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Spatial variability of POPs in European background air

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Abstract

Persistent organic pollutants (POPs) are recognized for their potential to create harmful effects in remote areas and several monitoring programs have been established which measure POPs in air. Active air sampling (AAS) has so far been the recommended method used under the EMEP (co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) measurement program. The number of EMEP AAS stations is still limited and mainly located in the north western part of Europe. Passive air sampling (PAS) methods, which have become increasingly popular in recent years, offer an opportunity as a complementary sampling strategy which could improve sampling coverage under EMEP. To gain further insight into spatial patterns of POPs in European background air and to evaluate PAS as an alternative sampling technique under EMEP, PAS were deployed at 86 European background sites during summer 2006. Duplicate PAS samplers were also deployed at EMEP AAS sites to allow for a comparison of results obtained using both methods. The PAS were analyzed for selected PCBs, HCHs, DDTs, PAHs, chlordanes and HCB, and air concentrations were calculated on the basis of losses of performance reference compounds. Air concentrations of PCBs were generally lowest in more remote areas of Northern Europe with elevated levels in more densely populated areas. γ-HCH was found at elevated levels in more central parts of Europe, whereas α-HCH, β-HCH and DDTs showed higher concentrations in the southeastern part. There was no clear spatial pattern in the concentrations for PAHs, indicative of influence by local sources, rather than long range atmospheric transport (LRAT). HCB was evenly distributed across Europe, while the concentrations of chlordanes were typically low or non-detectable. Co-deployed PAS samples showed a fair agreement between the duplicates, typically within 30%. Larger differences were seen when comparing results obtained on the basis of AAS and PAS. The latter results illustrated that coordinated PAS campaigns have the potential serve as a useful intercomparison exercise within and across existing monitoring networks. We furthermore adopted an existing

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Lagrangian transport model (FLEXPART) as recently modified to incorporate key processes relevant for POPs to evaluate potential source regions affecting observed PAS concentrations at selected sites. Using PCB-28 as an example, the model predicted concentrations which agreed within a factor of 3 with PAS measurements for all except 2 out of the 17 sites that were investigated in this analysis.

1 Introduction

Persistent organic pollutants (POPs) are a common group of chemicals that are semi-volatile, bio-accumulative, persistent and toxic (e.g. Vallack et al., 1998). A key feature of these components is their intrinsic potential for long range atmospheric transport (LRAT). Because of their ability to create detrimental effects in remote areas, two international agreements have come into effect to reduce future environmental burdens in remote areas. These are the global Stockholm Convention on POPs (UNEP, 2003) and the regional 1998 Aarhus Protocol on Persistent Organic Pollutants under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP). The latter Protocol entered into force in 2003, and its ultimate goal is to eliminate any discharges, emissions and losses of POPs to the environment. The Aarhus Protocol initially focuses on 16 substances which include eleven pesticides, two industrial chemicals and three by-products/contaminants (UNECE, 1998).

Within EMEP (co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) the current measurement programme for POPs is based on a limited network of conventional Active Air Samplers (AAS) at background sites, mainly located in the north-western part of Europe (Aas and Breivik, 2009). The high costs associated with AAS have in part motivated the development of passive air samplers (PAS), which has the potential to be used as a complimentary technique to conventional AAS. Over the last decade PAS have become increasingly popular (e.g., Shoeib and Harner, 2002a; Jaward et al., 2004b; Pozo et al., 2004; Harner et al., 2006b). Of key relevance to this study are the first European campaign

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using PAS (Jaward et al., 2004a,b) and the Global Atmospheric Passive Sampling (GAPS) studies (e.g., Pozo et al., 2009) which have measured POPs at both urban and rural sites on a European and global scale, respectively.

The objective of this study has been to improve the knowledge of spatial patterns of POPs in background air across Europe using PAS. Altogether 92 samplers were deployed for ~3 months at 86 sites in 34 European countries during the late summer of 2006. Unlike the former European-wide survey carried out in 2002 (Jaward et al., 2004a,b), our main focus is on the occurrence of POPs across Europe in the context of LRAT. This study therefore targets background sites only. As PAS were mainly located at established EMEP sites which additionally monitor POPs using AAS on a regular basis, this study offered a unique opportunity to investigate potential similarities and differences in levels and patterns on the basis of complementary air measurements.

The results of these investigations are also used to discuss limitations of the current EMEP measurement network with respect to spatial coverage. These results may also be used to evaluate LRAT models, both within EMEP (e.g., Malanichev et al., 2004) and beyond. As an illustration, we have also included an assessment of differences in predicted source-receptor relationships at selected sites as exemplified for PCB-28, using an existing model (Eckhardt et al., 2009).

2 Materials and methods

2.1 Theory

Polyurethane foam (PUF) disks have gained increasing use as passive air samplers (PAS) (Shoeib and Harner, 2002a; Harner et al., 2004, 2006b; Jaward et al., 2004b; Pozo et al., 2004, 2006; Motelay-Massei et al., 2005). These PUF disks have high affinity and capacity to sorb organic chemicals. Accumulation of a chemical during exposure is equivalent to the rate of uptake minus rate of loss. Uptake of POPs is airside controlled and is initially linear and a function of the mass transfer coefficient

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(k_A), the planar area of the sampling media (A_{PSM}) and concentration of the compound in air (C_A). Ideally, these are the functioning conditions to the sampler out in the field, but as the chemical builds up in the sampling medium, the rate of uptake will be reduced and finally reach equilibrium (Shoeib and Harner, 2002a). The duration of the linear phase is dependent on the octanol-air partition coefficient (K_{OA}), and chemicals with low K_{OA} will reach equilibrium with the atmosphere faster than chemicals with higher K_{OA} (Harner et al., 2004). Uptake is also found to increase at elevated wind speeds, as this causes an increase in the mass transfer coefficient (k_A) (Tuduri et al., 2006).

The PUF disk sampler typically contains a PUF foam disk placed between two stainless steel metal domes in a so called "flying saucer" design (Wilford et al., 2004). This design aims to protect the foam disk from precipitation, sunlight, wind speed effects and coarse particle deposition. Air flows through a gap between the two domes (Pozo et al., 2004). Different passive sampler housings have been tested, and a relatively recent study (Tuduri et al., 2006), shows that the "flying saucer" design dampens the wind speed effect adequately. The specific housing design used in this study with hollow metal tubes inside the sampler, offers the additional advantage that the width of the gap between the two domes is kept identical from site to site.

Because of the range of K_{OA} values for the compounds of interest and hence different sampling rates, the PUF disks were spiked with depuration compounds (Performance Reference Compounds – PRCs) prior to exposure (Huckins et al., 2002). PRCs are either isotopically labeled or non-native compounds. In addition the added PRCs have a range in volatility which makes them suitable to establish equilibrium for compounds with diverse physical-chemical properties. As a result, they can provide a more accurate quantitative sample volume and air concentration can be determined based on their loss rate during deployment (e.g., Tuduri et al., 2006).

2.2 Deployment and sample preparation

Samplers were exposed in the field for about 3 months in various European countries in a coordinated campaign during late summer 2006. The study region included 34

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countries and 86 sites, located from Spitsbergen (78° N) in the north to Cyprus (33° N) in the south, and from Greenland (38° W) in the west to Kazakhstan (75° E) in the east (see Table S1 in the Supporting Information (SI)). Most of the sites included in this study (N=71) are part of the EMEP (European Monitoring and Evaluation Program) measurement network (see e.g., Aas and Breivik, 2008) although additional remote sites (N=15) were included to improve spatial coverage in certain regions. PAS were additionally co-deployed with AAS at 6 EMEP sites where POPs are monitored under EMEP on a routine basis to evaluate possible differences in results, along with duplicated PAS samplers and field blanks.

