

OCEANS AND ATMOSPHERE AS GLOBAL SINKS OF PCDD/Fs

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs, dioxins and furans) are a priority group of compounds targeted by the Stockholm Convention on Persistent Organic Pollutants (POPs), adopted by the United Nations Environmental Program on May, 22, 2001¹. A better understanding of the sources, atmospheric behaviour and trends of POPs is sought by the Convention. Research should be undertaken as a means to better judge the long-range transport and environmental sinks of POPs.

Atmospheric transport is the main transport pathway for PCDD/Fs away from their emission sources to remote places². For example, PCDD/Fs have been measured in the Arctic and Antarctic atmosphere^{3,4}. Previous research has focussed on the terrestrial sink of PCDD/Fs^{2,5}. However, to derive a complete global inventory of PCDD/Fs, the role of oceans and atmosphere as sinks of PCDD/Fs need to be assessed. This was done by using a conceptual model, linking air-water exchange to phytoplankton-uptake with a net settling flux out of the mixed layer, as presented elsewhere⁷. Within the modelling framework, the fate of POPs in air and water is not solely controlled by temperature, but rather driven by the air-to-water-to-phytoplankton exchange, with phytoplankton-bound POPs being transported to the deep ocean⁷.

The distribution of PCDD/Fs between the gaseous and particulate phase determines their fate: While particle-bound PCDD/Fs are thought to be protected from atmospheric depletion reactions, gaseous PCDD/Fs will undergo OH-radical initiated atmospheric depletion reactions⁶. Once PCDD/Fs have moved away from the terrestrial ecosystems, their fate is decided in a competition of gaseous air-water exchange, particle-bound deposition and atmospheric degradation. The relative importance of these sink processes for PCDD/Fs were calculated and compared to the role of the terrestrial sinking flux of PCDD/Fs, which is regarded as their main environmental sink^{2,5}.

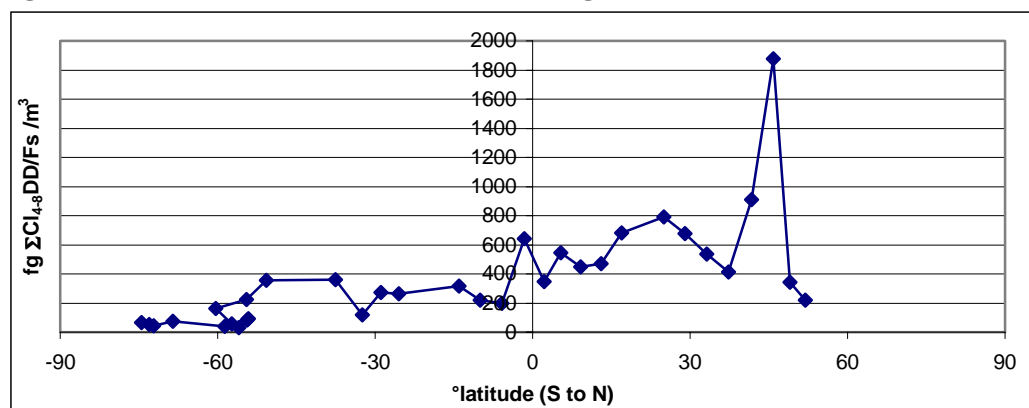
Materials and Methods

PCDD/F data: Atmospheric concentrations of PCDD/Fs were measured on an Atlantic North-South transect in October – December 1998 on-board the *RRS Bransfield*, on a cruise from England to the Antarctic (52 °N-72 °S). Samples were taken with a hi-vol sampler and separated into gaseous (adsorbed to PUF plugs) and particle-bound phases (retained by GFF filter). More details regarding the cruise itinerary, sampling and analytical procedure are given elsewhere³. A summary of the atmospheric concentrations of $\Sigma\text{Cl}_{4,8}\text{DD/Fs}$ along the North-South transect is shown in Figure 1. Concentrations were higher in the Northern Hemisphere (NH), off the European and African coasts. Lowest concentrations were measured in the remote Antarctic³.

Remote sensing and climatological data The global distribution of sea surface temperature (SST), chlorophyll *a* (Chl *a*) concentrations, and the mixed layer depth were obtained by remote sensing from satellites and climatological datasets. SST were obtained from the Along Track Scanning

Radiometer installed in the European Space Agency ERS-2 satellite⁸. SST images consist of monthly averaged data with a resolution of a half degree (360x720 pixels). Chl *a* concentrations were estimated from fluorescence signals obtained from the SeaWiFS satellite⁹ and were averaged monthly at 1°x1° resolution to estimate the spatial and seasonal phytoplankton biomass distribution in the surface mixed layer. Aerosol data has been obtained from the MODIS sensor of NASA on the Terra satellite. The present study was based on monthly averages of SST, wind speed, aerosol size distributions and Chl *a* concentrations corresponding to the sampling period of the experimental data (October-December 1998). These data were applied in a steady state model to predict the processes controlling the oceanic sink of POPs on a global scale⁷. The model takes into account air-water exchange, phytoplankton uptake and settling of organic matter.

