PAHs and nitrated PAHs in air of five European countries determined using SPMDs as passive samplers

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Abstract

The gas phase polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs in the atmosphere of five European countries (Austria, the Czech Republic, Poland, Slovakia and Sweden) were measured simultaneously during two 21-day passive sampling campaigns using semipermeable membrane devices (SPMDs). SPMD samplers, consisting of a pair of SPMDs covered by a metal umbrella, were deployed at 40 locations ranging from remote and rural to urban and industrial, at a similar time during each of the two sampling campaigns (autumn 1999, except in Poland, winter 1999, and summer 2000). The total amounts of PAHs and nitro-PAHs found in the SPMDs ranged between 5.0–1.2×10^3 and 1.1×10^{-3}–4.0 ng SPMD^{-1} day^{-1}, respectively. The measured environmental sampling conditions were similar between sites and, thus, the variations in the SPMD data reflected the spatial differences in gas phase concentrations of nitro-PAHs and PAHs within and between countries. The gas phase concentrations of nitro-PAHs and PAHs found in East Europe (Slovakia, the Czech Republic and Poland 1999) were 10 times higher than those measured in Sweden, Austria and Poland in 2000. In each country, the levels of PAHs and nitro-PAHs differed by one–three orders of magnitudes amongst sampling sites. The highest within-country spatial differences were found in Poland where levels of PAHs and nitro-PAHs were about one and two orders of magnitudes, respectively, higher in winter 1999 than in summer 2000, probably due to increasing emissions of coal combustion for residential heating. Differences in PAH-patterns between sites were visualized by the multivariate projection method, principal component analysis (PCA). However, no specific source patterns were found, probably since imissions rather than emissions were measured, so the PAHs detected at many sites originated from multiple sources.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic, moderately to highly lipophilic pollutants that are widely distributed in the environment. They are present in the atmosphere due to emissions from gasoline- and diesel-powered vehicles, municipal and commercial incinerators, residential heating systems that combust fuels such as coal, wood, gas and oil, various industrial processes and volatilization from polluted grounds. The main concern of PAHs is that some PAHs are reported to have carcinogenic properties that are associated with increasing size of the molecule (species with compounds of four or more benzene rings being especially carcinogenic) and their metabolic transformation to reactive dihydrodiol epoxides. Nitrated PAHs (nitro-PAHs) were first detected in atmospheric particulate matter in the 1970s (Pitts et al., 1978). The main concerns regarding these compounds are that many of them are reported to have direct mutagenic activity and carcinogenicity (Durant et al., 1996; Tokiwa et al., 1994). Nitro-PAHs are present in the atmosphere, originating from both primary sources, such as emissions in diesel vehicle exhaust (Bamford et al., 2003; Nielsen, 1984), and reactions of the parent PAHs in the atmosphere. Gas phase reactions of the parent PAHs are initiated by hydroxyl (OH) radicals during the day and by nitrate (NO_3) radicals (in the presence of NO_x) during the night (Arey et al., 1986; Atkinson et al., 1987; Atkinson and Arey, 1994; Nielsen, 1984). Parent PAHs associated with aerosols react with N_2O_5 or HNO_3 to produce nitro-PAHs (Kamens et al., 1990; Nielsen, 1983). Different nitro-PAH isomers are formed in the gas phase reactions (radical-initiated reactions) than those formed via particle phase reactions or emitted from primary sources (electrophilic nitration) (Atkinson et al., 1987; Atkinson and Arey, 1994; Feilberg et al., 1999, 2001; Gupta et al., 1996; Nielsen, 1983, 1984). Feilberg et al. (1999) analyzed diesel exhaust for the two nitronaphthalenes 1-nitronaphthalene (1-NN) and 2-nitronaphthalene (2-NN) and found only 1-NN in it, whereas Atkinson et al. (1987) found that gas phase reactions between naphthalene initiated by OH radicals produced 1-NN and 2-NN in nearly equal abundance. Concentration ratios can therefore be used to assess whether direct emissions or gas phase reactions have produced atmospheric nitro-PAHs (Bamford and Baker, 2003; Feilberg et al., 2001). In the atmosphere, both PAHs and nitro-PAHs display a wide range of gas–particle partitioning characteristics. PAHs with two or three rings, which have relatively low $\log K_{OA}$ values, are mainly associated with the vapor phase, 4-ring PAHs occur in both the gas and particle phases, whereas PAHs with five rings or more, which have high $\log K_{OA}$ values, are mostly bound to particles. Dimashki et al. (2000) measured nitro-PAHs in the atmosphere of

