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Oceanic Sink and Biogeochemical Controls on the Accumulation of Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans, and Biphenyls in Plankton

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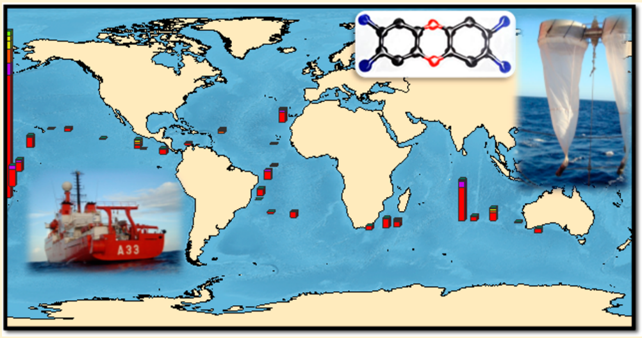
Supporting Information



ABSTRACT: Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) were measured in plankton samples from the Atlantic, Pacific, and Indian Oceans collected during the Malaspina circumnavigation cruise. The concentrations of PCDD/Fs and dl-PCBs in plankton averaged 14 and 240 pg g_{dw}^{-1}, respectively, but concentrations were highly variable. The global distribution of PCDD/Fs and dl-PCBs was not driven by proximity to continents but significantly correlated with plankton biomass, with higher plankton phase PCDD/F and dl-PCB concentrations at lower biomass. These trends are consistent with the interactions between atmospheric deposition, biomass dilution, and settling fluxes of organic matter in the water column (biological pump), as key processes driving POPs plankton phase concentrations in the global oceans. The application of a model of the air−water−plankton diffusive exchange reproduces in part the influence of biomass on plankton phase concentrations and suggests future modeling priorities. The estimated oceanic sink (Atlantic, Pacific, and Indian Oceans) due to settling fluxes of organic matter bound PCDD/Fs and dl-PCBs is of 400 and 10,500 kg y^{-1}, respectively. The atmospheric inputs due to gross diffusive absorption and dry deposition are nearly 3 and 10 times larger for PCDD/Fs and dl-PCBs, respectively, than the oceanic sink. These observations suggest that the coupling of atmospheric deposition with water column cycling supports and drives the accumulation of dl-PCBs and PCDD/Fs in plankton from the global oligotrophic oceans.

INTRODUCTION

Persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are semivolatile anthropogenic chemicals, reaching the remotest oceanic and polar regions.[1−8] PCDD/Fs and PCBs are also hydrophobic, and thus, they bioaccumulate and biomagnify in aquatic food webs,[9−11] being toxic even at trace concentrations.[12,13] The bioaccumulation and trophic transfer of PCDD/Fs and dl-PCBs have been studied previously in the marine environment.[14−20] However, most of these studies have not covered the lower levels of the marine food web. Phytoplankton and zooplankton, collectively named as plankton hereafter, are the first step for pollutant incorporation in the food chain.[21] The accumulation of POPs in plankton is thought to be dominated by water−lipid partitioning.[22,23] Additionally, plankton uptake of POPs and the subsequent settling flux of organic matter bound POPs are key controlling factors of the oceanic occurrence and sink of POPs.[24−28] Previous studies have reported the occurrence of organic pollutants, such as PCBs, polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) in plankton from the Mediterranean and Black Seas,[29−31] the Southern Ocean[2] and the Strait of Georgia.[25] However, the only assessments of PCDD/Fs in marine phytoplankton and zooplankton are those reported for coastal zones.[14,17,20]

Earlier works on the occurrence of POPs in plankton, usually focused on PCBs in lacustrine or local/regional marine

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environments, have described a strong dependence of concentrations on biomass, with and inverse correlation between pollutants concentration and amount of biomass in the water.[2,15,25,30,32,33] The lower concentrations found at sites with higher biomass reflects the depletion of POPs in the water column due the joint effect of biomass dilution and the biological pump. Biomass dilution reduce the POP concentrations due to larger amounts of lipids available for plankton–water partitioning, while the biological pump depletes the water column concentrations by settling of organic carbon bound POPs to deep waters.[2,24,28,29] The variability of POP concentrations in plankton has important implications for the accumulation of POPs at higher trophic level organisms through bioaccumulation and biomagnification. There are no previous studies on the accumulation of POPs in plankton for large oceanic regions of the Atlantic, Pacific, and Indian oceans that could confirm the previously proposed processes controlling POP concentrations in planktonic organisms. Specifically, it is not clear if POP concentrations in oceanic plankton follow the spatial distribution related to proximity to continental sources and atmospheric transport patterns, as observed for PCDD/Fs in the atmosphere,[8] or on the contrary, their global distribution is controlled by other physical and biogeochemical controls.

The objectives of this study are (i) to provide, for the first time, an assessment of the global occurrence of PCDD/Fs and dl-PCBs in plankton from the Pacific, Indian, and Atlantic Oceans and (ii) to assess the influence of atmospheric deposition and water column biogeochemical processes as drivers of POPs occurrence in oceanic plankton.

MATERIALS AND METHODS

Sample Collection. Sampling was carried out within the framework of the Malaspina Expedition 2010, which consisted of an oceanographic circumnavigation campaign sampling all open oceans between 40° N and 35° S. A total of 29 plankton samples were collected on board R/V *Hespérides* from December 2010 to July 2011. Transects covered the three main oceans collecting 10 samples from the Atlantic Ocean, 8 from Indian Ocean, and 11 from Pacific Ocean. Plankton samples were taken at the stations listed in Annex I of the Supporting Information using a double net trawl system with a 50 μm mesh size and performing several vertical tows from 20 m below the deep chlorophyll maximum (DCM), as identified from CTD casts, to the surface. The sampling depths ranged from 30 to 180 m (averaging 117 m depth, see Annex I, Supporting Information). Plankton biomass was transferred from the net beaker to a clean glass bottle and then filtered over precombusted 47 mm GF/D glass fiber filters (Whatman GE, U.K.). Filters were wrapped in aluminum foil, placed in zip bags, and stored at −20 °C until their analysis in the laboratory.

