2006

Quantifying the importance of the atmospheric sink for polychlorinated dioxins and furans relative to other global loss processes

Rainer Lohmann
University of Rhode Island, rlohmann@uri.edu

Elena Jurado

Jordi Dachs

Ulrike Lohmann

Kevin C. Jones

Quantifying the importance of the atmospheric sink for polychlorinated dioxins and furans relative to other global loss processes

Quantifying the importance of the atmospheric sink for polychlorinated dioxins and furans relative to other global loss processes

Rainer Lohmann,[1] Elena Jurado,[2] Jordi Dachs,[2] Ulrike Lohmann,[3] and Kevin C. Jones[4]

[1] Previous attempts to establish global mass balances for polychlorinated dioxins and furans (PCDD/Fs) have focused on the terrestrial sink, thereby neglecting deposition to the oceans and atmospheric losses. In this study, the atmospheric sink of polychlorinated dioxins and furans (PCDD/Fs) was calculated on the basis of their presence in soils. OH radical ([OH]) depletion reactions compete with atmospheric deposition fluxes for the fate of atmospheric PCDD/Fs. Three different steady state scenarios were considered: scenario A was a one-box atmosphere with globally averaged [OH], temperature (T), atmospheric lifetime (t_{life}), and a constant gas-particle partitioning (Φ); in scenario B, [OH], T, and Φ were averaged in a multibox atmosphere, with a constant t_{life}; and in scenario C, t_{life} was varied. In scenario A the strength of the atmospheric sink was 2400–2800 kg/yr; in scenario B it was $\sim$2100 kg/yr; in scenario C, it was $\sim$1,800 kg/yr (t_{life} = 5.4 days) to $\sim$2,800 kg/yr (t_{life} = 14 days). The majority of the atmospheric sink was due to the depletion of Cl_4DFs (1300–1400 kg/yr), followed by Cl_4DDs (360–380 kg/yr) and Cl_5DFs (230–240 kg/yr). On a global scale, major sinks for PCDD/Fs are the deposition to terrestrial soils and the oceans. For $Cl_{6-8}DDs$, deposition to soils outweighs depletion reactions in the atmosphere and ocean uptake. The more volatile $Cl_{4-5}DD/Fs$, however, are true "multimedia" compounds, with their estimated atmospheric sink being roughly as important as the terrestrial sink (in the case of Cl_5DD/Fs) or outweighing it (e.g., Cl_4DD/Fs).

1. Introduction

[2] 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 Programme (UNEP) on 22 May 2001 [*UNEP*, 2001]. Global emissions of PCDD/Fs are thought to be dominated by emissions into the atmosphere [*Brzuzy and Hites*, 1996]. Atmospheric transport is therefore the main transport pathway for PCDD/Fs away from their emission sources to remote places. For example, PCDD/Fs have been measured in the Arctic and Antarctic atmosphere [*Hung et al.*, 2002; *Lohmann et al.*, 2001]. Once PCDD/Fs have been emitted into the atmosphere, their fate is decided in a competition of depletion reactions versus dry and wet deposition to terrestrial and aquatic ecosystems. A better understanding of the sources, atmospheric behavior and trends of POPs is sought by the Convention. Research should be undertaken as a means to better judge the long-range transport and the environmental sinks of POPs.

[3] Attempts to quantify global sources and sinks have been undertaken for several POPs, such as PCBs, HCB and others [*Axelman and Broman*, 2001; *Axelman and Gustafsson*, 2002; *Bailey*, 2001; *Barber et al.*, 2005; *Breivik et al.*, 2002a; 2002b; *Jonsson et al.*, 2003; *Meijer et al.*, 2003; *Simonich and Hites*, 1995]. Some global budgets/sinks of POPs are relatively easy to quantify, such as the amount residing in the terrestrial environment. Numerous soil samples have to be taken, covering the different regions of the globe and appropriate scaling factors for global scale need to be found. For example, the annual deposition flux of PCDD/Fs to the terrestrial environment has been addressed in great detail in previous work [e.g., *Brzuzy and Hites*, 1996; *Wagrowski and Hites*, 2000].

[4] However, to derive complete global inventories of POPs, the role of oceans and atmosphere as sinks need to be

[1]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, USA.
[2]Department of Environmental Chemistry, Institut d'Investigacions Químiques i Ambientals de Barcelona, Consejo Superior de Investigaciones Científicas, Barcelona, Spain.
[3]Institute for Atmospheric and Climate Science, Eidgenössische Technische Hochschule Zurich, Zurich, Switzerland.
[4]Environmental Sciences Department, Lancaster University, Lancaster, UK.

Scenario	A	B	C
PCDD/F fluxes	regional	regional	regional
[OH·]	const.	0-2 km, 2-10 km per zone	0-2 km, 2-10 km per zone
temperature	const.	0-2 km, 2-10 km per zone	0-2 km, 2-10 km per zone
gas/particle distribution	const.	function of (T, [TSP])	function of (T, [TSP])
particle lifetime	const.	const.	range

Figure 1. Three scenarios used to quantify global atmospheric loss rates for PCDD/Fs.

assessed. For oceans, we have proposed using a conceptual model, linking the air-to-water flux of POPs with their uptake in phytoplankton and a subsequent settling flux out of the mixed layer into the deep ocean, as presented elsewhere [*Dachs et al.*, 2002]. Within that modeling 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 ocean [*Dachs et al.*, 2002]. Current research is underway to verify the predictive power of the modeling framework and derive inventories for the amount of POPs sequestered by oceans.

[5] Finally, deriving an estimate of the atmospheric sink of POPs combines the easiest and most difficult aspects of environmental chemistry. Ambient air measurements of POPs in general and PCDD/Fs in particular have been performed for decades [e.g., see *Lohmann and Jones*, 1998]. The presence of PCDD/Fs in air is easy to determine, as long as air volumes are sufficiently large to overcome detection limits. A particular difficult aspect of many POPs and notably PCDD/Fs is their semivolatility, resulting in their presence both in gas and particulate phase in the atmosphere. The correct determination and interpretation of measured gas-particle distributions is still subject to intense debate [e.g., *Dachs and Eisenreich*, 2000; *Lohmann and Lammel*, 2004; *Mader and Pankow*, 2002]. It is assumed that the distribution of PCDD/Fs between gas and particulate phase determines their fate: While particle-bound POPs are thought to be sheltered from atmospheric depletion reactions, gaseous POPs will undergo OH radical initiated atmospheric depletion reactions [*Atkinson*, 1996; *Brubaker and Hites*, 1997; *Lohmann and Lammel*, 2004].

[6] The aim of this study is to estimate the contribution of the atmosphere as a final sink of PCDD/Fs due to these above mentioned depletion reactions. Hence what is needed is not a measure of the presence of atmospheric PCDD/Fs, but rather of the rate of their disappearance. The problem is

to quantify the degradation of compounds, where there is no defined end-product available to determine the rate of conversion. Atmospheric depletion is one of the few "destructive" loss processes, together with biological transformation/mineralization. In contrast, we consider deep soils, deep sea sediments and the deep water column as "final" sinks of PCDD/Fs. Surface water and surface soils, on the other hand could, depending on air-soil/water fugacity gradients, be either temporary reservoirs or final sinks. Research suggests that PCDD/Fs in soil are in general far from equilibrium [e.g., *Cousins and Jones*, 1998].

[7] In short, quantifying the atmospheric sink of PCDD/Fs requires complimentary approaches other than direct measurements. Modeling offers a rather convenient way of estimating the importance of the atmospheric sink term, as long as sufficient knowledge is present. From laboratory studies, OH radical reaction constants with PCDD/Fs are known, and the reactions with NO_3 and O_3 should be of minor importance on a global scale [*Atkinson*, 1996]. Hence global OH radical concentrations are needed, coupled with temperature profiles and knowledge of the temperature dependency of the reaction rates, if any. Of key interest in such a model-based estimation is the role of the gas-particle distribution, and how the presence in either phase affects the atmospheric fate.