two cities and detected 2-ring nitronaphthalenes only in the vapor phase, the 3-ring nitro-PAH 9-nitroanthracene (9-NA) in both the gas and particle phases, whereas nitro-PAHs with four benzene rings or more (1-nitropyrene (1-NP), 2-nitrofluoranthene (2-NF) and 7-nitrobenz[*a*]anthracene (7-NBa)) were mainly bound to particles. Further, Feilberg et al. (1999) studied the gas–particle partitioning of 2-ring nitro-PAHs in a chamber and found that these compounds partition mainly to the gas phase. Nitro-PAHs appear to have lower vapor pressure than PAHs with corresponding numbers of benzene rings in their molecular structure since the 2-ring nitro-PAHs 1-NN and 2-NN elute between the 3-ring PAHs fluorene and phenanthrene from a DB-5 gas chromatographic column (J&W).

When measuring the atmospheric distribution of organic pollutants such as PAHs and nitro-PAHs at multiple sites on a global scale, passive air samplers are preferred to conventional active air samplers since they do not require electricity or maintenance and are less expensive. Passive air samplers can also be exposed for a long period of time and time-weighted average (TWA) concentrations can be determined. Many studies have used plant samples, e.g. bark (Simonich and Hites, 1995), lichen or pine needles (Kylin and Sjodin, 2003; Hellström et al., 2004; Ockenden et al., 1998b; Tremolada et al., 1996), to monitor ambient air concentrations of organic pollutants on a large scale, assuming that their spatial pollution distribution in the plants and the atmosphere will be closely related. However, the concentration capacity and sampling rate of plant tissues vary with the plant species and age, location and season. Therefore, these kinds of plant data are subject to several uncertainties, which complicate their interpretation and limit the potential of plants as monitoring tools. For this reason, man-made passive air samplers are preferred, despite their additional costs and that they have to be deployed, since the variability of samplers at different locations is low, and the sampling period can be controlled. In 2004, for instance, Jaward et al. (2004a, b) used man-made passive samplers to simultaneously monitor the atmospheric distribution of PAHs, polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), and organochlorine pesticides across Europe in a defined time period.

Semipermeable membrane devices (SPMDs) are passive samplers that have been used in spatial surveys of the atmospheric gas phase concentrations of organic pollutants by, for instance, Lohmann et al. (2001) and Meijer et al. (2003). The SPMD sampling rate (R_S) is affected by the physicochemical properties of the compound sampled. Furthermore, Söderström and Bergqvist (2004) found that high wind speeds/turbulences affect the amounts sequestered by the SPMDs. Chemicals bound to particles or aerosols can be trapped