Chemical Analysis. Prior to the extraction, plankton samples were freeze-dried, weighed, and spiked with known amounts of mixtures of $^{13}C_{12}$ PCDD/F (EPA-1613LCS, Wellington Laboratories, Guelph, Canada) and $^{13}C_{12}$ dl-PCB (WP-LCS, Wellington Laboratories, Guelph, Canada), which were used as recovery surrogates. Samples were Soxhlet extracted for ∼24 h using 400 mL of a mixture of toluene:cyclohexane. The organic extract was concentrated in a rotary evaporator and then transferred to *n*-hexane prior to cleanup, which was performed as described elsewhere (Annex II, Supporting Information).[8] The final extracts were rotary concentrated, reduced to dryness by a gentle stream of nitrogen, and reconstructed in a known amount of mixtures of $^{13}C_{12}$ PCDD/F (EPA-1613ISS) and $^{13}C_{12}$-dl-PCB (WP-ISS) used as internal standards for quantification. High resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS) was used for instrumental analysis. All analysis were performed on an Agilent 6890NT gas chromatograph (Agilent, Palo Alto, CA, U.S.A.) fitted with a 60 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 ms fused silica column for PCDD/Fs and dl-PCBs, coupled to an Micromass Ultima NT (Waters, Manchester, U.K.) HRMS controlled by a Masslynx data system. A positive electron ionization (EI+) source operating in the MID mode at 10,000 resolution (10% valley definition) was used for identification. Quantification was carried out by the isotopic dilution method. Further details on analytical methods and the list of the 17 PCDD/Fs and 12 dl-PCB quantified are described in Annex II of the Supporting Information.

Simultaneous to the plankton samples, atmospheric samples (gas and aerosol phase) were collected and analyzed as reported in a companion work.[8]

Quality Assurance and Quality Control (QA/QC). A strict quality assurance/quality control procedure (QA/QC) was followed, including regular analysis of analytical standards of target compounds in order to check mass spectrometer sensitivity and reproducibility, the analysis of certified reference materials in order to verify the accuracy of the method, and the analysis of blanks to avoid possible contamination during the analytical manipulation. Laboratory blanks covering the whole methodology and field blanks including also the transport and storage during the oceanographic campaign ruled out a possible contamination. There were no detected PCDD/F congeners in blanks except for 1,2,3,4,6,7,8-HpCDD and OCDD, which had values close to the detection limit. As expected from their higher environmental concentrations, there was a higher frequency of detected dl-PCB congeners than PCDD/Fs in blanks, being the congeners PCB-118, PCB-105, PCB-156, PCB-77, and PCB-167 detected in all the blank samples, but at concentrations always 1 order of magnitude lower than the concentrations in field samples. The mean blanks measured concentration was subtracted from the samples. The recoveries of the analytical procedure were between 33% and 127% for PCDD/Fs with an average of 85% and ranged from 50% to 138% for dl-PCBs with an average recovery of 95%. Limits of detection and surrogate recoveries are given in Annex II of the Supporting Information.

Analysis of Organic Carbon and Nitrogen. During the Malaspina campaign, plankton samples were also collected for the analysis of organic carbon (OC), nitrogen (N), and the carbon and nitrogen isotopes ($\delta^{13}C$, $\delta^{15}N$). Samples for OC and N analyzes were collected by vertical hauls of nets (30 cm diameter, 40 μm mesh size; 50 cm diameter, 200 μm mesh size) between 200 m depth and the surface just after the vertical tows performed for the plankton samples aiming at PCDD/Fs and dl-PCBs analysis. Details on sampling and analysis of OC, N, $\delta^{13}C$, and $\delta^{15}N$ can be found elsewhere.[34] Samples were size-fractionated using sieves of 200, 500, 1000, and 2000 μm. For this study, we computed total OC and N as the sum of all fractions and biomass-weighted averages of $\delta^{13}C$ and $\delta^{15}N$.[35] Even though the sampling depth for these samples was generally deeper than that of plankton samples used for POP analysis, these provide a measure of the variability of OC, N, $\delta^{13}C$, and $\delta^{15}N$ in plankton at oceanic scale. We also estimated the trophic position of the plankton in the size fraction 500–

1000 μm ($TP_{500-1000}$) as representative of the main primary consumers of plankton (copepods). TP was compared to PCDD/Fs and dl-PCBs concentrations at each station. The measured OC, N, $\delta^{13}C$, and $\delta^{15}N$ are given in Table S7 of the Supporting Information.

Plankton $TP_{500-1000}$ was estimated as

$$TP_{500-1000} = 1.5 + \frac{(\delta^{15}N_{500-1000} - \delta^{15}N_{40-200})}{3.4} \quad (1)$$

by assuming that $\delta^{15} N_{40-200}$ represents a mixture of phyto- and zooplankton at the base of the food web (TP = 1.5[36]) and that the average increase in $\delta^{15} N$ between TLs is 3.4‰.[37]

