Processes controlling diurnal variations of PCDD/Fs in the New Jersey coastal atmosphere

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Abstract

Consecutive 12 hour day–night air samples (~ 500 m\textsuperscript{3} each) were taken over 7 days at three land-based sites and an over-water site in coastal New Jersey (NJ) in July 1998, in a campaign designed to shed light on factors controlling ambient PCDD/F concentrations. The sampling sites were chosen to reflect contrasting environments: urban/industrial from the center of the New York (NY)–NJ metropolitan area (Liberty Science Center, LSC); coastal Atlantic (Sandy Hook, SH); suburban NJ (New Brunswick, NB); over-water in Raritan Bay (RB). Despite proximity to the major NY/NJ conurbation, ambient PCDD/F concentrations in the region were low compared to literature data for other urban locations. Mean $\sum$Cl\textsubscript{4–8}DD/Fs and $\sum$TEQ (in fg/m\textsuperscript{3}) were: 1400 and 16 at NB; 1000 and 9.5 over RB; 880 and 8.5 at LSC; and 830 and 6.6 at SH. Di- and tri-chlorinated dibenzo-p-dioxins and -furans (PCDD/Fs) were also measured and dominated the $\sum$Cl\textsubscript{2–3}DD/F concentrations. Air–water exchange calculations demonstrated the relative importance of Cl\textsubscript{3}DD volatilizing from the Lower Hudson River Estuary for ambient concentrations (~ 25% of advection), but was of minor importance for the other PCDD/Fs. The study provides evidence that advective transport, local inputs and atmospheric processes combine in a complex manner to control ambient PCDD/F concentrations. These processes generally dominate any local diurnal influence of OH-radical-mediated depletion, which we had hypothesized would be detectable by measuring higher night- and day-time concentrations. Rather, it is implied that changes in the mixed boundary layer height resulted in higher night- than daytime concentrations at the urban and coastal sites. A strong diurnal signal, dominated by the lower chlorinated dioxins and furans, was detected at the rural site (NB) during a period of lower wind speeds.

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1. Introduction

Polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs) are ubiquitous contaminants, released into the environment as by-products of incomplete combustion or as impurities in various chlorinated products (Ballschmiter and Bacher, 1996; Rappe, 1992). The last decade or so has seen major efforts in the US, Europe and elsewhere to reduce PCDD/F emissions to the atmosphere (e.g. US-EPA, 1998; Alcock et al., 1999). Recent US emission estimates, for example, suggest a reduction of 75% between 1987 and 1995 (US-EPA, 1998) in major primary sources, such as municipal solid waste incineration and metal industry activities, which...
have been targeted for control. As major primary emissions are reduced, diffusive primary sources (such as vehicle emissions, domestic burning, etc.) (Lee et al., 1999; Lohmann et al., 2000a) and possibly secondary/recycling sources (Cleverly et al., 1999; Lohmann et al., 2000b) may be expected to control ambient levels. However, it is unclear what the relative importance of these source categories is in controlling ambient PCDD/F concentrations, and what scope remains for further, cost-effective source reductions (Alcock et al., 1999; Lee et al., 1999; Lohmann et al., 2000a). To unravel this question, precise and sensitive ambient measurements are required. Such measurements can be targeted to investigate sources and the relative importance of loss processes, by spatial and temporal monitoring. Unfortunately, such studies are constrained by the sampling times needed to collect sufficient mass of PCDD/F for detection by HRGC-HRMS. Many monitoring programs have taken integrated samples over several weeks (e.g. Hiester et al., 1997; Hippelein et al., 1996), for example, thereby losing the resolution required to study sources and loss processes. However, if samples can be taken over shorter periods, for example, over hours (Lee et al., 1998) or a day or so (Lohmann et al., 1999a), the way is open to better understand sources/environmental fate.

Day–night samples can potentially provide clues about the relative importance of sources, but there are other potentially important variables that vary diurnally. Certain PCDD/F emission sources, such as vehicular traffic and the domestic burning of coal and wood, are expected to show a strong day–night cycle. The contribution of secondary sources can also vary diurnally. Air–water exchange of persistent organic pollutants (POPs) is less strongly affected by the day–night temperature cycle than air–soil or air–vegetation exchange, because the temperature of the water surface varies little. Water bodies may be sources of PAHs, PCBs and other POPs to the atmosphere (Zhang et al., 1999; Bamford et al., 1999; Dachs et al., 1999; Gigliotti et al., 2002). Air–water exchange is a source to the atmosphere of some PCDD/Fs (Lohmann et al., 2000b) and PCBs (Totten et al., 2002) in the Lower Hudson River Estuary (LHRE). It is unclear, however, how important the water–air exchange of PCDD/Fs is, compared to other local sources and advection in the area. Indeed, surprisingly little is known about the extent to which PCDD/Fs occur in the atmosphere of the New York/New Jersey (NY/NJ) conurbation or the eastern US, in general.