2.3 Analysis

In the following section, only a brief overview of the sample treatment and analysis will be given. More detailed information for the sample preparation; involving pre-cleaning and clean-up of the PUF disks and analysis is presented in the SI.

The PUF disks were pre-cleaned by soxhlet extraction, dried and spiked with PRCs prior deployment, and returned to the laboratory for clean-up and analysis after end of deployment (~3 months) (S1.1). A mixture of internal standards was added to the PUFs before Soxhlet extraction and further clean-up. The clean-up procedure involves separation into two extracts, with acid treatment and silica fractionation for analysis of the persistent compounds, and silica fractionation for the PAH extract (S1.2). The extracts were further concentrated by a gentle stream of nitrogen to ~50 µl and added recovery standards (S1.3). The isomer identification and quantification was carried out using a gas chromatograph coupled to a high resolution (PCBs, HCHs, HCB, DDTs) and low resolution (PAHs, chlordanes) mass spectrometer, with gas chromatograph conditions as explained in SI (Table S3, S1.3).

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2.4 Deriving concentrations in air/effective air sample volume

In order to back-calculate the actual air concentrations for individual compounds in air, information on the PUF characteristics, air temperature, measured loss of individual PRCs and their temperature dependent K_{OA}-values were used in an initial step to calculate site-specific sampling rates (e.g., Shoeib and Harner, 2002a; Pozo et al., 2004, 2009). The average air temperatures at each site for the exposure period are based on meteorological data from European Centre for Medium-Range Weather Forecasts (ECMWF) to ensure a consistent approach. Here, at 2 m a.g.l., the temperature was averaged every 3 h over the period for which the respective sample was taken. The altitude for each site (Table S1) was next compared against the model altitude. For five high altitude sites were large differences were noted (Jungfraujoch, Moussala, Zavizan, Chopok and Longobucco), the ECMWF data were adjusted by assuming a temperature decrease by altitude of −0.65 °C per 100 m. Loss of PRCs from individual samples was estimated on the basis of the ratio between the amount of PRCs in individual samples and the average amount of PRCs in the field blanks. For PCBs (23, 30, 32, 107, 198), temperature dependent K_{OA}-values were derived on the basis of data reported by Harner and Bidleman (1996) and relative retention times from Harju and collegues (1998). For PCB-12 and -14, we used data from Li et al. (2003), and for D6 γ-HCH information presented by Shoeib and Harner (2002b). Only PRCs which experienced a loss of 40% or more were used to calculate site-specific sampling rates (Pozo et al., 2009). These sampling rates were then used to convert measured values into air concentration as detailed by Shoeib and Harner (2002a). For a few sites experiencing insufficient loss of the PRCs (Nuuk, Summit, Spitsbergen, Sniezka), the default sampling rate proposed by Harner et al. (2006b) was used. The resulting air concentrations for these sites should be interpreted with caution. The air concentrations for each component were derived by dividing the amount by the respective effective air volume.

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2.5 Model

Simulations of atmospheric POP transport were made using the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005; Stohl and Thomson, 1999). FLEXPART was driven with analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF, 1995) with 1°×1° resolution (derived from T319 spectral truncation). Analyses at 00:00, 06:00, 12:00 and 18:00 UTC, and 3-h forecasts at 03:00, 09:00, 15:00 and 21:00 UTC were used. There are 23 ECMWF model levels below 3000 m, and 91 in total. FLEXPART calculates the trajectories of so-called tracer particles and accounts for turbulence, convection, deposition (wet and dry) and atmospheric reaction by hydroxyl (OH) radicals (Eckhardt et al., 2009). It was run in backward mode, in order to identify the source regions of air pollutants at a particular site (Stohl et al., 2003; Seibert and Frank, 2004). These were found by following all 4 million particles equally released over the sample duration, 20 days backward in time. These source regions are expressed as emission sensitivities (ES) in the footprint layer (0–100 m above ground) during each deployment period at different sites. Multiplying this ES with emission fluxes from the PCB-28 emission inventory (Breivik et al., 2007) yields the geographical distribution of sources contributing to the simulated concentration at the given measurement site. Emission contributions (EC), which gives the simulated air concentration at the receptor, may then be obtained by areal integration. For further details we refer to the original publications listed above.

3 Quality control/quality assurance (QC/QA)

The analytical procedures were monitored using NS/EN ISO/IEC 17025 accredited routines for quality assurance and quality control. A calibration solution was injected after every fourth sample, and was used to quantify the samples. Regarding PCBs, HCHs, DDTs, HCB and the chlordanes, a standard reference material (SRM 1588) from the National Institute of Standards and Technology (NIST) containing organic compounds

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in cod liver oil was analyzed routinely. In addition, for the quantification control, the retention for ^{12}C-labeled compound should not be more than 3 s later than its corresponding ^{13}C-labeled isomer. Furthermore the isotope ratio based on a 3:1 relationship between ^{12}C and ^{13}C, for the two monitored masses, must be within ±20% of the theoretical value. For the PAHs, the SRM solution, SRM 1491 (NIST) was analyzed during each run.

3.1 Method and field blanks values

Method and field blanks consisted of pre-cleaned PUF disks which were extracted and analyzed in the same way as the exposed samples. Method blanks were only stored at NILU, whereas field blanks were brought in field with the deployed samples but not exposed. The field and method blank values were converted into an air concentration by using the average sampling rate (4.9 m^3 day^{-1}), temperature (14°C) and exposure time (94 days). The method and field blank values had similar values.

3.2 Method detection limit (MDL)

The method detection limit (MDL) was calculated as the average of the field and method blank concentrations (N=18) plus 3 times the standard deviations (SD) (Table 1). When the target compound was not detected in the blanks (method blank and field blank), an instrumental detection limit (IDL) value derived from signal/noise values 3:1 divided by two, was used to derive a MDL (Pozo et al., 2009). This was not the case for the PAHs, here the lowest measured range for air samples for the instrument were 0.01–0.02 ng/m^3. For the components studied here (fluorene – benzo(a)pyrene) only 0.01 ng/m^3 was used. For values that fell below that, half of this measured value was used. Furthermore, when the target compound was not detected in the exposed samples, half of the MDL from the field and method blanks (amount/sample) was used to calculate air concentrations.

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3.3 Recoveries

Quantification is based on the added ^{13}C or ^{2}D-labeled internal standards and is therefore automatically corrected for recovery. Furthermore two types of recoveries were compiled, namely recovery for the internal standards and for the PRCs. See S1.4, S1.5 and Table S2 for additional information about these two types of recoveries. The concentrations were not blank corrected due to both low and not stable concentrations in the blanks, whereas they were automatically corrected for the recoveries.

