

Atlantic Ocean Surface Waters Buffer Declining Atmospheric Concentrations of Persistent Organic Pollutants

LUCA NIZZETTO,^{*,†,‡}
RAINER LOHMANN,^{*,§}
ROSALINDA GIOIA,[†] JORDI DACHS,^{||} AND
KEVIN C. JONES[†]

Centre of Chemicals Management, Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K., Norwegian Institute for Water Research, Gaustadalleen 21, 0349, Oslo, Norway, Graduate School of Oceanography, University of Rhode Island, Rhode Island 02882, and Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-24, Barcelona 08034, Catalunya, Spain

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Decreasing environmental concentrations of some persistent organic pollutants (POPs) have been observed at local or regional scales in continental areas after the implementation of international measures to curb primary emissions. A decline in primary atmospheric emissions can result in re-emissions of pollutants from the environmental capacitors (or secondary sources) such as soils and oceans. This may be part of the reason why concentrations of some POPs such as polychlorinated biphenyls (PCBs) have not declined significantly in the open oceanic areas, although re-emission of POPs from open ocean water has barely been documented. In contrast, results from this study show that several polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) have undergone a marked decline (2–3 orders of magnitude for some homologues) over a major portion of the remote oligotrophic Atlantic Ocean. The decline appears to be faster than that observed over continental areas, implicating an important role of oceanic geochemical controls on levels and cycling of some POPs. For several lower chlorinated PCDD/Fs, we observed re-emission from surface water back to the atmosphere. An assessment of the effectiveness of the main sink processes highlights the role of degradation in surface waters as potentially key to explaining the different behavior between PCDD/Fs and PCBs and controlling their overall residence time in the ocean/atmosphere system. This study provides experimental evidence that the ocean has a buffering capacity - dependent on individual chemicals - which moderates the rate at which the system will respond to an underlying change in continental emissions.

Introduction

Persistent Organic Pollutants (POPs) are ubiquitous pollutants which are prone to long-range transport, persistent in

the environment, capable of accumulating in biota and food webs, and toxic (1). The generic term POPs includes, among others, polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs).

POP movement away from sources is influenced by atmospheric transport and temperature dependent partitioning between the atmosphere and environmental media. Their ultimate fate depends on biogeochemical drivers such as photo- and biochemical degradation, and the sorption to carbon-rich depositing material which causes POPs burial in soils or sediments (2–4). Taken together, these sink processes determine the overall residence time of POPs in the environment (5).

National and regional regulatory actions, together with the globally binding Stockholm Convention have aimed to drastically reduce the synthesis and emissions of POPs. For example, production and use of PCBs - which were intentionally synthesized for diverse industrial applications - was banned and measures adopted to neutralize old stockpiles, while for PCDD/Fs (which are byproducts of various manufacturing and combustion processes (6)) this resulted in upgrading or shutting down of incinerators and various industrial chlorine-using processes and plants, especially in industrialized and postindustrialized countries (7, 8). Indeed, there is good evidence for a gradual decline in atmospheric concentrations of PCDD/Fs and PCBs in source regions, in Northern Europe, North America, and the Arctic (7, 9–13), with the exceptions of samples taken in rural/remote areas of the U.S. or England, where PCDD/F sources might be dominated by ongoing small-scale diffuse emissions or secondary sources (14, 15).

Because of their persistence and semivolatility, it has been argued that a decline in primary atmospheric emissions can result in re-emissions of POPs from 'environmental capacitors' or secondary sources such as soils, sediments, vegetation, and ocean waters which became contaminated in the past (e.g. ref 16). This may be the reason why concentrations of PCBs have not declined significantly in the atmosphere of the open Atlantic ocean areas, as recently reported by Gioia et al. (17), although re-emission of POPs from remote oceanic surface waters has barely been documented (18), so far, but some modeling exercises suggest it may be happening for some POPs such as DDT (19).

Determining time-trends of atmospheric concentrations in remote areas at large geographical scales is extremely helpful to help assess the relative importance of fresh primary versus old secondary sources and likely future trends in ambient levels and biota.

Our group undertook a ship-board sampling campaign across the Atlantic Ocean in October–November 2005 to determine concentrations of a range of POPs, including PCBs and PCDD/Fs (17), and compare results with those obtained from previous campaigns (20, 21). The aim of the study was to assess whether PCDD/F concentrations had declined during the past decade in the atmosphere of the open Atlantic Ocean. Comparisons between PCDD/Fs and PCBs were used to shed light on the role of different biogeochemical controls on the long-term fate of POPs in this environment.