on the membrane surfaces and thereby also influence the amount sequestered by the SPMD (Lohmann et al., 2001; Bartkow et al., 2004). In addition, Huckins et al. (1999) reported that in water, the R_S values of PAHs increased slightly when the temperature increased from 10 to 26 °C. Thus, the water temperature has a limited effect on the R_S values of PAHs, and we assumed that intermediate/warm temperature affects the R_S in air in a similar way as in water. Increasing temperature can also increase the gas phase partitioning of PAHs and nitro-PAHs that occur both in the gas and particle phases. In contrast to the R_S and the gas–particle partition coefficient, the gas phase concentrations, and thus, the amounts taken up by the SPMDs, can vary with temperature in complex ways since PAH-emission and source parameters can also change with ambient temperature, e.g. heating during colder periods. The sunlight exposure is another factor that should be considered during sampling because degradation of UV-sensitive compounds such as PAHs and nitro-PAHs can occur in the SPMDs (Orazio et al., 2002). In air, both the temporal and geographical variations over time in temperature, UV-radiation and wind speed/turbulence can be high. Particularly, the ambient temperature can vary significantly during the course of a day and between days. The site effects of particle deposition, UV-radiation and wind speed/turbulence can be reduced by covering the SPMDs with protective devices. Ockenden et al. (2001) and Söderström and Bergqvist (2004) demonstrated a reduction in wind speed by protecting the SPMDs with metal devices.

In the study reported here, SPMDs were used in two simultaneous 21-day passive sampling campaigns of the gas phase PAHs and nitro-PAHs in the air of five European countries (Austria, the Czech Republic, Poland, Slovakia and Sweden) with two main objectives. The first was to determine whether there were spatial differences in the concentrations of gas phase PAHs and nitro-PAHs within and between the countries and the second was to discern, if possible, the PAH-patterns of potential sources. The multivariate projection method principal component analysis (PCA) was used to visualize both the spatial differences in atmospheric PAH-levels and to identify PAH-patterns of potential sources (Jackson, 1991).

2. Experimental

2.1. Air sampling

Prior to the air sampling campaign, participating research groups discussed the air sampling protocols. In addition, each group received written sampling instructions and equipment for eight samplers from the Environmental Chemistry, Umeå University, Sweden.

A standard SPMD, used for sampling, consisted of a 91.4 cm long, 2.5 cm wide and 75–90 μm thick (wall thickness) layflat tube of low-density polyethylene (pore size ∼10 Å) filled with 1 mL (0.915 g) of >95% pure triolein (a neutral lipid). Each sampler included two standard 1 mL-triolein SPMDs (obtained from Expose-Meter AB, Trehörningen, Sweden) deployed on separate aluminum spiders, which were horizontally positioned on top of each other inside a metal umbrella. The SPMDs were transported and stored in sealed, solvent-cleaned tin cans at −18 °C, and were placed on the spiders at the sampling location. The metal umbrella was used to reduce the site effects of environmental conditions, e.g. to eliminate direct, and reduce indirect, exposure to particle deposition, sunlight and wind speed. For more detailed description of the sampler design, see Söderström and Bergqvist (2004). Air sampling was performed in each of the countries except Poland during two 3-week periods, one in the autumn of 1999 and the other in the summer of 2000. In Poland, 4-week samples were taken (at different locations) in the winter of 1999 and the summer of 2000. The SPMDs were deployed for 3–4 weeks to obtain linear uptake of most of the compounds in the SPMDs and thereby time-integrative sampling. However, the uptake of some of the most volatile PAHs, such as naphthalene, was in the curvilinear phase at the end of the sampling period and the calculated levels (ng SPMD^{-1} day^{-1}) of naphthalene were underestimates. In addition, time-integrative sampling of these compounds did not occur throughout the sampling. The average sampling temperature of each location was measured in parallel and other environmental conditions such as wind speed and wind direction were measured, if possible (Table 1). After each sampling period in each country the samplers were retrieved, the air-exposed SPMDs were placed in separate solvent-cleaned tin cans and stored at −18 °C until analysis.