■ RESULTS AND DISCUSSION

PCDD/Fs Occurrence in Plankton. Levels of ∑PCDFs and ∑PCDDs in plankton ranged from 1 to 93 pg g_{dw}^{-1} and from 0.2 to 94 pg g_{dw}^{-1}, respectively (Figure 1 and Figure S2, Supporting Information). Table 1 shows the average and range of concentrations for each PCDD/F congener and for each oceanic basin. The toxic equivalent ($WHO\text{-}TEQ_{2005}$) for PCDD/Fs in plankton ranged between 0.01 and 6.6 pg $WHO\text{-}TEQ_{2005}$ g $_{dw}^{-1}$. Octaclorodibenzo-*p*-dioxin (OCDD) was the predominant PCDD congener in all the plankton samples, followed by 1,2,3,4,6,7,8-heptaclorodibenzo-*p*-dioxin (HpCDD) (Table 1 and Figure S2, Supporting Information). Octaclorodibenzofuran (OCDF) was the dominant PCDF congener in plankton, followed by the two 2,3,7,8-substituted heptachlorodibenzofurans (HpCDFs) (Table 1 and Figure S2, Supporting Information). Therefore, the more hydrophobic PCDD/Fs dominate the pattern found in plankton. There were no significant differences ($p > 0.05$) of neither the PCDD nor PCDF concentrations in plankton among the different oceanic basins. The concentrations of PCDD/Fs in plankton from the open Atlantic, Pacific, and Indian oceans are 1 to 2 orders of magnitude lower than those reported for the Baltic Sea and Senday Bay in Japan.[17,20] However, the concentrations of PCDD/Fs in plankton reported here, all from the open oceans, were not correlated to distance to continents, suggesting that the decrease in concentrations occurs close to the coast. The pattern of individual PCDD/Fs in the open ocean plankton is less enriched in OCDD, HpCDD, and OCDF (Figure S3, Supporting Information) when compared with the reported profiles in plankton from Senday Bay, Bohai Bay, and the Baltic Sea.[14,17,20] The different patterns at the open ocean than at coastal sites likely reflect the larger influence of riverine/runoff at the coastal sites and the diverse loss processes of PCDD/Fs during atmospheric transport to remote regions. Both atmospheric dry deposition of aerosol bound chemicals and air−water diffusive exchange will diminish the abundance of the more hydrophobic compounds,[8] while atmospheric degradation due to reaction with OH radicals is more effective depleting PCDDs than PCDFs.[8,38,39]

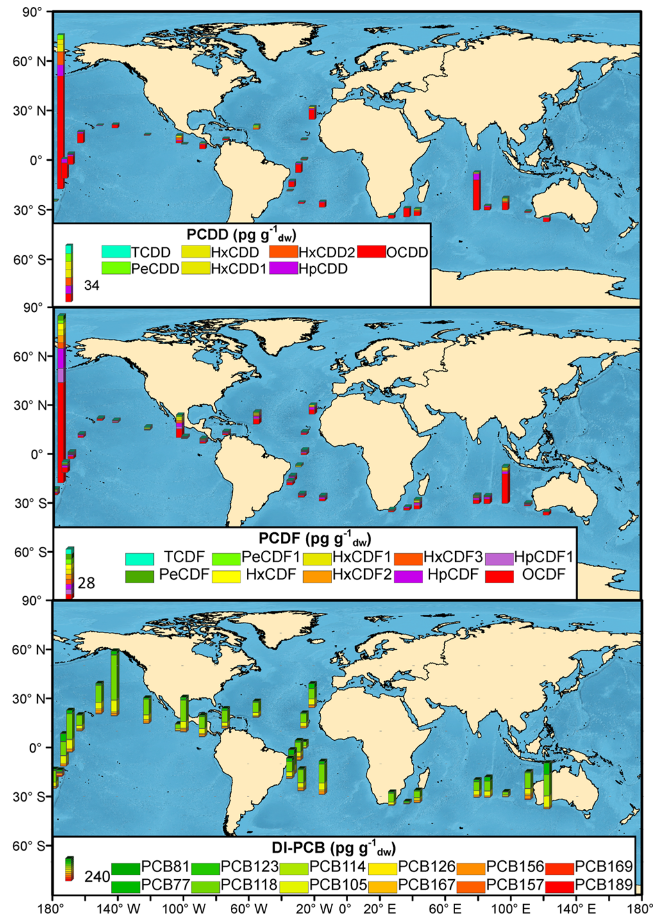

Figure 1. Global distribution of POPs concentrations in oceanic plankton. (Upper panel) Polychlorinated dibenzo-*p*-dioxins (PCDDs). (Middle panel) Polychlorinated dibenzofurans (PCDFs). (Bottom panel) Dioxin-like polychlorinated biphenyls (dl-PCBs).

dl-PCBs Occurrence in Plankton. Table 1 summarizes the mean and range of the 12 dl-PCBs concentrations in plankton for the different oceanic basins. The concentrations of ∑dl-PCB in plankton ranged from 30 to 692 pg g $_{dw}^{-1}$, while the dl-PCB $WHO\text{-}TEQ_{2005}$ in plankton ranged between 0.3 and 15 pg g $_{dw}^{-1}$. dl-PCB profiles are similar to those found in Senday Bay and Bohai Bay (Figure S4, Supporting Information), with a clear predominance of PCB-118 (around 50% of total dl-PCBs) followed by PCB-105 (20%). The global distribution of dl-PCB concentrations in plankton (Figure 1) shows a lack of significant differences among oceanic basins, with a more uniform spatial distribution across the different oceans than PCDD/Fs. The highest dl-PCB concentrations correspond to a North Pacific sample, while the lower value is located in the Indian Ocean. There was also a lack of significant influence of distance to continents on PCB levels in open ocean plankton. The concentrations of PCB-118 in the Atlantic, Pacific, and Indian oceans are comparable to those reported for the Southern Ocean[2] but 10 times lower than those described in the open Mediterranean and Black Seas[29] (Figure S5, Supporting Information).

Plankton Biomass as Descriptor of Variability of PCDD/F and dl-PCB Concentrations in Plankton. The global spatial distribution of PCDD/F concentrations in plankton (Figure 1) shows a remarkable variability and do not correspond with the spatial trends for gas and aerosol phase PCDD/F concentrations concurrently measured during the Malaspina campaign.[8] Gas and aerosol phase PCDD/Fs and dl-PCBs were generally higher at locations proximate to continents. Conversely, the highest plankton phase PCDD/Fs concentration was found in the open Pacific Ocean (Figure 1), and high values of PCDFs were also observed in the open Indian Ocean.