Experimental Section

Sampling

High-volume air and water samples for PCDD/Fs were collected between Bremerhaven (Germany) and Cape Town (South Africa) and stored as described elsewhere (20, 22)

* Corresponding author phone: (401)874-6612; fax: (401)874-6811; e-mail: lohmanna@gso.uri.edu (R.L.); phone: (+47) 98215393; e-mail: luca.nizzetto@niva.no (L.N.).

[†] Lancaster University.

[‡] Norwegian Institute for Water Research.

[§] University of Rhode Island.

^{||} IDAEA-CSIC.

(see also the Supporting Information). An earlier cruise in 1998 (20) provided reference atmospheric concentrations of PCDD/Fs along a similar track. In open Atlantic Ocean areas (namely between 30°N and 20°S) only 'clean' samples were compared (e.g., air sampler located upwind to the ship's stack to avoid ship board contamination (23). Even though the compared samples are in some cases at a different location of the oceanic gyre, only air masses originating from similar anticyclones systems and circulating for at least the previous 7 days over the open ocean before have been considered (24)). Therefore the different data sets were comparable and represented the atmospheric background concentrations of the central Atlantic Ocean.

Chemical Analysis

The analytical method for atmospheric samples was consistent with that used for the 1998 data set (20). The analysis of the two sets of samples was performed in the same laboratory and using the same facilities, analytical standards, and QA/QC measures. Data were reported as sum of congeners. Mono-CDD/Fs data were not considered due to possible breakthrough during sampling. For further details see ref 25 and text SI-1.

Assessment of the Geochemical Control on POP Fate

Four major geochemical controls on POPs were assessed here: degradation in air, degradation in water, settling with particles to deep waters, and air–water exchange (3).

The influence of these processes on the environmental fate of PCBs and PCDD/Fs was assessed by comparing their mass transfer coefficients or reaction velocities. Equations describing such velocities were parametrized with the scenario descriptors measured directly in the field and physicochemical properties from the literature. The selected environmental conditions were representative of the southern Atlantic gyre for the two weeks preceding the cruise (25 °C (T_{air})/26 °C (T_{water}) at the equator and 18 °C (T_{air})/19 °C (T_{water}) at 20°S; wind speed (11 ± 2 (SD) m s⁻¹) and direction ($139 \pm 10^\circ$ SD), with no precipitation). Air trajectories did not change during the 15 days prior to sampling in this region (24) with air masses coming from open ocean southern latitudes.

Reactions Velocity in Air, ν_{deg_A} (m d⁻¹). Reaction with $\cdot\text{OH}$ radicals is the key process controlling atmospheric half-life ($t_{1/2}$) of POPs (26). Following first order kinetics

$$J_{\text{deg}_A} = [\cdot\text{OH}] \cdot r_{\text{OH}} \cdot ABL \cdot C_A \quad (1)$$

where J_{deg_A} (mol m⁻² d⁻¹) is the flux of POPs lost by reaction, $[\cdot\text{OH}]$ (molecules cm⁻³) is the steady state concentration of $\cdot\text{OH}$ in the lower atmosphere; ABL (m) is the height of the atmospheric boundary layer, estimated to be ~150 m around the northern and southern gyres during the days of the cruise (24); r_{OH} (cm³ molecules⁻¹ d⁻¹) is the compound-specific reaction rate of the POP with $\cdot\text{OH}$ (26, 27), and C_A (mol m⁻³) is the gas-phase concentration of the POP. Average daily values of $[\cdot\text{OH}]$ for the Atlantic Ocean atmospheric boundary layer were obtained from Brauers et al. (28). Here, we assumed PCDD/Fs are mainly present in the gas phase, due to the low amount of organic and black carbon aerosols present in the remote marine boundary layer (22, 29). The term $[\cdot\text{OH}]r_{\text{OH}}ABL$ represents the velocity of the process, ν_{deg_A} (m d⁻¹). Previously reported atmospheric $t_{1/2}$ (30, 31) were also used to calculate ν_{deg_A} values and compared with those obtained here

$$\nu_{\text{deg}_A} = \frac{\ln(2)}{t_{1/2}} \times ABL \quad (2)$$

Reaction Velocity in Water, ν_{deg_W} (m d⁻¹). The velocity of the radical reactions in water, ν_{deg_W} , was estimated from reported overall water $t_{1/2}$ (30, 31) assuming a mixed layer depth (MLD) of 100 m (32) as follows

$$\nu_{\text{deg}_W} = \frac{\ln(2)}{t_{1/2}} \times MLD \quad (3)$$

The value of 100 m was taken from recent measurements performed in the same areas as this study (32).