Atmospheric OH-radical concentrations are greatest during daylight (e.g. Derwent, 1996); reactions with OH-radicals are considered by some researchers to be the dominant atmospheric loss process for PCDD/Fs (Kwok et al., 1995; Atkinson, 1997). The height of the mixed boundary layer also generally displays a strong diurnal cycle, with the height of the well-mixed atmosphere decreasing from ~1000 to 2000 m during the day to a few hundred meters or less during the night (Jacob, 1999; Lena and Desiato, 1999). Hence, local emissions to the atmosphere will be less well dispersed at night. Low wind speeds, coupled with a reduced height of the well-mixed atmosphere, favor an accumulation of near-ground emissions and result in increasing ambient concentrations. In one such episode, ambient PCDD/F concentrations increased 4–5-fold during the night (Lohmann et al., 2000a). There is considerable interest in studying the day–night variations of ambient PCDD/Fs, but so far, few—if any—studies have been designed which overcome the inherent sampling and analytical difficulties in doing so. One US study suggested that ambient PCDD/Fs exhibited a day–night cycle and proposed volatilization from soils as the likely reason for increased daytime concentrations (Cleverly et al., 1999).

However, the long sampling periods ('day' and 'night' samples were averaged over 28 days) would have integrated concentration variations arising from a range of factors, such as air mass origin (Lohmann et al., 1999a) and perhaps introduced sampling artifacts. The study also did not include the lower chlorinated PCDD/Fs, which are more susceptible to environmental remobilization.

We have reported previously on the use of sensitive and precise methods for determining PCDD/Fs in relatively small air volumes (Lohmann et al., 1999b), opening up the possibility of intensive short-term campaigns to investigate source/loss processes. We have also reported part of a study on PCDD/Fs in the NY/NJ area (Lohmann et al., 2000b). Here we describe a diurnal sampling campaign undertaken at three land-based sampling stations around the coastal NJ area and concurrently at an over-water site. At each site, consecutive 12 hour day (0800–2000 h) and night (2000–0800 h) samples were taken. The sampling sites were chosen to reflect contrasting environments (see Fig. 1): (i) center of the metropolitan NY/NJ urban/industrial complex (Liberty Science Center, LSC); (ii) coastal Atlantic (Sandy Hook, SH), located on a barrier spit separating the LHRE from the Atlantic Ocean; (iii) suburban (New Brunswick, NB), with a suburban site amidst intensely travelled roadways; and (iv) over water in Raritan Bay (RB). The over-water samples were taken to further investigate the role of the estuary in contributing to ambient PCDD/F concentrations (Lohmann et al., 2000b). Cl2–8DD/Fs and mono-CDFs were analyzed in all samples. The lower chlorinated homologues were included because of their relatively high Henry’s Law constants (HLCs) (1 to 7 Pa m3/mol) and log $K_{ow}$ values (4.9–6.4), which make them susceptible to terrestrial/aquatic surface–air exchange (Mackay et al., 2000; Govers and Krop, 1998).
2. Materials and methods

Sampling: The land-based air samples were taken over a week-long campaign, whilst additional over-water samples were being collected (Lohmann et al., 2000b). Thirteen samples were taken at both LSC and SH, 12 from NB and four over RB. The over-water samples were taken over the LHRE aboard the R.V. Walford in July 1998, while the boat was anchored facing into the wind. The first three samples were taken in RB, the fourth in the lower New York Harbor (see Fig. 1). The samples were collected with a modified organics Hi-Vol sampler (Graseby) equipped with quartz fiber filter (QFF) (20 × 24 cm²) and polyurethane foam (PUF; 10 × 8 cm² diameter) adsorbent. Each sample consisted of ca. 500 m³ (over water 350 m³) of air sampled at calibrated flow rates of ≈0.5–0.8 m³/min. Filters were pre-combusted at 400 °C for 4 h, equilibrated in constant humidity before and after deployment in the field and weighed. PUFs were cleaned by successive 24 hour extraction in acetone and petroleum ether and dried in glass vacuum desiccators. Samples were processed at Rutgers University immediately following collection and later analyzed at Lancaster University. Meteorological information was obtained from Newark Airport, ca. 20 km from the coast. Back trajectories (BTs) were obtained for the beginning and end of each sampling period employing the HYSPLIT Model at the NOAA Air Resources Laboratory’s Web site (www.arl.noaa.gov). The three-day endpoints of the BTs were at 850, 900 and 950 hPa for the NJ area (40.5°N, 74.0°W). Ambient temperature, wind speed/direction, relative humidity and air mass movement/origin are summarized for the sampling periods in Table 1.