This suggests that there are other physical and biogeochemical processes modulating POPs levels in the global oceans. Previous studies of POPs accumulation in plankton have mainly

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Table 1. Occurrence of PCDD/Fs and dl-PCBs in Plankton from the Atlantic, Indian, and Pacific Oceans and for the Global Oceans[a]

Ocean	North Atlantic	South Atlantic	Indian	South Pacific	North Pacific	Global
TCDFs	0.1 (0.1–0.2)	0.2 (0.1–0.2)	0.2 (0.1–0.3)	0.4 (0.2–0.5)	0.2 (0.1–0.3)	0.2 (0.1–0.5)
PeCDFs	0.5 (0.3–0.8)	0.4 (0.3–0.5)	0.5 (0.2–0.7)	1.9 (0.6–4.2)	0.5 (0.2–1.3)	0.6 (0.2–4.2)
HxCDFs	0.9 (0.2–1.8)	0.5 (0.2–0.8)	0.9 (0.2–2.0)	5.2 (0.7–14)	1.0 (0.3–3.5)	1.3 (0.2–14)
HpCDFs	0.9 (0.3–1.5)	0.6 (0.5–0.8)	0.9 (0.3–1.4)	6.9 (0.5–19)	0.8 (0.3–3.0)	1.5 (0.3–19)
OCDF	1.8 (0.8–2.8)	1.2 (0.9–1.7)	3.4 (0.5–17)	20 (1.2–56)	1.4 (0.3–4.9)	4.1 (0.3–56)
TCDDs	0.03 –	–	–	–	–	0.03 –
PeCDDs	0.6 –	0.1 (0.1–0.2)	0.5 (0.4–0.6)	2.7 –	0.5 –	0.7 (0.1–2.7)
HxCDDs	1.0 (0.1–1.9)	0.7 –	0.8 (0.1–2.3)	8.1 (0.5–16)	0.9 (0.2–2.6)	1.7 (0.1–16)
HpCDDs	0.3 (0.04–0.7)	0.4 (0.04–0.7)	0.8 (0.2–3.9)	4.6 (2.5–6.8)	0.5 (0.1–1.0)	0.8 (0.04–6.8)
OCDD	2.4 (0.4–6.0)	2.1 (0.1–5.1)	4.7 (0.5–18)	39 (9.4–69)	2.8 (0.4–5.8)	6.1 (0.1–69)
PCB-81	1.2 (0.5–1.9)	1.5 (1.1–1.9)	1.6 (0.3–4.4)	3.0 –	0.8 (0.4–1.2)	1.3 (0.3–4.4)
PCB-77	22 (8.3–49)	23 (2.3–51)	28 (4.0–116)	34 (12–78)	17 (4.5–36)	24 (2.3–116)
PCB-123	3.4 (2.3–4.7)	3.1 (2.0–4.4)	3.7 (2.1–6.3)	4.1 (3.3–5.2)	4.9 (1.9–9.1)	3.9 (1.9–9.1)
PCB-118	105 (90–120)	116 (41–196)	96 (8.5–218)	91 (7.2–146)	198 (45–475)	129 (7.2–475)
PCB-114	3.0 (2.5–4.4)	3.3 (1.0–5.0)	3.4 (1.7–8.1)	3.1 (1.9–4.3)	4.3 (1.9–8.0)	3.6 (1.0–8.1)
PCB-105	42 (35–58)	47 (14–71)	41 (5.3–114)	43 (5.2–80)	61 (15–117)	48 (5.2–117)
PCB-126	1.4 (0.8–2.0)	0.8 (0.4–1.4)	1.0 (0.8–1.2)	–	1.4 (0.8–2.4)	1.2 (0.4–2.4)
PCB-167	7.4 (5.6–10)	8.4 (2.7–14)	6.6 (0.9–17)	7.6 (6.6–8.8)	11 (2.7–15)	8.4 (0.9–17)
PCB-156	14 (9.5–18)	18 (5.8–26)	13 (3.2–32)	16 (13–19)	19 (5.4–28)	16 (3.2–32)
PCB-157	3.1 (2.1–4.2)	3.8 (1.1–5.3)	2.5 (1.0–5.1)	2.7 (2.2–3.1)	4.0 (1.3–5.7)	3.3 (1.0–5.7)
PCB-169	–	–	–	–	0.4 –	0.4 –
PCB-189	1.9 (1.0–3.2)	2.8 (0.8–4.7)	3.2 (0.9–7.0)	6.1 (2.1–13)	2.5 (1.1–4.3)	3.1 (0.8–13)
∑PCDFs	4.0 (1.7–6.8)	2.5 (1.2–3.1)	5.4 (1.5–21)	34 (3.4–93)	3.5 (1.4–13)	7.1 (1.2–93)
∑PCDDs	3.0 (0.6–7.8)	2.6 (0.4–5.8)	6.1 (0.8–23)	36 (0.5–94)	3.2 (0.2–6.9)	7.2 (0.2–94)
∑dl-PCBs	202 (163–257)	227 (71–356)	196 (30–491)	208 (70–346)	324 (79–692)	240 (30–692)
PCDD/Fs WHO-TEQ$_{2005}$	0.4 (0.1–1.1)	0.2 (0.1–0.4)	0.3 (0.01–1.1)	2.3 (0.2–6.6)	0.3 (0.1–1.4)	0.5 (0.01–6.6)
dl-PCBs WHO-TEQ$_{2005}$	3.5 (2.9–4.1)	3.8 (1.5–6.4)	3.2 (0.3–7.2)	3.2 (0.6–4.9)	6.5 (1.5–15)	4.3 (0.3–15)

