POLYCHLORINATED DIBENZO- DIOXINS, FURANS AND BIPHENYLS IN PLANKTON FROM THE GLOBAL OCEANS

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Introduction

The open oceans are one of the most pristine environments in the world, away from anthropogenic persistent organic pollutants (POP) sources, but not exempt of them because of the long range atmospheric transport (LRAT)[1]. Several families of POPs have been regulated by the Stockholm convention on POPs aiming at reducing or eliminating the production and use of these harmful substances[2]. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), commonly known as dioxins, are among the most toxic POPs listed in the Stockholm Convention. Besides dioxins, polychlorinated byphenils (PCB) are also included in the above-mentioned treaty; some of them (known as dioxin like PCB or dl-PCB) have similar toxic properties to dioxins due to their similar structure and planarity. The lipophilic nature and stability of POPs allow efficient assimilation and accumulation in the fat tissue of organisms leading to their biomagnification trough the food chain[3]. The trophic transfer of PCDD/F and dl-PCB has been studied previously[4] as well as bioaccumulation in the food chain[5,6]. In marine food webs, plankton is the lower trophic level, and the first step for the pollutant incorporation in the food chain[7]. Additionally, plankton uptake of POPs and the subsequent settling fluxes of organic matter bound POPs play an important role in the oceanic biogeochemical processes and as controlling factors of the oceanic occurrence of POPs[8,9]. Previous studies have reported the occurrence of POPs, such as PCBs, in plankton from the Mediterranean and black sea[10,11], Southern Ocean[12] and Strait of Georgia[13]. Despite PCDD/F have been studied in other marine organisms[14], no data on PCDD/F and dl-PCB are available in marine plankton except for some results from PCDD/F bioaccumulation studies[4,5,15].

The aim of this study is to provide for the first time the global oceanic plankton occurrence of PCDD/F and dl-PCB in the Pacific, Indian and Atlantic Oceans, and assess the influence of atmospheric deposition and water column biogeochemical processes as drivers of their occurrence in the oceanic plankton. Sampling was carried out within the framework of the Malaspina Expedition 2010, which consisted on an oceanographic circumnavigation campaign sampling all oceans between 40ºN and 35ºS. As part of the task included within the project, correlation with atmosphere occurrence is also intended to elucidate. More details on atmosphere are reported in "Background concentrations of PCDD/Fs and dl-PCBs in the oceanic atmosphere during the Malaspina circumnavigation" (also reported in this meeting).

Materials and methods

A total of twenty nine plankton samples were collected on board R/V *Hespérides* during the Malaspina oceanographic circumnavigation campaign in December 2010- July 2011. Transects covered the three main oceans: Atlantic, Indian and Pacific Ocean. Plankton samples were taken at sampling stations using a double net trawl system with a 50 µm mesh size and performing vertical tows from a variable depth (located 10 meters below the maximum chlorophyll depth) to the surface. Plankton biomass was transferred from net beaker to a clean glass bottle and then filtered with 47 mm GF/D glass fiber filters to remove the excess of water. Filters were stored frozen at -20ºC till the analysis started. Air samples were also collected in this oceanographic circumnavigation campaign and were composed of 2 parts: The quartz fiber filter (QFF) collected the particulate phase and the polyurethane foam (PUF) retained the gas phase.

Plankton samples were freeze-dried and weighted before starting the analytical procedure. Prior to extraction process, samples were spiked with known amounts of mixtures of 13C12 PCDD/F (EPA-1613LCS, Wellington Labs., Guelph, Canada) and 13C12 dl-PCB (WP-LCS, Wellington Labs., Guelph, Canada). After 2 h they were soxhlet extracted for ~24 h using 400 mL toluene:cyclohexane as solvent. After that, raw extract was cleaned up in order to remove interference substances and other matrix components. The clean-up and fractionation process was based on the sequential use of open chromatographic multilayer silica, basic alumina and carbon columns[16]. 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). Finally, high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS) was used for instrumental analysis. Quantification was carried out by isotopic dilution method.

Simultaneous to the plankton samples, atmospheric samples (gas and aerosol phase) were collected and analyzed as reported in “Background concentrations of PCDD/Fs and dl-PCBs in the oceanic atmosphere during the Malaspina circumnavigation” (also reported in this meeting). This allowed determining the atmospheric inputs of PCDD/F and dl-PCBs to the open ocean.

Results and discussion

PCDD/F occurrence

Levels of $\sum$PCDFs in plankton ranged from 0.3-11 pg/g dw and for $\sum$PCDDs concentrations varied from 3.4-14 pg/g dw. The toxic equivalent of plankton samples was between 0.01 and 0.8 pg WHO-TEQ2005/g dw. Only PCDD/F concentrations from few bioaccumulation studies in marine environments[4,5,15] could be used to compare our plankton concentrations. Plankton collected in Bohai Bay (North China)[4] has comparable levels to mean concentrations found in global oceans while Sendai Bay (Japan)[5] and Northern Baltic[15] studies had concentrations 1-2 orders of magnitude higher than those obtained in Malaspina circumnavigation.