[8] For atmospherically emitted PCDD/Fs, there are only two major pathways leaving the atmosphere: deposition/exchange to the Earth's surface (terrestrials soils and the oceans) or degradation in the atmosphere (we assume here that any other potential PCDD/F loss/destruction is negligible). Hence, if the global PCDD/F emissions were known, and the resulting settling fluxes to soils and oceans, the strength of the atmospheric sink could be deduced based on mass balance considerations, and yet the global source strength of PCDD/Fs is not known, although attempts are under way by the UNEP to assemble a global PCDD/F release inventory [e.g., *UNEP*, 1999; H. Fiedler, UNEP, personal communication, 2004]. Alternatively, it is possible to estimate the atmospheric sink of PCDD/Fs based on their known deposition fluxes to the Earth's surface, as long as there is a quantifiable relationship between their atmospheric settling and atmospheric depletion fluxes.

[9] At present, we know with reasonable certainty the annual deposition of PCDD/Fs to terrestrial surfaces, based on the work by Hites and his group [e.g., *Brzuzy and Hites*, 1995, 1996; *Wagrowski and Hites*, 2000]. This forms the basis of the research presented here; for PCDD/Fs emitted into the atmosphere, settling and OH radical destruction are the only removal processes considered. Other atmospheric depletion mechanisms (photolysis, reactions with other radicals, reactions in/on vegetation) are not considered. PCDD/Fs are removed from the atmosphere to either soils or water bodies through a combination of wet and dry deposition of gas phase and particulate congeners.

[10] Three complimentary approaches are pursued to derive estimates of the strength of the atmospheric OH radical depletion of PCDD/Fs (Figure 1). In each case, the deposition of PCDD/Fs to regionally classified soils is used to derive the fraction of PCFDD/Fs depleted in the atmosphere: (1) in scenario A, a rough estimate of the atmospheric sink is obtained based on globally averaged OH radical concentrations, temperature, atmospheric lifetime

Table 1. OH Radical Reaction Constants (k_{OH}) With Their Arrhenius Activation Energy (E_{act}), the Mean Retention Time Index (RTI) for the Calculation of the Octanol-Air Partitioning Constant (K_{oa}), and Their Calculated Values for $Cl_{4-8}DD/Fs$

	k_{OH} (298 K)[a]	E_{act}, kJ/mol	mean RTI	K_{oa} (298 K)
Cl_4DFs	7.00E-13	6.6	2307	9.4
Cl_5DFs	3.50E-13	7.1	2503	10.0
Cl_6DFs	1.50E-13	7.6	2710	10.6
Cl_7DFs	6.00E-14	8.1	2925	11.2
OCDF	3.00E-14	8.6	3152	11.9
Cl_4DDs	1.20E-12	14	2361	9.6
Cl_5DDs	6.00E-13	17	2561	10.2
Cl_6DDs	3.00E-13	21	2766	10.8
Cl_7DDs	1.30E-13	25	2979	11.4
OCDD	5.00E-14	28	3197	12.0

[a] Read 7.00E-13 as 7.00×10^{-13}.

and a constant gas-particle partitioning; (2) in scenario B, OH radical, temperature and gas-particle distributions are averaged in 2 atmospheric heights, with the deposition velocity being held constant; and (3) in scenario C, the atmospheric deposition velocity is varied.

[11] Possible limitations of this approach are the degree to which (1) other releases than atmospheric emissions account for the derived flux to the terrestrial environment, (2) relative and absolute rate of deposition versus depletion velocities are known, and (3) annual deposition fluxes to the terrestrial environments are precisely quantified. The limitations/validity of these assumptions will be addressed in more detail later. It is certain that atmospheric chemistry plays a major role as a sink of PCDD/Fs through OH radical depletion. In here, we offer a critical calculation of the atmosphere as a global destructive loss process of PCDD/Fs. Initially, the focus is on the OH radical depletion above soils. Then, PCDD/F deposition to and uptake by oceans are also considered, and the strength of OH radical depletion reactions over the oceans is estimated. In the end, this enables us to assemble a global picture of the different fluxes removing PCDD/Fs from the atmosphere.

2. Materials and Methods

2.1. Atmospheric Input Data

[12] Atmospheric temperature (T), and total suspended particulate matter concentrations [TSP] were based on modeled 5-year averages from an atmospheric general circulation model [*Lohmann et al.*, 1999]. Within the atmospheric general circulation model, monthly mean oxidant values including the OH radical [OH] are obtained from a chemical transport model as described by *Feichter et al.* [1996]. Average values were calculated for every month from 90°N in 3.75° increments to 90°S. Two well-mixed atmospheric compartments were assumed: the boundary layer (0–2200 m) and the troposphere (2200–10,500 m). A two-compartment model was chosen to minimize computing time. PCDD/Fs are emitted into the well-mixed boundary layer, and the combination of ambient temperatures and OH radical concentrations makes it the dominant reaction volume. Monthly area-weighted mean values were calculated from 6 different heights each, taking into account the pressure differentials with height.

2.1.1. Total Suspended Particulate Matter Concentrations

[13] [TSP] were obtained by summing up all the different aerosol species considered in the general circulation model. These were methane sulfonic acid, sulfate, dust in two size fractions (0–1 and 1–2 μm), sea salt in two size fractions (0–1 and 1–10 μm), and the hydrophobic and hydrophilic black carbon and organic carbon, respectively. In the first 2 km of the atmosphere, [TSP] < 1 $\mu g/m^3$ were found poleward of 70°S and concentrations < 10 $\mu g/m^3$ for 60–90°N and 0–90°S throughout the year. [TSP] > 20 $\mu g/m^3$ were found between 15 and 50°N, with [TSP] reaching 25–35 $\mu g/m^3$ from June–September between 19 and 45°N. These aerosols concentrations are in good agreement with the (near ground) values for fine aerosol (i.e., < 2 μm) summarized by [*Heintzenberg*, 1989]: < 5 $\mu g/m^3$ for remote, 15 $\mu g/m^3$ for nonurban continental and >30 $\mu g/m^3$ for urbanized regions. For 2–10 km height, [TSP] were < 2.0 $\mu g/m^3$ for the SH, and only exceeded 5.0 $\mu g/m^3$ from 15–50°N during June–September.

2.1.2. Atmospheric Temperature

[14] Mean atmospheric T (0–2 km) varied from 233 K in the southern winter near the South Pole to 297 K near 30°N in northern summer. In the upper 2–10 km, T varied from 214 K to 263 K.

2.1.3. OH Radical Concentrations

[15] [OH] values were taken from *Roelofs and Lelieveld* [1995] and are discussed in more detail by *Feichter et al.* [1996]. The 24-hour averages of [OH] in the first 0–2 km varied from close to zero at the poles during the respective winter seasons to > 2.0×10^6 molecules/cm^3 near 30°N from June to August. [OH] > 1.0×10^6 molecules/cm^3 were calculated for 15°S to 15°N throughout the year, The field of [OH] > 1.0×10^6 molecules/cm^3 extended up to 67.5°N during June and July. Between 2 and 10 km height, [OH] showed a similar spatial and temporal distribution, with values slightly below those in the 0–2 km height.

2.2. [OH] Reaction Rate Constants

[16] [OH] reaction rates were taken from *Brubaker and Hites* [1997] and *Kwok et al.* [1995]. The temperature dependency of the OH radical reactions was calculated by regressing the (Arrhenius) activation energy (E_{act}) against the number of chlorines (N° Cl) attached to the PCDD/Fs [*Brubaker and Hites*, 1997, 1998] (see Table 1). The following relationships were obtained:

PCDFs

$$E_{act} = 430 \times N° Cl - 40 (K) (n = 3) \tag{1}$$

PCDDs

$$E_{act} = 60 \times N° Cl + 550 (K) (n = 2) \tag{2}$$

These results are comparable to the E_{act} obtained for PCBs [see *Axelman and Gustafsson*, 2002]. It should be noted that the available database for OH radical reactions of PCDD/Fs is based on few measurements of lower chlorinated congeners, and has been extrapolated to the higher chlorinated compounds [*Atkinson*, 1996]. The situation is comparable for PCBs, where recent field evidence broadly

Table 2. Estimated Depositional Flux of PCDD/Fs to Soils in 1998 for Different Climatic Zones[a]

	Subtropical	New Temperate (a)	New Temperate (b)	Polar/Boreal	Tropical	Arid	Total (a)[b]	Total (b)[b]
Cl_4DFs	120	25	81	120	62	79	410	460
Cl_5DFs	210	72	160	94	38	36	450	540
Cl_6DFs	170	80	89	42	41	25	360	370
Cl_7DFs	210	96	110	43	54	30	430	450
OCDF	60	64	40	21	25	8.0	180	150
Cl_4DDs	4.0	0.8	20	16	55	8.0	84	100
Cl_5DDs	37	1.1	87	23	22	7.0	90	180
Cl_6DDs	130	370	270	62	110	48	720	620
Cl_7DDs	300	870	550	220	260	150	1800	1500
OCDD	1300	3200	2000	250	880	290	5900	4700
$\Sigma Cl_{4-8}DD/Fs$	2600	4800	3400	890	1500	680		
Sum of sums							10400	9100

[a]Modified from *Brzuzy and Hites* [1996]. Values are in kg/yr. Here (a) indicates mean U.S. decrease assumed for temperate regions, and (b) indicates 50% general decrease assumed for temperate regions.

