

## ADSORPTION ONTO BLACK CARBON DOMINATES THE GAS-PARTICLE PARTITIONING OF PCDD/Fs IN THE NEW JERSEY COASTAL ATMOSPHERE

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### Introduction

Describing the temperature-dependent gas-particle partitioning of PCDD/Fs and other semi-volatile organic compounds accurately remains one of the main challenges in our knowledge of their environmental distribution and fate. The distribution of PCDD/Fs between the gaseous and particulate phase determines their fate: OH-radical reactions are thought to occur exclusively in the gaseous phase, while particulate-bound compounds have, in general, shorter residence times in the atmosphere<sup>1</sup>.

We have reported previously on the use of sensitive and precise methods for determining PCDD/Fs in relatively small air volumes, opening up the possibility of intensive short-term campaigns to investigate source/loss processes<sup>2</sup>. We have also reported part of a study on PCDD/Fs in the New York / New Jersey (NY/NJ) area, highlighting the air-water exchange of PCDD/Fs in the lower Hudson River estuary (LHRE)<sup>3</sup>. Comparatively low ambient PCDD/F-concentrations were measured at three land-based sites in the coastal NJ region<sup>4</sup>. Cl<sub>2</sub>DDs 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<sup>3</sup>. Air-water exchange calculations demonstrated the relative importance of Cl<sub>2,3</sub>DD volatilising from the LHRE for ambient concentrations (~ 25% of advection), but was of minor importance for the other PCDD/Fs<sup>4</sup>.

Here we examine the gas-particle partitioning of PCDD/Fs in those diurnal samples. Gaseous and particulate PCDD/Fs were analysed separately, as defined by their presence in the PUF or GFF. Total suspended particulate matter (TSP), Organic Carbon (OC) and Elemental Carbon (EC) fractions were also determined, enabling a thorough examination of their role in determining gas-particle distributions in the New Jersey coastal atmosphere. Black Carbon (BC) itself is a incomplete combustion product, in a similar manner to PAHs or PCDD/Fs. It is as yet unclear to what degree the association of those pollutants and BC occurs directly at the emission source, during the particle formation, or at later stages during the atmospheric transport, settling in the water column or finally in the sediments themselves.

### Materials and Methods

**Sampling** The sampling sites were chosen to reflect contrasting environments: 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).

At each site, consecutive 12-hour day (0800-2000 hrs) and night (2000-0800 hrs) samples were taken. Thirteen samples were taken at both LSC and SH, 12 from NB and 4 over RB. The samples were collected with a modified organics Hi-Vol sampler (Graseby) equipped with quartz fiber filter (20 by 24 cm) and polyurethane foam (10 by 8 cm diameter) adsorbent. The analytical methods for extraction, clean-up and analysis of PCDD/Fs in GFFs and PUFs are detailed elsewhere<sup>3,4</sup>. Cl<sub>1,8</sub>DFs and Cl<sub>2,8</sub>DDs were analyzed in all samples. At air volumes of ~500 m<sup>3</sup> at 28°C, only Cl<sub>1</sub>DFs (50-100% relative to the front PUF), Cl<sub>2</sub>DFs (25%) and Cl<sub>2</sub>DDs (10%) were found on the back-up half. Separate samples were taken for OC and EC determination and analysed by a thermal-optical transmittance method at Rutgers University as described elsewhere<sup>5</sup>. Temperature-dependent K<sub>oa</sub>s for PCDD/Fs were measured by Harner *et al.* by the generator column method<sup>6</sup>.

The distribution of chemical between the gas and particulate phase is usually defined using the particle-gas partition coefficient,  $K_p = (F/A)/TSP$ , where F and A are the analyte concentrations on the GFF and on the PUF, respectively, and TSP is in µg/m<sup>3</sup>(<sup>7</sup>). Pankow and Bidleman noted that changes in the analytes' ambient air concentration and/or temperature during the sampling period may lead to adsorption/desorption of particulate-bound analytes and result in a measured particle-gas distribution that is not in equilibrium<sup>8</sup>. Our short sampling durations (12 hours) minimised fluctuations of temperature and analytes' concentrations as far as possible.