3.4 Uncertainties in the chemical analysis

Different factors influence the uncertainty in the chemical analysis: loss during sample extraction and clean-up, accuracy of the standard concentrations, instrumental parameters, in addition to interferences from other compounds and possible sample contamination. To compensate for possible loss of analytes due to sample clean-up, internal standards were used in combination with a recovery standard. Field blanks were used to evaluate possible contamination during transport, and the method blanks to evaluate the laboratory conditions (e.g. solvents, adsorbents), respectively. Different approaches were applied to assess these uncertainties, i.e. intra laboratory/inter laboratory evaluations or a step-by-step evaluation of all analytical steps. A total estimate for the uncertainty accumulates up to 35%, but will vary for different compounds/groups.

3.5 Uncertainties in back-calculated PAS air concentrations

The PAS results in this study are converted into air concentrations, rather than presented as sequestered amount per sampler, as this is essential to facilitate a direct comparison with AAS results (Sect. 4.2.2) and model outputs (Sect. 4.4). This introduces additional uncertainties which are likely to exceed those that are associated with the chemical analysis alone (Sect. 3.4). Past evaluations has suggested that the PAS method enables estimates of "true" air concentrations within a factor of 2–3 (Gouin

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et al., 2005a; Harner et al., 2006a; Klanova et al., 2008). Errors in estimated air concentrations reflect in part uncertainties in input parameters used to calculate uptake rates (e.g., Shoeib and Harner, 2002b), such as octanol-air partition coefficients and their temperature dependencies (e.g., Li et al., 2003), the use of modeled rather than measured chamber air temperatures (Kennedy et al., 2010), and in the selection/loss of PRCs (e.g., Bartkow et al., 2006a; Moeckel et al., 2009). Furthermore, there are uncertainties associated with sampling performance under variable environmental conditions, such as elevated wind speeds (Tuduri et al., 2006; Chaemfa et al., 2009b), sun-light intensity (Bartkow et al., 2006b), humidity (Santiago and Cayetano, 2007), temperatures (Klanova et al., 2008) and potential artifacts caused by inadvertent particle-phase sampling of POPs (e.g. Klanova et al., 2008; Chaemfa et al., 2009b). To further characterize uncertainties associated with uptake rates, a range of different field studies have previously been carried out whereby results obtained on the basis of AAS and PAS have been compared and contrasted (e.g. Gouin et al., 2005a, 2008; Klanova et al., 2008; Chaemfa et al., 2008, 2009a; Moeckel et al., 2009; Hayward et al., 2010). We refer to these studies for a more detailed account of uncertainties in uptake rates.

4 Results and discussion

4.1 Overall results

Table 1 shows the calculated air concentrations (average, median, range) of selected POPs at European background sites (N=86). PCBs 28, 52, and 101, α- and γ-HCH and HCB were detected in all samples, while for all other compounds some samples were below the method detection limit (MDL). The spatial variability in the overall results is initially evaluated by the ratio between maximum and minimum air concentrations (MMR). For samples with concentrations below the MDL, the minimum concentration was replaced by the MDL when calculating the MMR and set to 1/2 MDL for the calculation of average and median air concentrations in Table 1.

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PCBs

The average concentration of Σ_7PCBs was 21 pg/m^3 (SD±19 pg/m^3). The most abundant PCBs were PCB-52, -28, -101 and -153 which contributed 23%, 22%, 20% and 15% to the average concentration of Σ_7PCBs, respectively. Σ_7PCBs has a MMR of more than 55 which shows that there is still a marked spatial variability, even across European background sites. This may be interpreted as a continuing influence of primary emission on atmospheric levels. Alternatively, it cannot be excluded that some of the sites have been affected by the presence of one or more local emission sources. The range is smaller than previously reported for Σ_{29}PCBs in a similar study across Europe in 2002 (Jaward et al., 2004b). The former study reported a variability of more than 2 orders of magnitude between the highest and lowest samples, but included a combination of both urban areas as well as remote background sites. MMR furthermore tended to increase with increasing chlorination (Table 1), suggesting lighter PCBs to be more evenly distributed in European background air in comparison to their heavier counterparts. This may in part be seen as a reflection of a more limited long-range atmospheric transport potential of heavier PCBs, causing larger variability in air concentrations (and thus MMR) for these substances (Wania and Daly, 2002).

HCHs

The average concentration of Σ_3HCHs (α, β, γ) was 64 pg/m^3 (SD±59 pg/m^3). The concentration of Σ_3HCHs varied from 9–311 pg/m^3, with γ-HCH and α-HCH contributing on average 55% and 41%, respectively. β-HCH, which was close to MDL in some samples (Table 1), was less abundant and contributed only 4% on average. The median concentrations of γ-HCH and α-HCH were similar, although the average concentration for γ-HCH (38 pg/m^3) was higher than for α-HCH (26 pg/m^3). This illustrates a more homogenous distribution of α-HCH in European background air in comparison to γ-HCH, as also illustrated by the MMR for these two HCH isomers (Table 1). γ-HCH is less volatile than α-HCH (Xiao et al., 2004), which in turn may help to explain

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observed differences in air concentrations and environmental fates between the two isomers (Breivik and Wania, 2002). The results for β-HCH should be interpreted with caution as several samples (N=13) were below MDL (Table 1). However, the large spatial variability for this isomer (MMR>380) suggests a highly skewed distribution. This is noteworthy and may in part be attributed to the fact that β-HCH is much more water-soluble than the other two isomers and hence more easily subject to wash-out by rain in spite of a similar emission history to α-HCH (Li et al., 2002).

DDTs

The average concentration of Σ_4DDTs was 32 pg/m^3 (SD±62 pg/m^3), and ranged from 1.1 pg/m^3 to 356 pg/m^3 with p,p'-DDE as the major contributing isomer (67% on average). The second most prominent isomer was p,p'-DDT with an average contribution of 18%. MMRs were all high within the group of DDTs and ranged from >143 (o,p'-DDT) to >240 (p,p'-DDT).

PAHs

The average concentration of Σ_8PAHs was 6 ng/m^3 (SD±6 ng/m^3) and ranged from 0.2–35 ng/m^3. The more abundant PAHs include phenanthrene and fluorene which each contributed on average 49% and 29%, respectively. As expected, the contribution from heavier PAHs, such as benz(a)anthracene, chrysene and benzo(a)pyrene, was typically low with average contributions of 0.35%, 1.2% and 0.14% to Σ_8PAHs, respectively. This is also consistent with earlier studies (e.g. Halsall et al., 1994; Lohmann et al., 2000). MMR furthermore ranged from >15 (benzo(a)pyrene) and >153 (pyrene). The results for Σ_8PAHs compares favourably with similar results from the previous European campaign by Jaward et al. (2004a), which reported a measured range between 0.004 and 26 ng/m^3 for the same PAHs and also noted that lighter PAHs tended to dominate in the samples since they occur in the gas-phase and hence have greater higher ability for transport, while heavier PAHs (benzo(a)pyrene) are more related to the particle phase (Lohmann et al., 2000).

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HCB

HCB was detected in all samples with an average concentration of 49 pg/m^3 (SD±18 pg/m^3; range: 23–115 pg/m^3). The variability was limited with a MMR of 5, very similar to what has been previously reported for Europe (Jaward et al., 2004b). This has been interpreted as evidence of the long atmospheric lifetime of this volatile, compound combined with the absence of significant point sources of HCB in Europe (Jaward et al., 2004b). However, similar studies in Asia have reported larger variability, indicative of continuing emissions (Jaward et al., 2005). We also note that the range reported here (23–115 pg/m^3) is higher than previously reported for Europe (11–50 pg/m^3) by Jaward et al. (2004b). Interestingly, a recent study on levels and trends of POPs in Arctic air suggest an increase in HCB in recent years, and attribute this to a potential increase in worldwide usage of certain pesticides contaminated with HCB (Hung et al., 2010).