[b]Totals are named according to their corresponding temperate scenarios.

supported overall reaction rates and relative reactivities [*Mandalakis et al.*, 2003].

[17] For the loss calculation over the terrestrial environment, relative rates (depletion versus deposition) were taken as detailed by *Baker and Hites* [2000a]. Calculations were always performed per homologue group (i.e., combining all PCDD/Fs into groups with the same number of chlorines), and then combined to $\Sigma Cl_{4-8}DD/Fs$. Atmospheric emissions were assumed to be constant throughout the year.

[18] Here 1998 was chosen as a reference year for the calculations for better comparison of the results: Numerous ambient PCDD/F concentrations were measured that year, notably the Atlantic transect data [*Lohmann et al.*, 2001] which was used to estimate the oceanic sink of PCDD/Fs [*Dachs et al.*, 2002].

2.3. Other Loss Processes

[19] Photolysis of PCDD/Fs in the gas phase was not taken into account, due to a paucity of data [see *Atkinson*, 1996; *Lohmann and Jones*, 1998]. The role of vegetation in removing and destroying PCDD/Fs from the atmosphere is at present uncertain [*Niu et al.*, 2003; *Dalla Valle et al.*, 2004]. At least for PAHs, research has shown the importance of degradation reaction on the surface of leaves and the possibility of metabolism inside the stomata [*Wild et al.*, 2005a, 2005b]. It is unclear if vegetation is also important for the chlorinated, more recalcitrant compounds like OC pesticides, PCBs and PCDD/Fs; future research would be needed to address these questions.

3. Results and Discussion

3.1. Terrestrial Sink

[20] *Brzuzy and Hites* [1996] published the first global deposition estimate for PCDD/Fs. On the basis of over 100 soil samples, the global flux of $\Sigma Cl_{4-8}DD/Fs$ to soils was estimated to be 12,500 ± 1300 kg/yr. Fluxes were apportioned to different climate zones, with depositions to temperate soils (~6900 kg/yr) dominating the global depositional fluxes (Table 2). The derived deposition fluxes were calculated as the mean annual deposition over 60 years, until 1994. Numerous studies have shown a drastic decrease in ambient PCDD/F concentrations and their deposition in industrialized countries in the 1990s [e.g., *Alcock et al.*, 1999; *Alcock and Jones*, 1996; *Baker and Hites*, 2000b;

Hiester et al., 1997]. For example, the average deposition of $\Sigma Cl_{4-8}DD/Fs$ to Lake Siskiwit in Lake Superior (USA) decreased by 50% from the mean flux for 1935–1994 to 1998 (see Figure 2). The depositional flux in the temperate latitudes, thought to be dominated by European and North American emissions, was therefore reduced by (1) 50% across the homologue groups or (2) the mean decrease as measured in Lake Siskiwit (from ~30% for OCDD to > 90% for $Cl_{4/5}DDs$), which is taken to be representative for the whole US and Europe. There are no data available to justify a reduction of PCDD/Fs fluxes outside North America and Europe; hence the estimates were kept the same. Estimated depositional fluxes to the temperate environment in 1998 were in between 4800 kg/yr (based on the mean U.S. decrease) or 3400 kg/yr (based on a 50% decrease for all homologue groups).

[21] This resulted in a reduction of the global terrestrial deposition flux by ~20–30% (from 12,500 kg/yr to ~9100–10,400 kg/yr). Hence we suggest for 1998 that the best estimate of the global depositional flux of PCDD/Fs to soils is of the order of 9100–10,400 kg $\Sigma Cl_{4-8}DD/Fs$/yr (Table 2). The majority of that depositional flux was due to Cl_7DDs (1500–1800 kg/yr) and OCDD (4800–5900 kg/yr).

3.2. Predicted PCDD/F Gas-Particle Distributions

[22] Varying gas-particle distributions were calculated as a function of [TSP] and T. The particle-bound fraction Φ was calculated based on a correlation by *Finizio et al.* [1997] between the gas-particle partitioning coefficient, K_p, and that between octanol and air, K_{oa}. Φ was calculated based on the observed K_p value and [TSP]:

$$\Phi = K_P[TSP]/K_P[TSP] + 1 \qquad (3)$$

[23] K_p is defined as the ratio of the compounds' particulate (F) and the gaseous concentrations (A), normalized to [TSP] (in $\mu g/m^3$). The predicted [TSP] thus enables the calculation of gaseous and particulate fractions. The T dependency of the gas-particle partitioning was accounted for by calculating K_{oa} of the different PCDD/Fs at temperature T ($K_{oa}(T)$) relative to K_{oa} at 298 K ($K_{oa}(298)$) [*Harner et al.*, 2000]:

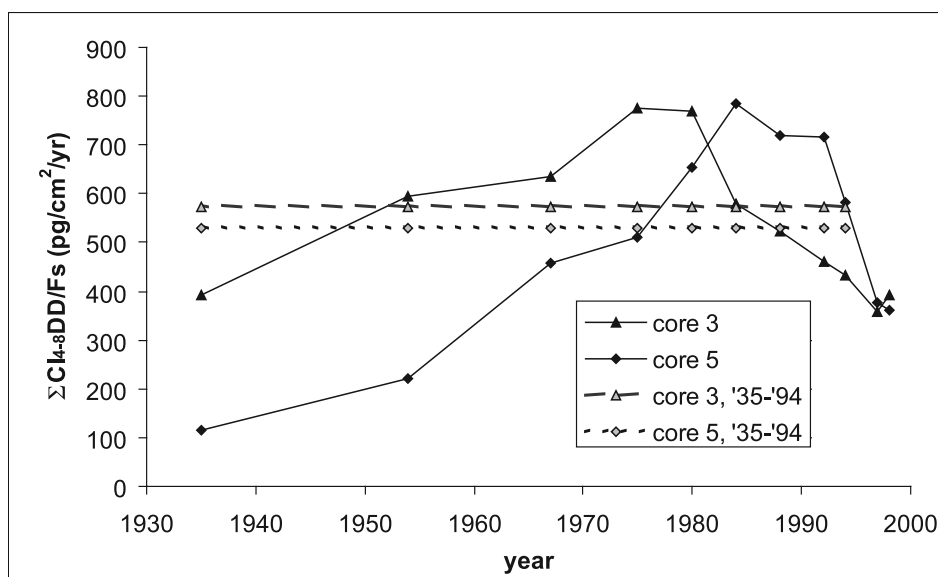$$\text{Log } K_{oa}(T) = A + B/T \text{ log } K_{oa}(298) \qquad (4)$$

Figure 2. Annual deposition of $\Sigma Cl_{4-8}DD/Fs$ to Lake Siskiwit. Shown are the calculated average flux 1935–1994 (dotted and dashed lines) and the measured decrease up to 1998.

[24] The correlation which was originally derived for PAHs was chosen here, as there is no generic one for PCDD/Fs. However, both PAHs and PCDD/Fs are planar compounds, originate mainly from combustion processes and show enhanced affinities for carbonaceous surfaces. Hence a comparable atmospheric partitioning between gaseous and particulate phase can be expected:

$$Log\ K_p = 0.79\ log\ K_{oa} - 10.01 \qquad (5)$$

[25] There is ongoing debate on the exact mechanisms (i.e., absorption into the organic carbon, adsorption onto the exterior surface of black carbon or a combination of both) governing the gas-particle distributions of semivolatile organic compounds, such as PAHs or PCDD/Fs [e.g., *Lohmann and Lammel*, 2004]. Because of the paucity of data, especially for PCDD/Fs, and questions pertaining to the quality of gas-particle distributions from field measurements [e.g., *Mader and Pankow*, 2000, 2001a, 2001b, 2002], it was decided to use a correlation that was based on measurements for a wider range of organic compounds, without an explicit assumption on the nature of the affinity for the aerosols in question.

