Atmospheric Distribution of Polychlorinated Dibenzo-p-dioxins, Dibenzofurans (PCDD/Fs), and Non-Ortho Biphenyls (PCBs) along a North—South Atlantic Transect

R. LOHMANN, W. A. OCKENDEN, J. SHEARS, AND K. C. JONES*†
Department of Environmental Science, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster LA1 4YQ, U.K., and British Antarctic Survey, High Cross, Cambridge CB3 0ET, U.K.

Air samples were taken on board the RRS Bransfield (typically for 24—72 h), during an Atlantic cruise from the U.K. to Antarctica in October—December 1998, to investigate the global scale distribution of PCDD/Fs and coplanar PCBs. Highest concentrations of Cl₂-ODD/Fs all occurred between 25 and 52° N; lowest concentrations were measured around ~ 65° S and further south. Cl₃DFs showed highest overall concentrations (up to 9800 fg/m³), followed by Cl₄DFs (up to 5300 fg/m³) and OCDD (up to 1300 fg/m³). Lowest concentrations, measured in the remote Southern hemisphere, were generally 2 orders of magnitude lower than their highest concentrations over the North Atlantic. Concentrations of PCB-77 were higher in the northern hemisphere, while PCB-126 and PCB-169 were higher in the northern hemisphere, while PCB-126 and PCB-169 showed highest overall concentrations (up to 9800 fg/m³), followed by Cl₄DFs (up to 5300 fg/m³) and OCDD (up to 1300 fg/m³). Lowest concentrations, measured in the remote Southern hemisphere, were generally 2 orders of magnitude lower than their highest concentrations over the North Atlantic. Concentrations of PCB-77 were higher in the northern hemisphere, while PCB-126 and PCB-169 showed highest overall concentrations (up to 9800 fg/m³), followed by Cl₄DFs (up to 5300 fg/m³) and OCDD (up to 1300 fg/m³).

Introduction

Polychlorinated dibeno-p-dioxins and -furans (PCDD/Fs) are ubiquitous contaminants that are released into the environment as byproducts of incomplete combustion or as chemical impurities. Diverse atmospheric emissions supply PCDD/Fs to the global atmosphere. Long-range atmospheric transport (LRAT) can move PCDD/Fs away from source regions to more remote locations. PCDD/Fs are among the Persistent Organic Pollutants (POPs) targeted for international source reduction by United Nations protocols because of concerns over their persistence and LRAT potential (1, 2). There are continuing uncertainties over the relative importance of different sources of PCDD/Fs; this includes primary and secondary source categories (3—7) as well as possible natural production and atmospheric reactions and formation mechanisms (7—9). There are also uncertainties about the loss mechanisms which control PCDD/F depletion from the environment (10).

Attempts have been made to make preliminary global budget calculations for PCDD/Fs, based on concentrations in soils and tree bark (11, 12) and by correlating PCDD/F emissions with the gross national product or CO₂ emissions (11). However, these studies rely heavily on information from the relatively well-known and “data rich” industrialized regions of the northern hemisphere (NH). Very few data are available from remote parts of the world, the southern hemisphere (SH) and over the oceans. It is likely that the SH has generally fewer emissions of PCDD/Fs than the more industrialized NH (13). LRAT is considered as a possible vector to move emissions from the NH to the SH. Ambient measurements can be used to help assess atmospheric emissions and obtain clues about the relative importance of different sources and processes controlling ambient levels. They provide a snapshot of the balance between current emissions/loss processes, whereas soils and tree bark provide a picture of longer-term, integrated atmospheric deposition. Caution is needed, however, because there is potential for confusion in interpreting data on regional/global PCDD/F distribution due to their persistence and possible atmospheric weathering.

The wide range of PCDD/F physicochemical properties makes them an interesting group to consider with respect to their gas/particle partitioning and susceptibility to undergo LRAT. Between the mono- and octa-CDD/Fs, their subcooled liquid vapor pressures (p) range from 10⁻² to 10⁻⁷ Pa and their octanol—air partition coefficients (KOA) from 10² to 10⁻¹² (10). The Cl₂₋₄DD/Fs are almost exclusively gas phase under ambient conditions in the U.K., while the Cl₂₋₄DD/Fs are predominantly particle bound (14). This has implications for their fate and behavior in the atmosphere, because the scope and importance of scavenging processes and reactions with OH-radicals depends on their phase distribution. Polychlorinated biphenyls (PCBs) are another group of semi-volatile compounds and are also targeted by the POPs protocols. Concentrations of non-ortho substituted PCBs-77, -126, and -169 are presented here.