Chlordanes

The average concentration for the Σ_4 chlordanes was 3.5 pg/m^3 (SD±2.7 pg/m^3). The concentrations varied from 0.2 pg/m^3 to 19.4 pg/m^3, with trans-nonachlor and cis-chlordane contributing 38% and 35%, respectively. The least abundant compound was cis-nonachlor with 5%. Concentrations of individual chlordanes were typically low in comparison to the other substances studied and MMR ranged from >11 (cis-nonachlor) to >104 (trans-chlordane).

4.2 Duplicate passive air sampling and comparison with active air sampling

Two passive air samplers were co-deployed close to each other at each EMEP-site (Košetice, Pallas, Storhofdi, Birkenes, Spitsbergen, Råö, Aspvreten) where POPs are monitored on a regular basis using conventional AAS techniques (Aas and Breivik, 2008). This was done to gain further insights into the reproducibility of the PAS method

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(e.g. Harner et al., 2006b) and to evaluate possible differences between PAS and AAS results (e.g. Gouin et al., 2005a,b; Mari et al., 2008).

4.2.1 Duplicate passive air samplers at selected sites

Figure 1a–f compares selected results for the six EMEP POPs sites where two samplers were co-located, while Table S4 additionally lists relative deviations, expressed as the percentage deviation from the average of these two parallels. The relative deviation for PCBs between the two replicates was less than 10% at four out of six sites and ranged from 4 (Košetice, Stórhöfdi) to 30% for Σ_nPCBs (Spitsbergen) (Table S4). Among individual PCBs, larger differences tended to occur for substances and sites experiencing lower concentrations (Spitsbergen, Pallas). However, differences of 20% or more were also seen for PCB-28 and 52 at the Råö site (Table S4) in spite of the relatively high air concentrations at this site (Fig. 1a). Differences in wind speed experienced between the two replicates may have contributed to some of the deviations observed (Tuduri et al., 2006), which could be more significant at the northern sites.

Figure 1b,c show results for α-HCH and γ-HCH. The relative deviations for α-and γ-HCH was always less than 20% and ranged from 1 to 13% and 2 to 18%, respectively (Table S4). These differences appear to be of a more random analytical character, rather than explained by differences in atmospheric concentrations and climatic conditions between the sites.

Figure 1d shows the results for Σ_nDDTs where n varies between the sites. Both replicates at Stòrhöfdi and Spitsbergen had concentrations below the MDL for all DDTs and are therefore not included in Fig. 1d. Concentrations under the MDL were also experienced at Birkenes and Pallas and hence a comparison for all four DDT isomers was only possible for Košetice and Råö. The larger deviations among the latter two sites were found for Råö where concentrations are much lower in comparison to Košetice (Fig. 1d).

Figure 1e shows the results for Σ_nPAHs, where n varies from 1 (Stòrhöfdi) to 8 (Košetice), while no comparison could be made for Spitsbergen. The relative deviation

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between the replicates ranged from 2% (Košetice) to 25% (Pallas) for Σ_nPAHs. The better agreement found for the Košetice (2%) site (Table S4) may be attributed to the higher concentration of PAHs experienced at this site (Fig. 1e).

Figure 1f shows the results for HCB. The difference between the two parallels ranged from 1 to 22%. A very good agreement was found at Stòrhöfdi, Košetice, Birkenes and Råö with 1, 2, 4 and 8%, respectively, while larger discrepancies (~20%) were observed at the northern sites at Pallas and Spitsbergen.

In general, we conclude that there is a reasonable agreement between the two replicates for most substances, with a tendency for better agreement for those substances (e.g. HCHs, HCB) and sites (e.g. Košetice) which tend to experience higher concentrations in air.

4.2.2 Passive air sampling in comparison with active air samplers

A key objective of this study has been to assess the potential of passive air sampling (PAS) as a complementary technique to conventional active air sampling (AAS) within the EMEP monitoring program. For this purpose direct comparisons of results obtained on the basis of AAS and PAS have been carried out. Although such comparisons have been reported previously (Gouin et al., 2005a; Mari et al., 2008), past evaluations of this kind have typically been carried out on the basis of results obtained at the same chemical laboratory. In this work, AAS results are mainly obtained on the basis of results originating from different chemical laboratories, hence both intra and inter laboratory uncertainties must be taken into account. Exceptions to this are the samples from the two Norwegian sites (Birkenes and Spitsbergen) which were both analyzed at the NILU laboratories. We should further note that the AAS monitoring strategies within EMEP vary in terms of temporal coverage (Table S5). Only Stòrhöfdi and Råö collect samples on a continuous basis. A direct comparison between AAS and PAS for the other EMEP sites is therefore difficult as the different samplers have been exposed to different air masses. Finally, we note again that all results for Spitsbergen obtained

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on the basis of PAS in this study may be questioned as they rely on the default uptake rate (Sect. 2.4).

Concentrations from the AAS were averaged over the same sampling period (or as close as possible) as for the passive air samplers (i.e. 3 months). The average air concentration for the two PAS parallels from each EMEP site were used, except for the Aspvreten site (one PAS sample only). Figure 2a–f illustrates the absolute differences between PAS and AAS results, while Table S5 include relative deviations $(C_{PAS}-C_{AAS})/C_{AAS}$. A positive deviation thus illustrates higher concentration in the PAS, relative to AAS.

PCBs

PCBs were reported for all sites. The results for Σ_nPCBs were found to be within a factor of ~2 for all sites (Fig. 2), but with some notable exceptions (e.g. 101, 138 and 153 at the Košetice site, Table S5). Deviations relative to AAS for Σ_nPCBs ranged from −59% (Pallas) to +86% (Košetice). Larger differences for Σ_nPCBs were also observed for Stòrhöfdi (−51%) and Råö (+47%). A plausible explanation for the large deviations seen at the Košetice site is that the AAS is only operating one day per week (Table S5) and hence the air masses sampled deviate significantly between the AAS and the PAS. This effect may be particularly significant at Košetice as this site is located close to major source regions in Europe (Breivik et al., 2007). Air concentrations at this site may thus be expected to fluctuate significantly over time as the air masses would be expected to be less well-mixed. However, if difference in sampling coverage was the only factor to consider, significant deviations would also be expected at those other sites which do not operate the AAS on a continuous basis (Birkenes, Aspvreten, Pallas and Spitsbergen). The best agreement between AAS and PAS for Σ_nPCBs was obtained for Birkenes (−5%) (Table S5), which may be due to a combination of air concentrations being well above MDL and the fact that the samples being analyzed at the same chemical laboratory. It must be cautioned that this comparison is of limited significance for Spitsbergen and Pallas as some PAS results were close to or below MDL (Table S5).

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HCHs

α- and γ-HCH were also reported for all sites (Fig. 2b,c). The percentage deviation relative to AAS for the α- and γ-HCH isomers ranged from −43% (Birkenes) to +318% (Stòrhöfdi) and from −48% (Birkenes) to +85% (Košetice) for these two isomers, respectively (Table S5). With the exception of Birkenes, Pallas and Stòrhöfdi (latter only for γ-HCH), positive deviations were typically observed ($C_{PAS}>C_{AAS}$) for these two isomers. For the α-HCH isomer, minor deviations were seen for Råö (+19%), Spitsbergen (+23%) and Pallas (−17%). Likewise, good agreement for γ-HCH was found for Stòrhöfdi (−8%), Spitsbergen (+22%) and Råö (24%). Given that the AAS at Stòrhöfdi operates on a continuous basis it is difficult to offer an explanation for the large differences seen for α-HCH at but not for γ-HCH at this site.