[26] PCDD/Fs on particles were assumed not to react with OH radicals. This was inferred from studies showing a reduced reactivity of PAHs on carbonaceous particles (1) with OH and NO_2 radicals [*Esteve et al.*, 2004, 2006] and (2) in photolysis experiments [*Behymer and Hites*, 1988]. Hence we assume that the averaged "aged" particle will effectively shield PCDD/Fs from OH radicals, possibly due to an outer ring made of secondary organic aerosols, and different salts [see also *Lohmann and Lammel*, 2004].

3.3. Predicted Particulate Fraction (Φ) of PCDD/Fs

[27] Φ varied both with latitude (i.e., T and [TSP]) and homologue groups. The relative spatial and temporal trends of Φ were constant for the various PCDD/F homologue

groups: Lowest Φ were predicted from 25°S to the equator from October to June. Conversely, highest Φ were predicted for 34°N to ~75°N from October to June, with some high values of Φ around 60°S and near 90°S during May to September. Φ increased within the homologue groups with increasing degree of chlorination, with PCDFs having slightly lower values of Φ for the same number of chlorines attached. This predicted behavior can be explained by the decrease in volatility with an increasing number of chlorines attached and has regularly been observed in field studies [see *Lohmann and Jones*, 1998].

[28] The predicted Φ between 0 and 2 km for Cl_4DDs ranged from 0.03 (near equator) to > 0.30 (35°N to 75°N), with values around 0.25 around 57°S. For Cl_5DDs, minimum values of Φ were 0.07, with highest values of > 0.60 in the NH. Φ for Cl_6DDs ranged from < 0.20 to > 0.80 and for Cl_7DDs from < 0.50 to > 0.90. OCDD was predicted to have Φ of at least 0.70 near the equator to values close to 100% in the NH. Predicted Φ for PCDFs were in generally lower by ca 0.05 compared to those for PCDDs. Between 2 and 10 km predicted Φ for all homologue groups were higher, indicating that the decrease in [TSP] (which would result in a decrease in Φ) was outweighed by the decrease of temperature and its effect of increasing K_{oa} values. The increase in predicted Φ was nonlinear, i.e., more pronounced in colder regions and those with higher [TSP]. For example, for Cl_4DDs, predicted Φ reached > 0.50 for north of 40°N for most of the year, with predicted Φ < 0.10 within a narrow region south of the equator for most of the year. For Cl_5DDs, Φ > 0.75 were predicted north of 40°N and south of 80°S for most of the year, with minimum values of ~0.15 near the equator. For Cl_6DDs, Φ > 0.90 were predicted north of 40°N and south of 80°S, with lowest values of Φ of around 0.40 in between 5°S and 30°S during March to June. During those months, Φ < 0.75 and ~0.90 were predicted near the equator for Cl_7DDs and OCDD, respectively.

3.4. Predicted Versus Measured Particulate Fractions

[29] The following studies were selected which determined actual gas-particle distributions in coastal/rural or remote environments: (1) results from rural Lancaster (UK, 54°N), taken in November/December 1998 [*Lohmann et al.*, 2000], (2) annual means from rural Bayreuth (Germany, 52°N), taken in 1995 [*Hippelein et al.*, 1996], (3) results from coastal Sandy Hook (NJ, USA, 40°N), take in June 1998 (R. Lohmann et al., Assessing the importance of ab- and adsorption to the gas-particle partitioning of PCDD/Fs, with a case study in the New Jersey urban atmosphere, submitted to *Atmospheric Environment*, 2006, hereinafter referred to as Lohmann et al., submitted manuscript, 2006), (4) results from a trans-Atlantic cruise from England (53°N) to the Antarctic (74°S), taken from October to December 1998 [*Lohmann et al.*, 2001], (5) the annual mean from Barbados (13°N) in 1996/1997 and Bermuda (32°N) in 1993/1994 [*Baker and Hites*, 1999], and (6) annual mean from rural Bloomington, determined in 1986 (40°N, USA) [*Eitzer and Hites*, 1989]. A comparison of predicted (mean 0–2 km) and measured (near ground) land-based particulate fractions (ϕ) showed good agreement (Figure 3).

[30] For example, for Cl_5DDs at Lancaster (UK, 54°N) in November/December, Φs of 57–62% were predicted, and Φs ranging from 44 to 99% were measured [*Lohmann et al.*, 2001]; at the New Jersey coast (USA, 40°N) in June/July, Φs of 38–47% were predicted, and Φs ranging from 25 to 60% were measured (Lohmann et al., submitted manuscript, 2006). These trends can be seen for all land-based stations. Φ determined in Barbados and Bermudas (13 and 32°N, USA) were below the predicted values, though the long sampling duration might have affected the measured distributions. On the contrary, results for Lancaster tended to be above the predicted values, but the samples taken were not representative for the winter season. Instead rather cold spells were targeted, to minimize the temperature fluctuation during the 24-hour sampling periods [*Lohmann et al.*, 2000]. Most importantly, the comparison with the gas-particle distribution as determined on a trans-Atlantic cruise showed the mean value close to the predicted one [*Lohmann et al.*, 2001] for all homologue groups (Figure 3): for Cl_4DDs, predicted was 12% (range 4–25%), and measured 17% ± 18% (±1 standard deviation), for Cl_5DDs, predicted were 28% (12–51%), measured were 41% ± 30% and finally for Cl_6DDs, predicted were 54% (30–76%), measured were 46% ± 33%.

3.5. Atmospheric Loss Over Terrestrial Environment

[31] The atmospheric OH radical depletion over the terrestrial environment was calculated based on the relative OH radical reaction rates [*Baker and Hites*, 2000a], relating the amount deposited (S_D) to the amount emitted (S_E) through a combination of particulate deposition and gaseous depletion. Atmospheric deposition was described through a single settling velocity (k_D) for the particle-bound fraction (ϕ), and atmospheric depletion through a pseudo-first-order OH radical reaction constant (k'_{OH}) for the gaseous PCDD/Fs ($1-\phi$). For the terrestrial environment, the total amount deposited ($S_{D, terre.}$) is known through the detailed study by [*Brzuzy and Hites*, 1996]. The total amount depleted ($S_{depl, terre.}$) over the terrestrial environment can be calculated assuming that PCDD/Fs detected in the

remote soil samples arrived exclusively through atmospheric deposition, with gaseous depletion through OH radicals being the only other loss process limiting their deposition.

$$S_{depl,terre.} = S_{D,terr.} \left(\frac{k'_{OH}(1 - \phi)}{k_D \phi} \right) \qquad (6)$$

3.5.1. Scenario A: One-Box Atmosphere Model (Constant T, [OH], and Gas-Particle Partitioning)

[32] This approach follows *Brubaker and Hites* [1997] and *Baker and Hites* [2000a] by assuming a globally constant [OH] of 9.7×10^5 molecules/cm^3, a constant T (298K) and a universal gas-particle partitioning of PCDD/Fs as determined at Bloomington [*Eitzer and Hites*, 1989]. OH radical depletion was calculated to be a major sink for Cl_4DDs and Cl_4DFs: Less than 20% were calculated to deposit onto soils (120 and 540 kg/yr), with the majority being degraded in the atmosphere (400–500 and 1700–1900 kg/yr, respectively). For Cl_5DD/Fs, OH radical depletion was already far less important, with at most a third reacting in the atmosphere. Slow atmospheric reactions times for gaseous $Cl_{7-8}DD/Fs$, coupled with their preponderance on particles, rendered atmospheric loss processes for these compounds negligible. In total, the atmospheric sink over the terrestrial environments was calculated to be on the order of 2400–2800 kg/yr for $\Sigma Cl_{4-8}DD/Fs$, most of which was due to Cl_4DFs and Cl_4DDs (Table 3). A breakdown of the importance of OH radical depletion shows a roughly equal importance of subtropical (~650 kg/yr), polar/boreal (~610 kg/yr) and tropical zones (~560 kg/yr). The estimation for the temperate zone depended strongly on the scenario assumed for the recent decrease. Taking the observed decrease, the atmospheric sink term was rather small (~160 kg/yr), while assuming a general 50% decrease for all congeners resulted in a much higher atmospheric sink (~570 kg/yr). This reflects the disproportionate decrease of the Cl_4DD/Fs compared to the total PCDD/F depositional flux.