[a] The average, minimum, and maximum concentrations (pg $g^{-1}{}_{dw}$) do not take into account the nondetects. The list of the measured 17 PCDD/Fs is found in Annex 2 of the Supporting Information.

been centered in the study of PCBs and PAHs.[2,15,27,29,30,32,40] Generally, these previous works suggest that an increase in plankton biomass results in a decrease in the measured POP concentrations in plankton, while the highest POPs concentrations in plankton are found at sites with the lowest plankton biomass. These trends have been explained by a biomass dilution effect of the concentrations, which is modulated by atmospheric inputs and the biological pump.[29]

Following the approach proposed by Berrojalbiz and coworkers[29] for PCBs in plankton from the Mediterranean Sea, which has already been adopted in other works,[2,25] planktonic concentrations (C_p, pg g $_{dw}$ $^{-1}$) were correlated to plankton biomass (B, mg_{dw} L^{-1}) by

$$\log C_p = a - m \times \log B \quad (2)$$

where m is the slope, and a is the independent term from the least-squares linear regression fitting the values of C_p and B. Figures 2 and 3 and Figure S6 of the Supporting Information show the strong dependence of PCDDs, PCDFs, and dl-PCBs concentrations on plankton biomass, with higher concentrations when the biomass was lower. The compound specific slopes (m) for PCDDs and PCDFs depend on the hydrophobicity of the compound, with larger absolute m values (more influence of biomass) for the more hydrophobic compounds as measured by the octanol–water partition constant (K_{OW}) (central panels in Figures 2 and 3). Although plankton phase concentrations of dl-PCBs also depended on B, there was not a significant correlation of dl-PCBs m values with log K_{OW} if dl-PCBs were considered alone, probably due to the narrow range of K_{OW} for dl-PCBs (less than one logarithmic unit) (Figure S6, Supporting Information). However, when m values for PCDD/Fs and dl-PCBs are considered together, all m values fit in a single linear correlation with the corresponding K_{OW} (Figure S8, Supporting Information), consistent with previous studies for PCBs.[2,25,29]

The present study shows that there are biogeochemical and physical controls on the occurrence of hydrophobic POPs in the water column, other than distance to continental sources, as reflected by the influence of plankton biomass as a descriptor of PCDD/F and dl-PCB concentrations in plankton (Figures 2 and 3 and Figures S6 and S7, Supporting Information). It is remarkable that a single regression including the samples from the different oceanic basins can describe the variability of PCDD/Fs and dl-PCBs in plankton for the global oceans.

Indeed, plankton biomass explains between 26% and 68% of the variability of PCDDs in plankton and between 25% and 53% of PCDF concentrations in plankton (Figures 2 and 3 and Figure S7, Supporting Information). Plankton biomass also accounts for up to 37% of the variability of dl-PCB concentrations in the global oceans (Figure S6, Supporting Information). If the concentrations of PCDD/Fs and dl-PCBs are corrected by the OC content ($C_{p,OC}$, pg $g^{-1}{}_{OC}$), instead of the dry weight biomass, in order to take into account the variability of the fraction of biomass with higher affinity to POPs, similar regressions between $C_{p,OC}$ and B (as OC

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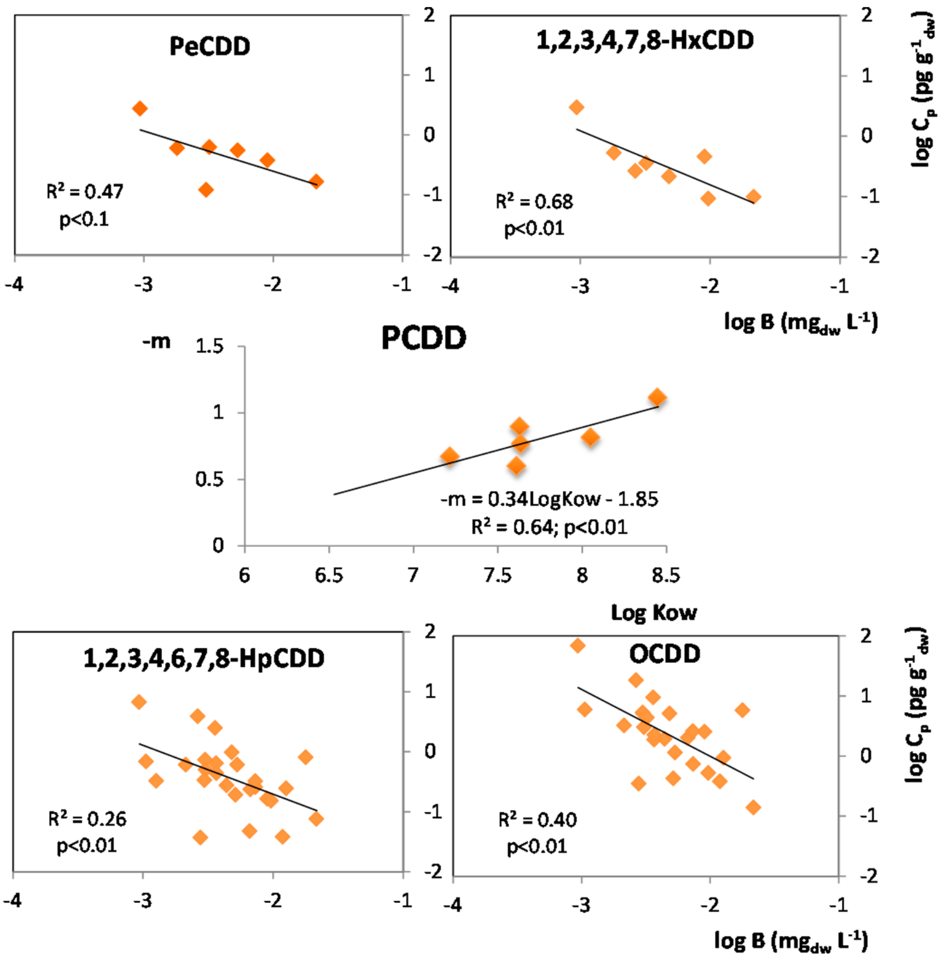

Figure 2. Influence of plankton biomass (B) on the PCDD concentrations in plankton (C_p) is shown in upper and lower panels. The central panel shows the relationship between m (slope of regressions of log C_p versus B) against the octanol–water partition constants (log K_{OW}) for all the 2,3,7,8-substituted dioxin congeners.

concentrations) are obtained for PCDD/Fs and dl-PCBs (Figures S9, S10, and S11, Supporting Information).