DDTs

As several DDTs were either not reported by AAS, or because several results from PAS were found to be below MDL (Table S5, Fig. 2d), a comparison was only possible for Košetice, Råö and Aspvreten. Hence the sum of DDTs (i.e. p,p'-DDD, p,p'-DDE, p,p'-DDT) also vary from site to site. The percentage deviation for Σ_nDDTs varies from −34% (Aspvreten) to +282% (Košetice). Again, the large deviations seen at Košetice may in part be due to the different air masses sampled by AAS and PAS.

PAHs

For the same reasoning as for the DDTs, the comparison for PAHs had to be carried out for a variable number of compounds (phenanthrene, anthracene, fluorathene, pyrene, benzo(a)pyrene, benz(a)anthracene) and limited to four stations (Košetice, Råö, Aspvreten and Pallas), see Fig. 2e. The percentage deviations relative to AAS for Σ_nPAHs (Table S5) ranged from +45% (Råö) to +216% (Košetice). The relative deviations for the individual PAHs were mostly positive, except pyrene and benz(a)anthracene at

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Aspvreten, and benzo(a)pyrene at Košetice. The best agreement between the two air sampling techniques was found for Råö and Pallas (+45% and +52% for Σ_nPAHs, respectively).

HCB

Results for HCB obtained on the basis of AAS are only available for Košetice, Birkenes, Spitsbergen and Stòrhöfdi (Fig. 2f). For all these sites, except for the latter, the relative deviation was between +36% and −31% (Table S5). This is in striking contrast to Stòrhöfdi for which C_{PAS} exceeded C_{AAS} by as much as +1540%. Hung et al. (2010) recently pointed out that all Arctic monitoring stations showed similar air concentrations after year 2000, with annual average air HCB concentrations between 29 and 76 pg/m^3, while Stòrhöfdi had much lower concentrations (2 to 6.8 pg/m^3). As the PAS results for the other three sites compare favourably with AAS results, the large discrepancy for HCB at Stòrhöfdi merits further investigation. This example also illustrates how coordinated PAS campaigns has the potential to serve as an intercomparison effort within and across existing monitoring programs and which could complement other relevant efforts, e.g. inter laboratory comparisons.

4.3 Spatial patterns

As most EMEP monitoring stations reporting POPs in air are mainly located in the northwestern part of Europe (Aas and Breivik, 2008), an additional objective of this study was to evaluate potential limitations in the current EMEP measurement network with respect to spatial coverage. Improved spatial coverage is not only considered important to support relevant modelling activities within EMEP (e.g., Malanichev et al., 2004) and beyond, but it may also provide useful information for future monitoring strategies within EMEP.

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PCBs

Figure 3a shows the results for Σ_7PCBs while Fig. S1a–g presents the spatial patterns of individual PCB congeners across Europe. Similar to past studies, elevated levels of PCBs were typically found in more densely populated areas in central parts of Europe (Jaward et al., 2004b). Lower levels of PCBs tended to occur along the western coast of Scandinavia, the British Isles and to some extent Spain/Portugal, which may be explained by the prevailing wind regimes with transport from west to east. Elevated levels of Σ_7PCBs (>50 pg/m^3) were detected at sites in Belgium, Germany, Italy, Netherland and Ukraine, while the highest concentrations were observed at a site in Denmark (121 pg/m^3). However, it is important to keep in mind that the number of sites in each country is too limited to use the data to infer any background concentrations in individual countries. Whenever significantly elevated levels are measured at a specific site, this may indicate an influence from one or more nearby sources as may be the case with the elevated levels seen at the Danish site.

HCHs

The spatial patterns for Σ_3HCHs and individual HCHs across Europe are shown in Fig. 3b and Fig. S2a–c, respectively. HCHs are insecticides which have been extensively used in Europe (Breivik et al., 1999) and the rest of the world (e.g., Li et al., 1996, 1999). The results for Σ_3HCHs shows a fairly consistent pattern with low levels (<20 pg/m^3) at most Scandinavian and Arctic sites. Elevated levels (>200 pg/m^3) were recorded at certain sites in France, Moldova and Ukraine. HCHs ultimately originate from the production and use of technical HCH (55–80% α-HCH, 2–16% β-HCH, 8–15% γ-HCH) or lindane (>99% γ-HCH) (Breivik et al., 1999). Hence, while the occurrence of γ-HCH may be attributed to either technical HCH or lindane, α- and β-HCH only originates from technical HCH. In general terms, lindane usage tended to dominate in the western part of Europe, while technical HCH tended to dominate in the eastern part (Breivik et al., 1999). This pattern is also reflected in the results, whereby

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elevated levels of α- and β-HCH are mainly seen at some sites in the southeastern areas of Europe (Fig. S2a,b). Elevated atmospheric concentrations of β-HCH may hence be a more useful indicator than α-HCH to identify proximity to regions or areas that are affected by ongoing or past historical usage of technical HCH as β-HCH is more easily washed out by rain. Elevated levels of γ-HCH tend to occur across central parts of Europe (Fig. S2c). Given the remoteness from key source areas, relatively high levels of α-HCH are also observed at the sites in Iceland, Greenland and Spitsbergen, which may be seen as a reflection of the elevated long-range atmospheric transport potential of this isomer (Li et al., 2002; Wania and Mackay, 1996; Beyer et al., 2000).

DDTs

The spatial patterns of Σ_4DDTs and individual DDTs are presented in Fig. 3c and Fig. S3a–d, respectively. The technical mixture of DDT contains up to 80–85% of the p,p'-DDT isomer and only small amounts of the o,p'-DDT isomer (15–20%) (Motelay-Massei et al., 2005) and was banned in Europe in the 1970s and 1980s (Pacyna et al., 2003). Levels of Σ_4DDTs were generally low and frequently below the MDL in Northern Europe (Fig. 3c) but with increasing air concentrations towards Central and Eastern Europe (Fig. 3c). Concentrations of Σ_4DDTs above 100 pg/m^3 occurred at sites in the Czech Republic, Greece, Hungary, Moldova, Poland and Ukraine (Fig. 3c). The spatial pattern for individual isomers (Fig. S3) generally reflected that of Σ_4DDTs, although absolute air concentrations varied. A p,p'-DDE/p,p'-DDT ratio lower than 1 has been proposed as an indication of fresh use of technical DDT (Pozo et al., 2006). This ratio is shown in Fig. S3e). Jaward (2004b) previously noted a low p,p'-DDE/p,p'-DDT ratios in European air, which suggest a fresh p,p'-DDT signal. This is in contrast to our results, which indicates a more weathered signal with an average ratio of 3.8 (range 0.9–8.5) for our samples collected four years later (Fig. S3e). A ratio higher than 1 is also in better accordance with observations based on active air sampling from various EMEP sites (Košetice, Pallas, Storhofdi, Spitsbergen and Råö) which show a mean value for this ratio in the range between 1.3 and 10.9 during 2006 (Aas and Breivik,

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2008). The ratio o,p'-DDT/p,p'-DDT (Fig. S3f) has previously been used to evaluate possible influence from dicofol, a miticide which contains 10% by weight of the o,p'-DDT isomer (Becker, 2008; Gillespie et al., 1994; Qiu et al., 2005). Several countries in Europe (e.g. Italy, United Kingdom, Spain and Turkey) utilize dicofol in agriculture (Gillespie et al., 1994; Turgut et al., 2009). This study confirms several sites which had higher values for the o,p'-DDT isomer in comparison to the p,p'-DDT isomer. The average ratio (±SD) was 0.86±0.26 and spanned from 0.3–1.6 which may suggest some influence from dicofol at certain sites. A ratio higher than 1 was found at sites in Austria, Denmark, Finland, France, Ireland, Italy, Kazakhstan, Lithuania, Moldova, Netherland, Norway, Poland, Sweden and United Kingdom (Fig. S3f).