Analytical procedure: The QFFs were extracted with toluene and the PUFs with dichloromethane in a Soxhlet apparatus. QFFs and PUFs were spiked with 13C12-labelled PCDD/F standards (Promochem, Welwyn Garden City, AL7 1SS, UK) prior to extraction. The extracts were reduced to ≈1 ml, transferred to gas chromatographic (GC) vials and transported to Lancaster University. They were cleaned upon a mixed silica column and fractionated on a basic alumina column (for details see Lohmann et al., 1999b). Field blanks (n = 12), laboratory blanks (13) and spiked blanks (6) were routinely included and treated as the other samples.

All samples were analyzed by HRGC-HRMS on a Micromass AutoSpec Ultima, operated at a resolving power of ≈10,000. PCDD/Fs were quantified relative to a full suite of 13C12-labelled congeners (isotope dilution method). The Cl₂–8DD/Fs and mono-CDFs were separated and quantified on a 30 m DB-5 column; the 2,3,7,8-substituted congeners on a 60 m SP-2331 column. Mean recoveries of the various 13C12-labelled congeners were generally 50–100%, but in some samples recoveries of 12C12–2,3,7,8-TCDD were <50%. New, wider alumina columns were found to have caused the problem. In those samples, Cl₂DDs were quantified against 13C12–2,3,7,Cl₁-Cl₂DD. At detection limits of ≈0.1–0.6 pg/sample for the 2,3,7,8-substituted congeners (based on the noise of the baseline), only trace amounts of Cl₇/₈DDs were detected in the blanks. There was no consistent difference between laboratory and field
blanks. Method detection limits for the homologue groups, expressed as the mean blank level plus three times its standard deviation were generally 1–2 pg/sample, but higher for OCDD (13 pg/sample) and Cl2DFs (60 pg/sample). The low detection limits permitted detection of virtually all homologue groups; only OCDF had several non-detects. Mean recoveries for Cl2–8DD/Fs in the spiked blanks were between 90% and 105%. On two occasions, the breakthrough of PCDD/Fs was tested, using a split PUF-cartridge and analyzing the halves separately. At air volumes of 500 m³ at 28°C, only Cl2DFs (25% relative to the front PUF) and Cl2DDs (10%) were found on the back-up half. Breakthrough was therefore not a concern for these samples.

3. Results and discussion

General comments on concentrations: Table 2 presents a summary of the concentration data for each site. Mean (and range) ∑Cl₄–₈DD/F concentrations (in fg/m³) were: NB, 1400 (450–3700); RB, 1000 (190–2700); LSC, 880 (290–1800); and SH, 830 (72–6300). The range was greatest at SH, with Cmax/Cmin > 90, but < 10 at the other sites. The range in concentrations is also reflected

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Ambient temperature (T), wind speed (w.s.) and direction (w.d.), relative humidity (r.h.) and air mass movement according to 3 day BTs for the individual sampling periods (D-day; N-night)</th>
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<td>Sampling period</td>
<td>T (°C)</td>
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</tr>
<tr>
<td>5 July, N</td>
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</tr>
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<td>20.1</td>
</tr>
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<td>21.7</td>
</tr>
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<tr>
<td>11 July, D</td>
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</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Ambient PCDD/F concentrations (gas + particle phase; in fg/m³) in Coastal New Jersey</th>
</tr>
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<tbody>
<tr>
<td>New Brunswick (n = 12)</td>
<td>Sandy Hook (n = 13)</td>
</tr>
<tr>
<td>Mean</td>
<td>s.d.</td>
</tr>
<tr>
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<tr>
<td>Cl2DFs</td>
<td>3200</td>
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<td>1000</td>
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<tr>
<td>Cl6DFs</td>
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<tr>
<td>Cl7DFs</td>
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<td>Cl7DDs</td>
<td>1400</td>
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<td>∑TEQ*</td>
<td>16</td>
</tr>
<tr>
<td>∑TEQ*</td>
<td>16</td>
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</table>

