Observation and origin of organochlorine compounds and polycyclic aromatic hydrocarbons in the free troposphere over central Europe

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Abstract

On Zugspitze (2670 m a.s.l.), Alps, higher concentrations were observed during a winter than during a summer measurement campaign of PAHs, chlorobenzenes (43.6 vs. 2.0 pg m\(^{-3}\)) and DDTs (3.7 vs. 1.2 pg m\(^{-3}\)), while hexachlorocyclohexanes and PCBs were found at similar levels. The PCB, HCH and DDT levels are among the lowest ever reported from outside the Arctic. Mostly lower levels were found in samples collected in summer than in winter despite a significant boundary layer air influence, but no such influence on samples collected during the winter campaign. Boundary layer influence was quantified by Lagrangian particle dispersion model retroplume analyses. Photochemical lifetimes corresponding to \(k_{OH} < 1.5 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\) are found for \(p,p'-\text{DDE}\) and \(k_{CH} < 1 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}\) for \(p,p'-\text{DDD}\). Persistent organic pollutants have been observed at a mountain site in the Alps showing that very low concentrations can be found in the free troposphere.

1. Introduction

Many organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), as well as polycyclic aromatic hydrocarbons (PAHs) are considered to be ubiquitous in the global atmosphere, and they have been observed far from emission areas, notably in high latitudes (e.g. Hung et al., 2002; AMAP, 2004; Becker et al., 2006) and at high altitude sites (e.g. Weiss et al., 2000; Grimalt et al., 2001; Daly and Wania, 2005). Many of these substances are considered persistent organic pollutants (UNEP, 2003). Despite their often small fractions of the total environmental burden stored in air, long-range transport (LRT) occurs to a large extent in air. Semivolatility \((P_{sat} = 10^{-6}–10^{-2} \text{ Pa})\) in combination with persistence in ground compartments implies that atmospheric LRT is enhanced due to the potential of more than one cycle (multi-hopping, grasshopper effect; Wania and Mackay, 1993; Semeena and Lammel, 2005). At high remote mountain sites, pollutant levels are expected to be determined by long-range advection rather than local air/surface exchange (e.g. Carlson and Hites, 2005). Whether the balance between pollutant input by deposition and output by (re-)volatilization and advection is determined by substance vapour pressure (Blais et al., 2000; Grimalt et al., 2001) or by atmospheric transport processes (as found to explain the accumulation of the OCP hexachlorocyclohexane in high latitudes, i.e. so-called global distillation; Semeena and Lammel, 2005) is not yet decided.

The free troposphere (FT) is the middle and upper part of the troposphere. FT air is not in contact with the ground, as vertical mixing is limited to the lower part of the troposphere, the planetary boundary layer (BL). Typical BL heights are 500–2000 m in the afternoon and 50–200 m during the night. In the summer BL maxima can reach > 3000 m (e.g. Stull, 1988). Due to higher wind speeds transport is faster in the FT (Wenig et al., 2003). Concentrations of substances which are emitted at the ground should be substantially lower in the FT than in the BL, in particular when subject to photochemical degradation and according to transport time (‘age’). Sources for OCPs and PCBs in the FT are mixing with BL air and sinks are wet and dry deposition and photochemical degradation. For PAHs, emissions from aircraft cruising the FT is an additional, direct source. For most OCPs photochemical degradation is slow. Insufficient knowledge exists with regard to degradability in air of PCBs (e.g. Mandalakis et al., 2003) and PAHs (e.g. Tsapakis and Stephanou, 2007) as laboratory based rates seem to be contradicted by at least some of the field observations at remote locations.
sites, possibly related to gas-particle partitioning and the influence of the particulate matter matrix on degradation kinetics (Pöschl et al., 2001; Ding et al., 2007; WHO, 2002). Early generic multimedia box model based estimations of the LRT potential of OCPs and PCBs had neglected transport in the FT (e.g. Beyer et al., 2000). Recent comprehensive multicompartment model results, however, suggest substantial transport of OCPs and PAHs in the upper troposphere and lower stratosphere, at least if the photochemical degradability of the particle associated fraction was assumed to be negligible (Semeena et al., 2006; Sehili and Lammel, 2007).