To obtain data on the atmospheric distribution of PCDD/Fs in remote, oceanic locations, including the SH, air samples were collected on a British Antarctic Survey (BAS) research vessel as it travelled from the U.K. to Antarctica in October—December 1998 (see Figure 1). A total of 53 samples were taken, between 52° N, 1° E and 75° S, 20° W, as the ship sailed from Grimsby, U.K., passed parts of Europe, Africa, and South America, and visited islands in the southern Atlantic, before reaching the BAS Halley research station on the Brunt ice shelf in Antarctica.

Materials and Methods

Air Sampling. The air sampler was installed on the monkey deck immediately above the bridge deck (ca. 20 m above sea level). For the majority of samples, air was collected while...
24 h periods around Signy Island (60° S). A week long sample was taken for the entire period the ship was moored in port, namely at Montevideo (Uruguay, 34° S, 55° W), Port Stanley (Falkland Islands, 51° S, 58° W), Bird Island (54° S, 37° W), and South Georgia (54° S, 37° W). A week long sample was taken around Signy Island (60° S, 47° W). More details about the sample numbers, the average position for each sample, air volumes taken, and meteorological conditions are given in the Supporting Information. On three occasions, a glass fiber filter was installed on the stack outlet and exposed for 12 h in toluene. The DCM and toluene extracts were combined for the cleanup procedure.

Of the 53 samples taken, 12 were blanks. They were firmly sealed and stored at temperatures of 25 °C overnight; breakthrough occurred for Cl1DFs, with similar amounts on the first and second PUF plug. For every five samples, a field blank was taken by assembling two PUFs and a GFF in a module next to the air sampler. For every 10 samples a laboratory blank was taken, representing the unopened PUFs and GFF. Field and laboratory blanks were incorporated in the analytical procedure and used to derive detection limits as mean blank plus 3 times the standard deviation of the mean concentration in the blanks. There was no significant difference between field and laboratory blank levels for the GFFs; for the PUFs, concentrations of Cl1-DFs were consistently lower in the field blanks. The mean concentrations found in the laboratory and field blanks were subtracted from the samples; in the case of Cl1-DFs the field blanks were used. For most homologues and PCBs-126 and -169, mean blank concentrations were 0.1–1.0 pg/sample, but higher for Cl1DFs, OCDD, and PCB-77 (see Table 1). In the gaseous phase, Cl2-DDDs were generally at least 10× blank levels, with fewer (southern) samples 5× blank levels. In the particulate phase, Cl2-DDs/Fs were generally 5–10× blank levels, with fewer detects for OCDF. Detection limits were <2 pg/sample for most homologues but higher for Cl1DFs (4.0 pg/sample), Cl2DFs (35), Cl3DDs (2.6), Cl4DFs (2.5), Cl2DDs (2.2), and OCDD (7.6) in the PUFs. Detection limits for the 2,3,7,8-substituted Cl4DDs were in general at least 10× blank levels, with <1 pg/sample for the 2,3,7,8-Cl4DDs; the field blanks were used. For most non-ortho PCBs, they were 36 (27) pg/sample for −77 on PUFs (GFFs), <1 pg for −126 and <0.3 pg for −169. In contrast to observations by Kallenborn et al. (16), the long transport times on the ship (>6 months) before samples taken arrived in the laboratory did not affect the blanks, validating the use of tin cans as a storage medium.

Mean recoveries for the 13C12-2,3,7,8-substituted PCDD/Fs were between 58 and 85%. 57% for Cl2-2,7-DiCDD, 61% for Cl2-2,8-DiCDF, 61% for Cl2-2,7,8-TCDF, 55 and 57% for Cl2-PCBs-77, -126, and -169 (all at 100 pg each) and a range of 13C12-labeled PCBs (28, 52, 101, 153, 138, 180 each at 325 pg) were spiked onto the samples immediately prior to extraction. PUFs were extracted in DCM for 16 h; GFFs were extracted consecutively for 12 h in toluene. The DCM and toluene extracts were combined for the cleanup procedure.

The general circulation, local back trajectories and sampling locations

**FIGURE 1.** Mean sampling location of each sample (ITCZ = intertropical convergence zone).

The analytical method employed has been described elsewhere (15). However, it was improved to include the reliable detection of Cl1DFs for this study. PUFs and GFFs were extracted separately. Briefly, all 13C12-2,3,7,8-substituted PCDD/F congeners; 13C12-2,8-DiCDF, 13C12-2,7-DiCDD, 13C12-2,3,7,8-TCDD, and 13C12-PCBs-77, -126, and -169 (all at 100 pg each) and a range of 13C12-labeled PCBs (28, 52, 101, 153, 138, 180 each at 325 pg) were spiked onto the samples immediately prior to extraction. PUFs were extracted in DCM for 16 h; GFFs were extracted consecutively for 12 h in toluene. The DCM and toluene extracts were combined for the cleanup procedure. The extracts were put through a mixed silica column and were fractionated for PCDD/F and non-ortho PCB analysis on a basic alumina column (see ref 4 for details). All PCB and PCDD/F standards were obtained from Promochem (U.K.); solvents and reagents were pesticide grade/high purity. PCDD/Fs and non-ortho PCBs were analyzed by HRGC–HRMS using an HP 6890 GC connected to a Micromass Autospec Ultima high-resolution instrument at a resolving power of ~10 000 (for more details see refs 4 and 15).