The influence of plankton biomass on the occurrence of POPs in plankton is due to a number of processes. First, there is a biomass dilution due to plankton–water partitioning of POPs. If there is a larger amount of biomass, the concentrations in plankton will tend to be lower.[15,29] In a volume of water with no inputs and losses of chemicals, the biomass dependence of concentrations of hydrophobic POPs will result in a value of m equal to −1.[29] However, the observed slopes in this study for PCDD/Fs and dl-PCBs ranged from 0.015 to 1.114, being these values correlated with the POPs hydrophobicity (K_{OW}) (Figures 2 and 3 and Figure S8, Supporting Information), similarly to what was found in earlier works for PCBs in marine plankton.[2,25,29] Hence, there are other processes than biomass dilution that modulate the influence of biomass on plankton phase concentrations.

POPs reach the open ocean by atmospheric deposition,[8,41] with a major contribution of diffusive air–water exchange in the subtropical and tropical oceans (Figure S12, Supporting Information).[41] If PCDD/Fs in air, water, and plankton were close to equilibrium, there would be no dependence of plankton phase concentrations on biomass, and the spatial variability of concentrations in plankton would resemble that observed for the atmosphere. On the contrary, there are no significant correlations between PCDD/F and dl-PCB concentrations in plankton with those in the gas and aerosol phase (p > 0.05). However, since diffusive air–water exchange is faster for the less hydrophobic (more volatile) compounds, the atmospheric inputs can compensate in part the decrease in plankton phase concentrations due to biomass dilution. Therefore, atmospheric inputs result in a lower dependence of plankton phase concentrations on biomass (lower m absolute values), especially for dl-PCBs and the less hydrophobic PCDD/Fs. The biological pump is an important sink of hydrophobic organic compounds, and settling of organic matter bound POPs reduces the concentrations of POPs in the water column. This process is more effective for the more hydrophobic chemicals.[24,28] In consequence, a stronger dependence of plankton phase concentrations on biomass (higher m absolute values) will occur for the more chlorinated PCDD/Fs. The observed dependence of PCDD/F concentrations on biomass is the result of biomass dilution, but its strength is modulated by atmosphere–ocean exchanges and settling fluxes of organic carbon bound POPs.

The potential role of diffusive air–water exchange supporting the PCDD/F and PCB concentrations in plankton was evaluated with a model that accounts for the coupling of air–water exchange, water–particle partitionin, and settling fluxes as described previously.[24,29,41] This approach allows to predict the plankton phase concentrations from the gas phase concentrations,[29] which were measured simultaneously with the

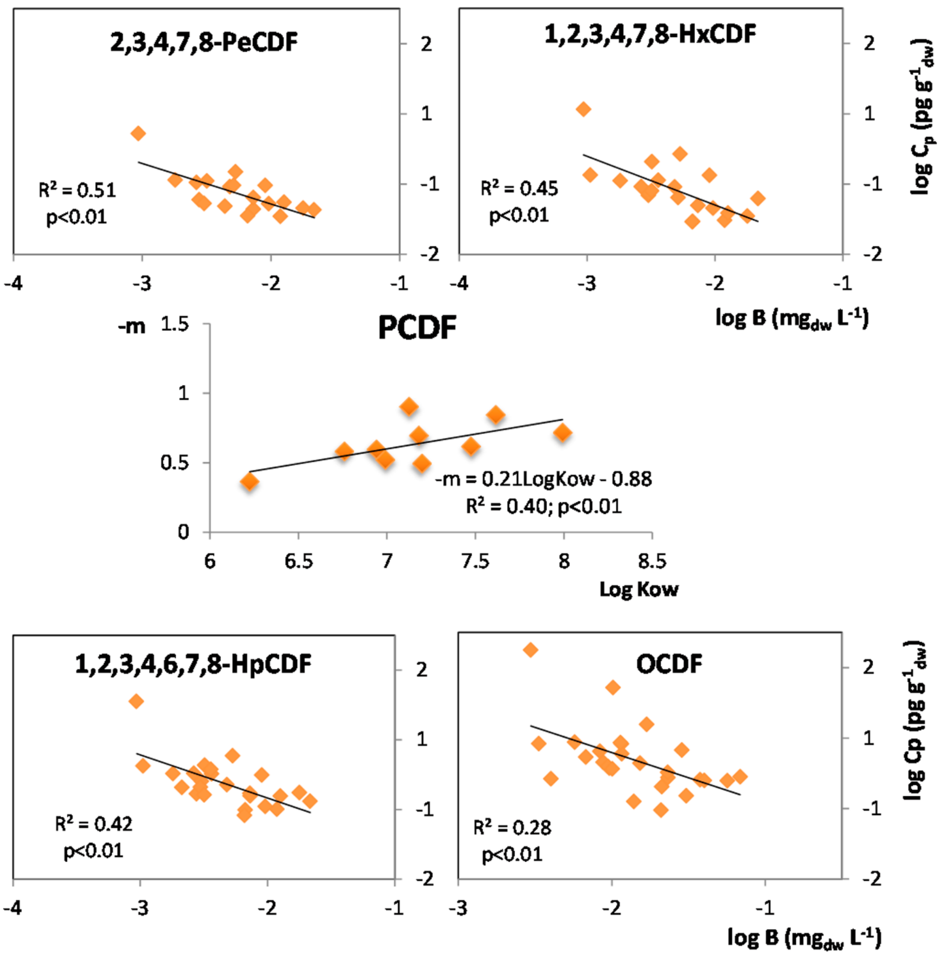

Figure 3. Influence of plankton biomass (B) on the PCDF concentrations in plankton (C_p) is shown in upper and lower panels. The central panel shows the relationship between m (slope of regressions of log C_p versus B) against the octanol−water partition constants (log K_{OW}) for all the 2,3,7,8-substituted furan congeners.