Little is known about the vertical distribution of POPs and their occurrence in FT air: OCPs and PCBs have been measured from aircraft over the western North Atlantic ocean and the northeastern USA (Knap and Binkley, 1991) and at high mountain sites on the Canary Islands, the Pyrenees (van Drooge et al., 2002, 2005) and in the Himalayas (Li et al., 2006). PAHs have been measured in the Pyrenees, Alps (Fernández et al., 2002) and in the Himalayas (Ciccioli et al., 1996). The aim of the present study is to add concentration data of OCPs, PCBs and PAHs in FT air and gain insights about LRT and atmospheric lifetimes of these substances.

2. Methods

2.1. Sampling

High volume (Digitel) air samples were taken during a 2 week period in each of the summer 2007 (19.–29.6.) and winter 2008 (11.–21.2.) on the terrace of the Schneefernerhaus observatory (SFH, 47°25.0’N/10°58.9’E). SFH is located on a steep slope close to Zugspitze summit (Fig. 1a). No roads, populated houses or other possible emission sources are in the vicinity within some 4 km. Local emissions from the station are limited to the hours between 7 am and 7 pm. During the summer campaign the local emissions were very limited and were dominated by minor construction activity (with up to two diesel engines in operation). During the winter campaign, snow crawlers servicing the ski slopes near the cable car station (mostly in the morning and in the evening) produced significant local emissions, as reflected in NOx levels up to 15 ppbv (30-min mean; cf. Table 1) during peak activities. Occasionally, helicopter flights to and from the station occurred during afternoons in winter.

Day-time and night-time samples were collected, such that FT and BL air was separated between samples and periods of local pollution, morning and evening hours, were largely excluded (times given in the Supplementary material, Table ESM-1). One sample was excluded from the analysis of the winter night-time data subset (see text below, Section 3, and Table 1). Gas and particulate phases were collected separately on one glass fibre filter (GFF, Whatman) and two polyurethane foam plugs (PUFs), together 10 cm high, in series. GFFs were deployed as purchased.

Fig. 1. Location of Mt. Zugspitze in the Alps and of the site, Schneefernerhaus (SFH).
Table 1

Statistics of meteorological parameters and trace substance levels during sampling intervals in the form time-weighted mean \( \pm \) standard deviation (minimum–maximum).

All data are averaged for the air sample times. For values < LOQ, LOQ/2 was used for the calculation of the mean value.

<table>
<thead>
<tr>
<th></th>
<th>Summer</th>
<th>Winter</th>
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<tbody>
<tr>
<td></td>
<td>Day (mixed air)</td>
<td>Night (mixed air)</td>
</tr>
<tr>
<td>No. of samples</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Duration of samples (h)</td>
<td>13.8 ± 8.4 (7–27)</td>
<td>10.5 ± 5.5 (6–16)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>4.9 ± 4.8 (–1.4–9.7)</td>
<td>6.2 (1.6–7.8)</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>88 ± 10 (75–99)</td>
<td>72 (70–78)</td>
</tr>
<tr>
<td>Time in FT (%) during 10 h (120 h) before arrival</td>
<td>85 ± 15 (78 ± 8)</td>
<td>46 (79)</td>
</tr>
<tr>
<td>Particle number concentration ( N_{\text{air}–\text{soot}} ) (( 10^3 ) cm(^{-3} ))</td>
<td>1.66 ± 0.60 (0.67–2.47)</td>
<td>1.28 (1.20–1.53)</td>
</tr>
<tr>
<td>Aerosol surface concentration ( S_{\text{air}–\text{soot}} ) (( 10^3 ) cm(^{-3} ))</td>
<td>8.53 ± 3.37 (3.62–11.2)</td>
<td>4.76 (4.54–5.43)</td>
</tr>
<tr>
<td>Ozone (ppbv)</td>
<td>50 (6–44.57)</td>
<td>51 (50–52)</td>
</tr>
<tr>
<td>NO (ppbv)</td>
<td>0.18 ± 0.15 (0.04–0.13)</td>
<td>0.09 (0.04–0.10)</td>
</tr>
<tr>
<td>( \text{NO}_x ) (ppbv)</td>
<td>1.40 ± 0.23 (1.00–1.59)</td>
<td>0.94 (0.86–1.20)</td>
</tr>
<tr>
<td>HCHs (sum of 4, pg m(^{-3} ))</td>
<td>&lt; 8.8 ± 3.6 (&lt;0.4–24.8)</td>
<td>&lt;14.0 (&lt;10.5–&lt;23.8)</td>
</tr>
<tr>
<td>PCBs (sum of 7, pg m(^{-3} ))</td>
<td>&lt; 9.6 ± 2.9 (&lt;5.0–&lt;19.4)</td>
<td>&lt;11.2 (&lt;8.0–&lt;20.2)</td>
</tr>
<tr>
<td>DDTs (sum of 6, pg m(^{-3} ))</td>
<td>1.14 ± 1.05 (&lt;1.08–2.02)</td>
<td>1.48 (2.6–4.2)</td>
</tr>
<tr>
<td>( \text{C}<em>{\text{Cl}} + \text{C}</em>{\text{HCl}} ) (pg m(^{-3} ))</td>
<td>2.23 ± 2.31 (&lt;2.0–7.1)</td>
<td>0.87 (1.2–3.3)</td>
</tr>
<tr>
<td>PAHs (sum of 24, pg m(^{-3} ))</td>
<td>79 ± 6 (30–165)</td>
<td>98 (73–170)</td>
</tr>
</tbody>
</table>