**Quality Control.** For every five samples, a field blank was taken by assembling two PUFs and a GFF in a module next to the air sampler. For every 10 samples a laboratory blank was taken, representing the unopened PUFs and GFF. Field and laboratory blanks were incorporated in the analytical procedure and used to derive detection limits as mean blank plus 3 times the standard deviation of the mean concentration in the blanks. There was no significant difference between field and laboratory blank levels for the GFFs; for the PUFs, concentrations of Cl1-DFs were consistently lower in the field blanks. The mean concentrations found in the laboratory and field blanks were subtracted from the samples; in the case of Cl1-DFs the field blanks were used. For most homologues and PCBs-126 and -169, mean blank concentrations were 0.1–1.0 pg/sample, but higher for Cl1DFs, OCDD, and PCB-77 (see Table 1). In the gaseous phase, Cl2-DDDs were generally at least 10× blank levels, with fewer detects for OCDF. Detection limits were <2 pg/sample for most homologues but higher for Cl1DFs (4.0 pg/sample), Cl2DFs (35), Cl3DDs (2.6), Cl4DFs (2.5), Cl2DDs (2.2), and OCDD (7.6) in the PUFs. Detection limits for the 2,3,7,8-substituted Cl4DDs were in general at least 10× blank levels, with <1 pg/sample for the 2,3,7,8-Cl4DDs; the field blanks were used. For most non-ortho PCBs, they were 36 (27) pg/sample for −77 on PUFs (GFFs), <1 pg for −126 and <0.3 pg for −169. In contrast to observations by Kallenborn et al. (16), the long transport times on the ship (>6 months) before samples taken arrived in the laboratory did not affect the blanks, validating the use of tin cans as a storage medium.

Mean recoveries for the 13C12-2,3,7,8-substituted PCDD/Fs were between 58 and 85%. 57% for Cl2-2,7-DiCDD, 61% for Cl2-2,8-DiCDF, 61% for Cl2-2,7,8-TCDF, and between 55 and 57% for Cl2-PCBs-77, -126, and -169. Recovery problems affected 13C12-2,3,7,8-TCDF; mean recoveries were only 23%. New, wider alumina columns were found to have caused the problem. 2Cl1DDs were therefore quantified against 13C12-2,3,7,8-TCDF. Of the total of 115 samples, eight had to be rejected (recoveries of several congeners <50%).

**Breakthrough.** In six samples, breakthrough of analytes from the first to the second PUF plug was assessed. Breakthrough occurred for Cl1DFs, with similar amounts on both PUF plugs for sample volumes of ~300 m³ at ambient temperature of 25 °C. We therefore decided not to report Cl1DF-concentrations. PCBs and Cl1-DFDs on the back-up PUF plug accounted for ≤10% of the amount on the first plug in all samples considered. In sample 50 the back-up PUFs showed a profile unlike any gas-phase samples and was not considered for assessing breakthrough.
TABLE 1. Mean, Median, Maximum, Minimum, and Mean Blank Concentrations (fg/m³) of Cl₂, ₃DFs and Non-Ortho PCBs-77, -126, and -169

<table>
<thead>
<tr>
<th></th>
<th>GFF – PUF</th>
<th>mean</th>
<th>median</th>
<th>max.</th>
<th>sample no.</th>
<th>min.</th>
<th>sample no.</th>
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<tr>
<td>Cl₂DFs</td>
<td>6.6</td>
<td>13</td>
<td>1500</td>
<td>990</td>
<td>#9</td>
<td>66</td>
<td>#53</td>
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<td>0.2</td>
<td>110</td>
<td>79</td>
<td>#9</td>
<td>3.2</td>
<td>#53</td>
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<tr>
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<td>0.2</td>
<td>23</td>
<td>13</td>
<td>#9</td>
<td>0.88</td>
<td>#44</td>
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<tr>
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<td>0.3</td>
<td>24</td>
<td>12</td>
<td>#4</td>
<td>1.1</td>
<td>#46</td>
</tr>
<tr>
<td>OCDF</td>
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<td>0.4</td>
<td>9.2</td>
<td>6.9</td>
<td>#4 &lt; 3.0</td>
<td>#44, 46, 49, 50</td>
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<tr>
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<td>0.9</td>
<td>100</td>
<td>76</td>
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<td>8.6</td>
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<td>2.7</td>
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<td>#44</td>
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<td>1500</td>
<td>1100</td>
<td>#11</td>
<td>180</td>
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<tr>
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<td>0.5</td>
<td>27</td>
<td>25</td>
<td>#21</td>
<td>0.9</td>
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<tr>
<td>-169</td>
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<td>0.1</td>
<td>2.1</td>
<td>1.0</td>
<td>#21</td>
<td>0.2</td>
<td>#48</td>
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* Based on average air volume of samples 40–51 (~750 m³).