3.5.2. Scenario B: Multibox Atmosphere Model (Variable T, [OH], [TSP], and Gas-Particle Partitioning)

[33] In a second, more refined approach, OH radical depletion was calculated as a function of globally modeled monthly OH radical concentrations at the respective ambient temperature. The gas-particle partitioning was calculated as a function of T and [TSP] (see above). No depletion of PCDD/Fs occurred in the particulate phase. Atmospheric depletion versus deposition factors were averaged over the range of latitudes best representing the climatic zones and their spatial coverage (Table 4).

[34] The soil climatic zones were placed in the atmospheric circulation pattern in which the majority was found: the polar/boreal zone between 60°N and 90°N (polar cell), the temperate zone between 30°N and 60°N (Ferrel cell), the subtropical zone between 0°N and 30°N covering the northern branch of the Hadley cell, the tropical zone in the 60°S–30°N zone, and the arid zone again in the 0°–30°N cell. The differences between the arid and the subtropical zone are based on their different PCD/F content in the soils, while the atmospheric chemistry is the same. Atmospheric transport in these zones is fast longitudinally, so well-mixed FCDD/F concentrations can be assumed both horizontally and across the zone. However, the latitudinal
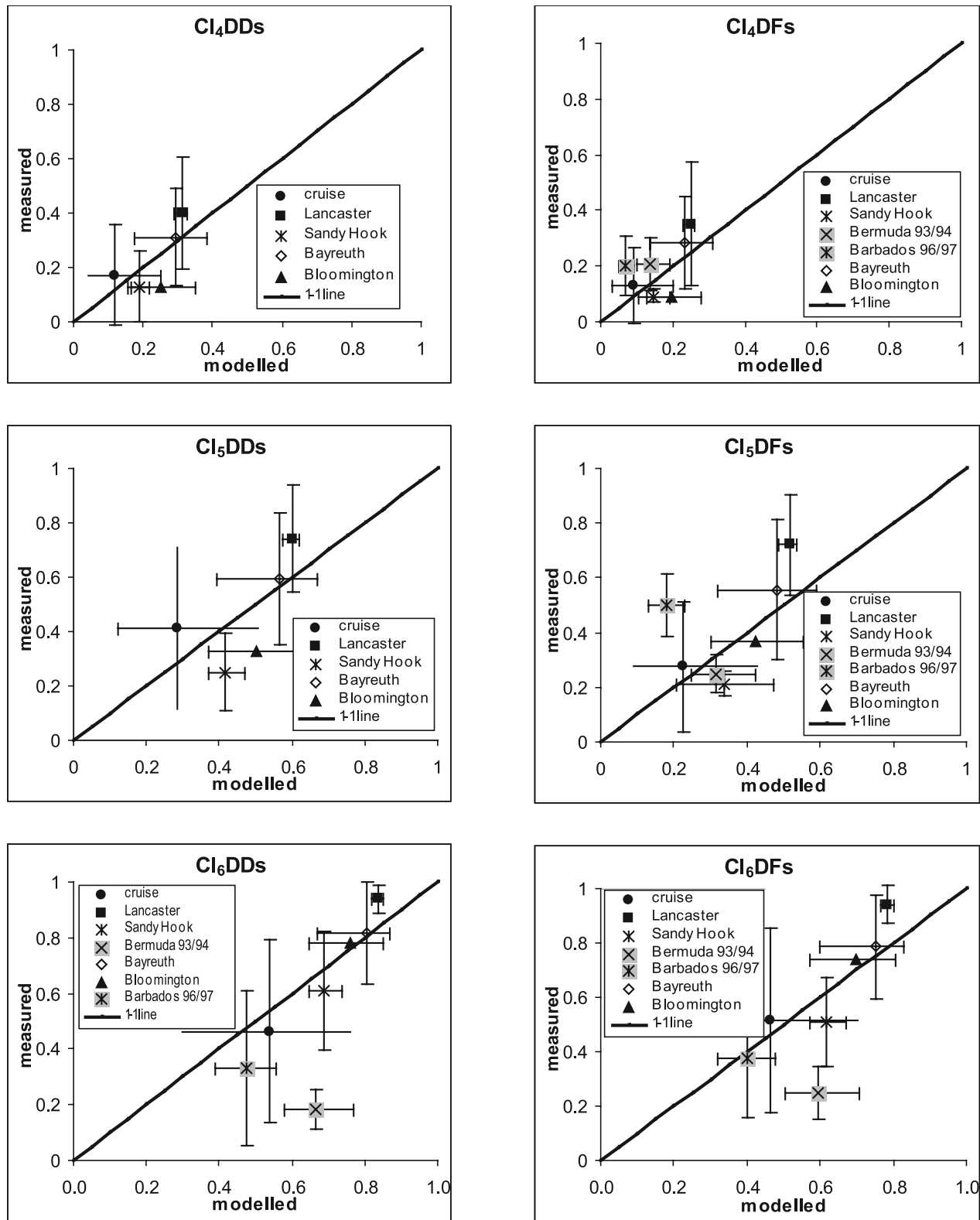
Figure 3. Comparison of predicted and measured gas-particle distributions for selected PCDD/F homologue groups.

Table 3. Calculated OH Radical Depletion Fluxes of PCDD/F Homologue Groups Based on Constant Temperature, OH Radical Concentration, and Gaseous Fraction[a]

	Subtropical	Temperate (a)	(b)	Polar/Boreal	Tropical	Arid	Total (a)	Total (b)
T_{air}, K	298							
[OH], molec/cm^3	9.7 e5							
v_{dep}, 1/s	1.45 e-6							
Φ	as determined for Bloomington							
Cl_4DFs	520	110	340	480	260	330	1700	1900
Cl_5DFs	72	24	55	32	13	12	150	180
Cl_6DFs	6	3	3	1	1	1	13	13
Cl_7DFs	1	0.3	0.4	0.2	0.2	0.1	2	2
OCDF	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Cl_4DDs	19	4	94	75	260	38	390	480
Cl_5DDs	28	1	66	17	17	5	68	130
Cl_6DDs	7	19	14	3	5	2	36	31
Cl_7DDs	1	2	2	1	1	0	5	4
OCDD	0.5	1	0.7	0.1	0.3	0.1	2	2
$\Sigma Cl_{4-8}DD/Fs$	650	160	570	610	560	390	2400	2800

[a]Here (a) indicates mean U.S. decrease assumed for temperate regions, and (b) indicates 50% general decrease assumed for temperate regions. Values are in kg/yr.

exchange between atmospheric cells is much slower, hence the separation into cells.

[35] The yearly loss of gaseous PCDD/Fs due to OH radical reactions through this more detailed calculation gave results that compare surprisingly well with those derived by using single values for ϕ, T and [OH·] (see Table 4). The strength of the atmospheric sink of PCDD/Fs was on the order of 2100 kg/yr, as compared to 2400–2800 kg/yr by the "one-box atmosphere" model. However, major shifts were apparent in the regions in which PCDD/Fs were depleted in the atmosphere. The "one-box atmosphere" model showed similarly high loss fluxes for subtropical, polar/boreal, tropical and temperate climate zones. In the "multibox" atmosphere with different T, [OH], and [TSP], the atmospheric depletion of PCDD/Fs was concentrated in the subtropical (810 kg/yr), tropical (710 kg/yr) and to some

degree arid zones (440 kg/yr). Lower temperatures and higher [TSP] combined to decrease the gas-phase atmospheric depletion over the temperate and polar/boreal regions (with effects on both the reaction rates and the gas-particle distribution). The majority of the atmospheric depletion was still due to the depletion of Cl_4DFs (1300–1400 kg/yr), followed by Cl_4DDs (360–380 kg/yr) and Cl_5DFs (230–240 kg/yr). Thus the different assumptions regarding the terrestrial deposition flux of PCDD/Fs to the temperate environment were less important in this scenario.