\( ^{*} \) Standard deviation not defined (n = 2).

\( ^{b} \) 1 sample excluded from the data subset, because of contamination by local sources, i.e. at SFH itself.

\( ^{c} \) n = 3.

\( ^{d} \) n = 7.

PUFs were cleaned (8 h-extraction in acetone and twice 8 h in dichloromethane), dried in the hood with filtered air circulation, wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to extraction. PUFs were cleaned (8 h-extraction in acetone and twice 8 h in dichloromethane),...puematic model data, FLEXPART (Stohl et al., 1998, 2005). Hereby, 40 000 air parcels per 3 h are followed 20 days backwards in time. The model output reflects an upper estimate for a 3-D emission sensitivity distribution (if no chemical removal or deposition processes had occurred en route). Fig. 2 shows the emission sensitivity in the lowest model layer, the footprint layer. The emission sensitivity is a measure of the concentration in air at the measurement site that a source of unit strength in a given area would produce (units of ns/kg). High values (reddish colors) thus indicate areas where emissions would be most effective in contributing to the measured mixing ratios. The co-location of strong emission sources and a high emission sensitivity would produce the greatest mixing ratio at the Zugspitze station. BL heights in the model are calculated using a combined Richardson number and lifting parcel technique (Vogelzang and Holtslag, 1996). The fraction of parcels above and below the calculated BL height is budgeted and used hourly.

Night-time samples were only taken when the observatory was in the FT. In accordance with on-site long-term observations, pollution level criteria (visibility > 5 km, particle number concentration \( N_{\text{PNC–PM}} < 1500 \) cm\(^{-3} \) and meteorological criteria (local wind components, negative evening atmospheric relative humidity trend \( \Delta h_{\text{RH–PM}} < 35 \)%) were applied on site in order to identify the most ideal times to sample air representative of the FT, as opposed to the BL. Episodes of advection of FT air occurred during 4 nights in summer (combined to 2 samples) and during all but one night in winter (8 samples). 5 day-time samples were collected in winter and 6 in summer. The summer day-time samples were BL air mixed with FT air and the winter day-time samples were mostly FT air. The latter were, however, influenced by local pollution (as was apparent based on the particle and NO\(_x\) measurements).

2.3. Organic trace substances analyses and quality assurance

GFF and PUF filters were extracted separately with 120 mL of dichloromethane in an automatic extractor (Buchi B-811). The pairs of PUF plugs were not analyzed separately as previous work indicated negligible breakthrough. Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene, PCB 30 and PCB 185) were spiked on each PUF and GFF prior to extraction. The volume was reduced after standards (D8-naphthalene, D10-phenanthrene, D12-perylene, PCB 30 and PCB 185) were spiked on each PUF and GFF prior to extraction. The pairs of PUF plugs were not analyzed separately as previous work indicated negligible breakthrough. Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene, PCB 30 and PCB 185) were spiked on each PUF and GFF prior to extraction. The volume was reduced after