Interference of Stack Emissions. The three stack samples taken did not exhibit consistent profiles; in two of the samples, only Cl₂-₃DFs were detected, while the third displayed a full range of PCDD/Fs (at ~1 pg/sample for PCDDs and 2 pg for OCDF to 19 pg Cl₁DF). Non-ortho PCBs exhibited concentrations slightly above the detection limits (23–33 pg of –77, 0.5–1 pg ~126 and 0.07–1.4 pg ~169). For most samples taken, the ship’s emissions did not interfere with the sampling (by visual observation of the GFF). The samples for which interference was noticed, namely samples 4, 44, 50, and 53 did not show higher concentrations of Cl₂-₃DFs than the samples taken before or after it. Although we cannot exclude sample contamination from the ship’s stack, we believe that it is of minor importance for the samples taken, including samples 4, 44, 50, and 53. Principal components analysis confirmed this but separated sample 47 from the rest of the samples. That sample displayed unusually high concentrations of PCDD/Fs and PCBs -126 and -169 and has therefore been excluded.

Meteorological Information. Air and sea temperature (Tair, Tsea) and atmospheric pressure were obtained from 4-hourly observations. Wind direction (wind) and wind speed (w.s.) were estimated from the roughness of the sea surface every 4 h (Beaufort scale). Back-trajectories (BTs) were obtained from the British Atmospheric Data Service. Five-day BTs were run every 12 h with the endpoints at 950 hPa.

Surface Trade Winds. The individual air masses sampled during the cruise reflect different global surface wind patterns. It therefore seems appropriate to group the samples together according to their air mass origin/surface wind patterns (see Figure 1). In the NH, the ship traversed consecutively the “westerlies” (55–30 °N), with winds coming from westerly directions (samples 1–5). At around 30 °N, winds changed, due to a high-pressure system (“subtropical anticyclone”, sample 7); further south were the easterly trade winds with air masses coming off the African coast (~30 °N to near the inter-tropical convergence zone, ITCZ; samples 8–13). The ITCZ identifies a ribbon of atmosphere with persistent convection, separating the (atmospheric) NH from the SH (sample 14). In the SH, samples taken reflected the “East-erlies” with air masses coming off the South Atlantic, from the ITCZ to 20–30 °S (samples 15–21). A stationary high-pressure system at around 30 °S (sample 22) marked the beginning of another change of wind direction: the strong “westerlies” (“roaring forties”, “furious fifties”) from 40 to 55 °S (samples 23–31). Further south, polar winds prevailed, with the air coming from a southwesterly direction (samples 33–51).

As a direct result from the ship crossing the different surface wind patterns, the individual samples taken represent very differently “aged” air masses. BTs showed some air masses arriving at the sampler from the Atlantic Ocean for at least 5 days (samples 2–7, 15, 21, 46, 53), while in others, the air had been over land (and hence emissions) ~1–2 days beforehand (samples 8–13). For samples 23–31, the air masses had a partly continental, partly oceanic influence; in samples 32–44, the air masses had spent the last 5 days above the South Atlantic and some had moved over Tierra del Fuego.