3.5.3. Scenario C: Multibox Atmosphere Model, Variable Particle Lifetime

[36] The biggest uncertainty regarding the atmospheric sink was rather in the actual value of the particle life time (affecting the relative rate of deposition versus [OH] depletion). On average, particle life time is ∼1 week in the lower

Table 4. Calculated OH Radical Depletion Fluxes of PCDD/F Homologue Groups Based on Their Deposition Flux According to Climatic Zones as a Function of Variable Temperature, OH Radical Concentrations, and Gas-Particle Partitioning[a]

	Subtropical	Temperate	Temperature (b)	Polar/Boreal	Tropical	Arid	Sum (a)	Sum (b)
Zone	0–30°N	30–60°N		60–90°N	0–60°S	0–30°N		
Mean T_{air} (range), K	291 (281–294)	278 (260–293)		265 (249–283)	282 (263–292)	291 (281–294)		
Mean [OH] (range), molec/cm^3	1.4 e6 (4.7e5–2.2e6)	9.0 e5 (1.0e4–2.3e6)		2.4 e5 (0–1.4e6)	8.30 e5 (4.4e3–2.1e6)	1.4 e6 (4.7e5–2.2e6)		
v_{dep}, 1/s	1.45 e-6							
Φ	function of T, [TSP]							
Cl_4DFs	570	23	74	40	340	360	1300	1400
Cl_5DFs	150	10	23	5	33	27	230	240
Cl_6DFs	16	1	2	0.3	5	2	25	25
Cl_7DFs	2	0.2	0.2	0.0	0.7	0.3	4	4
OCDF	0.1	0.0	0.0	0.0	0.0	0.0	0.2	0.2
Cl_4DDs	19	0.8	18	5	300	38	360	380
Cl_5DDs	26	0.1	11	1	17	5	49	60
Cl_6DDs	13	7	5	0.4	12	5	37	35
Cl_7DDs	4	2	1	0.1	4	2	11	10
OCDD	2	0.7	0.5	0.0	1	0.4	4	4
$\Sigma Cl_{4-8}DD/Fs$	810	46	140	52	710	440	2100	2100

[a]Here (a) indicates mean U.S. decrease assumed for temperate regions, and (b) indicates 50% general decrease assumed for temperate regions. Values are in kg/yr.

Table 5. Calculated OH Radical Depletion Fluxes of PCDD/F Homologue Groups Based on Different Atmospheric Particle Lifetimes[a]

| | Mean Atmospheric Sink (Soils) | | | |
	t_{life} = 4.0 days	t_{life} = 8.0 days	t_{life} = 14.0 days	Atmospheric Sink (Ocean)
Cl_4DFs	1000	1400	1800	1400
Cl_5DFs	190	240	310	190
Cl_6DFs	20	25	32	22
Cl_7DFs	3	4	4	3
OCDF	0.1	0.2	0.2	0.2
Cl_4DDs	300	370	480	770
Cl_5DDs	46	55	67	61
Cl_6DDs	32	36	43	41
Cl_7DDs	10	11	12	12
OCDD	4	4	5	5
$\Sigma Cl_{4-8}DD/Fs$	1600	2100	2800	2400

[a]For comparison, the estimated atmospheric sink based on a comparable PCDD/F deposition to the oceans is shown.

troposphere, though actual particle life time varies with altitude from several days to weeks [*Jaenicke*, 1988; *Textor et al.*, 2005]. To give a better estimation of the range of the atmospheric sink term two values covering the range of particle life times (4 and 14 days) were chosen (Table 5). The range given by these different settling velocities varied the strength of the OH radical depletion of PCDD/Fs from ~1600 kg/yr for fast settling particles to ~2800 kg/yr for the slower particle settling velocity. Recent results from the aerosol climate model ECHAM5-HAM developed at the Max-Planck-Institute of Meteorology suggest on average lifetimes of 5.4 days for both organic and black carbon [*Stier et al.*, 2005], which was in good agreement with other predictions. Using a particle lifetime of 5.4 days, the atmospheric sink of PCDD/Fs was just under 2000 kg/yr (1800–1900 kg/yr). In summary, based on a particle life time of 8 days, the strength of the atmospheric sink of PCDD/Fs is estimated to be on the order of ~2,100 kg. Differing particle life times affect that mean value by roughly a third (1600–2800 kg/yr).

[37] So far we have estimated the fate of OH radical depleted PCDD/Fs based on their depositional flux to the terrestrial environment. It is evident from inspecting the deposition velocities used here that some fraction of atmospheric PCDD/Fs will be transported across the oceans and deposited there; and this has indeed been observed [e.g., *Baker and Hites*, 1999; *Hung et al.*, 2002; *Lohmann et al.*, 2001]. Following the logic used above, for every fraction of PCDD/Fs deposited to the global oceans, a corresponding fraction will have been depleted in the atmosphere. This will add to the atmospheric depletion fluxes derived above for the deposition to the terrestrial soils. However, no measured data exist for the settling fluxes of PCDD/Fs to sediments or the deep water in the oceans.

3.6. Atmospheric Loss Over Oceans

[38] The atmospheric deposition fluxes of PCDD/Fs over the oceans were calculated based on the measured transect data of PCDD/Fs over the Atlantic (for details, see *Jurado et al.* [2004, 2005]). Highest atmospheric concentrations of $Cl_{2-8}DD/Fs$ all occurred between 25 and 52°N; lowest concentrations were measured around ~60°S and further south. In these calculations, extrapolated to the global scale, total deposition to the oceans accounted for ~16,000 kg/yr, dominated by wet deposition (~10,000 kg/yr), followed by

gas phase uptake by the oceans (~3500 kg/yr), and dry deposition (~2800 kg/yr). As these calculations were based on single point measurements extrapolated to the world's oceans, the uncertainty of the resulting PCDD/F deposition flux is rather high, around a factor of 3. Nonetheless, the calculated oceanic settling fluxes of PCDD/Fs suggest that the total PCDD/F deposition to the world's oceans could match their deposition to terrestrial soils.

[39] It is appropriate to consider how representative the atmospheric Atlantic concentrations measured in this study are for other locations of similar latitude. *Baker and Hites* [1999] measured PCDD/Fs on Bermudas and Barbados from the clean, "eastern" sector, and reported PCDD/F concentrations which were on average lower by a factor of 5 than those reported by *Lohmann et al.* [2001]. Assuming both measurements were correct, this suggests that (1) PCDD/Fs do indeed travel long distances over water, (2) *Baker and Hites* [1999] likely underestimated the "true" deposition of PCDD/Fs, at least to the North Atlantic Ocean, as PCDD/Fs had to undergo deposition, depletion, and air-water exchange processes before reaching their sampler near the American coast, and (3) global atmospheric background concentrations will lie in between these two data sets. We are not aware of published PCDD/F measurements over the Pacific or Indian Ocean.