*Van den Berg et al. (1998)
in the standard deviations of the mean values: the standard deviation was twice the mean value at SH, but comparable to the mean at NB and RB and only half the mean value at LSC (see Table 2). Mean WHO-TEQ (Van den Berg et al., 1998) concentrations were lowest at SH (6.6 fg \( \sum \text{TEQ/m}^3 \)), see Table 2) and highest at NB (16 fg \( \sum \text{TEQ/m}^3 \)). These values are low for an urban center, and actually more typical of rural/remote areas (Lohmann and Jones, 1998). For example, \( \sum \text{Cl}_4–8 \text{DD/F} \) concentrations of \( \sim 500 \text{ fg/m}^3 \) (3–4 fg \( \sum \text{TEQ/m}^3 \)) were measured at the remote western Irish coast and were \( \sim 1000 \text{ fg/m}^3 \) (\( \geq 10 \) fg \( \sum \text{TEQ/m}^3 \)) near Lancaster, a city of 100,000 inhabitants on the north-west coast of England in May 1997 (Lohmann et al., 1999b). Ambient PCDD/Fs in the NY/NJ complex were therefore only 2–3 times higher than at the remote Irish site. It is obviously of interest to consider why these low levels were measured in this study. It is first worth noting that Baker et al. (1999) measured very similar concentrations (300–3400 fg \( \sum \text{Cl}_4–8 \text{DD/Fs/m}^3 \)) at sites in NJ, including NB and LSC, in August 1999. This suggests the data are ‘real’ and sampling and/or analytical artifacts have not significantly affected the results.

Ambient PCDD/Fs have been shown to display a seasonal cycle, with lower concentrations in summer (Lohmann and Jones, 1998): this campaign was conducted in the height of the summer. In the 1990s, a number of US studies reported ambient \( \sum \text{Cl}_4–8 \text{DD/Fs} \sim 10 \text{ pg/m}^3 \) or less (see Lohmann and Jones, 1998). For example, Smith et al. (1992) measured concentrations of 3.9 pg/m\(^3\) for air taken in NY State for 1986–1990. Due to emission abatement measures taken in the US and Europe, PCDD/Fs have decreased on the order of \( \sim 10\% \) a year (Alcock and Jones, 1996). Clearly, lower concentrations are to be expected for more recent measurement programs. Recent US-EPA air monitoring found low annual average \( \sum \text{TEQ} \) concentrations (12 fg \( \sum \text{TEQ/m}^3 \)) in the rural US (Cleverly et al., 1999). Although PCDD/F-contaminated sediments have been reported in part of the Hudson River and adjacent waters, they were largely contaminated by direct discharges into the water, rather than via ambient emissions and deposition. Presumably ambient levels in the NY/NJ area are influenced by ‘dilution’ of advected air moving off the Atlantic.

Although lower chlorinated homologues are not usually quantified by analytical laboratories, when they are, they dominate the PCDD/F profile (e.g. Ballschmiter and Bacher, 1996; Lee et al., 1999; Lohmann et al., 2000a). In this study, either \( \text{Cl}_2 \text{DFs} \) (at NB), \( \text{Cl}_1 \text{DFs} \) (LSC) or \( \text{Cl}_2 \text{DDs} \) (SH, RB) dominated, with concentrations reaching 21 pg/m\(^3\) (\( \text{Cl}_2 \text{DFs} \)) and 7.6 pg/m\(^3\) (\( \text{Cl}_2 \text{DDs} \)). The \( \text{Cl}_1 \text{DFs} \) and \( \text{Cl}_2 \text{DFs} \) were the next most important homologue groups, with mean concentrations of 300–2600 fg/m\(^3\) (see Table 2). The \( \text{Cl}_2 \text{DD/Fs} \) were more abundant than the sum of all other PCDD/Fs, and the \( \text{Cl}_3 \text{DD/Fs} \) alone often contributed as much as \( \sum \text{Cl}_4–8 \text{DD/Fs} \) in a given air sample. Mean \( \text{Cl}_2–4 \text{DD} \) concentrations were highest for over-water samples while mean \( \text{Cl}_7–8 \text{DD} \) concentrations were highest for the SH samples.

In summary, there was a marked spatial and temporal variation in the concentrations and mixture of PCDD/Fs (see Fig. 2a). Various sources/processes are therefore implicated as influencing the ambient concentrations. It is appropriate to examine each site in more detail and comment on likely controlling influences.