Results and Discussion

General Comments on Atlantic Air Concentrations. Mean, median, minimum, and maximum concentrations of each PCDD/F homologue group are given in Table 1. 2Cl₁₄-₃DD/Fs displayed a gradient with concentrations decreasing from the NH to the SH (regression versus latitude; r² = 0.47 significant at P < 0.01, slope 6.0, intercept 460). Highest concentrations of Cl₂-₃DFs all occurred between 25 and 52 °N; lowest concentrations were measured around ~60 °S and south of that (see Table 1). Cl₂DFs showed highest overall concentrations (up to 9800 fg/m³), followed by Cl₁DFs (up to 5300 fg/m³) and OCDD (up to 1300 fg/m³). Lowest concentrations were measured in the remote SH, with ambient concentrations as low as 66 fg/m³ for Cl₂DFs and ~11 fg/m³ for Cl₁DFs—in general 2 orders of magnitude lower than their highest concentrations over the North Atlantic (see Table 1). 2Cl₁₄-₃DD/Fs varied, on average, in the NH from 750 in the westerlies to 630 fg/m³ in the easterlies and decreased to 450 fg/m³ in sample 14 (ITCZ). In the SH, mean 2Cl₁₄-₃DD/Fs decreased further, from 380 in the easterlies to 310 fg/m³ in the westerlies and were lowest in the south polar winds with 2Cl₁₄-₃DD/Fs of 84 fg/m³. Relative to other PCDD/F ambient air measurements, these low concentrations, as typically found in remote locations (16, 17). PCDDs were generally more abundant than PCDFs. PCDF concentrations generally decreased with increasing degree of chlorination; PCDDs were dominated by OCDD and Cl₁DDs.

Toxic Equivalents (TEQs). Most samples (28 of 41) were analyzed for the individual 2,3,7,8-substituted congeners, enabling the calculation of WHO-TEQ (18). Although the concept of TEQs was not developed for abiotic matrices,
different congeners, the 2,3,7,8-substituted Cl7DD/Fs and Cl17DD/Fs (footnote 22). In marked contrast to PCDD/Fs and PCB-77, non-ortho PCBs-126 and -169 exhibited highest concentrations around the equator (see Figure 2b). They were strongly correlated with ambient T (PCB-126: \( r^2 = 0.89 \); PCB-169: \( r^2 = 0.69 \), significant at \( P < 0.01 \). Highest concentrations around the equator may be indicative of a dominating role for air-water exchange, but it is not clear why this should be more important for these compounds than others.

**Emissions from Africa.** Cl2- and Cl2-DDs displayed highest concentrations in air masses coming off Africa, while Cl17- DDs and Cl16-DDs were highest in the samples taken off the European coast (see Table 1). This may be indicative of different PCDD/F sources in Europe and Africa. In the air masses coming off Africa, mean Cl12DF and Cl17DF-concentrations were 3100 and 5800 fg/m³, respectively. The homologue profile indicates low-temperature combustion processes, such as the domestic burning of coal and wood (4, 19, 20) as probable sources. Given the atmospheric depletion, deposition, and dilution processes, which would influence the air mass as it moved away from Africa over the sea to the ship, these data suggest significant releases of PCDD/Fs in west Africa. Samples 8 and 9 had the highest concentrations of Cl2-3DD/Fs. Back-trajectories showed that these had come straight off the African continent. Their mean gaseous concentrations were used to model the change in concentrations, due to the combined effects of particle deposition and OH-radical initiated depletion of gaseous PCDD/Fs (“weathering”, for more detail see in ref 3), to crudely derive the emissions from West Africa. Extrapolating samples 8 and 9 backward by 2–4 days, yields concentrations of \( \approx 10 \) pg/m³ for Cl2-DDs and 1–2 pg/m³ \( \Sigma \)Cl17-DD/Fs (\( \Sigma \)TEQ \( \approx 10 \) fg/m³). If these concentrations were representative of an annually well-mixed atmospheric boundary layer (750 m height) of a 250 km stretch along the West coast of Africa (ca. 4000 km long) with a constant wind speed of 5 m/s, then emissions of the order of \( \approx 5 \) kg \( \Sigma \)TEQ would be released in West Africa annually. This is comparable to the estimated \( \Sigma \)TEQ emissions for the entire U.S.A. for 1995 (20).

**The Occurrence of PCDD/Fs in the Southern Hemisphere.** This sample set adds considerably to the range of sites we have studied from various parts of the world by the same methods. PCDD/F concentrations at Montevideo, the capital of Uruguay with ca. 1.3 million inhabitants, were comparatively high and reached levels detected in U.K. winter samples from Lancaster (city of ca. 100 km inland near the equator (21)) as probable sources. Given the atmospheric emission of low-temperature solid fuel combustion being partly responsible for ambient PCDD/F concentrations there. Interestingly, while Cl2-DDs at Montevideo reached levels comparable to those in Manchester, Cl6-DD/Fs were lower by factors of \( \approx 5 \). Baker and Hites (7) have argued that Cl6-DD/Fs might be produced from PCP in the atmosphere and hence this might reflect a lower usage of PCP in Uruguay.