Fig. 2. Characteristic examples for surface contact distributions (‘footprint’ emission sensitivity in m/kg, 3-h time average) according to 20-days 3-D retroplumes, arrival height at 2650 m a.s.l. during the campaigns (a) 19.6.–22.6.07, (b) 23.6.–28.6.07, (c) 29.6.07, (d) 11.–15.2.08 and 17.–20.2.08, (e) 16.2.08, (f) 21.2.08. The asterisk marks the location of the Zugspitze station. Numbers indicate the area of the retroplume centroid.
extraction under a gentle nitrogen stream at ambient temperature and two aliquots were taken for the separate analysis of PAHs and organochlorines. Fractionation was achieved on a silica gel column (30 cm length, 1 cm i.d., 5 g of silica). Silica gel (porosity 60A, grains 0.063–0.200 mm) has been extracted for 8 h in dichloro-
methane in the Soxhlet extractor, dried on the aluminium foil in a hood, and acti-
vated for 12 h in the oven before use (150 °C). It was stored in the tightly closed glass container for not more than 24 h. Activated silica was further modified using the sulfuric acid (50 g of silica and 22 ml of H2SO4 was left overnight in the shaker) for the PCB/OCP analysis. Samples for organochlorine analysis were eluted from the column with 40 ml of the mixture dichloromethane – hexane (1:1), PAHs were eluted with 20 ml of dichloromethane after removal of the aliphatic hydrocarbons with 10 ml of hexane. Samples were concentrated to the final volume of 100 and 200 µL for the winter and summer campaigns, respectively, and analyzed using an HP 5975 gas chromatograph coupled with a mass spectrometer in the electron impact ionization mode. It was equipped with an autosampler and a J&W Scientific fused silica column DB-SMS (50 m x 0.25 mm, 0.25 µm film thickness). PCDDs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180), OCPs (a-HCH, f-HCH, p-HCH, y-HCH, p,g-DDE, p,p-DDE, p,p-DDD, p,p-DDT, p,p-DDE, p,p-DDE, p,p-DDE, p,p-DDE, p,p-DDE, p,p-DDE, p,p-DDE), HCB and 22 3–6-ring PAHs (acenaphthene, fluorene, phenanthrene, anthracene, flu-
oranthene, pyrene, retene, benzo(b)fluorene, benzo(g,h)anthracene, benzo(a)pyrene, cyclopenta(c,d)pyrene, benzo(a)anthracene, triphenylene, chrysene, benzo(b,fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g)fluoranthene, benzo(a)pyrene, perylene, indeno(12,3cd)pyrene and benzo(g,h,i)perylene) were determined. Terphenyl and PCB 121 were used as internal standards for PAHs and PCBs analyses, respectively. The samples (1 µL) were injected at 80 °C oven temperature and 280 °C injector and transfer line temperature. After 2 min, the temperature was raised at 15 °C/min to 180 °C, then at 5 °C/min to 300 °C and to the final temperature of 320 °C for 20 min. The carrier gas was He at a flow of 0.2 ml/min. Data were collected in selected ion monitoring mode.

Method recoveries derived from the recovery of surrogate standards varied between 88 and 100% for PCBs, 85–98% for OCPs, and 76–102% for PAHs. Correction factors have not been applied.

Method blanks were determined and they stayed below the limit of quantifi-
cation (LOQ, 0.05–0.5 ng per sample) for all investigated compounds. For all organochlorines and higher molecular weight PAHs (starting with benzo(a)anthracene) they stayed below the instrument detection limit (IDL; 0.01–0.1 ng per sample).

10% of filters were analyzed for the blank levels before taking them to the field. For OCPs, the blanks concentrations stayed at the same level as the method blanks. For chlorinated compounds and higher molecular weight PAHs in PUF samples no blank concentrations were detected. For acenaphthene, fluoranthene and pyrene these were below LOQ, while for acenaphthylene, fluorene and phenanthrene these were below 2 ng per sample. The mean of 5 field blank values was subtracted from the blank and all samples. The LOQ for indi-
vidual filter or PUF samples was defined as the mean field blank value plus 3 standard deviations, if field blank exceeded IDL, else on instrument IDL/2 (cf. Table ESM-1 for quality assessment parameters). Total PAHs could be underestimated by up to 50% in the gas-phase and by up to 25% in the particulate phase due to losses related to oxidation of sorbed PAH by ozone (Tsapakis and Stephanou, 2003; Galanneau et al., 2006).

2.4. Other trace contaminants and meteorological parameters

Aerosol surface concentrations, S/V (cm⁻¹), were derived from particle number concentrations, N/V (cm⁻³), in 35 size bins between 12 and 600 nm of aerodynamic diameters measured using a differential electric mobility spectrometer (TSI 3080). Assuming sphericity, in combination with a condensation nucleus counter (TSI 3010). For continuous quality assurance the total particle number concentration N/0.5-1000 nm was measured with a second particle condensation nucleus counter (TSI 3772). Ozone was measured with a UV absorption method, NO and total oxidized N (NOx) by chemiluminescence (CL). NOx was measured by CL as NO equivalent after reduction with a Cranox gold convertor. Meteorological parameters were determined at the observatory as well as on Zugspitze summit (2060 m a.s.l.).