Sinking Velocity with Settling OC, ν_{set} (m d⁻¹) in the Water. The vertical fluxes of POPs (J_{set} , mol m⁻² d⁻¹) were modeled assuming equilibrium between dissolved and OC-bound phases

$$J_{\text{set}} = C_w K_{\text{OC}} \times 10^{-6} \times F_C \quad (4)$$

where C_w (mol m⁻³) is the water dissolved phase concentration, K_{OC} (L × kg⁻¹) is the compound specific OC-water partition coefficient, the coefficient 10^{-6} is a conversion factor to provide consistent units, and F_C (g m⁻² d⁻¹) is the daily average export flux of OC from the surface water. $K_{\text{OC}}F_C$ 10^{-6} represents the mass transfer coefficient of this process (ν_{set} , m d⁻¹). K_{OC} values were based on field results (33), corrected for temperature and salinity. Values of F_C were estimated for the MLD from the values reported in ref 34 and ranged from 0.020–0.053 g m⁻² d⁻¹ for the oligotrophic region considered here.

Air–Water Exchange Mass Transfer Coefficient, ν_{a-w} (m d⁻¹). The overall mass transfer coefficient of the air–water gaseous exchange of POPs was estimated by describing it as the inverse of the overall resistance to the diffusion of PCDD/Fs through thin boundary layers (films) at the interface between air and water (35)

$$\frac{1}{\nu_{a-w}} = \frac{1}{\nu_a K_{\text{AW}}} + \frac{1}{\nu_w} \quad (5)$$

where ν_a and ν_w (m d⁻¹) are the mass transfer coefficient of the gaseous compounds in the air and water films (estimated as reported in the SI), respectively, and K_{AW} is the temperature corrected dimensionless air–water equilibrium partition coefficient (Henry's Law constant) (37, 38).

Results and Discussion

PCDD/Fs in Air and Water

Concentrations of PCDD/Fs in air and surface water are reported in Tables SI1 and SI2. Concentrations in water were only measured in 2005 and ranged from 15–120 fg L⁻¹ (ΣPCDFs) and 4–70 fg L⁻¹ (ΣPCDDs), with the highest values generally measured in proximity to the European coasts. In the water, dissolved concentrations of di-CDFs > tri-CDFs, with most other PCDFs being at or below detection limits. No clear trends were apparent for dissolved PCDDs, where most congeners were at or below detection limits.

Atmospheric concentrations in the open Atlantic were 7–35 fg m⁻³ for ΣPCDFs and 0.5–7 fg m⁻³ for ΣPCDDs. They were 2 to 3 orders of magnitude lower than in 1998 (20). Tetra- to octa-chlorinated congeners, routinely detected in 1998, were often below the detection limits in 2005. Only those air samples collected close to Europe and with recent back trajectories showing movement off the land mass, presented comparable concentrations to those collected in 1998. In 2005, ambient concentrations ranged from 80–700 fg m⁻³ for ΣPCDFs and 85–285 fg m⁻³ for ΣPCDDs (5–10 times lower than in 1998) (20), reflecting the influence of continental primary and/or secondary sources. The decline observed here (with an estimated $t_{1/2}$ between 0.7 and 1.1 years, assuming first order decline) appears much faster than