Figure 1: Ambient concentrations of $\Sigma\text{Cl}_{4,8}\text{DD/Fs}$ (fg/m^3)



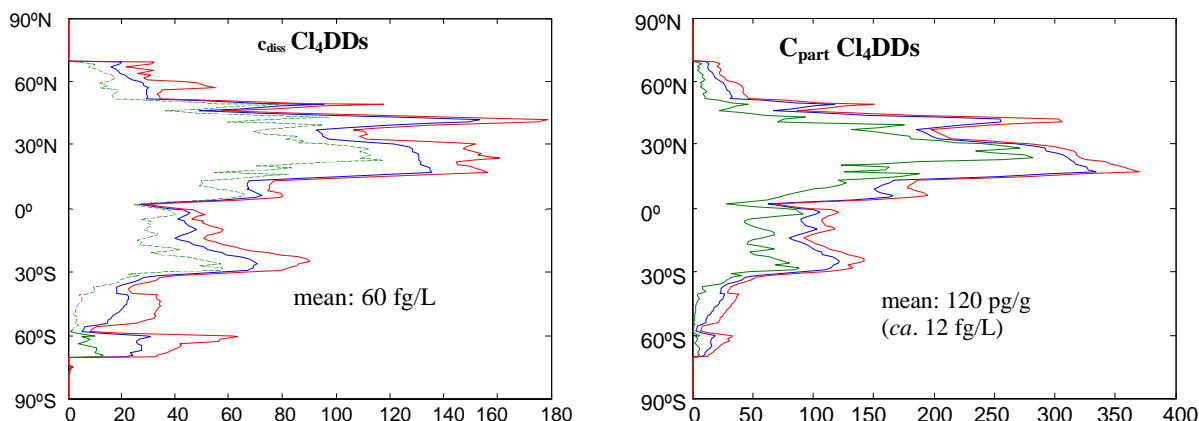
Results and Discussion

The measured atmospheric PCDD/F concentrations above the Atlantic were deemed representative of the global marine background. They were applied to all Oceans by driving air-water exchange and consequent partitioning to phytoplankton in a steady-state calculation. Air water exchange has hitherto been neglected in the estimation of global PCDD/F emissions, though dry deposition of particles was estimated by Baker and Hites¹⁰. The resulting profiles of the dissolved and phytoplankton-bound concentration are illustrated for Cl₄DDs in Figure 2. Highest dissolved and phytoplankton-bound concentrations were obtained for the NH, around 30°N.

$\Sigma\text{Cl}_{4,8}\text{DD/Fs}$ in the dissolved phase were on average ~280 fg/L, which is comparable to reported measurements from the River Elbe¹¹, Baltic Sea¹² and off the Japanese Coast¹³ (all ~ 100 – 300 fg/L), but lower by an order of magnitude relative to measurements in the Hudson River and its Estuary¹⁴ (~ 3000 fg/L). Rivers and coastal waters display far higher concentrations of organic carbon (OC), resulting in lower dissolved concentrations due to partitioning of the PCDD/Fs into the OC fraction of the phytoplankton / suspended particulate matter.

Predicted phytoplankton-bound concentrations, on the other hand, were ~ 900 pg/g $\Sigma\text{Cl}_{4,8}\text{DD/Fs}$, lower than reported measurements for River Elbe¹¹, Hudson River and its estuary¹⁴ (~ 3000-6000 pg/g). Hence, total (dissolved + phytoplankton-bound) aqueous concentrations predicted by the air-water-phytoplankton exchange model for the Atlantic Ocean were lower than those reported for other, more anthropogenically affected rivers and coastal waters.

Figure 2: Monthly mean results (Oct. – Dec. '98) from the steady-state model for (a) dissolved and (b) phytoplankton-bound concentrations of Cl₄DDs in the global Oceans



The predicted homologue profiles of the dissolved and phytoplankton-bound PCDD/Fs are dominated by the less chlorinated homologue groups, notably Cl₄DFs, Cl₅DFs and Cl₄DDs. This mirrors the composition of the gaseous phase, which drives the aqueous concentrations through air-water exchange. Dry deposition was calculated by multiplying aerosol-phase concentrations by the sedimentation velocity. The latter was estimated from the size distribution of aerosols over the ocean as given from remote sensing observations. These dry particle deposition fluxes, on the other hand, were dominated by the higher chlorinated congeners, especially OCDD, Cl₇DDs and the highest chlorinated PCDFs.