Spatial and temporal trends at each site: The trends in \( \sum \text{Cl}_4–8 \text{DD/Fs} \) are shown in Fig. 2a and are clearly different at each site. For example, PCDD/F concentrations at NB peaked on the days of 6/7 July, with \( \sum \text{Cl}_4–8 \text{DD/Fs} \) of \( \sim 4 \text{ pg/m}^3 \); none of the other sites peaked at this time. Similarly, at SH, \( \sum \text{Cl}_4–8 \text{DD/Fs} \) peaked on the night of 9 July, but not at the other sites. The LSC site showed the least variation over the course of the sampling campaign.

Sandy Hook: This coastal site provided clear evidence of the influence of air mass origin and advection on concentrations and profiles, together with outgassing of lower chlorinated homologues from nearby water bodies. Concentrations varied most at this site, as air mass origin changed. On 5/6 June, air masses originated from the N/NE and \( \sum \text{Cl}_4–8 \text{DD/Fs} \) decreased to 0.1 g/m\(^3\), but increased to 6.3 pg/m\(^3\) on the night of 9 July when air came from the west, over urban/industrial NY–NJ. The air mass episodes displayed distinctly different homologue patterns (see Fig. 3). Air from the N/NE was dominated by PCDFs. During gentle breeze episodes, \( \text{Cl}_1 \text{DFs} \) alone contributed >50% of all homologue groups, and \( \text{Cl}_1 \text{DDs} \) were the only PCDDs contributing >10%. The preponderance of less chlorinated compounds was the result of long-range transport, characterized by preferential removal of the higher chlorinated, particulate-bound PCDD/Fs and depletion of PCDDs relative to PCDFs (‘weathering’) (Lohmann et al., 1999a; Brubaker and Hites, 1997). In contrast, PCDD/F air masses transported from the urban/industrial NJ–NY area showed the other extreme, dominated by PCDDs, particularly \( \text{Cl}_7–8 \text{DD/Fs} \) — a strong pentachlorophenol signal (Baker and Hites, 2000). The \( \text{Cl}_2–3 \text{DDs} \) were an exception, with stable concentrations and \( C_{\text{max}}/C_{\text{min}} \) of 3–4. We interpret this as being due to volatilization from the LHRE (Lohmann et al., 2000b).

Over water: The \( \text{Cl}_2 \text{DDs} \) dominated the PCDD/F profile over the LHRE, consistent with earlier observations of outgassing from the water body (Lohmann et al., 2000b). This is discussed further below.

Liberty Science Center: Ambient PCDD/F concentrations at LSC displayed the least variation of all land-based sites: \( C_{\text{max}}/C_{\text{min}} \) of \( \text{Cl}_2–6 \text{DFs} \) and \( \text{Cl}_3–5 \text{DDs} \) were...
only $\sim 5$ over the entire sampling campaign; only Cl$_1$DFs, Cl$_2$DDs, Cl$_6$–8DDs and OCDF displayed $C_{\text{max}}/C_{\text{min}} > 10$. This is also reflected in the relative standard deviations, which were in general smallest at the LSC. The temporal stability of lower chlorinated Cl$_2$–6DD/F concentrations implies proximity to ongoing, local source(s).

**New Brunswick:** Concentrations at NB were highest during the daytime samples of 6/7 July. In marked contrast to the other land-based sites, concentrations at NB did not decrease to their lowest concentrations during the calm days of 7/8 July. The initial $\sum$TEQ concentrations were low at $\sim 3$ fg $\sum$TEQ/m$^3$, but increased during the daytime of 6–8 July to 55, 20 and 23 fg $\sum$TEQ/m$^3$, respectively. For all samples, PCDF dominated contributions to the $\sum$TEQ (on average 73%). Based on characteristic emission profiles by the US-EPA, such profiles could be attributed to vehicular traffic, secondary lead smelters and/or residential oil furnaces (US-EPA, 1998). Proximity to roads and vehicular emissions (and/or another local diurnal source) may be important at this site, contributing to the daytime peaks in concentration.

The importance of air–water exchange of dioxins to the atmosphere above the LHRE has been implicated as being responsible for relatively stable atmospheric concentrations of Cl$_2$–3DDs above the LHRE. In the following, an approximation as to the relevance of this source relative to advectively transported PCDD/Fs is attempted. Two scenarios were considered. Firstly (event A), the period from 6 July during the day (D) to 8 July, D: This scenario had air coming from $\sim 150^\circ$ to $180^\circ$ with wind speeds measured at 10 m height ($u_{10}$) of 2.0–3.6 m/s. Secondly (event B), the period of 11 July
D and N, when the wind originated from 330° at 5.0–7.5 m/s ($u_{10}$). For both events, the air masses were sampled twice, before and after it moved over the LHRE.