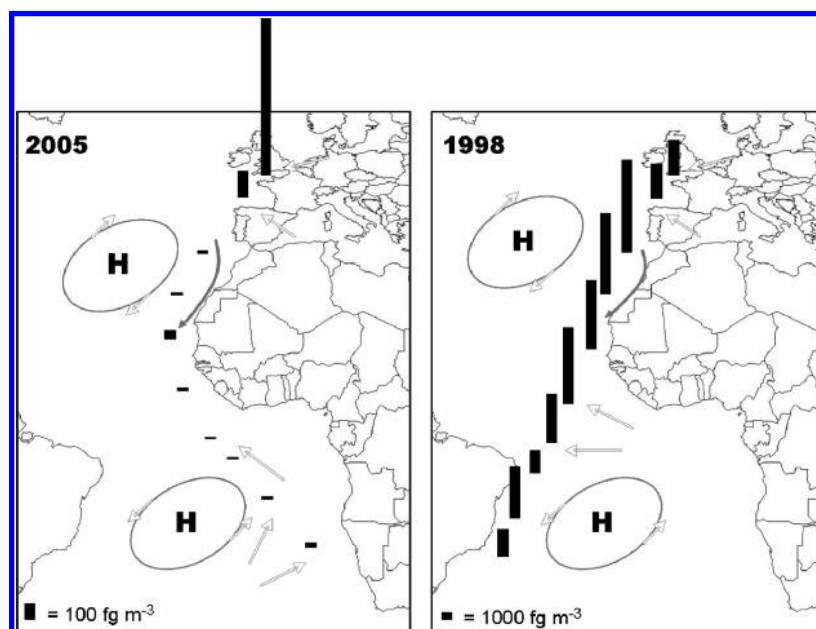


FIGURE 1. Atmospheric concentrations of PCDD/Fs in the 2005 and 1998 campaigns (sum of di- to octa- congeners). The dominant atmospheric systems during the campaigns are schematically represented (H = high pressure system), and wind direction is indicated by the arrows.

that observed for PCDD/Fs in continental areas (e.g., ambient air close to an upgraded incinerator: $t_{1/2} \sim 3$ years (7); deposition to alpine lakes: $t_{1/2} \sim 7$ years (11), vegetation samples in central Europe: $t_{1/2} \sim 10$ years (9), coastal benthic organisms: $t_{1/2} \sim 12$ –22 years (10)). In contrast to PCDD/Fs, our recent assessment of time trends of PCBs in the Atlantic Ocean atmosphere during the last ten years did not show any decline (17). This is despite PCBs having decreased ($t_{1/2} \sim 4$ years) in background air concentrations across northern Europe (13). These results suggest that biogeochemical processes in the ocean are likely to be responsible for the different fate observed here for PCBs and PCDD/Fs.

Oceanic Biogeochemical Controls

Atmospheric concentrations of POPs in remote areas are the result of the dynamic balance between advection, re-emission from environmental surface compartments, and environmental sinks. The biogeochemical control of the ocean on POPs fate has been detailed by Dachs et al. (3). Here, atmospheric $\cdot\text{OH}$ radical depletion, degradation in water, and removal to deep waters via OC settling fluxes are considered as the key sink processes. The partitioning of compounds between the surface water and the atmospheric gas phase buffers concentration changes in either compartment. Ultimately, a combination of compound specific (30) physicochemical properties and environmental mass transfer coefficients controls the interactions with the biogeochemical cycles and various loss/sink processes. Determining loss rates of POPs from environmental compartments (and their relative importance) is subject to large uncertainties (30, 31). Therefore the relevance of oceanic sink processes was assessed by estimating the order of magnitude of the mass transfer coefficients and reaction velocities to better understand the different behavior between PCDD/Fs and PCBs.

Figure 2 presents the estimated loss/sink velocities for a range of PCBs and PCDD/Fs congeners. Wide confidence intervals - typically over 1 order of magnitude - were derived from the uncertainty of the parameters in the calculations or from the literature (38). This analysis showed that i) indirect photolysis with $\cdot\text{OH}$ radicals in air is the fastest degradation pathway; ii) reaction in surface water is much faster (1–2 orders of magnitude) for PCDD/Fs than for PCBs, represent-