3. Results and discussion

3.1. Meteorological situations

The weather during the summer measurements was deter-
mined by a cyclone over western Europe bringing warm and later on cooler air from W. The observatory was within clouds during a large part of the campaign. Rain fell occasionally during short periods, sometimes mixed with snow. The winter measurements took place during a very stable anticyclone which dominated almost the entire European continent and was centered over Germany or southern Norway. Unusual high temperatures, almost cloudless skies and easterly and northerly wind directions prevailed until the anticyclone was disturbed by a cold front which reached from west on 20.2.08. Precipitation (snow) was <5 mm and lasted to the last 24 h of the campaign. The local orography in the vicinity of SFH almost prevents extreme wind velocities. The mean wind velocities during the sampling intervals varied between 0.5 and 5.5 m s⁻¹. Almost calm situations occurred only in winter. An overview of the meteorological and pollution conditions is provided in Table 1.

3.2. Sampling the FT and long-range atmospheric transport analysis

During the summer measurement period the sampling site received air from within the BL during the day and from the FT during most of the nights. Note, that in mountain regions a so-
called injection layer exists above the BL in summer, into which valley air is injected during daytime due to thermally induced local circulation systems (Henne et al., 2004). Therefore, air sampled during the night from the FT (or injection layer), had been included in the BL during the previous day. This is reflected in similar frac-
tions of residence time in the FT for the day-time samples and the night-time samples (note that the latter were only collected when the site was in the FT) when budgeted over the last 120 h before arrival (Table 1). When budgeted over the last 10 h before arrival, longer times in FT result for the day-time samples than for the night-time samples, because of longer night-time than day-time periods within the preceding 10 h. Thus, in summer the lower FT is often contaminated with BL air by these daytime injections. Long distance advection was via and with BL contact limited to south-
western and western Europe and the North Atlantic (Fig. 2a,b) or, on the last day of the campaign, the Arctic (Fig. 2c). In conclusion, during the summer campaign only mixed BL and FT air samples were taken which had resided 78–83% in FT.

Mixing reached less high during the winter campaign, as BL was less deep (partly visible from clouds), an anti-cyclonic situation produces descending air masses, and an injection layer above the mountain range is largely absent. Air parcels which passed during the first days had almost exclusively been residing in the FT, even when budgeted over as much as 20 days prior to arrival. This is reflected in extremely small extensions of the footprint emission sensitivities (Fig. 2d) or long distance advection via north with BL contact only in the Arctic (Fig. 2e). On the time horizon of days (last 120 h before arrival), for all samples except one it is found that air had resided >95% in FT. For one sample, the one collected after the front had reached the site on 20.2.08, mixed BL (20%) and FT (80%) air is allocated. BL influence during this last-night-time sampling period was obvious as indicated by the highest condensation nuclei and NOx levels measured during winter nights and ground surface influences from southern Europe (Fig. 2f). It was also the only sampling period with precipitation and the sample was accordingly depleted of OCPs, PCBs and PAHs. Therefore, this sample was excluded from the data subset.

3.3. Pollutant levels

POP levels were higher in winter (FT air) than in summer (mixed BL and FT air) for DDT, chlorobenzenes and PAHs (Table 1, Fig. 3, Tables ESM-2 and -3) and in both sample subsets clearly lower than measured at a continental central European site, Kosei, Czech Republic, and comparable to levels at an Arctic station (Table 2). Indicators for air pollution in general, particle number (N/V) and NOx concentrations, were not significantly different between seasons. Similar ranges of N/V in winter and summer (at least during the day) were corresponding with significantly lower aerosol surface concentrations (S/V) in winter than in summer.
This should be seen as related with much more humid air and significant influence of BL air in summer, both enhancing S/V.

OCP accumulation in winter could be related to the unusually stable anticyclone which prevented trace substance loss due to precipitation. During the first days of the winter campaign (advection of pure FT air, cf. Fig. 2 d), when least BL influence prevailed, slightly higher POP levels were measured than during the following days, when BL influence from Arctic was indicated (cf. Fig. 2e, Table ESM-3), namely 7.3, 6.0 and 3.8 pg m$^{-3}$ respectively, (first days) in contrast to 5.3, 2.7 and 3.4 pg m$^{-3}$ of PCBs, HCHs and DDTs, respectively (following days). This means that air masses which had been influenced by sparse emission sources in the Arctic carried even less pollutants than air masses which did not receive any influence from ground surfaces within 20 d back. A possible explanation for that might be influence from the tropical and/or subtropical BL even longer back. Even lower levels under advection situations observed in summer (reflected by the footprint emission sensitivities of Fig. 2a and b) suggest that clean air resided in the marine BL of the North Atlantic and also the BL over parts of western and southwestern Europe.

