another explanation can be that when ambient levels are low, PCDD/Fs emissions from ships crossing the Mediterranean may act as a local source. Ship emissions (0.1 ng kWh^{-1} PCDD/Fs WHO-TEQ emission factor for residual oil engine, corresponding to $\sim 0.5 \text{ ng kg}^{-1}$ fuel WHO-TEQ) are relatively low compared to other sources (39). However, concentrations (derived from PCDD/Fs emissions from residual oils or gasoil powered ships) ranging from 5–30 and 3–5 pg m^{-3} WHO-TEQ, respectively, have been reported (39). According to the Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC), around 200 000 vessels cross the Mediterranean annually (26). The combination of low atmospheric concentrations, volatilization of some PCDD/Fs congeners from seawater surface and this intense maritime traffic may explain the source pattern observed. There is therefore a necessity of further investigating the PCDD/Fs ship emission influence in the open sea pollution. For example, there is no current ship emission inventory for PCDD/Fs in the Mediterranean Sea. That will allow to better assess the relative influence of this source compared to other PCDD/Fs sources in open waters such as the advection of continental air masses coming from North and central Europe or North Africa or revolatilization from seawater surface.

Atmospheric Deposition. Diffusive air–water exchange was calculated by estimating the PCDD/Fs absorption (F_{AWAb} , $\text{pg m}^{-2} \text{ d}^{-1}$) and volatilization (F_{AWVol} , $\text{pg m}^{-2} \text{ d}^{-1}$) fluxes as follows:

$$F_{\text{AWAbs}} = -10^{-3} k_{\text{ol}} C_{\text{g}} / H' \quad (1)$$

$$F_{\text{AWVol}} = k_{\text{ol}} C_{\text{w}} \quad (2)$$

Where k_{ol} is the air–water mass transfer coefficient (m d^{-1}), C_{g} (fg m^{-3}) and C_{w} (fg L^{-1}) are the pollutant concentration in the gas and dissolved phases, respectively, and H' the dimensionless Henry's law constant. H' values and their temperature dependence as well as K_{ol} values have been estimated as explained elsewhere (8, 40), and the nonlinear influence of wind speed has been taken into account by correcting the water-side mass transfer coefficient using a Weibull distribution of wind speeds (see SI Text S5) (41). The fact that PCDD/F dissolved concentrations were below LODs for most samples/congeners (in particular low chlorinated PCDD/Fs) only allow to provide net air–water exchange fluxes for seven compounds in four transects. (Figure 3A). Dry deposition fluxes were calculated by estimating the aerosol-bound PCDD/F fluxes as follows:

$$F_{\text{DD}} = v_{\text{d}} C_{\text{aerosol}} \quad (3)$$

Where C_{aerosol} is the volumetric concentration of PCDD/F in aerosols (ng m^{-3}) and v_{d} is the deposition velocity of aerosols.

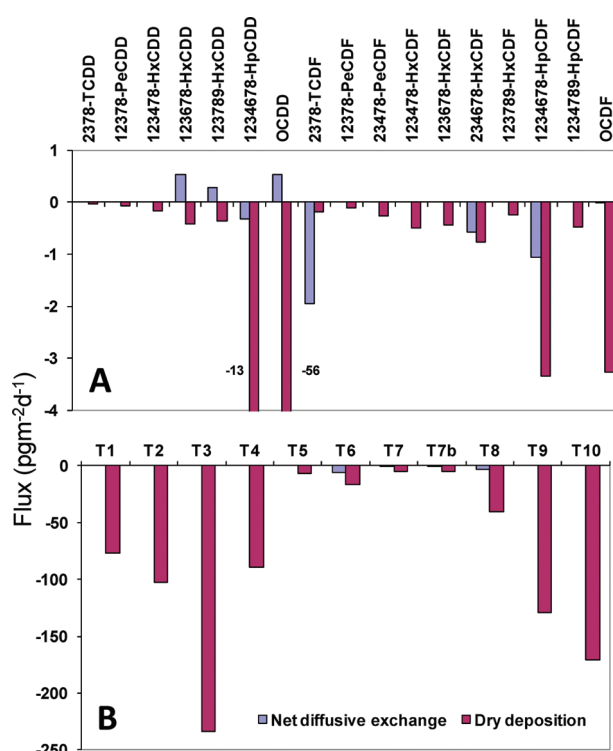


FIGURE 3. Average diffusive air–water exchange (only from samples where PCDD/Fs water concentrations were available) and dry deposition fluxes of 2,3,7,8-PCDD/F congeners to the Mediterranean Sea during both cruises (A) and total deposition (Σ 2,3,7,8-PCDD/F) fluxes for all transects (B).