4. Conclusion and Outlook

[40] A comparison of the different sink strength and homologue profiles shows the dominance of terrestrial soils and oceans as sinks for most PCDD/Fs (Figure 4). For $Cl_{6-8}DDs$, deposition to soils outweighs depletion reactions in the atmosphere and ocean uptake. It is suggested that for $Cl_{6-8}DFs$, deposition to the oceans is their major global sink. The more volatile $Cl_{4-5}DD/Fs$, however, are true "multimedia" compounds, with their estimated atmospheric sink being roughly as important as the terrestrial sink (in the case of Cl_5DD/Fs), or outweighing it (e.g., Cl_4DD/Fs). These tetrachlorinated and pentachlorinated homologue groups are calculated to have a strong gas-to-water uptake by oceans. As a direct consequence, it is suggested that attempts to establish global mass balances for PCDD/Fs have to consider atmospheric loss processes and uptake by oceans. For 1998, we estimate the importance of the atmospheric sink to be on the order of ~2100 kg/yr, based
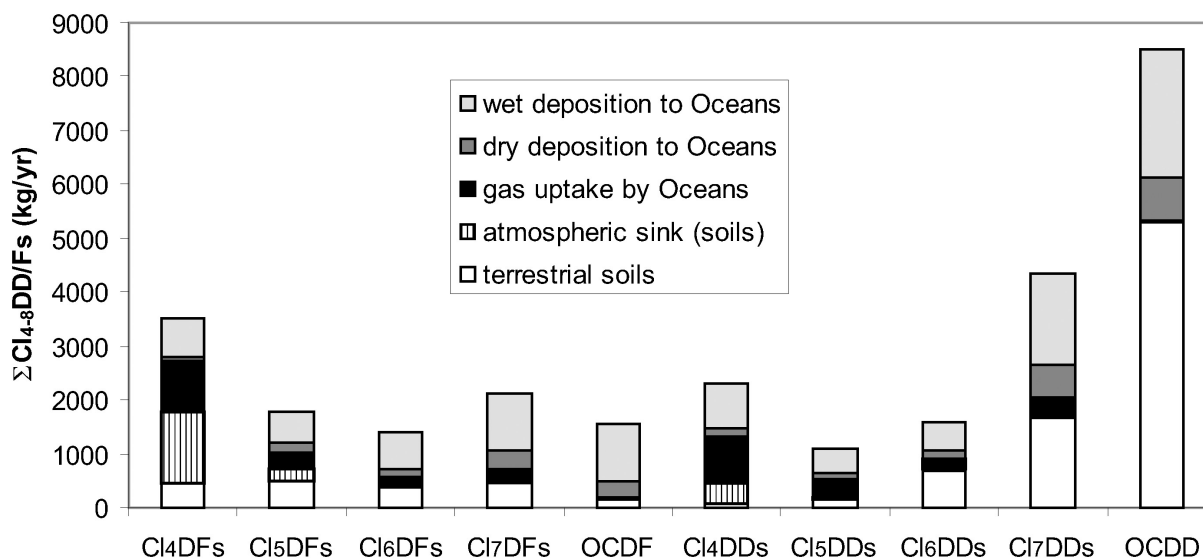
Figure 4. Comparison of global PCDD/F sinks, deposition to terrestrial soils and oceans, and the calculated corresponding OH radical depletion fluxes.

on the deposition of PCDD/Fs to terrestrial soils. Depending on the magnitude of the PCDD/Fs settling and gas uptake fluxes to oceans, the atmospheric sink calculations performed here could be twice as high.

[41] Estimated global PCDD/F emissions needed to be on the order of 12,000 kg $\Sigma Cl_{4-8}DD/Fs$/yr in 1998, solely to balance the deposition to terrestrial soils and the corresponding atmospheric depletion calculated here. In addition, deposition and gas uptake to the global oceans and their corresponding atmospheric depletion reactions could add up to another 18,000 kg $\Sigma Cl_{4-8}DD/Fs$/yr (Figure 4).

[42] It is interesting to compare the global fate of PCDD/Fs summarized here with work carried out for PCBs. For example, *Mandalakis et al.* [2005] derived a mass balance for PCBs in the eastern Mediterranean, and argued that atmospheric depletion was the biggest removal mechanism of PCBs ($\sim$6700 kg/yr), much more important than wet and dry deposition (together $\sim$1600 kg/yr) or deep-sea settling ($\sim$300 kg/yr). The importance of the atmospheric depletion of PCBs in the Mediterranean does not contradict the results of our study. The fraction of particle-bound PCBs has been observed to be lower than for PCDD/Fs of similar Koa [e.g., *Lohmann et al.*, 2000], resulting in higher depletion reactions in their study. Furthermore, in contrast to our study their study region did not include terrestrial soils, which are considered one of the main PCB reservoirs.

[43] Global PCDD/F emissions were derived through emission inventories. *Brzuzy and Hites* [1996] calculated emissions on the order of 3,000 kg/yr (certain within a factor of 3). Later research suggested that the preponderance of OCDD, and other $Cl_{6-8}DD/Fs$ can be explained by their atmospheric condensation reaction from pentachlorophenol [*Baker and Hites*, 2000a]. A global emission inventory based on adding up national emission inventories is currently undertaken by the UN EP. On the basis of a few countries, these added up to a few thousand kg $\Sigma Cl_{4-8}DD/Fs$/yr in 1999 [*UNEP*, 1999]. In light of the binding commitment of

the international community to decrease emissions of PCDD/Fs, it seems certain that additional PCDD/F emissions exist, beyond those accounted for in the national emission inventories.

References

Alcock, R. E., and K. C. Jones (1996), Dioxins in the environment: A review of trend data, *Environ. Sci. Technol.*, *30*, 3133–3143.

Alcock, R. E., et al. (1999), Improvements to the UK PCDD/F and PCB atmospheric emission inventory following an emissions measurement programme, *Chemosphere Global Change Sci.*, *38*, 759–770.

Atkinson, R. (1996), Atmospheric chemistry of PCBs, PCDDs and PCDFs, in *Chlorinated Organic Micropollutants*, *Issues Environ. Sci. Technol.*, vol. 6, edited by R. E. Hester and R. M. Harrison, pp. 53–72, R. Soc. of Chem., London.

Axelman, J., and D. Broman (2001), Budget calculations for polychlorinated biphenyls (PCBs) in the Northern Hemisphere—A single-box approach, *Tellus, Ser. B*, *53*, 235–259.

Axelman, J., and O. Gustafsson (2002), Global sinks of PCBs: A critical assessment of the vapor-phase hydroxy radical sink emphasizing field diagnostics and model assumptions, *Global Biogeochem. Cycles*, *16*(4), 1111, doi:10.1029/2002GB001904.

Bailey, R. E. (2001), Global hexachlorobenzene emissions, *Chemosphere Global Change Sci.*, *43*, 167–182.

Baker, J. I., and R. A. Hites (1999), Polychlorinated dibenzo-p-dioxins and dibenzofurans in the remote North Atlantic marine atmosphere, *Environ. Sci. Technol.*, *33*, 14–20.

Baker, J. I., and R. A. Hites (2000a), Is combustion the major source of polychlorinated dibenzo-p-dioxins and dibenzofurans to the environment? A mass balance investigation, *Environ. Sci. Technol.*, *34*, 2879–2886.

Baker, J. I., and R. A. Hites (2000b), Siskiwit Lake revisited: Time trends of polychlorinated dibenzo-p-dioxin and dibenzofuran deposition at Isle Royale, Michigan, *Environ. Sci. Technol.*, *34*, 2887–2891.

Barber, J. L., et al. (2005), Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes, *Sci. Total Environ.*, *349*, 1–44.

Behymer, T. D., and R. A. Hites (1988), Photolysis of polycyclic aromatic-hydrocarbons adsorbed on fly-ash, *Environ. Sci. Technol.*, *22*, 1311–1319.

Breivik, K., et al. (2002a), Towards a global historical emission inventory for selected PCB congeners—A mass balance approach 1. Global production and consumption, *Sci. Total Environ.*, *290*, 181–198.

Breivik, K., et al. (2002b), Towards a global historical emission inventory for selected PCB congeners–A mass balance approach 2. Emissions, *Sci. Total Environ.*, *290*, 199–224.

Brubaker, W. W., and R. A. Hites (1997), Polychlorinated dibenzo-p-dioxins and dibenzofurans: Gas phase hydroxyl radical reactions and related atmospheric removal, *Environ. Sci. Technol.*, *31*, 1805–1810.

Brubaker, W. W., and R. A. Hites (1998), OH reaction kinetics of poly-cyclic aromatic hydrocarbons and polychlorinated dibenzo-p-dioxins and dibenzofurans, *J. Phys. Chem. A*, *102*, 915–921.

Brzuzy, L. P., and R. A. Hites (1995), Estimating the atmospheric deposi-tion of polychlorinated dibenzo-p-dioxins and dibenzofurans from soils, *Environ. Sci. Technol.*, *29*, 2090–2098.

Brzuzy, L. P., and R. A. Hites (1996), Global mass balance for polychlori-nated dibenzo-p-dioxins and dibenzofurans, *Environ. Sci. Technol.*, *30*, 1797–1804.

Cousins, I. T., and K. C. Jones (1998), Air-soil exchange of semi-volatile organic compounds (SOCs) in the UK, *Environ. Pollut.*, *102*, 105–118.

Dachs, J., and S. J. Eisenreich (2000), Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, *34*, 3690–3697.

Dachs, J., et al. (2002), Oceanic biogeochemical controls on global dynamics of persistent organic pollutants, *Environ. Sci. Technol.*, *36*, 4229–4237.