While PAHs levels in Europe are higher in winter because of higher emissions (home heating) and slower atmospheric degradation (photoc incumbency; e.g. Fernández et al., 2002), OCPs levels at European continental and coastal sites are usually higher in summer, probably dominated by the temperature dependence of volatilization from ground compartments, where most of the total environmental burden of these substances is stored (e.g. Holoubek et al., 2007). The mean concentration in June divided by

Table 2
Statistics of measurements at high altitudes (Fernández et al., 2002; van Drooge et al., 2002, 2005; Li et al., 2006) and at a central European (Holoubek et al., 2007, and own, unpublished data) and Arctic (EMEP, 2007) background site, mean values (pg m$^{-3}$).

<table>
<thead>
<tr>
<th></th>
<th>Izala, Tenerife, Canary Islands (2367 m a.s.l.)</th>
<th>Redd, Pyrenees (2250 m a.s.l.)</th>
<th>Gossenkölle, Alps (2413 m a.s.l.)</th>
<th>Mt. Everest, Himalayas (4400–4976 m a.s.l.)</th>
<th>Zugspitze, Alps (2670 m a.s.l.)</th>
<th>Kosecke, Czech Republic (534 m a.s.l.)</th>
<th>Zeppelinfjell, Svalbard (474 m a.s.l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBs (sum of 7)</td>
<td>16.9</td>
<td>44.4</td>
<td>44.4</td>
<td>8.8</td>
<td>5.2</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>p,p'-DDT + p,p'-DDD</td>
<td>=26</td>
<td>=50</td>
<td>=26</td>
<td>=50</td>
<td>=50</td>
<td>=50</td>
<td></td>
</tr>
<tr>
<td>HCB</td>
<td>8.9</td>
<td>8.9</td>
<td>8.9</td>
<td>8.9</td>
<td>8.9</td>
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</table>

$^a$ Total sampling time of 2 d during each of the sampling periods on Zugspitze.

$^b$ Total sampling time of 8 d.

$^c$ Sum of 24, including naphthalene.
concentration in February for the years 2003–07 at the central European background station, Kosetice, Czech Republic (400 km NE of SFH), for example was 1.70 and 2.15 for DDTs and HCB, respectively, while in this study 0.32 and 0.07, respectively, are found. In the same months, June 2007 and February 2008, 0.74 and 0.19, respectively, were observed in Kosetice (Table 2). This trend reflects the reduced significance of air/soil exchange for OCP levels in FT as compared to BL air. It may also be influenced by a larger difference in temperature between the two months in Kosetice than at Zugspitze, where temperatures were similar (Table 1). Most notably, the chlorobenzenes, and among these in particular PeCB, were elevated in winter at Zugspitze for unknown reason. While there it was found PeCB/HCB ¼ 1.0, this ratio was 0.17 in Kosetice (not shown). The explanation for elevated HCB levels in winter (also at the background site, Kosetice, cf. Table 2) might be that it is a wood combustion by-product (Hedman et al., 2006).

The PCB, HCH and DDT levels found in this study (see Table 1, disaggregated for seasons and day/night) are among the lowest ever reported from outside the Arctic (Table 2; AMAP, 2004; Wenzel et al., 2006; EMEP, 2007). Previous observations at high mountain sites reported 44.4 pg m⁻³ PCBs, 16.9 pg m⁻³ HCHs, and 5.2 pg m⁻³ DDTs (sum of only p,p'-DDT and p,p'-DDE) on the Canary Islands with little or no difference between air masses advected from the ocean as compared to from the European and African continents (van Drooge et al., 2002; cf. Table 2) and 26.9 pg m⁻³ of α- and γ-HCHs and 8.8 pg m⁻³ for the sum of p,p'-DDT and p,p'-DDE in the Himalayas (Li et al., 2006; Table 2).

3.4. Diel variation

In winter day-time levels of PCBs, OCPs and PAHs exceeded night-time levels by 70, 55 and 26%, respectively (Table 1). NO and particle concentration levels and their daily cycle confirm the understanding that this must have been related to local emissions at the site. Opposite trends were found in summer, which is consistent with the then less significant local emissions, but is not considered a significant finding, as samples were only collected in 4 out of 10 nights of the summer campaign.