As expected, octaclorodibenzo-p-dioxin (OCDD) was the predominant PCDD/F congener in all the plankton samples. This prevalence is remarkable in PCDD/F profiles shown in Figure 1. Comparing the plankton profiles with phytoplankton and zooplankton profiles from bioaccumulation studies[4,5,15] we notice that the same pattern is followed.

Global distribution of PCDD/F plankton concentrations is presented in Figure 1. For PCDD, there is a single sample in Pacific Ocean that stands above the rest. This sample also highlights in PCDF map together with another Indian Ocean sample. Conversely, low concentrations were found in the North Pacific and Southern Atlantic. The main descriptor of the variability of PCDD/F concentrations is related to the biomass abundance in the water column (see discussion below).

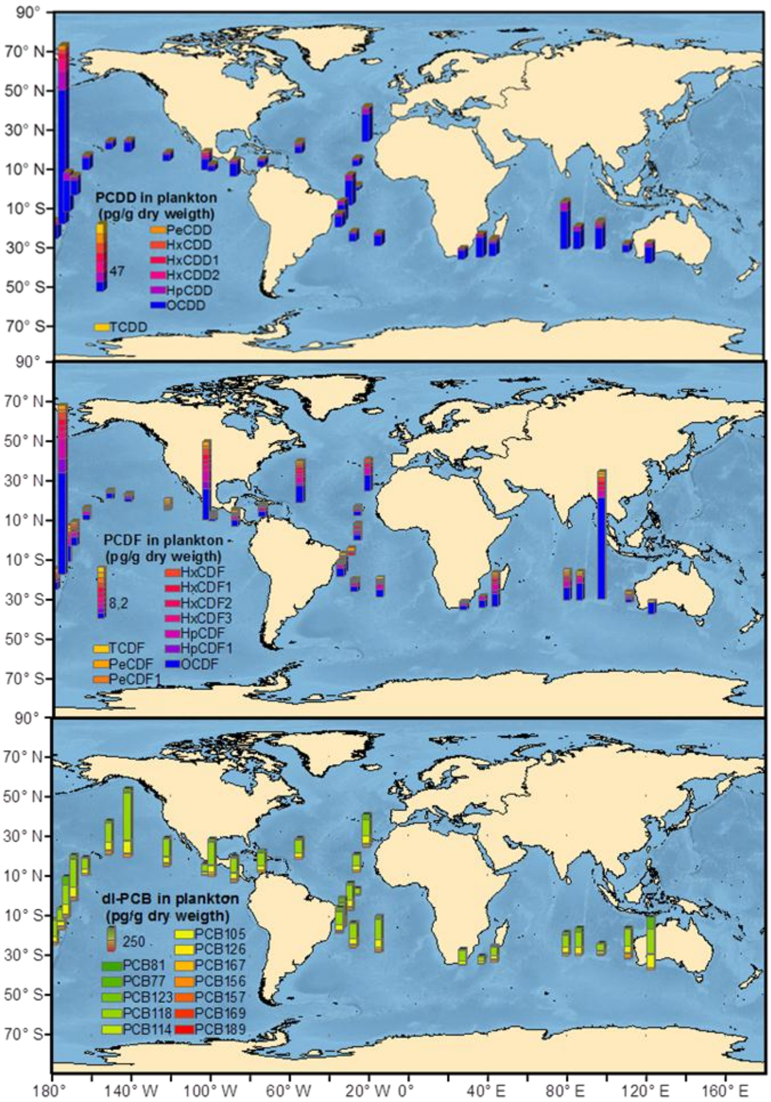

Figure 1. Global distribution of PCDD/F and dl-PCB concentrations in plankton (pg/g dw)

Dl-PCB occurrence

The concentrations of ∑dl-PCB in plankton from the global oceans ranged from 27 to 439 pg/g dw while the toxic equivalent of plankton samples was between 0.4 and 9.6 pg WHO-TEQ2005/g dw. The concentrations obtained were consistent with the unique dl-PCB plankton values published in two biomagnification studies in Senday Bay (Japan)[5] and Bohai Bay (North China)[4] despite only a pair of samples was analyzed in each study (1 fitoplankton + 1 zooplankton). A better comparison could be done with PCB#118 which is included in ICES PCB congeners and reported in two oceanic studies in plankton[10,12]. Concentrations found in Southern Ocean[12] have similar values to those reported in this paper, despite the maximum concentration in the southern ocean was 4 times the maximum concentration found in PCB#118 in our study (300 pg/g dw). As we expected, PCB#118 levels obtained in the Mediterranean and Black Sea[10] were in general one order of magnitude higher (and up to 2 orders of magnitude in the hottest points) than those obtained in the open Oceans.

Dl-PCB profiles (Figure 1) are similar to profiles found in Senday Bay and Bohai Bay, with a clear predominance of PCB#118 (around 60% of total dl-PCB) followed by PCB#105 (20%).

Global distribution of dl-PCB plankton concentrations is given in Figure 1. It could be observed a fairly uniform distribution across the 3 oceans without points protruding above or below the media exaggeratedly (contrary to the PCDD/F). The highest dl-PCB value corresponds to a North Pacific sample while the lower value is located in the South Pacific Ocean.