### Results and Discussion

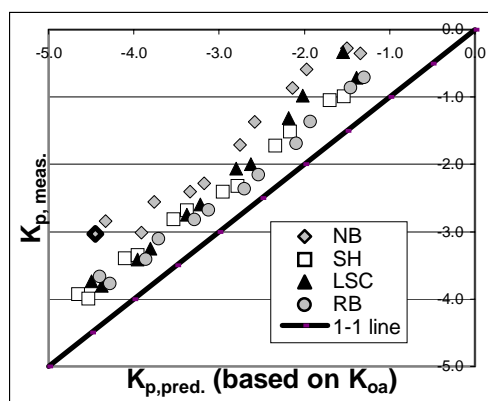
The spatial and temporal trends in ambient PCDD/Fs in the NJ atmosphere is described in more detail elsewhere<sup>4</sup>, and only summarised here. Despite proximity to the major NY/NJ conurbation, ambient PCDD/F concentrations in the region were low compared to literature data for other urban locations<sup>9</sup>. Mean ΣCl<sub>4,8</sub>DD/Fs and ΣTEQ (in fg/m<sup>3</sup>) were: 1,400 and 16 at NB; 1000 and 9.5 over RB; 880 and 8.5 at LSC; and 830 and 6.6 at SH. The lower chlorinated homologue groups dominated gaseous concentrations: Cl<sub>2</sub>DFs occurred at 1000s of fg/m<sup>3</sup> at all sites. TSP-concentrations (all in µg/m<sup>3</sup>) ranged from ~ 30 to 100 at most sites, [OC] ranged from <1 to > 20 at the different sites, and [EC] ranged from < d.l. (0.13) to almost 3.0. Average TSP, OC and EC concentrations were comparable to those reported for other continental US-locations<sup>10</sup>.

The average % of PCDD/Fs in the particulate phase increased with increasing degree of chlorination. Exceptions were OCDD and OCDF, which were either below or at similar % in the particulate phase as Cl<sub>7</sub>DDs and Cl<sub>7</sub>DFs, respectively. On average, Cl<sub>2,4</sub>DD/Fs were 1 - 21% on particulate matter, Cl<sub>3</sub>DD/Fs 21-50%, Cl<sub>6</sub>DD/Fs 51-80%, and Cl<sub>7,8</sub>DD/Fs > 72%.

Log K<sub>p</sub>s increased with increasing degree of chlorination. NB had highest log K<sub>p</sub> values; LSC and SH displayed the lowest log K<sub>p</sub> values. The log K<sub>p</sub>s obtained at the NJ sites are similar to selected literature values, with NB displaying consistently higher log K<sub>p</sub>s, and LSC and SH at the lower end of the range. The literature values display quite consistent values for a given homologue group, despite sampling times (air volumes) varying from 1-2 days (1000-1500 m<sup>3</sup>)<sup>11</sup>, 3-4 days (600- 1000 m<sup>3</sup>)<sup>12</sup> and up to 6 weeks (~ 2500 m<sup>3</sup>)<sup>13</sup>.

Log K<sub>p</sub> was significantly correlated with log K<sub>oa</sub>: All but 5 samples were highly significant (at P < 0.001), and the other significant at P < 0.01. Assuming an ideal, octanol-like behaviour of the fraction of organic matter (f<sub>OM</sub>), the gas-particle partitioning according to<sup>14</sup>:  $\log K_p = m_r \log K_{oa} + \log f_{om} - 11.91$ . As can be seen in Figure 1, the measured log K<sub>p</sub>s are in general above the 1-1 trendline, exceeding the prediction by a factor of 3 (<sup>1</sup>/<sub>2</sub> log unit for LSC; SH) up to 1 order of magnitude (NB). All homologue groups follow a straight line for a given site. Figure 1 indicates

that measured gas-particle distributions have far lower gaseous concentrations than predicted based on the  $K_{oa}$ -approach.