PAHs

Figure 3d shows the spatial pattern for Σ_8PAHs across Europe while included compounds are plotted individually in Fig. S4a–h. PAHs are by-products from incomplete combustion processes and have many different sources (Lohmann et al., 2000). No clear trend in spatial patterns could be found, and it seems likely that the sites which are experiencing elevated concentrations are mainly affected by local sources. Elevated concentrations of Σ_8PAHs (>20 ng/m^3) where observed at sites in Finland, Greece, Netherland and Spain (Fig. 3d). Hence, many of the sites included may not be considered true background sites with respect to PAHs.

HCB

The spatial pattern for HCB is presented in Fig. 3e. HCB is highly volatile, persistent in air and expected to be extensively re-emitted from secondary sources like soil and vegetation (Bailey, 2001; Barber et al., 2005). As previously recognized in this study (Table 1) and elsewhere (Jaward et al., 2004b) concentrations are relatively uniform across Europe. Elevated air concentrations (>100 pg/m^3) occurred at four sites, two of which are found at high elevation (Summit, Spitsbergen). Yet, as the uptake rate

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for these two sites rely on the default value, we suspect air concentrations may have been overestimated as the true uptake rates at these exposed sites may have been underestimated due to wind speed effects (Tuduri et al., 2006).

Chlordanes

The spatial pattern for $\Sigma_4$chlordanes is presented in Fig. 3f, and for individual compounds in Fig. S5a–d. The technical mixture of chlordane consists mainly of trans-chlordane, cis-chlordane and trans-nonachlor (Sovocool et al., 1977; Dearth and Hites, 1990). Chlordane were formerly used in agriculture as an insecticide and termiticide up to the mid 1980s (Bidleman et al., 2002). The levels of the individual chlordanes were typically low and several sites were below MDL. The predominating compounds in the PAS were cis-chlordane and trans-nonachlor, while cis-nonachlor were found at lowest levels. Elevated levels of $\Sigma_4$chlordanes (>10 pg/m^3) were found at sites in Belgium, Greece and Netherlands. The trans-chlordane/cis-chlordane (TC/CC) ratio is 1.56 in the technical chlordane mixture (Bidleman et al., 2002). Trans-chlordane is more easily degraded than cis-chlordane in the environment and ratio values for TC/CC close to 1 implies a weathered signal. Consequently elevated ratios may indicate fresh usage of technical chlordane (Pozo et al., 2004). The average ratio (±SD) was 0.5±0.4 and spanned from 0.03–2.6 indicating there were some sites which experienced higher levels of the trans-chlordane component. Sites with ratio >1.56 were found in Moldova (1.57), Netherlands (1.61, 1.63) and Malta (2.58).

4.4 Model evaluations

The atmospheric transport model FLEXPART was used in a time-reverse mode to identify the source regions responsible for the PCB-28 loading at the respective sampling site in addition the meteorological parameters driving the transport. In contrast to classical trajectory calculations (Gouin et al., 2005a) turbulence, convection and removal processes (dry and wet deposition, reaction with OH) are taken into account. In this

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manner the source regions for each sample can be identified and an emission sensitivity (ES) map can be derived. Combining this information with the PCB-28 emission inventory (Breivik et al., 2007) a concentration for each receptor can be predicted resulting in a emission contribution (EC) map. We selected PCB-28 to illustrate the model as (a) unlike several compounds included in this study, PCB-28 exists solely in the gaseous state in the atmosphere, and (b) a spatially resolved emission inventory is available which is essential as model input. The model was run for 17 of the sites included in this study, including all EMEP AAS to also facilitate a comparison between model and measurements derived using on the basis of both AAS and PAS. Table S6 presents the sites and predicted and observed concentrations, including percentage deviation between model and PAS measurement results, while Fig. 4 shows the modelled versus observed air concentrations (PAS only). The agreement between PAS and model results were found to be within a factor of 3 for 15 out of 17 sites, with most results within a factor of 2. It is possible that the overestimation of the model is caused by too high emissions in the inventory (Fig. 4). The overall results show that the model predicted values in comparison to AAS results were 2–3 times higher at four out of seven sites (Košetice, Birkenes, Råö, Aspvreten) and 1–12 times lower for the other sites (Pallas, Stòrhöfdi, Spitsbergen).

In a recent study by Eckhardt et al. (2009) the same method was used in order to identify source regions contributing to the loadings of PCB-28 at the Birkenes site (for sampling times of 24 h). Here, Košetice and Birkenes (Fig. 5) where chosen for further discussion of the model results, while additional model results can be found in the SI, Fig. S6 to S20. The ES maps in Fig. 5a,b shows the residence time of the air masses in the so called the footprint layer (0–100 m a.g.l.) where potential uptake of emissions can take place. Looking at the source regions of the air masses influencing the two sites (upper row) it can be seen for both that the local influence gives the greatest contribution and the prevailing westerly winds extend the source region towards North America. Air masses flow in both cases over the British Isles. For Košetice, also Southern and Eastern Europe is an important influence. This can

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be seen when looking at the EC-maps (Fig. 5 c,d), where emission fluxes (Breivik et al., 2007) are incorporated. Integrating over the maps shown in the lower row of Fig. 5 yields an estimated concentration of 4.7 pg/m^3 and 13.6 pg/m^3 for Birkenes and Košetice, respectively (Table S6). The influence of Southern and Eastern Europe is larger for Košetice than for Birkenes.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/10/22585/2010/ acpd-10-22585-2010-supplement.pdf.

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Table 1. Concentrations of selected PCBs, HCHs, DDTs, chlordanes and HCB (pg/m^3) and selected PAHs (ng/m^3) at European background sites.