2.2. Sampling locations

Five European countries (Austria, the Czech Republic, Poland, Slovakia and Sweden) were included in this air sampling campaign. In total, air sampling was performed at 40 locations; eight sites per country, at similar periods of time in two different seasons (Fig. 1). The eight sampling locations, ranging from remote to urban, were chosen by participating research group from each country, with guidance, to cover a wide range of pollutant situations. The degree of air pollution varied between countries and the definitions of remote, rural and urban areas for each country were somewhat subjective. However, within each country the sampling locations were highly diverse, ranging from forest to industrial areas. In addition, the research group from each country was recommended to choose

Table 1
Description of the pollutant and environmental situations of the sampling locations in Sweden (SE), Austria (AU), the Czech Republic (CZ), Poland (PL) and Slovakia (SK) in 1999 and 2000

Site	Pollutant situation	Date[a]	(°C)[b]	(ms^{-1})[c]
SE1	Urban area with aluminum industry	0919–1011, 0608–0630	8.7/14.1	–/2.6
SE2	Semi-rural area with metal industries	0918–1008, 0609–0703	7.1/13.4	–/2.9
SE3	Urban area with traffic	0922–1013, 0626–0719	6.5/16.7	–/–
SE4	Urban area with pulp mill	0918–1008, 0609–0703	7.6/13.5	2.5/3.4
SE5	Semi-rural area with agriculture/aluminum industry/traffic	0919–1011, 0608–0630	8.7/14.1	–/2.6
SE6	Rural area with agriculture/pulp-mill/traffic	0918–1010, 0612–0703	7.6/13.6	2.5/3.4
SE7	Rural area with agriculture	0923–1015, 0629–0719	5.9/15.9	–/–
SE8	Remote area with forested region	0916–1011, 0626–0719	6.0/–	4.2/–
AU1	Urban area with high traffic	0921–1012, 0626–0717	14.8/18.6	–/1.0
AU2	Urban area with cement industry	0921–1012, 0626–0717	13.7/17.5	0.8/0.9
AU3	Urban area with steel industry	0921–1012, 0626–0717	12.2/16.0	0.45/0.5
AU4	Urban area with steel/chemical industry	0923–1014, 0623–0714	14.4/18.2	1.5/1.6
AU5	Rural area with agriculture	0923–1014, 0623–0714	9.8/12.7	2.4/2.9
AU6	Rural area with agriculture	0922–1013, 0621–0712	14.9/18.8	–/–
AU7	Rural area with agriculture	0922–1013, 0621–0712	14.5/19.8	3.8/3.8
AU8	Remote area with forested/mountain region	0921–1012, 0626–0717	9.6/12.3	1.3/1.4
CZ1	Urban area with the industry DEZA plant/tar products/local combustion	1007–1028, 0628–0718	7.2/15	1.8/2.4
CZ2	Urban area with steel works/coal mining/traffic	1001–1021, 0630–0720	7.4/17.2	–/3.0
CZ3	Urban area with heavy traffic	1005–1026, 0707–0728	8.5/16.9	2.3/3.9
CZ4	Urban area with local combustion/traffic	1013–1104, 0703–0724	9.7/18.2	0.5/0.8
CZ5	Rural area with intensive agriculture/local combustion/traffic	1001–1021, 0630–0720	8.8/17.8	3.4/1.7
CZ6	Urban area with intensive agriculture/local combustion/traffic/chemical industry	1006–1027, 0703–0724	8.8/18.4	–/3.6
CZ7	Rural area with forested region/agriculture (1/2)	1013–1104, 0607–0727	9.4/17.8	–/–
CZ8	Remote area with forested region/agriculture (2/1)	1005–1026, 0703–0724	8.1/16.5	0.5/2.2
SK1	Semi-rural area with non-ferrous industry	1006–1027, 0619–0709	6.3/14.8	–/–
SK2	Semi-rural area with coal power plant	1006–1027, 0619–0709	9.8/21.0	–/–
SK3	Urban area with iron industry	1007–1028, 0620–0710	8.6/21.3	–/–
SK4	Urban area with traffic/petrochemical industry	1008–1029, 0626–0716	10.2/19.0	–/
SK5	Urban area with petrochemical industry and agriculture	1007–1028, 0622–0712	10.1/19.8	–/–
SK6	Rural area with traffic and agriculture	1006–1027, 0619–0709	7.7/17.1	–/
SK7	Rural area with agriculture	1007–1028, 0620–0710	9.0/19.9	–/–
SK8	Remote area with forested region	1006–1027, 0619–0709	4.7/14.2	–/–
PL1	Urban area with traffic and residential coal heating (W)/rural area (S)	1118–1216, 0731–0828	0.7/17	0.8/0.9
PL2	Urban area with traffic and residential coal heating (W)/urban area with high traffic (S)	1118–1216, 0731–0827	0.7/17	1.1/1.7
PL3	Urban area with traffic and residential coal heating (W)/rural area (S)	1118–1216, 0731–0827	0.7/15	1.0/1.9
PL4	Urban area with traffic and residential coal heating (W)/rural area (S)	1118–1216, 0731–0828	0.7/17	2.1/1.1
PL5	Urban area with traffic and residential coal heating (W)/rural area (S)	1118–1216, 0731–0828	0.7/17	2.2/0.9
PL6	Urban area with traffic and residential coal heating (W)/urban area with traffic (S)	1118–1216, 0731–0828	0.7/17	1.8/0.6
PL7	Urban area with traffic and residential coal heating (W)/urban area with high traffic (S)	1118–1216, 0731–0828	0.7/17	1.6/1.1
PL8	Urban area with traffic and residential coal heating (W)/rural area (S)	1118–1216, 0731–0827	0.7/15	2.1/0.9