Dalla Valle, M., J. Dachs, A. J. Sweetman, and K. C. Jones (2004), Max-imum reservoir capacity of vegetation for persistent organic pollutants: Implications for global cycling, *Global Biogeochem. Cycles*, *18*, GB4032, doi:10.1029/2004GB002334.

Eitzer, B. D., and R. A. Hites (1989), Polychlorinated dibenzo-para-dioxins and dibenzofurans in the ambient atmosphere of Bloomington, Indiana, *Environ. Sci. Technol.*, *23*, 1389–1395.

Esteve, W., et al. (2004), Relative rate constants for the heterogeneous reactions of OH, NO_2 and NO radicals with polycyclic aromatic hydro-carbons adsorbed on carbonaceous particles. Part 1: PAHs adsorbed on 1–2 mu m calibrated graphite particles, *Atmos. Environ.*, *38*, 6063–6072.

Esteve, W., et al. (2006), Relative rate constants for the heterogeneous reactions of NO_2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a, *Atmos. Environ.*, *40*, 201–211.

Feichter, J., et al. (1996), Simulation of the tropospheric sulfur cycle in a global climate model, *Atmos. Environ.*, *30*, 1693–1707.

Finizio, A., et al. (1997), Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols, *Atmos. Environ.*, *31*, 2289–2296.

Harner, T., et al. (2000), Measurements of octanol-air partition coefficients for PCDD/Fs: A tool in assessing air-soil equilibrium status, *Environ. Sci. Technol.*, *34*, 3109–3114.

Heintzenberg, J. (1989), Fine particles in the global troposphere, A review, *Tellus, Ser. B*, *41*, 149–160.

Hiester, E., et al. (1997), Pronounced decrease of PCDD/PCDF burden in ambient air, *Chemosphere*, *34*, 1231–1243.

Hippelein, M., et al. (1996), Baseline contamination assessment for a new resource recovery facility in Germany. Part II: Atmospheric concentra-tions of PCDD/F, *Chemosphere*, *32*, 1605–1616.

Hung, H., et al. (2002), Measurement of particle-bound polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in Arctic air at Alert, Nunavut, Canada, *Atmos. Environ.*, *36*, 1041–1050.

Jaenicke, R. (1988), Aerosol physics and chemistry, in *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology New Series Group V*, vol. 4, *Geophysics and Space Research*, edited by G. Fischer, pp. 391–457, Springer, New York.

Jonsson, A., et al. (2003), Global accounting of PCBs in the continental shelf sediments, *Environ. Sci. Technol.*, *37*, 245–255.

Jurado, E., et al. (2004), Atmospheric dry deposition of persistent organic pollutants to the Atlantic and inferences for the global oceans, *Environ. Sci. Technol.*, *38*, 5505–5513.

Jurado, E., et al. (2005), Wet deposition of persistent organic pollutants to the global oceans, *Environ. Sci. Technol.*, *39*, 2426–2435.

Kwok, E. S. C., et al. (1995), Rate constants for the gas-phase reactions of the OH radical with dichlorobiphenyls. 1. Chlorodibenzo-p-dioxin, 1,2-dimethoxybenzene, and diphenyl ether- estimation of OH radical reaction-rate constants for PCBs, PCDDs, and PCDFs, *Environ. Sci. Technol.*, *29*, 1591–1598.

Lohmann, R., and K. C. Jones (1998), Dioxins and furans in air and deposition: A review of levels, behaviour and processes, *Sci. Total Environ.*, *219*, 53–81.

Lohmann, R., and G. Lammel (2004), Adsorptive and absorptive contribu-tions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended parametrization for modeling, *Environ. Sci. Technol.*, *38*, 3793–3803.

Lohmann, R., et al. (2000), Gas-particle partitioning of PCDD/Fs in daily air samples, *Atmos. Environ.*, *34*, 2529–2537.

Lohmann, R., et al. (2001), Atmospheric distribution of polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs), and nonortho biphenyls (PCBs) along a North-South Atlantic transect, *Environ. Sci. Technol.*, *35*, 4046–4053.

Lohmann, U., et al. (1999), Predicting the number of cloud droplets in the ECHAM GCM, *J. Geophys. Res.*, *104*, 9169–9198.

Mader, B. T., and J. F. Pankow (2000), Gas/solid partitioning of semi-volatile organic compounds (SOCs) to air filters. 1. Partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans and polycyclic aromatic hydrocarbons to teflon membrane filters, *Atmos. Environ.*, *34*, 4879–4887.

Mader, B. T., and J. F. Pankow (2001a), Gas/solid partitioning of semi-volatile organic compounds (SOCs) to air filters. 2. Partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and polycyclic aromatic hydrocarbons to quartz fiber filters, *Atmos. Environ.*, *35*, 1217–1223.

Mader, B. T., and J. F. Pankow (2001b), Gas/solid partitioning of semivo-latile organic compounds (SOCs) to air filters. 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOCs and organic carbon (OC) when using teflon membrane filters and quartz fiber filters, *Environ. Sci. Technol.*, *35*, 3422–3432.

Mader, B. T., and J. F. Pankow (2002), Study of the effects of particle-phase carbon on the gas/particle partitioning of semi-volatile organic com-pounds in the atmosphere using controlled field experiments, *Environ. Sci. Technol.*, *36*, 5218–5228.

Mandalakis, M., et al. (2003), Direct evidence for destruction of polychlor-obiphenyls by OH radicals in the subtropical troposphere, *Environ. Sci. Technol.*, *37*, 542–547.

Mandalakis, M., M. Apostolaki, E. G. Stephanou, and S. Stavrakakis (2005), Mass budget and dynamics of polychlorinated biphenyls in the eastern Mediterranean Sea, *Global Biogeochem. Cycles*, *19*, GB3018, doi:10.1029/2004GB002403.

Meijer, S. N., et al. (2003), Global distribution and budget of PCBs and HCB in background surface soils: Implications or sources and environ-mental processes, *Environ. Sci. Technol.*, *37*, 667–672.

Niu, J. F., et al. (2003), Photodegradation of PCDD/Fs adsorbed on spruce (*Picea abies* (L.) Karst.) needles under sunlight irradiation, *Chemosphere Global Change Sci.*, *50*, 1217–1225.

Roelofs, G. J., and J. J. Lelieveld (1995), Distribution and budget of O-3 in the troposphere calculated with a chemistry general-circulation model, *J. Geophys. Res.*, *100*(D10), 20,983–20,998.

Simonich, S. L., and R. A. Hites (1995), Global distribution of persistent organochlorine compounds, *Science*, *269*, 1851–1854.

Stier, P., et al. (2005), The aerosol-climate model ECHAM5–HAM, *Atmos. Chem. Phys.*, *5*, 1125–1156.

Textor, C., et al. (2005), Analysis and quantification of the diversities of aerosol life cycles with AeroCom, *Atmos. Chem. Phys. Disc.*, *5*, 8331–8420.

United Nations Environment Programme (1999), UNEP chemicals: Dioxin and furan inventories—National and regional emissions of PCDD/Fs, report, Nairobi.

United Nations Environment Programme (2001), Stockholm convention on persistent organic pollutants, *Rep. UNEP/POPs/CONF/PM/4/Rev.1*, Nairobi.

Wagrowski, D. M., and R. A. Hites (2000), Insights into the global distribu-tion of polychlorinated dibenzo-p-dioxins and dibenzofurans, *Environ. Sci. Technol.*, *34*, 2952–2958.

Wild, E., et al. (2005a), Direct observation of organic contaminant uptake, storage, and metabolism within plant roots, *Environ. Sci. Technol.*, *39*, 3695–3702.

Wild, E., et al. (2005b), Real-time visualization and quantification of PAH photodegradation on and within plant leaves, *Environ. Sci. Technol.*, *39*, 268–273.

————————————

J. Dachs and E. Jurado, Department of Environmental Chemistry, IIQAB-CSIC, Jordi Girona 18-24, E-08034 Barcelona, Catalunya, Spain.

K. C. Jones, Environmental Sciences Department, Lancaster University, Lancaster LA1 4YQ, UK.

R. Lohmann, Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA. (lohmann@gso.uri.edu)

U. Lohmann, Institute for Atmospheric and Climate Science, ETH Zurich, CH-8092 Zurich, Switzerland.