Table 1: Global sinks of PCDD/Fs (kg/year)

	Air-water exchange*	Oceanic dry deposition*	Oceanic dry deposition ^a	Terrestrial deposition ^b	Atm. loss* (above land)	Atm. loss* (above ocean)
Cl ₄ DFs	1500	10	10	540	2000	500
Cl ₅ DFs	390	20	10	700	220	120
Cl ₆ DFs	150	35	20	450	20	20
Cl ₇ DFs	59	50	10	550	/	/
OCDF	10	46	20	190	/	/
Cl ₄ DDs	430	45	/	120	640	390
Cl ₅ DDs	180	14	5	260	160	80
Cl ₆ DDs	100	27	20	890	60	20
Cl ₇ DDs	130	88	40	2,000	/	/
OCDD	10	220	70	6,800	/	/
ΣCl ₄₋₈ DD/Fs	2,900	540	200	12,500	3,100	1,100

* this study; a – ref. 10; b - ref. 2

Assuming that the measured atmospheric PCDD/Fs were representative for background Ocean air, the global oceanic air-to-water flux of PCDD/Fs was calculated. This is summarised in Table 1. A total of ~ 3000 kg/yr Σ Cl₄₋₈DD/Fs were estimated to partition into the global oceans. Cl₄DFs account for roughly 50% the total flux, with Cl₄DDs and Cl₅DFs together accounting for another 25%. Based on this estimation, air-water exchange adds another 30% to the current global emission estimation based mainly on the terrestrial sinking flux, as derived by Brzuzy and Hites². The terrestrial sinking flux is dominated by the heavier, particle-bound congeners, especially OCDD and Cl₇DDs. This reflects the much shorter atmospheric lifetimes of particle-bound PCDD/Fs and their preferential deposition close to source relative to their gaseous fraction. Hence the terrestrial sink is believed to dominate over air-water exchange and the dry particle deposition flux over the oceans. The dry deposition flux estimated in this study (~ 540 kg/yr) exceeds an earlier estimation by Baker and Hites (~ 200 kg/yr)¹⁰, which reflects the lower particle-bound PCDD/F concentrations used in the latter study.

The atmospheric loss process over the terrestrial environment was calculated based on the relative OH-radical reaction rates as reported by Baker and Hites¹⁵. Less than 20% of the relatively labile Cl₄DD/Fs were calculated to deposit onto soils, with the majority being degraded in the atmosphere. Long atmospheric life times for gaseous Cl₇₋₈DD/Fs, coupled with their preponderance on particles, renders atmospheric loss processes for these compounds negligible⁶. Atmospheric degradation over the oceans was calculated relative to their air-water exchange and deposition fluxes.

These calculation suggest that oceans and atmosphere are both equally important as global sinks of PCDD/Fs (ca. 3,000 – 4,000 kg/yr, see Table 1). As a direct consequence, it is estimated that global emissions of Σ Cl₄₋₈DD/Fs are on the order of ~ 20,000 kg/yr.

References

1. www.pops.int/ 5 June 2001.
2. Brzuzy, L. P.; Hites, R.A. **1996** *Environ. Sci. Technol.* 30, 1797-1804.
3. Lohmann, R.; Ockenden, W.A.O.; Shears, J.; Jones, K.C. *Environ. Sci. Technol.* **2001**, 35, 4046-4053.
4. Hung, H.; Blanchard, P.; Poole, G.; Thibert, B.; Ciu, C.H. *Atmos. Environ.* **2002**, 36, 1041-1050.
5. Wagrowski, D. M.; Hites, R.A. *Environ. Sci. Technol.* **2000**, 34, 2952-2958.
6. Brubaker, W. W.; Hites, R.A. *Environ. Sci. Technol.* **1997**, 31, 1805-1810
7. Dachs, J.; Lohmann, R.; Ockenden, W.A.O. ; Mejanelle, L.; Eisenreich, S.J. ; Jones, K.C. **2002** *Environ. Sci. Technol.* 36, 4229-4237.
8. ATSR project web page <http://www.atsr.rl.ac.uk>
9. <http://seawifs.gsfa.nasa.gov/SEAWIFS.html>
10. Baker, J. I.; Hites, R.A. **1999** *Environ. Sci. Technol.* 33, 14-20.
11. Götz, R.; Enge, P.; Friesel, P.; Roch, K.; Kjeller, L.-O.; Kulp, S.E.; Rappe, C. *Chemosphere* **1994**, 28, 63-74.
12. Broman, D.; Näf, C.; Rolff, C.; Zebühr, Y. *Environ. Sci. Technol.* **1991**, 11, 1850-1864.
13. Hashimoto, S.; Matsuda, M.; Wakimoto, T.; Tatsukawa, R. *Chemosphere* **1995**, 30, 1979-1986.
14. Lohmann, R.; Nelson, E.; Eisenreich, S.J.; Jones, K.C. *Environ. Sci. Technol.* **2000**, 34, 3086-3093.
15. Baker, J. I.; Hites, R.A. **2000** *Environ. Sci. Technol.* 34, 2879-2886.