Concentrations of 330 fg Cl6-DD/Fs/m³ were detected in the Falkland Islands and were similar to PCDD/Fs measured at the remote Irish coast (15). Although low, PCDD/F-concentrations at the Falkland Islands were still higher by factors of 2–5 than those found south of 40 °S. Other measurements of marine background concentrations detected \( \Sigma \) Cl6-DD/Fs in the order of \( \approx 20 \) fg/m³ in the North Atlantic in 1997 (22) and \( \approx 67–100 \) fg/m³ in the Northern Hemisphere in 1995 (23). The detection of PCDD/Fs in the remote south provides further evidence of ongoing emissions in the SH. On average it takes about a year for gases in the NH to be exchanged to the SH (24). Published half-lives of gaseous PCDD/Fs (with respect to OH-radical attack, for 298 K and 10⁸ mol./cm³) vary from \( \approx 1.5 \) days for Cl2-DDs to 10–20 days for Cl17-DDs (25, 26), making any exchange of PCDD/Fs released in one hemisphere to the other unlikely and insignificant compared to local releases.

**Relative Homologue Profiles.** Figure 3 shows the relative contribution of the tri- to octachlorinated homologues to the \( \Sigma \)Cl17-DD/Fs, for selected air measurements from the SH and NH. The average profile from Manchester mirrors the “typical” ambient air profile as described in much of the literature for the temperate industrialized countries (see ref 17). The relative contribution of PCDDs decreases with increasing chlorination, while the relative contribution of each homologue increases with increasing chlorination for the PCDDs. However, the samples from off Africa, the ITZ, Montevideo, the Falkland Islands, and near Halley were all dominated by Cl12DFs, contributing \( \approx 40 \% \) of the total (as compared to \( \approx 20 \% \) for Manchester). At Montevideo, each PCDD homologue contributed \( < 10 \% \) of the total; Cl17DDs were in higher abundance than OCDD. This likely reflects different local PCDD/F sources to the atmosphere. Samples

\[ \Sigma \text{TEQ} \] is frequently used for comparison and characterization of air samples from different areas (see ref 17). Of the 17 different congeners, the 2,3,7,8-substituted Cl7DD/Fs and OCDD were most frequently detected, followed by most 2,3,7,8-substituted PCDFs and 1,2,3,7,8-Cl5DD. The other 2,3,7,8-substituted PCDDs were rarely above detection limits. Nondetected congeners were not considered for the derivation of \( \Sigma \)TEQ. Highest \( \Sigma \)TEQ concentrations over the Atlantic were measured off the African coast (11 fg \( \Sigma \)TEQ/m³-sample 9) and the lowest \( \Sigma \)TEQ (where most congeners were > d.l.) was measured nearest the Antarctic (0.50 fg \( \Sigma \)TEQ/m³-sample 53). In general \( \Sigma \)Cl17-DD/Fs and \( \Sigma \)TEQ covary (see Figure 2a), with \( \Sigma \)Cl17-DD/Fs/\( \Sigma \)TEQ being on the order of \( \approx 10 \). All individual PCDD/F concentrations, separated into gas and particulate phase, are given in the Supporting Information.

**Non-Ortho PCBs.** Concentrations of PCB-77 were higher in the NH, with concentrations up to \( \approx 5400 \) fg/m³. In the SH, ambient concentrations were around 1000 fg/m³ (see Figure 2b). In marked contrast to PCDD/Fs and PCB-77, non-ortho PCBs-126 and -169 exhibited highest concentrations around the equator (see Figure 2b). They were strongly correlated with ambient T (PCB-126: \( r^2 = 0.89 \); PCB-169: \( r^2 = 0.69 \), significant at \( P < 0.01 \). Highest concentrations around the equator may be indicative of a dominating role for air–water exchange, but it is not clear why this should be more important for these compounds than others.

**Figure 2. a. \( \Sigma \)Cl17-DD/Fs (fg/m³) and PCDD/F \( \Sigma \)TEQ (fg \( \Sigma \)TEQ/m³) and b. PCB-77, -126, and -169 (fg/m³) as a function of latitude.**
from off Africa and the ITCZ were strongly dominated by Cl$_3$DFs (90%), confirming their relatively long characteristic travel distance (CTD) (27, 28). Samples from the Falkland Islands and near Halley showed profiles being dominated by Cl$_3$DFs (~40% of the total) and OCDD (~20% of the total). These are the most persistent PCDD/Fs, occurring predominantly in the gaseous and particulate-bound phase and the profile therefore likely represents the pattern found in "old air masses" (i.e. after passage away from land, and weathering due to degradation/ deposition during atmospheric transport (29)).