Compounds	Average±SD	Median	Measured range: Deployed samples	Measured range: Blanks	MDL	% above MDL	Max/min ratio (MMR)
PCB-28	5±4	4	0.6–20	0.06–0.3	0.4	100	34
PCB-52	5±4	4	0.8–20	0.05–0.3	0.3	100	25
PCB-101	4±5	3	0.4–34	0.03–0.3	0.3	100	84
PCB-118	1.5±1.5	1.0	0.1[1)]–8.3	0.001[2)]–0.2	0.2	95	>55
PCB-138	2.1±2.4	1.2	0.1[1)]–18.3	0.001[2)]–0.2	0.2	95	>102
PCB-153	3±4	2	0.2[1)]–28	0.004[2)]–0.3	0.3	94	>87
PCB-180	0.8±1.0	0.6	0.03[1)]–6	0.001–0.04	0.05	98	>122
Σ_7PCBs	21±19	17	2–121				>55
α-HCH	26±24	21	5–156	0.1–0.8	1	100	33
β-HCH	2±7	1	0.06[1)]–49	0.01–0.2	0.13	85	>380
γ-HCH	36±38	19	1.8–170	0.1–1.3	1.3	100	94
Σ_3HCHs	64±59	46	9–311				>36
p,p'-DDE	21±47	6	0.8[1)]–281	0.06–2	1.6	74	>177
p,p'-DDD	0.5±1.1	0.2	0.03[1)]–10	0.004[2)]–0.07	0.06	79	>169
o,p'-DDT	5±7	2	0.14[1)]–39	0.001[2)]–0.3[4)]	0.3	87	>143
p,p'-DDT	6±9	2	0.1[1)]–46	0.001[2)]–0.2	0.2	86	>240
Σ_4DDTs	32±62	11	1.1–356				>312
Fluorene	1.7±1.8	1.0	0.06[1)]–9.7	0.01[2)]–0.1	0.1	98	>83
Phenanthrene	3±3	2	0.07[1)]–20	0.01[2)]–0.1	0.1	95	>147
Anthracene	0.07±0.1	0.03	0.003[1)]–0.9	0.007[3)]	0.007	88	>130
Fluoranthene	0.7±0.8	0.4	0.02[1)]–3.5	0.01[2)]–0.03	0.03	95	>117
Pyrene	0.4±0.4	0.2	0.01[1)]–2.4	0.01[2)]–0.02	0.02	99	>153
Benz[a]anthracene	0.02±0.03	0.01	0.002[1)]–0.2	0.004[3)]	0.004	68	>49
Chrysene	0.07±0.07	0.04	0.002[1)]–0.3	0.005[3)]	0.004	95	>58
Benzo[a]pyrene	0.008±0.01	0.002	0.002[1)]-0.06	0.005[3)]	0.004	43	>15
Σ_8PAH	6±6	4	0.2–35				>205
HCB	49±18	45	23–115	0.2–3	3	100	5
trans-Chlordane	0.8±1.1	0.4	0.03[1)]–7.3	0.003[5)]–0.1	0.07	95	>104
cis-Chlordane	1.2±0.7	1.2	0.05[1)]–4.6	0.006[5)]–0.1	0.1	98	>46
trans-Nonachlor	1.3±1.0	1.2	0.05[1)]–7.0	0.002[5)]–0.08	0.1	98	>77
cis-Nonachlor	0.16±0.1	0.15	0.02[1)]–0.5	0.001[5)]–0.04	0.05	87	>11
$\sum$chlordanes	3.5±2.7	3.2	0.2–19.4				>114

[1)] 1/2 of the MDL value.
[2)] The lower limit is 1/2 of the IDL (instrument detection limit).
[3)] The component were not detected in the blanks.
[4)] Interference in one of the blanks.
[5)] Lower and upper concentrations in the blanks were below IDL.

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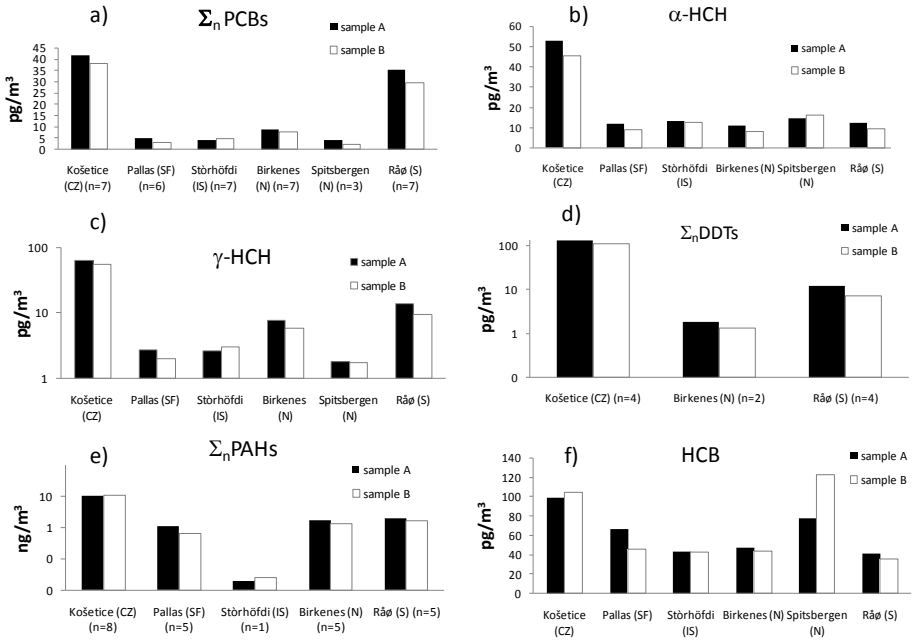

Fig. 1. Comparison of selected PAS results for two parallels at six EMEP sites. Note that results for γ-HCH **(c)**, DDTs **(d)** and PAHs **(e)** are expressed on a logarithmic scale due to large variability across sites. Secondly, the sum of PCBs, DDTs and PAHs only includes those substances (n) for which both samples at a given site were found to be above MDL.

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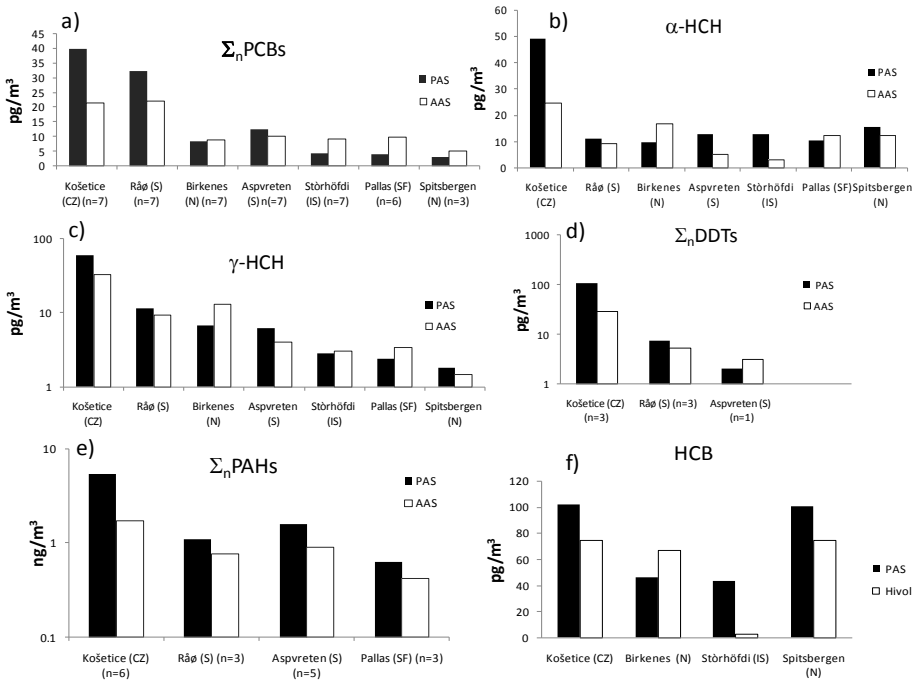

Fig. 2. Comparison of results obtained on the basis of PAS (average of two parallels) and AAS.