The v_{d} values for PCDD/F will be similar to those of aerosol organic and black carbon since these phases dominate the gas-particle partitioning of PCDD/Fs (42, 43). There are few reports on deposition velocities of PCDD/F and other POPs (8). The only v_{d} values available for open sea conditions ($\sim 0.1 \text{ cm s}^{-1}$) have been reported for PAHs, which show a similar gas-particle partitioning than PCDD/Fs. However, significantly higher v_{d} values during sea salt formation events were reported (44). Other v_{d} measurements for PAH at NW Mediterranean coastal sites ranged between 0.1 and 0.5 cm s^{-1} (45). Presumably, the v_{d} values during the sampling cruises ranged from 0.1 (open sea conditions) to 0.3 (coastal sites). Therefore, a value of 0.2 cm s^{-1} for v_{d} has been chosen as representative of marine aerosols at high sea but influenced by continental sources. The uncertainty associated to dry deposition fluxes is then of an order of two, due to the lack of measurements of v_{d} during the Mediterranean cruises. Figure 3A shows the average PCDD/Fs dry deposition flux for all transects and the net diffusive fluxes (average of four samples) to the Mediterranean Sea during both cruises.

The overall flux is dominated by those of the more dominant compounds which are OCDD and 1,2,3,4,6,7,8-HpCDD followed by OCDF and 1,2,3,4,6,7,8-HpCDF. Dry deposition clearly dominated for higher chlorinated compounds (hepta- and octa-CDD/Fs). Net diffusive fluxes were from sea to air (positive value, thus volatilization fluxes) for hexa- and octa-PCDDs whereas a net absorption (negative value) for tetra-, hexa-, and hepta- PCDFs was estimated (see SI Text S7 and Figure S3).

In order to determine the significance of the net flux direction the ratios of fugacity in air over fugacity in water ($f_{\text{g}}/f_{\text{w}}$) were estimated. When $f_{\text{g}}/f_{\text{w}}$ ranges from 0.3 to 3, gas and dissolved phases can be assumed close to equilibrium. The criteria adopted in order to ensure a flux direction was that of considering a net direction from air to water when $f_{\text{g}}/f_{\text{w}} > 3$ and a net direction from water to air when $f_{\text{g}}/f_{\text{w}} < 0.3$.

0.3 (see SI Text S6). SI Table S10 shows the fugacity ratios for all transects and samples. Fugacity ratios were generally within the range 0.3–3 for hexa-, hepta-, and octa-PCDDs indicating than air and water are close to equilibrium in most cases. Conversely, fugacity ratios were higher than 3 for tetra (only one transect)-, hexa-, and hepta-PCDF, pointing to a significant net absorption flux from the atmosphere. SI Table S10 also shows the estimated fugacity ratios using LODs for calculating the fugacity in water (f_w) (providing therefore a lower estimate of these fugacity ratios, since real dissolved phase concentrations will be lower than the LOD). For most transects and compounds where C_w were below LOD (except for tetra-, penta-, and some hexa-PCDDs in most samples and the tetra-PCDFs in four transects) a $f_g/f_w > 3$ was obtained and thus a net absorption can be assumed. For tetra- to hexa-PCDD and PCDF in some samples, it is not possible to ensure whether there is a net absorption or volatilization from the sea surface. In any case, considering the dry deposition and diffusive exchange together (Figure 3A and B), overall the Mediterranean sea is a sink of PCDD/Fs due to the relevance of dry deposition fluxes of PCDD/Fs (chemicals with high affinity to bound to aerosols).

These trends are similar to those described for the Atlantic Ocean (8). The total depositional fluxes (dominated for the higher chlorinated compounds) for the different transects are shown in Figure 3B. $\Sigma 2,3,7,8$ -PCDD/F dry deposition fluxes in the Mediterranean Sea ranged from 5 to 170 $\text{pg m}^{-2} \text{d}^{-1}$, whereas the highest flux (234 $\text{pg m}^{-2} \text{d}^{-1}$) corresponded to the Black Sea (T3). The lower values of the estimated fluxes are similar to the dry deposition fluxes (1–7 $\text{pg m}^{-2} \text{d}^{-1}$) reported for the Atlantic Ocean (8) and higher than those reported for remote North Atlantic marine atmosphere (1.5 $\text{pg m}^{-2} \text{d}^{-1}$) (46). The annual $\Sigma 2,3,7,8$ -PCDD/F deposition fluxes (only dry) to the Mediterranean and Black Seas are estimated to be 4–156 and 210 kg year^{-1} , respectively. The dry deposition fluxes in the Marmara and Black Seas are from 2 to 55 times higher than the fluxes in the Mediterranean Sea. The presented values are the background deposition fluxes but PCDD/Fs atmospheric inputs are expected to be higher in coastal areas and during precipitation events, where wet deposition of contaminants become more relevant (8).

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Supporting Information Available

Additional data and information on the data sets, different sampling approaches and details on analytical methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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