(1) *Air–water exchange*: Air–water diffusive fluxes of Cl$_{1–5}$DD/Fs were calculated using a modified two-layer resistance model (e.g. Zhang et al., 1999; Bamford et al., 1999; Dachs et al., 1999; Gigliotti et al., 2002; Totten et al., 2002). Volatilization and absorption fluxes were treated separately in the mass balance, as follows:

$$\text{volatilization} = k_{ol} \times c_{\text{diss}},$$

$$\text{absorption} = k_{ol} \times (c_{\text{gas}}/H'),$$

where $c_{\text{diss}}$ and $c_{\text{gas}}$ are the dissolved and gas-phase concentrations, respectively. A mean $c_{\text{diss}}$ was calculated from Lohmann et al. (2000b). The $H'$ value is the dimensionless HLC for each of the Cl$_{1–5}$DD/Fs and $k_{ol}$ is the mass transfer coefficient (m/day). Values for $k_{ol}$ were calculated using ambient wind speeds and the diffusivities of the PCDD/Fs in water and air, respectively (for details see Zhang et al., 1999). $H'$ values for 25°C were taken as reported in the literature (Govers and Krop, 1998). A temperature correction of $H'$, though warranted, was not performed due to a lack of data. Mean volatilization fluxes for the LHRE (area 3.8 x 10$^8$ m$^2$) were (in pg/m$^2$/day) 4200 for Cl$_2$DDs, 680 for Cl$_1$DFs, 180 for Cl$_2$DFs and $\leq 50$ for Cl$_3$–5DD/Fs. Gaseous adsorption was one order of magnitude lower, on the order of less than 10 up to 150 pg/m$^2$/day for Cl$_2$DDs. A summary of the parameters used in the air–water exchange calculation and the resulting fluxes is given in Table 3. As is obvious from these calculations, the LHRE is an important, continuous

### Table 3

<table>
<thead>
<tr>
<th>Cl$_x$DD/Fs</th>
<th>$k_{ol}$ ($u_{10}$) (cm/day)</th>
<th>HLCs (at 298 K)</th>
<th>$c_{\text{water}}$ (ng/m$^3$)</th>
<th>$c_{\text{gaseous}}$ (fg/m$^3$)</th>
<th>Volatilization (pg/m$^2$/day)</th>
<th>Adsorption (mg/m$^2$/day)</th>
<th>Volatilization (fg/m$^3$)</th>
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<tr>
<td>Cl$_1$DFs</td>
<td>21</td>
<td>4.0E–03</td>
<td>3.2</td>
<td>600</td>
<td>680</td>
<td>31</td>
<td>56 (38–110)</td>
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<td>180</td>
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<td>13</td>
<td>2.4 (1.6–4.9)</td>
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<td>Cl$_5$DFs</td>
<td>13</td>
<td>7.0E–04</td>
<td>0.20</td>
<td>24</td>
<td>26</td>
<td>5.9</td>
<td>2.3 (1.5–4.6)</td>
</tr>
<tr>
<td>mean $u_{10}$</td>
<td>3.4E + 07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$_2$DDs</td>
<td>16</td>
<td>1.0E–03</td>
<td>27</td>
<td>1300</td>
<td>4200</td>
<td>150</td>
<td>360 (240–720)</td>
</tr>
<tr>
<td>Cl$_3$DDs</td>
<td>13</td>
<td>6.8E–04</td>
<td>0.40</td>
<td>19</td>
<td>52</td>
<td>3.6</td>
<td>4.5 (3.0–9.1)</td>
</tr>
<tr>
<td>Cl$_4$DDs</td>
<td>12</td>
<td>5.5E–04</td>
<td>0.08</td>
<td>10</td>
<td>9.2</td>
<td>2.6</td>
<td>0.8 (0.5–1.6)</td>
</tr>
<tr>
<td>Cl$_5$DDs</td>
<td>11</td>
<td>5.1E–04</td>
<td>0.04</td>
<td>5</td>
<td>4.6</td>
<td>1.3</td>
<td>0.4 (0.3–0.8)</td>
</tr>
</tbody>
</table>

Note: Gaseous adsorption is calculated based solely on the advective flux.