3.5. Substance patterns

The substance ratios DDT/total-DDTs and α-HCH/total HCHs in winter, 0.19 and 0.31, are found similar to the study at Izaïa (= 0.2 and ±0.35, respectively) and can be considered typical for recent measurements in Europe. An influence of the contribution of BL air is not significant, and would be unexpected as no fresh emissions of technical HCH and DDT should occur in Europe. These indicative ratios were higher, 0.42 and 0.71, respectively, in the Himalayas indicating more recent application of both technical HCH and DDT (or dicrof) in south Asia than in Europe or Africa, and/or faster degradation of γ-HCH than α-HCH in the environment.

Most notably, in winter PeCB was at the same level as HCB, but only one third of HCB in summer. PeCB levels observed in the FT even exceed those measured at a number of source sites and background sites in Germany in 1995–96 (Wenzel et al., 2006), when the levels of OCPs had been higher than a decade later. While HCB is produced in substantial amounts in Europe (8.0 and 18.2 kt a⁻¹ in 1990 and 2000, respectively), PeCB is not produced, but is a by-product of combustion processes (AMAP, 2004; Wenzel et al., 2006; Denier van der Gon et al., 2007) and might be formed in the environment by dechlorination of HCB (Sugiura et al., 1984). At the background site Kosetice, the ratio PeCB/HCB was 0.32 in the annual mean and 0.72 in the winter mean (2003–07).

The PAH pattern is largely unchanged between the seasons (Fig. 3). The exception are the heavier compounds indeno(123cd)pyrene and benzo[g,h,i]perylene whose seasonal ratio, winter/summer, was clearly above average. Ratios of certain PAHs, indicative for various combustion sources were not significantly different in winter (FT air) and summer (mixed air), except the ratio between fluoranthene and pyrene, which was higher in winter (Table 3). This ratio is believed to distinguish between the petrogenic sources (Ό.4) and petroleum combustion (0.4–0.5), wood and coal (Ό.5). Hence, wood and coal burning are indicated sources in winter but not in summer. Similarly, the ratio between retene and chrysene should distinguish between petroleum (Ό.15), coal (0.3–0.45) and wood (0.8–0.96) combustion (Zencǎk et al., 2007). Values in the range 0.45–0.90 were found in both summer and winter.

3.6. Gas-particle partitioning

As expected, OCPs and PCBs were higher concentrated in the gas-phase (Fig. 3). For the partitioning ratios, θ = c_{part}/c_{total} in winter vs. summer we found DDTs (θ = 0.54 vs. 0.12), HCHs (θ = 0.09 vs. 0.29), chlorobenzenes (θ = 0.00 vs. 0.03) and PCBs (θ = 0.26 vs. 0.12). This trend is not unplayable, because temperatures were not lower in winter than in summer, but were in the same range (Table 1). The Junge–Pankow empirical formula,

$$\theta = \frac{c(S/V)}{c(S/V) + pe^{\alpha T_{amb} - T}}$$

(with T and T_{amb} standing for the ambient and melting temperatures; Pankow, 1987), was tested for c = 17.2 Pa cm using the S/V data and it was found that prediction matched the observed θ values for the light PCBs, overestimated for the heavier PCBs and the OCPs. Partitioning is steered by various interactions on the molecular level (Goss, 2004), i.e. by particulate matter chemical surface properties. No in-depth investigation of gas-particle partitioning is possible, because of lack of particulate matter chemical composition data.

3.7. Atmospheric lifetimes

The ratio of concentrations in FT (at Zugspitze) over in BL (at Kosetice) air winter values (Table 3) tell about the balance of sources (emissions) and sinks (degradation and deposition): 0.5 are found for PCBs and HCB, 0.2–0.3 for HCH and DDT, and 0.05 is found for PAHs. The big gradient for PAH may reflect the short

### Table 3

<table>
<thead>
<tr>
<th></th>
<th>Summer</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day (mixed air)</td>
<td>Night (mixed air)</td>
</tr>
<tr>
<td>ANTV + ANT</td>
<td>-0.03 (-0.01–0.10)</td>
<td>-0.04 (-0.03–0.042)</td>
</tr>
<tr>
<td>ANTV + ANT</td>
<td>0.76 (0.71–0.94)</td>
<td>0.86 (0.80–0.89)</td>
</tr>
<tr>
<td>ANTV + ANT</td>
<td>0.35 (0.26–0.55)</td>
<td>0.27 (0.26–0.27)</td>
</tr>
<tr>
<td>ANTV + ANT</td>
<td>0.00 (0.45–0.90)</td>
<td>0.80 (0.76–0.80)</td>
</tr>
</tbody>
</table>

