A Comparative Study of the Gas-Particle Partitioning of PCDD/Fs, PCBs and PAHs

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Introduction
The atmospheric fate of POPs is primarily governed by their gas-particle partitioning. Wet and dry deposition, photolysis and reaction with OH radicals act differently on gas- and particle-bound semi-volatile organic compounds, thereby affecting the efficiency and scope of their long range atmospheric transport (1).

Materials and methods
Sampling Locations The study sites were chosen to encompass a range of aerosol types and potential sources of POPs. They were: i) Manchester, an urban centre, comprising ~3 million inhabitants with traffic and heavy industries (site A) and ii and iii) Clapham and Austwick, small villages in the Yorkshire Dales National Park (sites B and C) with a strong impact of domestic burning. At both villages, domestic burning of coal and wood is extensive during the winter months (for more details on the sites see in 2).

Air sampling Four high volume (hi-vol) air samples were collected concurrently for 72 to 96 hours at all three sites in February 1998. Air samples were taken with GPS-1 air samplers (Graseby Andersen) equipped with a Whatman glass fibre filter (GFF, 10cm diameter) for collecting particle-bound compounds and two polyurethane foam plugs (PUF, 5cm diameter, 6.25cm length) in series for retaining compounds in the gaseous phase. For more details on the sampling and analytical procedures see 2.

Sub-cooled liquid vapor pressures (p_L) T-dependent p_L values were taken from Eitzer and Hites (for PCDD/F; 3), Yamasaki et al. (PAHs; 4) and Falconer and Bidleman (PCBs; 5).

Octanol-air partition coefficients (K_{oa}): Dimensionless K_{oa} values for PAHs were calculated at a temperature (T) of 298 K according to $K_{oa} = K_{ow}RT/H$, where K_{ow} is the octanol-water partition coefficient, H is the Henry's Law constant, and R is the universal gas constant. T-dependent K_{oa} values for PCBs were taken from Harner and Bidleman (6) and for PCDD/Fs from Harner et al. (7).

Results and discussion
Ambient air concentrations of PCDD/Fs, PAHs and PCBs varied widely over the 4 sampling events: Highest concentrations of $\Sigma Cl_{4-8}DD/Fs$ and $\Sigma PAHs$ were observed on event I. Concentrations on events II - IV were factors of 3-8 lower for PCDD/Fs and decreased by factors of 2-4 for PAHs. At the Manchester site (A), ΣPCB levels increased with increasing T from 370 (event I, ~2 °C) to 720 pg/m³ (event IV, ~12 °C). At sites B and C, ΣPCB levels were generally

low, at ~50-85 pg/m^3, and were not correlated with T.

Results of a related study showed that local sources at the villages (sites B and C), accounted for ~25% of the PCDD/F-ΣTEQ (WHO-TEFs, Ref. 8) and ~75% of the ΣPAHs (2). This was mostly attributed to local domestic burning. No site-specific PCB signal was found. Urban site A was found to be a source area for all three POPs classes studied (2).

<u>Comparison of p$_L$ and K$_{oa}$ as descriptors of partitioning</u> Gas-particle partition coefficients, K$_P$, were calculated according to K$_p$= (F/A)/TSP, where F and A are the analyte concentrations on the GFF and on the PUF, respectively, and TSP are total suspended particles in μg/m^3 (9). Log K$_p$ values were regressed against the T-corrected log p$_L$ and log K$_{oa}$ of the compounds. Regression coefficients (r^2) were similar for PCBs and PAHs, while r^2 for PCDD/Fs were in general higher using p$_L$, but still highly significant for log K$_p$-log K$_{oa}$ regressions. The higher r^2 using p$_L$ may indicate a significant <u>ad</u>sorptive contribution for low f_{om} aerosols for which p$_L$ is a better descriptor than K$_{oa}$.

Based on the K$_{oa}$ absorption model it is possible to calculate f_{om} in the aerosols. The mean PCDD/F-intercepts from sites A to C correspond to a f_{om} of 4% (site A), 20% (B) and ~ 100% (C) in the aerosol. A higher f_{om} can be expected for the predominantly low-temperature aerosols (associated with wood burning) at the rural sites.