plankton phase concentrations. Figure 4 shows the predicted and measured concentrations of 2,3,4,7,8-PeCDF and PCB-118 in plankton, showing that the predicted plankton phase concentrations from the measured gas phase concentrations are of the same order of magnitude as the measured concentrations in plankton. The average relative error of predictions is of 84% and 150% for 2,3,4,7,8-PeCDF and PCB-118, respectively. In addition, the estimated plankton phase concentrations of most dl-PCBs (including all major congeners) are correlated with the plankton biomass, with this explaining between 16% and 35% of the variability of predicted plankton phase concentrations ($p < 0.05$). The model do predict low concentrations in plankton at high biomass for all compounds. However, for some PCDD/Fs, the model tends to overpredict concentrations in plankton for some samples with intermediate biomass (Figure 4). In addition, the model fails to predict the highest measured PCDD/Fs, concentrations and to lesser extend the highest dl-PCBs concentrations. This is probably due to the fact that part of the sampled plankton was below the thermocline, a feature not accounted in the model. The thermocline is an additional resistance, especially for dissolved POPs transfer to deeper waters, favoring the importance of biomass dilution of plankton phase concentrations below the thermocline. In any case, the thermocline is not seasonally persistent, and this resistance is also lowered during periods of higher turbulence due to higher wind speeds or currents. In addition, this model does not account for the atmospheric inputs due to dry deposition, which is important for PCDD/Fs. Finally, the parameterization is better for PCBs than for PCDD/Fs likely due to previous modeling efforts.[24,29,41] Future work should focus on the development of dynamic models that take into account the role of the previous history of physical and biogeochemical controls as drivers of POP concentrations in plankton and how these interact with the different atmospheric depositional processes.

Bioaccumulation in Planktonic Food Web. Since hydrophobic POPs biomagnify in the food web, the trophic level is also an important factor to be considered. The plankton samples collected during the Malaspina cruise consisted in a pool of organic matter containing phytoplankton, zooplankton, and aggregates of organic matter. This plankton originated from diversity of nutrient sources, as reflected by the large range of δ^{15}N values, but the overall trophic structure was essentially the same, as indicated by the small range in trophic positions (from 1.2 to 1.9) estimated for the 500−1000 μm size-fraction eq 1. The concentrations of individual PCDD/Fs and dl-PCBs were not correlated with neither δ^{15}N nor the trophic position, probably due to the bigger influence of plankton biomass as commented above. If we remove the influence of biomass (or organic carbon), the residuals were not correlated neither with δ^{15}N nor the trophic position. This is consistent with both phytoplankton−water and zooplankton−

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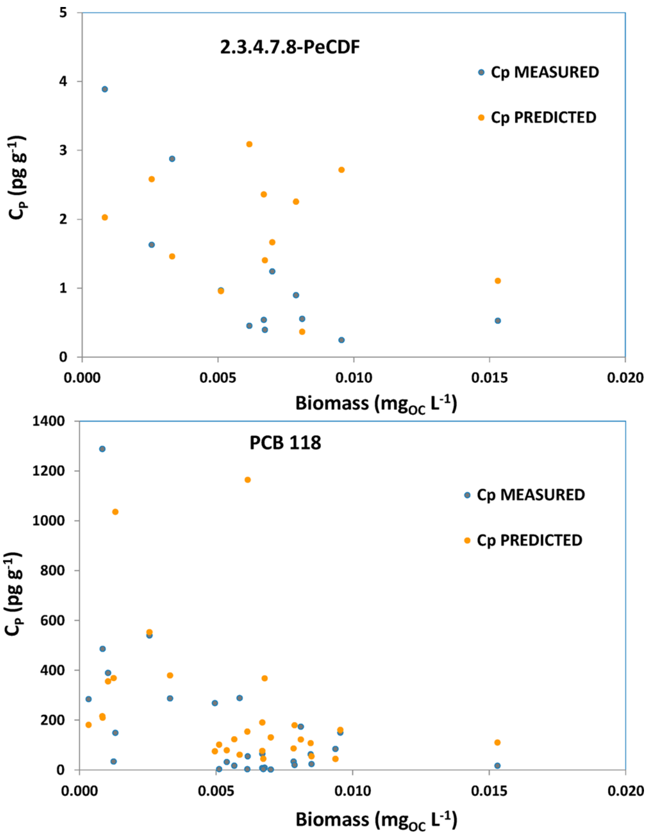

Figure 4. Predicted and measured plankton phase concentrations (pg g_{OC}^{-1}) of 2,3,4,7,8-PeCDF (upper panel) and PCB 118 (lower panel) versus biomass (mg_{OC} L^{-1}).