Ratios of PAH (total) concentrations in the FT and BL (including mixed) air sample subsets as time-weighted mean (range). ANTV = antracene, ANTV = benzo(a)anthracene, CHR = chrysene, FLT = fluoranthene, PHE = phenanthrene, PYR = pyrene, RET = retene.
atmospheric lifetimes of these substances, as limited by deposition of particles (high $\theta$) and partly rapid photochemical degradation. No conclusions can be drawn, however, because of the inhomogeneous distribution of various PAH ground sources in central Europe and the possible impact of airborne sources (aircrafts). Lower limits for atmospheric lifetimes, $\tau_\text{air}$, of OCPs and PCBs as limited by deposition and photochemical degradation can be derived from the observations in FT and BL air, however:

$$\tau_\text{air} = \frac{\Delta t}{\ln(c_0/c(t))}$$

with $\Delta t$ = time since emission, $c_0$ and $c(t)$ concentrations after emission and at a receptor site, given by the BL (at Kosetice) and FT (at Zugspitze) concentrations. For winter $\Delta t > 5$ d applied. The actual transport time since ground contact would be accessible through the Lagrangian particle dispersion model retroplume analysis. It is, however, not useful as for $\Delta t > 5$ d the back-trajectories anyway reach beyond the European continent. Therefore, the levels measured in BL air in central Europe would not be representative for the BL in question. Considering that POPs emissions in central Europe are certainly higher than in northern and western Europe and the surrounding seas (e.g. EMEP, 2007), the levels at Kosetice represent upper limits for $c_0$, the mean background of the entire continent and BL air beyond the European continent. Therefore, lower limits for $\tau_\text{air}$ are derived. These are $\tau_\text{air} = 2.4–3.5$ days for $p,p'$-HCH, $\gamma$-HCH, PCB 28, PCB 52, PCB 118 and PCB 153, 6.5–8 d for PCB 101, HCB and $p,p'$-DDT, and $\tau_\text{air} = 15–20$ d for $p,p'$-DDE and $p,p'$-DDD. Assuming winter-time climatological OH levels for the Alps (Spivakovsky et al., 2000), $1.0 \times 10^{10}$ OH cm$^{-3}$, these correspond to $k_{OH} < 1.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $p,p'$-DDD and $k_{OH} < 0.75 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $p,p'$-DDE and $p,p'$-DDD. Assuming the validity of the lower limits found here, although other congeners had been studied. The BL–FT gradient of PCBs represent upper limits for $c_0$, the mean background of the entire continent and BL air beyond the European continent. Such data could be used for model validation.

4. Conclusions

OCPs, PCBs and PAHs are transported in the free troposphere over Europe. The concentrations observed in winter 2008 and, even more in summer 2007 were to our knowledge lower than observed elsewhere in the mid latitudes or tropics. This applies also to the PAHs. These, however, might have been higher concentrated, up to 50%, due to negative sampling artefacts and blank problems for samples analyzed in winter. As a consequence of length of sampling periods and meteorology, these cannot be considered representative of normal summer/winter weather conditions. For substances without primary emissions on the continent, the levels observed in FT air (winter) represent the continental background, eventually even the intercontinental, northern mid latitudes background in the middle troposphere. Such data could be used for model validation.

The usage of the lower limits for atmospheric lifetimes of $p,p'$-DDE, $p,p'$-DDD and $p,p'$-DDT inferred in this study rather than the usage of structure–activity relationship (SAR) method-based lifetimes can be recommended in modelling DDT environmental fate. The origin of a possibly increasing temporal trend of PeCB levels should be studied.

Acknowledgements

We are grateful to Thomas Kautselsky and his team (SFH) and Johannes Werhahn (FZK-IMK, Garmisch-Partenkirchen) for logistic support, to Steffen Knabe and Ralf Sohmer (Umweltbundesamt, Zugspitze) for measurement data. This project was supported by the Ministry of Environment (SP/1a3/29/07) and the Ministry of Education (MSMT 0021622412) of the Czech Republic. Andreas Stohl was supported by the Norwegian Research Council in the framework of the FLEXPO-P project.

Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envmon.2009.05.028.

References


References