<u>Comparison of sites</u> Both the p$_L$- and the K$_{oa}$-model agreed that PAHs were closest equilibrium at site C. Both models showed PCBs closest to equilibrium at site A: mean p$_L$- m$_r$ values were -0.64 at site A, but only ~ -0.5 at the other sites. K$_{oa}$- m$_r$ values for PCBs were on average 0.58 at site A, but only ~ 0.4 at the other sites. We hypothesise that the shallow slopes for PCBs at the rural sites is due to slow re-equilibrium of advected PCBs to freshly emitted particulate matter (see Figure 1). The rural sites were not significant sources of PCBs, which were mostly introduced by advective transport and will have already approached gas-particle equilibrium (see line 1). However, the rural sites released particulate matter (with few PCBs) from domestic burning, which offset the established gas-particle equilibrium (line 2). Initially, this will result in a lower value for K$_P$ and thus reduce the intercept value in log K$_p$- log p$_L$/log K$_{oa}$ plots. Consecutively, the more volatile PCBs will re-equilibrate faster and thus alter the slope of the log K$_p$- log p$_L$/log K$_{oa}$ plots. This rapid redistribution of the more volatile PCBs to the new particulate matter will result in slopes more shallow than -1 (p$_L$) or +1 (K$_{oa}$) (see line 3):

Figure 1: Influence of TSP on log K_p - log K_{oa} trendlines

log K_{oa}
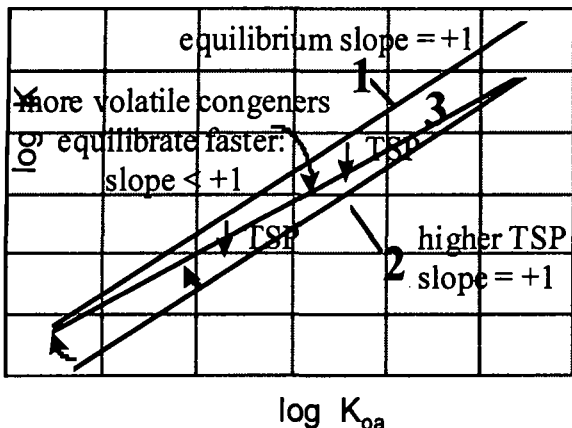
Comparison of events For event I, when favourable meteorological conditions (i.e. low ambient T and wind speed) increased PAH and PCDD/F-concentrations by factors of 2-4, the partitioning of PAHs and PCDD/Fs was similar: K_{oa}-regression slopes were 0.83 (PAHs) and 0.87 (PCDD/Fs) and significantly different from +1. Cold ambient temperatures may have slowed down the exchange between the gaseous and particulate fraction. Clearly, local emissions will not have reached equilibrium while 'aged', regional background concentrations had more time to partition between the gaseous and particulate phase. A simple model illustrates this in Figure 2. The two 'ideal' partitioning lines represent POPs arriving by

Figure 2: Non-equilibrium in log K_p - log K_{oa} trendlines
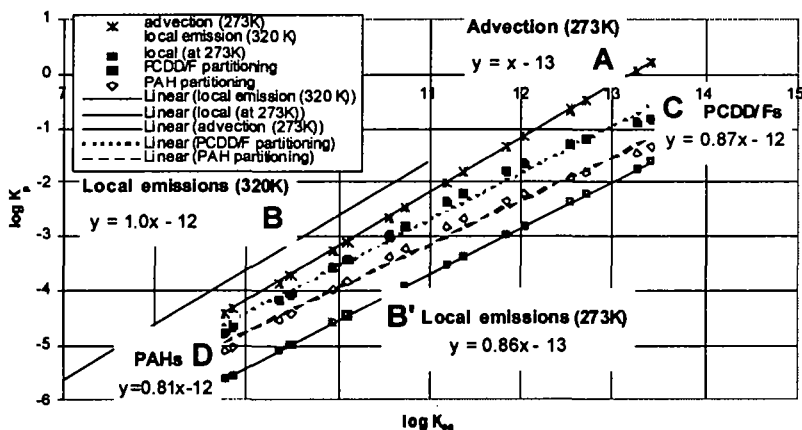
advective transport (line A: at 273 K, f_{om} 0.05, TSP 30 µg/m^3) and local emissions (line B: at 320 K, f_{om} 0.20, TSP 60 µg/m^3). For PCDD/Fs, we assumed 75% advective transport and 25% local emissions; for PAHs 25% advective transport and 75% local emissions. At the rural sites, the locally released TSP, PAH and PCDD/F emissions mix with those arriving by advective transport. The resulting partitioning lines reflect that the mixed PCDD/Fs and PAHs have not yet reached equilibrium between the warm, local emissions and the cold, advective ambient air masses: For PAHs, the locally released 75% still reflect the partitioning at 320K, i.e a higher proportion in the gaseous phase than the 'advective' PAHs at 273 K. Line B' depicts the partitioning of these locally released PAHs at the ambient T of 273K which results in a slope <1.

In that case, slopes shallower than +1 result for PCDD/Fs (line C: +0.87) and PAHs (line D: +0.81). A combination of advection and local releases during cold ambient T could explain why PCDD/Fs were closer to equilibrium than PAHs, which were predominantly locally released.

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