The atmospheric half-life of Cl$_3$DFs at 298 K and 10$^6$ OH-radicals/cm$^3$ has been estimated to be ~3.9–6.7 days (25, 26). After emission from land-based sources Cl$_3$DFs have the propensity to be advected for relatively long periods of time without being subject to significant depletion or deposition processes. Indeed, their CTD, where the concentration in air has dropped off to 1/e, is estimated to be in the order of 2300 km (27, 28). Concentrations measured over the open ocean should reflect air–water partitioning. It is therefore possible that the high concentrations encountered are influenced by outgassing of aqueous dissolved Cl$_3$DFs. Selected samples taken over the open ocean (i.e. 16, 34, 38, and 47) were compared with respect to the composition of the Cl$_3$DF-traces. All samples were similarly dominated by a single congenер, suggesting that Cl$_3$DFs had a common (likely land-based) origin.

**Gas-Particle Distribution.** Cl$_3$-DD/ Fs were on average >90% in the gaseous phase and Cl$_2$-DD/ Fs predominantly in the particulate phase. Cl$_4$-DD/ Fs showed the widest range of distributions, their fraction in the gas-phase varying from 10 to 90% between locations. The relative distribution between the gaseous and particulate phases obviously depends strongly on ambient temperature, the properties, and concentration of ambient particles. Around the equator (>25 °C), even Cl$_3$-DD/ Fs were >50% in the gaseous phase. In the samples from the temperate north, Cl$_4$DFs and Cl$_6$DFs were ~65% and 15% in the gaseous phase, respectively. This share increased to almost 100% around the equator, before decreasing to ~60% (Cl$_4$DFs) and 15% (Cl$_6$DFs) in the samples taken further south than 40°S. The plot of percent Cl$_3$DFs in the gaseous phase versus latitude is given as Figure A in the Supporting Information. To examine the partitioning in more detail, the logarithm of the gaseous (V) over the particulate (P) phase versus 1/T were plotted for a range of

PCDFs. As expected, lower ambient T resulted in increased partitioning to the particulate phase (and lower log(V/P) coefficients) and statistically significant correlations (at P ≤ 0.01) were obtained for Cl$_3$-DD/ Fs (shown in the Supporting Information as Figure B).

PCB-77 was predominantly in the gaseous phase—even south of 40°S only 10–20% of PCB-77 was particulate-bound. The particle-bound fraction of PCB-126 and -169 varied strongly with the latitude/ambient temperature. Their particulate fraction accounted for <10% around the equator, when ambient temperatures were >25 °C but increased to over 50% south of 50 °S.

**PCDD/Fs in the Particulate Phase.** Concentrations of PCDD/Fs in the particulate phase were generally low, with most homologue groups rarely exceeding 50 fg/m$^3$ (see Figure 4a for Cl$_3$DF and OCDD concentrations). Apart from one or two samples, concentrations of Cl$_{1-2}$DD/ Fs on particles varied little along the north–south transect. These fairly constant concentrations of the particle-borne Cl$_{1-2}$DD/ Fs suggests a consistent background concentration of fine particles (<1 μm) above the Atlantic ocean (30). We interpret this as indicative of LRAT of Cl$_{1-3}$DD/ Fs, which are small enough not to be deposited close to emission sources and can therefore effectively act as vapor phase species. However, we have no accompanying aerosol measurements to support this suggestion. Heintzenberg (31) estimated total fine particle (<1 μm) concentrations in the remote marine boundary layer to be ~5 μg/m$^3$, of which 11% is organic carbon.

**OH-Radicals.** Figure 5 shows average monthly OH-radical concentrations at 30°W between the surface and 30 m, obtained from a chemical general circulation model (32, 33). Modeled OH-radical concentrations fall away sharply outside the zone 40°N to 40°S during the ship’s cruise. Beyond these latitudes, gaseous deactivation reactions would be much less important for PCDD/F atmospheric fate. Interestingly, concentrations of most gaseous PCDD/Fs were uniform south of 40°S. This can be interpreted as evidence that this loss mechanism is indeed limited beyond these latitudes. It takes
the remote SH (as opposed to 2.4 days at 298 K and [OH] of 1.6×10^6 mol/cm^3). Cl2/3DDs displayed relatively low concentra-
tions around 5°S. This could be indicative of reactions/depletion with OH-radicals where their concentrations and temperature are highest. PCDDs are less stable than the equivalent PCDF homologue with respect to degradation by OH-radical attack (15, 24, 25).