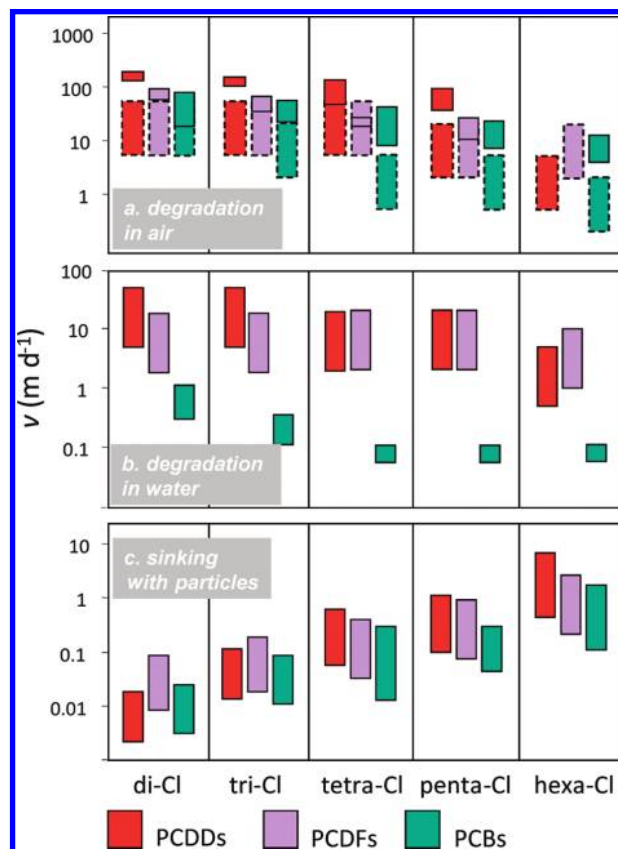


FIGURE 2. Velocities of the main loss/sink processes for POPs. Bands represent the range of the estimates. In the panel the solid lined bands refer to estimates of reaction velocity from eq 1, while dotted bands are from refs 26 and 27.

ing the major difference between the two classes; iii) export from surface water with settling OC was in general the slowest sink process, and it was relatively important compared to degradation in water only for the PCBs with >3 chlorines and PCDD/Fs with >6 chlorines; iv) degradation in surface water represented the largest loss flux for di- to penta-CDD/Fs in the system, given that typically 2–3 orders of magnitude

more of a given pollutant is present in a unit volume of water compared to air (Tables SI1 and SI2). This process represents therefore the dominant geochemical control on the system's resilience. Clearly photodegradation in these oligotrophic waters is also promoted by enhanced light penetration due to relatively low particle derived scattering. The photic zone in the Atlantic gyres is in fact typically more than 100 m deep. In other oceanic regions, with different trophic status, the relative importance of the different biogeochemical drivers will vary. For example, settling fluxes can be orders of magnitude higher in upwelling zones and other high productivity regions. In addition, PCDD/F could sorb strongly to carbonaceous particles such as soot carbon. The settling fluxes estimated here assume that organic matter is the major carrier of vertical transport of PCDD/F and PCB in the water column. Soot carbon concentration in remote oceanic waters are unknown but are probably extremely low. Nonetheless, due to the high affinity of coplanar compounds to soot carbon, it could be possible that settling fluxes are enhanced, especially for the highest chlorinated PCDD/Fs.

Biodegradation is not expected to play a significant role in these oligotrophic waters. Rather, indirect photochemical reaction with $\cdot\text{OH}$ is likely driving the degradation of POPs. The $\cdot\text{OH}$ photoproduction during daytime is dependent on the irradiation of chromophores present in the surface water dissolved organic matter (DOM) (39). It was shown that the $\cdot\text{OH}$ attack positions on the PCDD/Fs ring where the four C atoms neighbor the O atom(s) (40). This enhanced reactivity of PCDD/Fs explains their shorter $t_{1/2}$ compared to PCBs which lack these structures. This implies a key role of the ocean's DOM in controlling the fate of POPs at the global scale, given that DOM represents one of the planet's largest OC reservoirs. More research is required to understand the interactions between OH, DOM, and POPs.

Implications for the Atmospheric Concentrations

An important implication of these findings is that, because degradation in air is faster than any other sink process in oligotrophic regions, it is reasonable to expect that when declining atmospheric advective fluxes no longer support net deposition, the air-surface water system shifts toward a situation in which atmospheric concentrations of PCBs and PCDD/Fs are controlled by degassing from the surface water. Indeed, for PCDD/Fs there is experimental evidence that this has occurred across a large part of Atlantic Ocean in 2005. The fugacity ratio f_a/f_w between the air and water for POPs' concentrations measured in 2005 was calculated as follows

$$\frac{f_a}{f_w} = \frac{C_A}{C_w K_{aw}} \quad (6)$$

where f_a and f_w are the POPs' fugacities in air and water, respectively.

Values of $f_a/f_w < 1$ indicate the potential for re-emission of compounds from surface water. Considering the associated uncertainties with the ratios (38), it was assumed that $0.3 < f_a/f_w < 3$ is not significantly different from the equilibrium condition. Due to the frequent occurrence of concentrations below the limit of the detection, it was possible to calculate f_a/f_w only for a limited number of congeners and only in the location in which compounds were detected both in the water dissolved phase and in the gas phase. f_a/f_w was < 0.3 for PCDD/Fs across a large portion of the Atlantic (from 30°N to equator), indicating re-emission of low chlorinated PCDD/Fs from surface water (Figure 3). This is documented for the first time in open ocean areas and indicates that surface waters reacted to declining atmospheric levels by re-emitting PCDD/Fs to the air. In the rest of the oceanic regions, with the