Factors affecting POPs occurrence

Some studies focused on the processes driving the variability of POPs in plankton have observed that high plankton biomass (B) corresponded to low POPs concentrations in plankton (C_p)[9,10,12,17]. This trend to decrease C_p at high B is thought to be the result of the coupling between atmospheric deposition inputs and settling in the water column due to the biological pump, leading to an apparent "biomass dilution effect"[17]. Using a similar approach to that of Berrojalbiz et al. (2011)[10], concentrations in plankton were fitted by least-squares versus the biomass supporting that, in general, C_p decreased with increasing B following a power function:

$$log[C_p] = a - m \cdot log[B]$$

The slope *m* depends on the compound physical-chemical properties. PCDD/F had higher *m* values than dl-PCB, which suggest a higher control of C_p by plankton biomass for PCDD/F, while lower dl-PCB values of *m* denote a major independence of C_p on B. This could be observed in Figure 1 with the remarkable C_p differences in PCDD/F global maps while dl-PCB had similar concentrations despite the different B. The best correlations concentration versus biomass were achieved for PCDD/F (R^2=0.5, p<0.01). Dl-PCB correlations were not so high on average (R^2=0.2, p<0.09), but some dl-PCB congeners were in the same order than those obtained for PCDD/F.

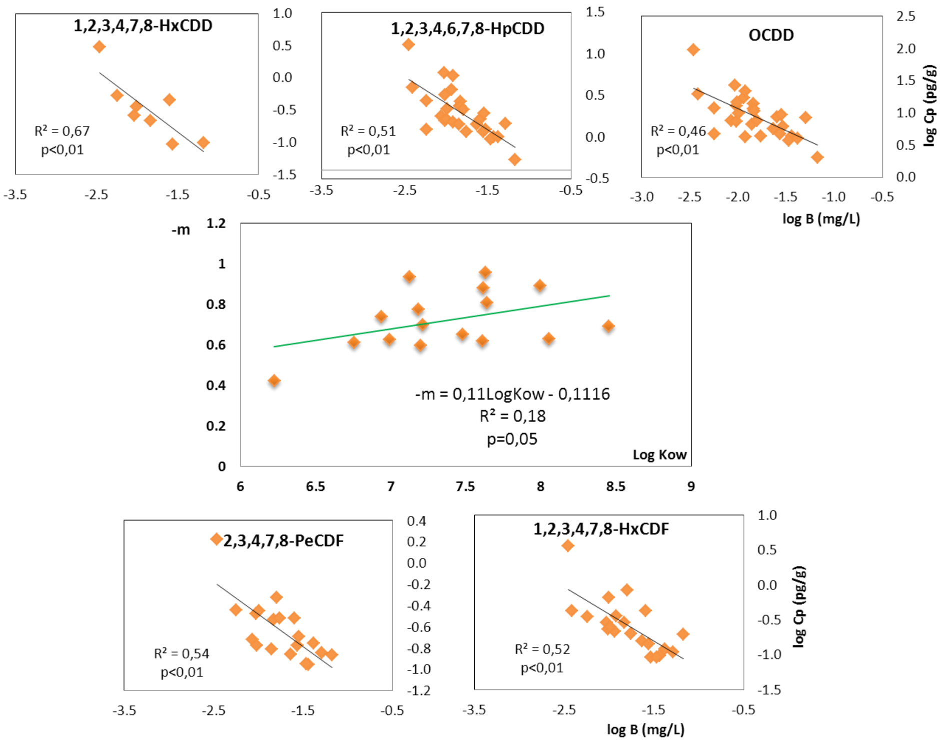

Figure 2. Influence of plankton biomass (B [mg/L]) on the concentrations of PCDD/F in plankton (C_p [pg/g dw]). The central panel shows the dependence of m on the chemical hydrophobicity (K_{OW}) for plankton samples from Atlantic, Indian and Pacific Ocean.

Those better congeners were PCB#81 and PCB#77 which belong to non-ortho dl-PCB group, more similar to PCDD/F.

To assess the influence of PCDD/F affinity to organic matter in these processes, *m* was plotted against the corresponding octanol-water partition coefficient (K_{OW}) (Figure 2). The central panel shows the dependence of *m* on the chemical hydrophobicity for plankton samples. If these trends were due to “biomass dilution”, the value of m would be the same for all compounds, while it varies depending on K_{OW}. For the more hydrophobic congeners, as PCDD/F air-water exchange is a slower process while the settling could be an important loss due to the higher fractions of sorbed chemical in particles and its settling fluxes (biological pump)[9,18]. This means that atmospheric deposition cannot support the fast sinking fluxes of PCDD/F when the biomass is higher, leading to lower concentrations in plankton. Because the concentrations in plankton reflect the occurrence of PCDD/F in the water column (fast water-plankton partitioning), the results demonstrate that the occurrence of PCDD/F in the global oceans is controlled by the coupling of atmospheric deposition and the settling fluxes of PCDD/Fs, and not by the distance to sources.

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