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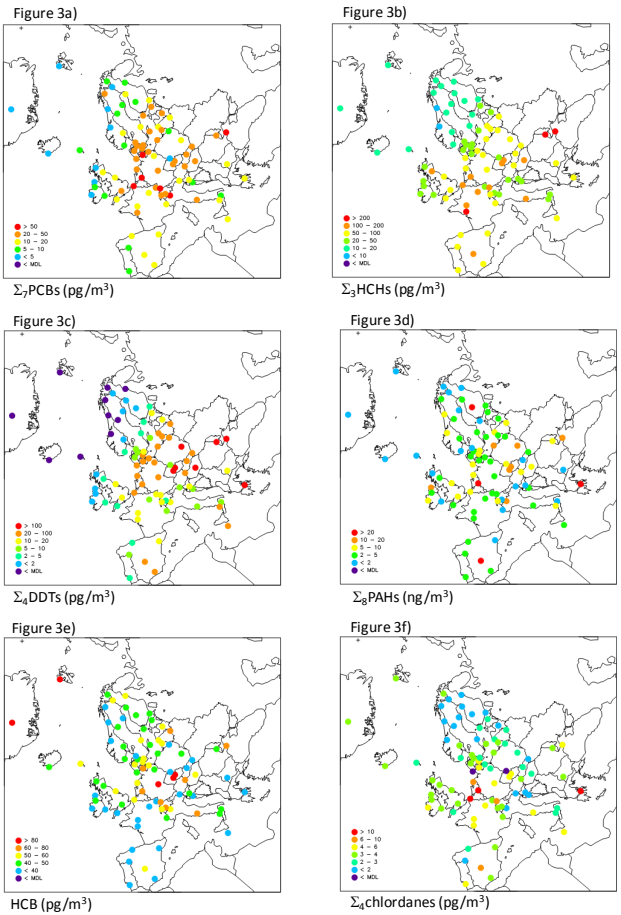

Fig. 3. Spatial patterns of Σ_7PCBs, Σ_3HCHs, Σ_4DDTs, Σ_8PAHs, HCB and $\Sigma_4$chlordanes in European background air.

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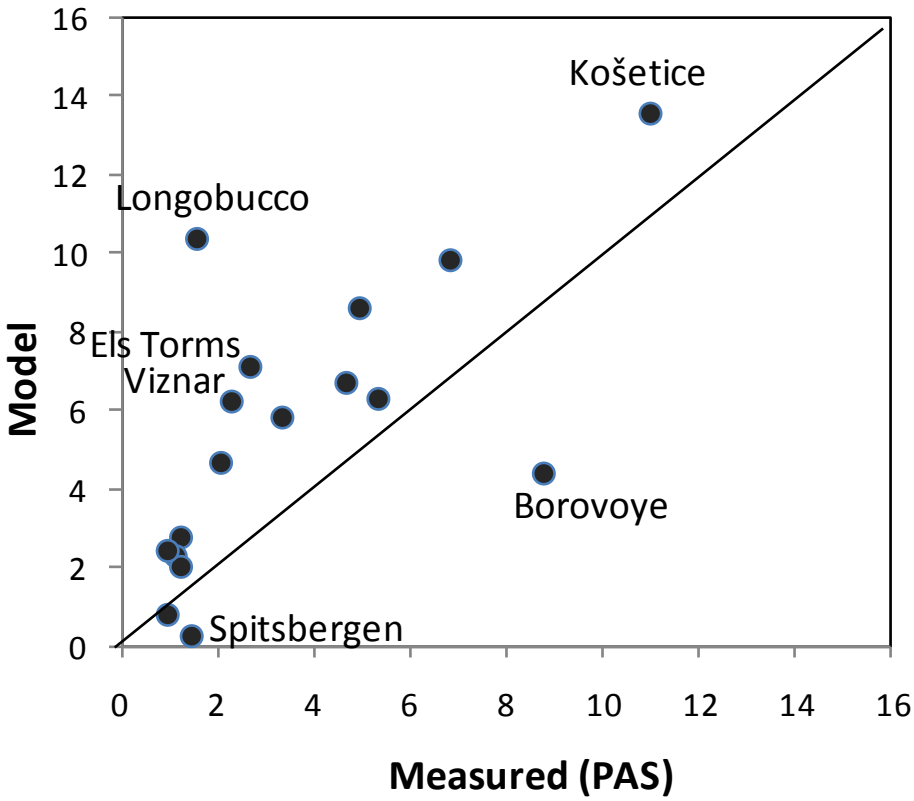

Fig. 4. Predicted versus observed (PAS) air concentrations for PCB-28 at selected sites (in pg/m^3).

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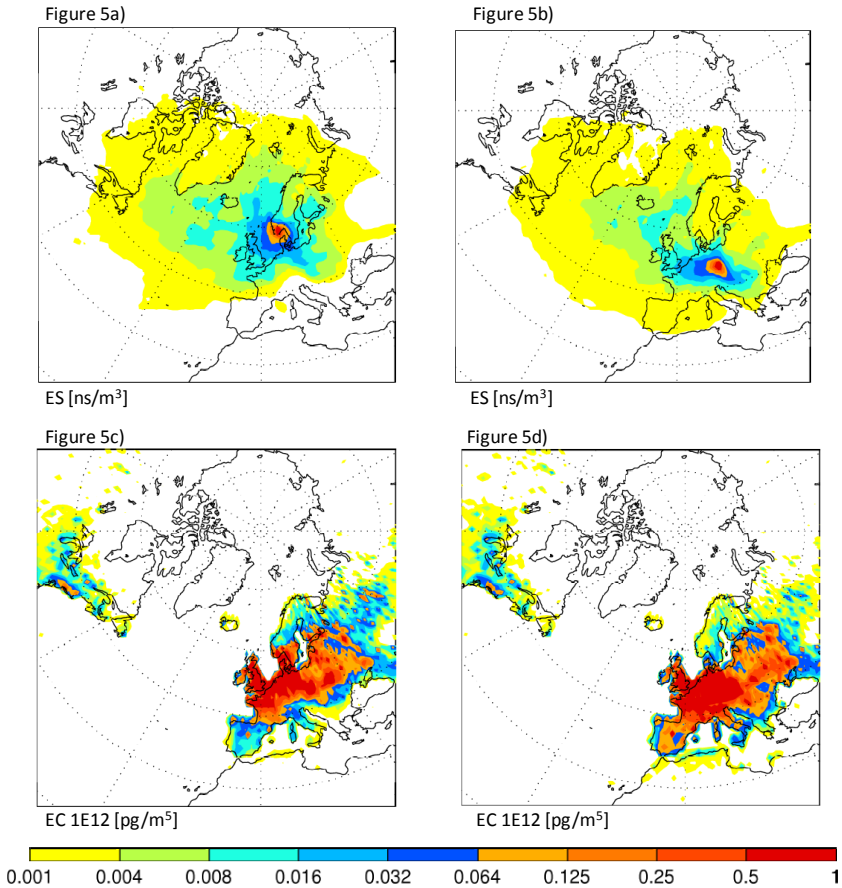

Fig. 5. Footprint ES (emission sensitivity) maps [ns/m^3] **(a,b)** and EC (emission contribution) maps [pg/m^5] **(c,d)** for PCB-28 averaged over calculations for the sampling period (July–October) for Birkenes and Košetice, respectively.

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