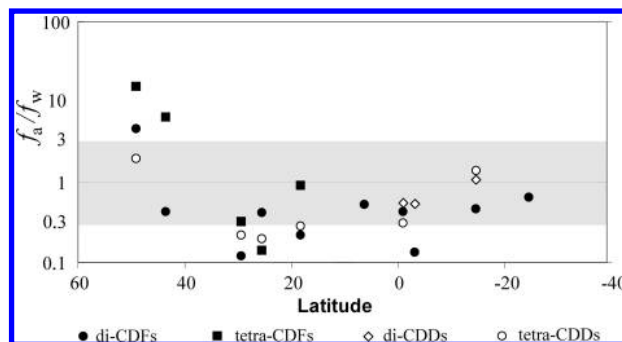


FIGURE 3. Values of the fugacity ratios between air and water as measured in 2005. The dotted area represents confidence boundaries (0.3 and 3) for the condition of partitioning equilibrium.

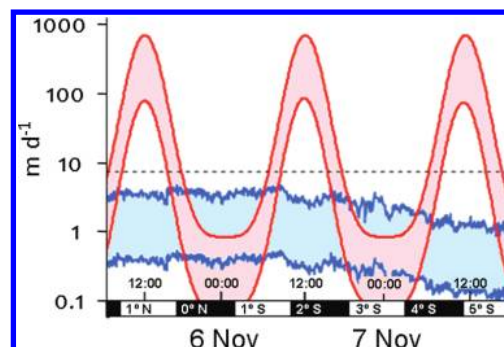


FIGURE 4. Dynamic comparison of the velocities of the air-water exchange v_{a-w} and reaction in atmosphere with OH radicals v_{degA} for a tetrachlorinated dioxin in the subequatorial leg of the cruise. The area in blue represents the range of estimates of v_{a-w} , while the red one represents the estimates of v_{degA} . The dotted line represents the overall average v_{degA} . The comparison has been performed for the period between the 5th and the 8th of November 2005, while the ship was cruising between 1°N and 5°S. Spatial and temporal scales are reported on the x axis.

exceptions of mid latitudes in the northern hemisphere, the f_a/f_w values ranged between 1 and 0.3, suggesting close to equilibrium conditions tending to revolatilization.

A necessary condition for the occurrence of low f_a/f_w is that the gaseous exchange between air and water is kinetically limited. In other words, the mass transfer coefficient v_{a-w} (m d^{-1}) of the air-water exchange must be slower than the degradation in air. We compared these two parameters by assessing their value during the transect of the cruises between 0 and 5°S. This is shown in Figure 4 with 2,3,7,8-TCDD taken as an example. The value of v_{a-w} was calculated as described in the Supporting Information, and the velocity of reaction in air v_{degA} was estimated from $[\cdot\text{OH}]$ diel trends (28) as a harmonic function. This transect encompasses 3 days and 3 nights, and the dynamic comparison was performed considering day and night periods because v_{degA} fluctuate dramatically between light and dark. During the daytime, v_{a-w} for PCDD/Fs was 1–2 orders of magnitude lower than v_{degA} for all di- to hexa-PCDD/Fs congeners, consistent with the low f_a/f_w measured above. During the night-time, atmospheric degradation is expected to be negligible due to the lack of reactive radicals. The results indicate that air-water exchange may therefore replenish the atmosphere with PCDD/Fs at night, potentially driving a day/night oscillation in air concentrations as has been observed in the literature (21). It should be noted that this will not apply to the hepta- and octa-DD/Fs, as these are controlled by particle settling both in air and water.

It is possible to show that such condition is verified also for the selected PCBs, although their f_a/f_w were found to be