![Fig. 3. Relative contribution of the homologue groups to $\sum$Cl$_x$DD/Fs at Sandy Hook for selected samples.](image-url)
source of lower chlorinated PCDD/Fs, especially C12DDs, to the atmosphere. But how important is it relative to advective inputs?

(2) *Advection inputs:* For both events, the concentrations measured prior to movement over the LHRE (at the SH site for scenario 1, LSC for scenario 2) were taken as representative of the mean advection input to the atmosphere above the LHRE. The relative change of \(h_{abl}\) from one sampling event to the next was estimated as (given here for the nighttime relative to the preceding daytime sample)

\[
h_{abl,N} = h_{abl,D}(v_a(H_2O)_N/v_a(H_2O)_D)(r.h._D/r.h._N)
\]

with \(v_a(H_2O)\) the transfer velocity of water in air and r.h. the measured relative humidities for day (\(D\)) and night (\(N\)), respectively. The transfer velocity \((\text{in cm/s})\) was calculated according to

\[
v_a(H_2O) = 0.2 \times u_{10} + 0.3
\]

as approximated in Schwarzenbach et al. (1993). These approximations show a decrease in \(h_{abl,N}\) by \(\sim\) a factor of 2 compared to the previous day (\(h_{abl,D}\)). Reduced mixing heights during the nights are needed to accommodate a decreased water flux into the atmosphere (due to decreased wind speeds), while measured relative humidities increased (see Table 1). The choice of the initial \(h_{abl}\) value is critical to the mass budget calculations. For the day of 6 July, \(h_{abl,D}\) was set to 1000 m (Jacob, 1999), which resulted in, \(h_{abl,N}\) of around 500 m. These \(h_{abl,N}\) are higher by a factor of 2 compared to those derived according to Lena and Desiato (1999) for stable nocturnal layers above Milan, Italy. Given the more dynamic coastal system at NJ/NY, an increased boundary layer seems reasonable. In general, volatilization was of minor importance and accounted for only \(\sim 10\%\) (range of 5–20\%) of the advective flux (see Table 3). Volatilization was more important for C12DDs and C12DDs, for which it equaled roughly 25\% of advection (range of 20–50\%).

*Interpreting day–night variations:* It is clear from the preceding discussion that there are numerous factors influencing PCDD/F concentrations spatially and temporally in the NY/NJ region. As noted in the Introduction, several factors potentially vary diurnally. These include: certain primary emissions (e.g. traffic; several combustion sources); secondary emissions and deposition (e.g. volatilization from soil/vegetation; partitioning to surfaces); atmospheric boundary layer heights (\(h_{abl}\)); the strength and direction of advection (particularly near large water bodies); and atmospheric reactions with OH-radicals. Assuming all other factors are constant over 24 hour, if reactions with OH-radicals exert an important influence on ambient levels, the ratio of night/day concentrations \(R_{N/D}\) should be \(>1\) and highest for the lower chlorinated homologues. The lighter homologues react more rapidly with their OH-radicals than their heavier counterparts; for example, the reaction half-lives for C12DDs and C12DDs have been reported at ~1.5 and 15 days, respectively (Kwock et al., 1995; Atkinson, 1997). In contrast, if the \(h_{abl}\) exerts an over-riding influence on ground-level concentrations, then \(R_{N/D}\) should be \(>1\), but quite consistent across homologues. \(R_{N/D}\)’s were calculated for each site as the ratio of \(c_{day}\) relative to the two encompassing \(c_{night}\)’s, and the mean values are discussed here. There was no dominating trend visible explaining nighttime/daytime ratios for all sites and homologue groups (see Fig. 4a). Rather, site-specific differences were apparent: At NB, most homologue groups were below or around a 1:1 ratio, with the \(Cl_6\) to \(DF\)s reaching ratios of \(>2\). \(R_{N/D}\)’s at SH were around a 1:1 ratio, with the exception of the highest chlorinated PCDDs, which were due to the strong PCP-signal from the NJ–NY area (see above). Finally, at LSC, \(R_{N/D}\)’s were fairly tight: 10 homologue groups were within 20\% of a 1:1 ratio, with only C12DDs (1.8), Cl7/7DDs (1.6) and Cl2DFs (0.7) deviating more. However, there were no significant trends \((P<0.05)\) present (see also single standard deviations in Fig. 4a).

In summary, over the course of a week-long sampling campaign, concentration changes linked to advective air mass transport dominated any local source signals and expected day–night variations (especially at NB and SH), though LSC displayed less variability than the other sites.