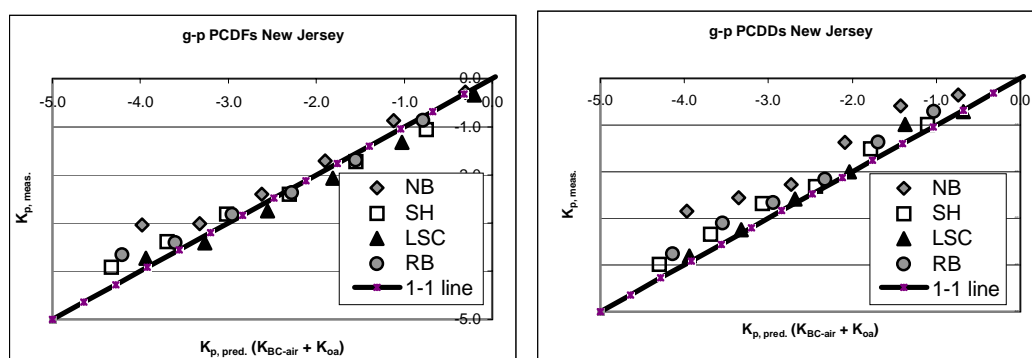
**Figure 1: Measured  $\log K_p$  versus  $f_{OM} K_{oa}$  predictions for the different sites in New Jersey**

$K_{BC-air}$ s for PCDD/Fs were based on  $K_{BC-w}$ s measured by Barring *et al.*<sup>15</sup>. The  $K_{BC-w}$ s were divided by the respective dimensionless Henry's Law Constants (HLC'<sup>16</sup>) to obtain the corresponding  $K_{BC-air}$ s:  $K_{BC-air} = K_{BC-w} / HLC'$ . The calculated  $K_{BC-air}$ s increase with increasing degree of chlorination, but increase faster than the corresponding  $K_{oa}$ s. Affinities to BC surpass those to octanol by 1-2 orders of magnitude; with PCDFs preferring BC more strongly than PCDDs (see Table 1).

homologue	Cl <sub>2</sub> DFs	Cl <sub>3</sub> DFs	Cl <sub>4</sub> DFs	Cl <sub>5</sub> DFs	Cl <sub>6</sub> DFs	Cl <sub>7</sub> DFs	OCDF
$\log K_{oa}$	8.3	8.8	9.4	10.0	10.6	11.2	11.9
$\log K_{BC-air}$	9.7	10.4	11.1	11.9	12.7	13.5	14.4

**Table 1: prediction of black carbon-air partitioning coefficients for PCDFs**

Considering both absorption into  $f_{OM}$  and adsorption onto  $f_{BC}$  results in the following prediction of the gas-particle partitioning:  $K_p = f_{om} K_{oa} / (10^{12} \rho_{oct}) + f_{BC} K_{BC-air} / (10^{12} \rho_{BC})$ , with  $\rho_{BC}$  the density of BC. Inclusion of adsorption onto BC increased the partitioning to particles, which was in-line with the observations of this dataset. The mean of the measured  $\log K_p$ s were plotted as a function of those predicted using the above equation, and is shown in Figure 2. The partitioning prediction was improved considerably compared to those based solely on absorption into  $f_{OM}$  (see Figure 1). Data from NB displayed  $K_p$ -values above the prediction, with data from LSC falling below the prediction lines for PCDFs. For PCDDs, NB again displayed the lowest  $K_p$ -values, with the LSC data being exactly predicted by the above equation. For PCDFs, all data were within a factor of 2 (0.3 log units) of the predicted values, with the exception of the Cl<sub>2</sub>DFs, which displayed stronger deviations. For PCDDs, data from LSC, SH and LHRE were within 0.3 log units, with the data from NB being above the prediction by ca. 0.5 log units (factor of 3). Compared to the  $K_{oa}$ -model, the gas-particle partitioning of PCDD/Fs was best predicted by the dual sorption model, improving the predictions by almost an order of magnitude for all samples. Differences between PCDDs and PCDFs were observed, with PCDFs being better predicted by the dual sorption model than PCDDs.



**Figure 2:** Measured log  $K_p$  versus predictions based on absorption ( $f_{OM} K_{oa}$ ) plus adsorption ( $f_{BC} K_{BC-air}$ ) for PCDFs and PCDDs at the different sites in New Jersey

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