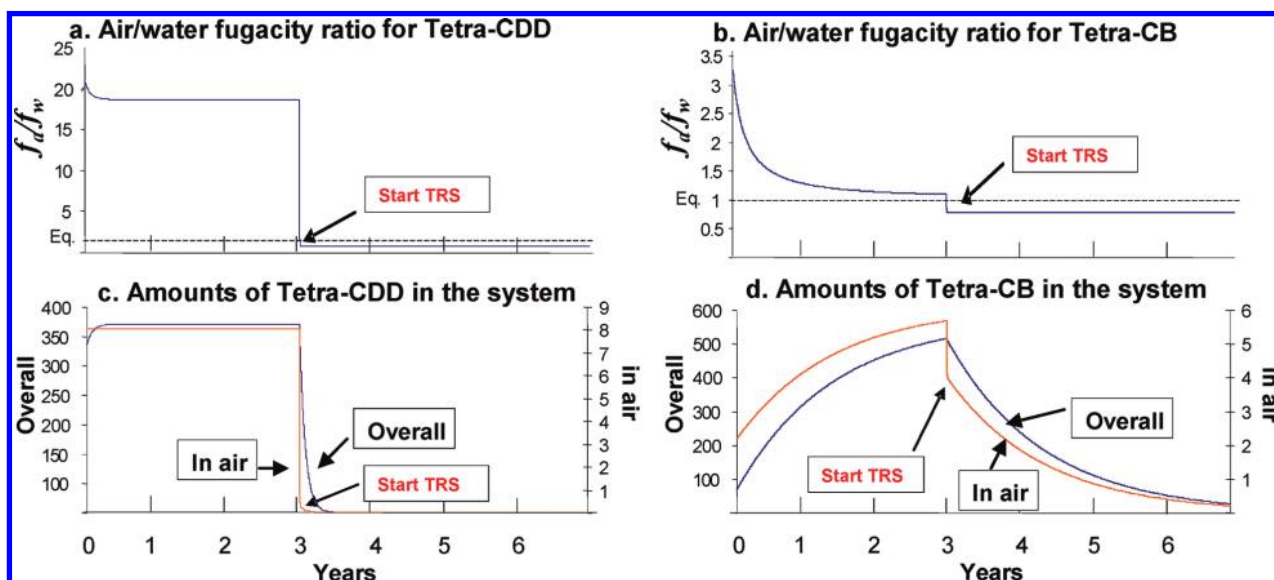


FIGURE 5. Simulation results for a generic tetrachlorinated dibenzo-*p*-dioxin (left) and a tetrachlorinated biphenyl (right). Upper plots represent the simulated value of f_a/f_w . Lower plots reported the time trends of the simulated amounts in arbitrary mass units. Overall amount = amount in air + amount in bulk water.

not significantly different from the equilibrium (17) condition. Compared to PCDD/Fs, PCBs have much longer half-lives in water and higher K_{aw} (log K_{aw} for di- to hexa-chlorinated congeners ranges: -2.38 and -3.28 for PCDD/Fs (36) and -1.91 and -2.26 for PCBs (37)). For these reasons it is reasonable to expect that surface waters have buffered declining atmospheric concentrations much more efficiently for PCBs than for PCDD/Fs.

Assessing the Oceanic Buffering Capacity

To better understand the buffering ability of the ocean surface water, we employed the kinetic parameters assessed earlier in a dynamic model of the ocean air/surface water system.

Details of this model are reported in the SI. Briefly, the model is comprised of three compartments (air, surface water, and OC in water); the sink processes and the scenario descriptors are those described earlier. The model considers a 1 million km² portion of the open ocean. Simulations are performed as follows: an initial arbitrary advective flux of pollutants to the atmosphere is set constant in order to load the system with POPs until it reaches a steady state. After this, atmospheric advective fluxes are turned off (e.g., fluxes entering and leaving the system; i.e. advective wind speed is set to 0). Under this condition the system can be considered “closed” (with the exception of export with settling particles to deep water). The clearance phase of POPs from atmosphere and water is then only controlled by sink processes. This is clearly a simplified approach, however, the goal here is to use a mathematical tool to dynamically and quantitatively compare the different behavior of PCBs and PCDD/Fs in terms of the time necessary for the ocean-atmosphere system to recover after the sources of pollutants are switched off. The advantages of adopting a “closed” system scenario for the clearance phase are the following: i) only the main sink processes (degradation in air and water and settling with OC) are considered. Advection in air and water can have a dominant influence on environmental levels, but they are not sink processes and do not differentiate between PCBs and PCDD/Fs given that the advection vector leaving the system will have the same determinants (velocity and direction) both for PCBs and PCDD/Fs; ii) the sink processes considered here do not depend on the geographic spatial scale of the model; therefore, the simulated clearance time for the compounds is an “intensive” property of the system;

iii) excluding air and water advective fluxes allow the problem of setting boundary conditions to be avoided. This is important given that information on intensity and location of sources is missing.