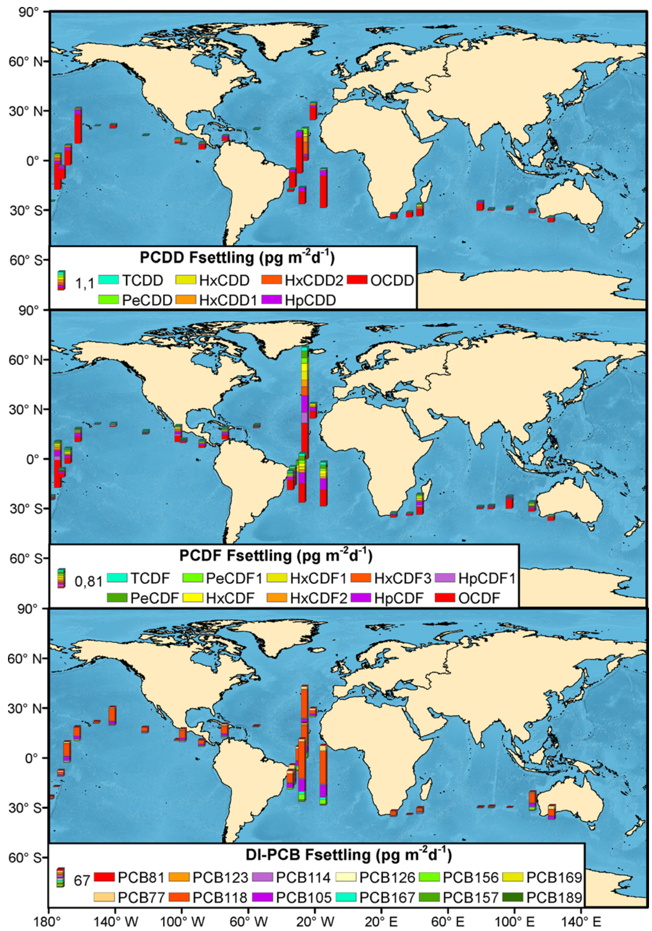

Figure 5. Estimated settling fluxes (pg $m^{-2}d^{-1}$) of PCDDs (upper panel), PCDF (middle panel), and dl-PCB (lower panel) in the global oceans.

water partitioning being driven by passive partitioning,[22,23] which implies that POP concentrations do not vary due to changes in the relative importance of phytoplankton or zooplankton on the overall sample biomass.

Oceanic Sink and Atmospheric Deposition of PCDD/Fs and dl-PCBs. The biological pump is thought to be the main oceanic sink for persistent and hydrophobic chemicals such as PCBs and PCDD/Fs.[24,28,41] The settling fluxes ($F_{Settling}$, pg m^{-2} d^{-1}) of PCDD/Fs and dl-PCBs can be estimated from $C_{p,OC}$, assuming that these are representative of the concentrations in settling particles, and the vertical fluxes of organic carbon (F_{OC}, g_{OC} m^{-2} d^{-1}) by

$$F_{Settling} = C_{p,OC} \times F_{OC} \tag{3}$$

F_{OC} values have been obtained from the recently published climatology for the global oceans.[42] Figure 5 shows the estimated settling fluxes of PCDD/Fs and dl-PCBs for the global oceans. Settling fluxes ranged from 0.003 to 2.13 pg m^{-2} d^{-1} for PCDD/Fs and from 0.014 to 135 pg m^{-2} d^{-1} for dl-PCBs. The spatial variability of these fluxes reflects the variability in $C_{p,OC}$ and F_{OC}. The spatially and annually extrapolated global oceanic sinks of PCDD/Fs and dl-PCBs due to the biological pump in the global oceans (Atlantic, Pacific, and Indian oceans) are of 400 kg y^{-1} and 10,500 kg y^{-1}, respectively. The atmospheric inputs due to dry deposition of aerosol bound PCDD/Fs and dl-PCBs are of 360 and 900 kg y^{-1}, respectively.[8] The inputs due to wet deposition and the net diffusive air−water exchange cannot be estimated from this study. However, it is possible to estimate the gross diffusive absorption (Figure S12, Supporting Information) from the gas phase concentrations. Diffusive atmospheric inputs of PCDD/Fs and dl-PCBs are of 1100 and 100,000 kg y^{-1}, respectively. Therefore, atmospheric inputs are 3 and 10 times higher than the biological pump sink, and thus, its magnitude is sufficient to control water column dynamics of PCDD/Fs and dl-PCBs and their accumulation in plankton. Previous works have suggested close to air−water equilibrium and even volatilization of PCBs from the oligotrophic Atlantic and Pacific oceans,[43,44] but there is probably a net deposition in some regions of the subtropical oceans.[45] Regardless of the net direction and magnitude of diffusive fluxes, gross absorption fluxes are much higher than dry deposition and settling fluxes, influencing water column levels of PCDD/Fs and dl-PCBs.[41] For PCDD/F, degradation in the water column could play a relevant role, while it is negligible for PCBs.[43] Therefore, the settling fluxes estimated here are a lower-end estimate of the oceanic sink of PCDD/F and dl-PCBs also because atmospheric inputs to the oceans and the settling fluxes are particularly high at higher latitudes than those covered by the Malaspina campaign.[28,46]

There are more than three decades of research efforts to elucidate the influence of atmospheric deposition on organic pollutant concentrations in aquatic environments.[47,48] There are landmark field studies showing the unequivocal importance of atmospheric inputs of POPs, such as those performed at Siskiwit Lake (Isle Royale, Lake Superior).[49,50] The present study further elucidates the importance of atmospheric deposition as supporting the accumulation of POPs in biota

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in the remote oceans. The concentrations in the water column are not directly related to remoteness to primary sources[51] but depend mainly on the physical and biogeochemical controls affecting the atmospheric deposition and cycling of POPs in the lower atmosphere and surface ocean, even though it is not yet possible to predict all the observed variability in concentrations. These biogeochemical controls also exert an important influence on the relative concentrations of the different dl-PCBs and PCDD/Fs in the water column biota and their oceanic sequestration, thus probably affecting the fractionation of POPs at oceanic scales.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The complete data set of PCDD/Fs and dl-PCBs concentrations and additional figures and tables. This material is available free of charge via the Internet at http:/pubs.acs.org.The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01360.

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Notes

The authors declare no competing financial interest.

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