Comments on Air–Sea Exchange of PCDD/Fs. Compounds in the gas and particle phase will be deposited to surface seawater. PCDD/Fs in the surface waters can accumulate over time and—in the absence of degradation or removal mechanisms such as scavenging by organic carbon and deposition into the deep ocean (35)—will approach equilibrium with the air above it. If concentrations in the overlying air then decline, outgassing from the surface water back to the atmosphere may then be important in controlling the air concentrations over the oceans (as has been noted for POPs in the Great Lakes (35, 36) and for lower chlorinated PCDD/Fs in the Lower Hudson River Estuary (6)). Outgassing of PCBs from the Great Lakes is occurring, because peak primary emissions in the 1960/1970s loaded up the lake burden and—in principle—similar mechanisms can be envisaged for the PCDD/Fs, for which the peak primary emissions were in the 1960/1970s (37). However, ocean systems may be very different, with organic carbon scavenging POPs from surface waters to deeper waters and ultimately sediments. Another area of uncertainty is whether PCDD/Fs can be converted or formed in the oceans, yielding PCDD/Fs which can be released from the water column to the overlying air. Adrieans and co-workers have reported the dechlorination of heavier homologues in sediments, forming Cl2DDs (38), which can volatilize from water–air (6). PCDD/Fs in surface waters can also enter the atmosphere in sea spray notably during high winds/storms. However, there is no evidence from this study that these pathways are dominant in influencing air composition over the open ocean.

Estimation of the Global Atmospheric PCDD/F Burden. The measured PCDD/F air concentrations represent, with few exceptions (see above), general ocean background concentrations. These were used to calculate the mass of PCDD/Fs in the global background/oceanic atmosphere. For each group of samples, i.e., N-Westerlies, N-East Trade winds, S-East Trade winds, S-Westerlies, and S-Polar winds, the median ambient Atlantic concentrations were calculated (see Table 2). Of crucial importance to this estimation is the height of the atmosphere containing PCDD/Fs, for which concentrations measured at ~20 m above sea-level are representative. As a conservative estimate, the height of the well-mixed atmospheric boundary layer was limited to 1.5 km for these calculations. The volume of the air in each zone was calculated based on a sphere of radius 6370 km.

It is appropriate to consider how representative the concentrations measured in this study are for other locations of similar latitude. PCDD/Fs will be higher over land, i.e. closer to the principle release areas. BTs for the majority of our samples indicate that PCDD/Fs have been moving over water for at least 5 days, thereby reflecting "true" remote concentrations. We are not aware of published PCDD/F measurements over the Pacific or Indian Ocean. While Pacific air and water concentrations are significantly lower than the North Atlantic for PCBs, ambient PCDD/Fs in Japan are routinely among the highest found for industrialized countries (e.g. ref. 13).

These assumptions lead to an estimate that the global atmosphere carries thousands of kilograms of Cl2/3DFs and tens of kilograms of Cl2DDs and OCDD at any one time (see Table 2). The total burden of Cl2/3DFs is on the order of ~350 kg, with the ΣTEQ being lower by a factor of ~100 (3.3 kg). It should be noted that the calculation of ΣTEQ excluded all congeners <d.l.; in other words, this understimates the ΣTEQ in most Atlantic air samples. As shown in Table 2, two-thirds of the global atmosphere is in the region 30°N to 30°S. Hence, PCDD/F concentrations around the equator
TABLE 2. Surface Wind Groups, Their Respective Air Volumes, and Median Ambient Concentrations (fg/m$^3$) of Selected PCDD/Fs

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* Concentrations assumed to be similar to S-Polar zone. * Reference 18.

Concluding Remarks. This study has shown that PCDD/Fs are globally distributed in the atmosphere and can be detected, with sufficiently sensitive techniques, in the most remote parts of the world. Higher atmospheric concentrations were measured in air masses coming off the African coast and close to South America, providing evidence for current releases on those continents. Air mass BTs confirm the effective separation of the NH and SH atmosphere: this implies that emissions in the SH must be of a similar order, though lower, to those in the NH. The majority of samples reflected Atlantic background concentrations. Concentrations of the particulate-bound Cl$_2$-DD/Fs were fairly constant over the ocean, while gaseous PCDD/Fs decreased from the NH to the SH. We estimated the global background atmospheric PCDD/F burden to be on the order of 350 kg for $\Sigma$Cl$_4$-DD/ Fs and 3–4 kg for $\Sigma$TEQ. The influence of OH-radical initiated depletion reactions of gaseous PCDD/Fs was not as evident as expected. It is important to include seasonally and latitudinally adjusted OH-radical concentrations in atmospheric transport and fate calculations of compounds such as PCDD/Fs. Only Cl$_2$-DDs displayed lower concentrations around the equator, i.e., a zone of highest OH-radical concentrations. Samples taken in the remote south suggest that gaseous depletion reactions are likely to be slower than the time it takes the air masses to become well mixed (in the order of a few weeks).

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Supporting Information Available

PCDD/F gas and particle phase concentrations, together with sample details (sample numbers, the average position for each sample, air volumes taken, and meteorological conditions) and plots of the gas-particle partitioning of some homologues. This material is available free of charge via the Internet at http://pubs.acs.org.

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