Figure 5 shows as an example the simulation for generic tetra-PCDD and PCBs. After switching off atmospheric advection, air concentrations of tetra-CDDs decline very quickly (order of few days) (panel c) until a new phase of the environmental clearance is reached, controlled by re-emission from the surface ocean. The theoretical frame of this phase of the environmental clearance of pollutants has been defined by Stroebe et al. (5) as the “temporal remote state” (TRS). During the TRS, the relative fractions of the pollutant burden in the different compartments are constant with time, because they show identical decline rates. The two conditions (steady state dominated by advection vs TRS) are therefore characterized by constant (in time) f_a/f_w but with very different values. In fact the fugacity ratio for PCDD/Fs shifted from $f_a/f_w = 10$ – 20 (with advection dominant) to 0.4 – 0.7 (with degassing dominant, in the TRS) depending on congeners (Figure 5, panel a). Sudden changes in the magnitude of PCDD/Fs’ advective fluxes to the open ocean, followed by shifts in the direction of the air–water exchange fluxes, could therefore generate sharp and quick (time scale of days) changes in atmospheric concentrations of 1–2 orders of magnitude, followed by a more gradual decline controlled by the surface water buffering.

PCBs also showed a two phase decline but with very different features. The initial fast decline consists in a drop of 20 to 70% (depending on congeners) of the atmospheric concentration of the steady state condition controlled by advection (Figure 5 panel d). This is translated in f_a/f_w values passing from 1.2–1.4 (with advection dominant) to 0.5–0.8 (at TRS) (Figure 5 panel b). In both cases, the TRS is reached rapidly, given the relatively short half-life in air and gaseous exchange across the air–water interface.

Once the TRS is reached, the overall PCDD burden in the air/water system will decline by an order of magnitude over 1–2 months, by means of the relatively short half-life in water. In contrast, this would take 1–3 years for PCBs, depending on the congeners, resulting in a longer and more efficient buffering of the decline in atmospheric concentrations. For this reason, declining emissions in continental areas are more

likely to be reflected in remote oligotrophic ocean regions for PCDD/Fs than for PCBs.

Implications for the Global Decline of POPs

Given the short persistence of PCDD/Fs in the surface water compared to PCBs, it can be deduced that their atmospheric levels over the ocean reflect a highly dynamic system and that the observed re-emission of PCDD/Fs from surface water is likely a temporary condition. However, it must be noted that, theoretically, the inversion of the air–water net exchange toward re-emission, can occur when the decline rate of the atmospheric advection is faster than the decline rate of the chemicals in the surface water. This explains why it is more likely to observe degassing of PCDD/Fs than of PCBs. On the other hand, as shown in the previous model exercise, given the enhanced reactivity in water, for PCDD/Fs ($t_{1/2} \sim 1$ month) the inversion of f_a/f_w can not be achieved by gradually declining background concentrations. Therefore, for PCDD/Fs a reversal of the air–water exchange gradient leading to net volatilization is most likely caused by sudden changes in the atmospheric transport trajectories. Atmospheric advective fluxes from continental areas add burdens of pollutants to the open ocean, whenever polluted air masses reach the remote ocean regions. Such pulses can temporarily reverse the air water exchange toward net deposition, as observed in the coastal region near Europe (Figures 1 and 3). As soon as the advective pulse dissipates, atmospheric PCDD/Fs are rapidly depleted by reaction with $\cdot\text{OH}$, and the system shifts back to re-emission from surface water in the time scale of weeks.

To us, this suggests that re-emission of PCDD/Fs from surface water and the low levels measured in 2005 compared to 1998 are likely the residual effect of long-range atmospheric transport pulses which occurred sometime in the months prior to the cruise.

It is nevertheless reasonable that under declining atmospheric emissions in continental source areas, such advective pulses were less frequent and effective in 2005 than in 1998, and this can explain the different atmospheric concentration observed for PCDD/Fs during the two campaigns.

Clearly, despite PCBs and PCDD/Fs being grouped together (within and between classes) as ‘POPs’ because of their common traits, they exhibit very different behavior here. PCDD/Fs can undergo rapid changes in atmospheric concentrations and air-surface exchange directions because of their relatively low persistence in surface water. Instead, for those compounds (such as for example PCBs) which are effectively buffered by re-emission from ocean surface water such changes are more difficult to detect. This study provides powerful evidence that the global environment has a buffering capacity - which varies between ecosystems (oceanic regions) and for individual chemicals - able to moderate the rate at which the global system will respond to an underlying change in primary emissions.

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Supporting Information Available

Additional information on analytical methods, PCDD/F concentrations, and a detailed model description. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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