Further clues as to the importance of local sources, changes in \(h_{abl}\) and degradation reactions might be gained from a special time-window within our sampling set, from the night sample of 6 July through to the night of 8 July. During that period, wind speeds were low (2.1–3.6 m/s, see Table 1) and advection was less important than for the remainder of the study. \(R_{N/D}\) values were calculated as above, and the mean of the two values are plotted in Fig. 4b. Day–night differences were apparent at the three sites: \(R_{N/D}\) was \(>1\) for SH (1.7) and LSC (1.2) and \(<1\) (0.5) at NB. Though rigorous statistics cannot be applied here due to the limited sample numbers, an approximate significance can be gained by applying probability theory. In the absence of a diurnal source or sink, \(R_{N/D}\)’s should be distributed at random and be evenly distributed around 1. At NB, however, 14 (out of 15) homologue group ratios were \(<1\) (significant at \(P<0.01\)); at SH 15/15 were \(>1\) (significant at \(P<0.01\)) and at LSC 13/15 were \(>1\) (significant at \(P<0.01\)). This suggests that daytime sources were present at NB, resulting in consistently higher day- than nighttime PCDD/F-concentrations over these 2 days. At LSC and especially SH, on the other hand, nighttime concentrations were higher than during the day. Within the homologue groups at either site, there is no trend visible supporting the OH-radical initiated degradation of the less relative to the more chlorinated congeners, or of PCDDs relative to PCDFs.
For both sites, this implies that changes in the $h_{abl}$ were the most probable cause for the higher night- than daytime concentrations during these 2 days.

**Re-examination of OH-radical initiated depletion reactions:** The Cl$_2$–3DDs were the only homologue groups for which nighttime concentrations were often higher than daytime concentrations. This occurred at LSC but was not seen at either NB or SH, and the data are shown in Fig. 2b. Earlier, we interpreted this signal as evidence for OH-radical-initiated breakdown (Lohmann et al., 2000c). After a thorough re-examination of the data, it is suggested that the observed day–night fluctuations are best explained by changes in the boundary layer height, and this is detailed below.

We attempted to model changes in ambient, gaseous concentrations above the LHRE, considering advection and water-to-air exchange as input or source terms, with gaseous deposition and OH-radical-initiated depletion constituting the loss terms (data not shown): In the mass balance calculation, OH-radical depletion of gaseous PCDD/Fs imposed a day–night fluctuation on the ambient concentrations, with nighttime concentrations generally higher than during the day. This was rarely found in the measured concentrations, with the exception of Cl$_2$–3DDs. However, the best correlations for

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Fig. 4. Ratios of night- over daytime concentrations ($R_{N:D}$) for the three sites for all samples (a) and during 6–8 July (b).
Cl₂–3DDs at LSC were not obtained with the modelled concentrations, but rather with relative humidity. Relative humidity was positively correlated to Cl₂DDs (r² = 0.54, significant at P ≤ 0.10) and Cl₃DDs (r² = 0.60, P ≤ 0.05), highlighting the importance of a similar origin, namely the water-to-air transfer for these compounds. A nighttime increase in relative humidity was interpreted as indicative of a reduced height of the boundary layer, resulting in an increase in relative humidity and Cl₂–3DDs due to their constant water-to-air fluxes from the LHRE.

In summary, we measured comparatively low ambient PCDD/F-concentrations at three land-based sites in the coastal NJ region. Cl₂DDs dominated ambient concentrations at the Atlantic coast (Sandy Hook) and over the LHRE and fluctuated little, with water-to-air exchange as the likely cause. Air–water exchange calculations demonstrated the relative importance of Cl₂–3DDs volatilizing from the LHRE for ambient concentrations (~25% of advection), but was of minor importance for the other PCDD/Fs. OH-radical depletion of gaseous compounds, as applied in a mass balance model, cannot explain the day–night cycle of Cl₂–3DDs. Rather, it is suggested that changes in the mixed boundary layer height resulted in higher night- than daytime concentrations at the urban and coastal sites. During a period of low wind speeds, the rural site (New Brunswick) showed a strong daytime source signal, dominated by the lower chlorinated furans and dioxins. To gather field evidence for the role of OH-radical depletion on ambient POPs, it is suggested to measure its breakdown products rather than the fluctuation of the POPs themselves or to choose a location (i.e. the open ocean) where local source influences are removed.

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References


NOAA, see under: http://www.arl.noaa.gov/ready/disclaim.html


US-EPA: The Inventory of Sources of Dioxin in the United States, EPA/600/P-98/002Aa.