Note that the sampling sites in Poland differed in 1999 (W) and 2000 (S).

[a]Sampling period.

[b]Average air temperature (°C).
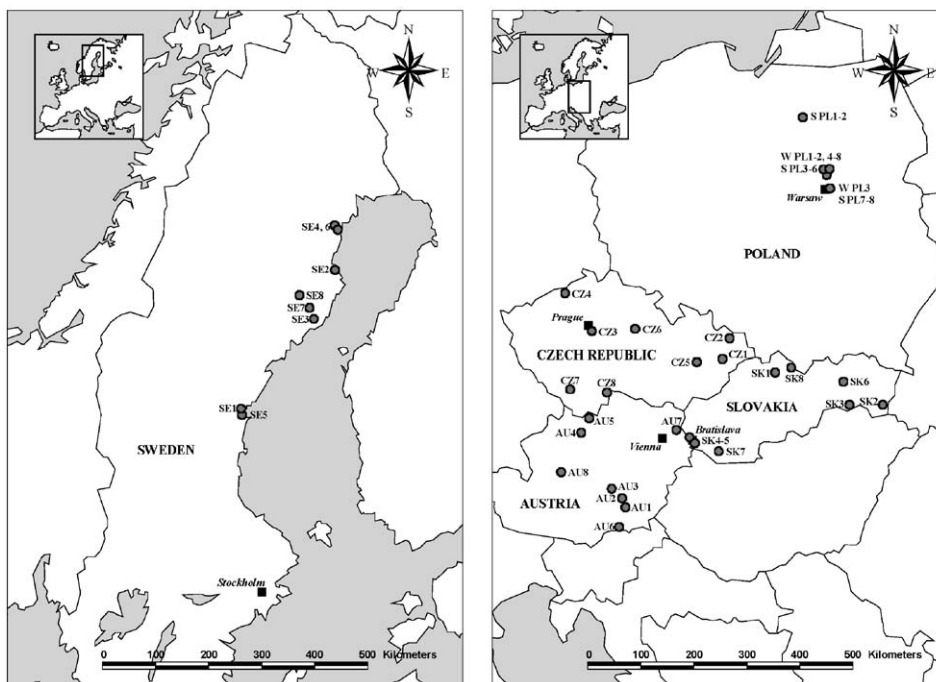
[c]Average wind speed (ms^{-1}) in 1999 and 2000.

Fig. 1. Locations of the sampling sites in Sweden (SE), Austria (AU), the Czech Republic (CZ), Slovakia (SK) and Poland (W-PL and S-PL).

sampling locations in the vicinity and upwind of at least three different potential sources of PAHs. Generally, the measurements were performed about 1 km from the point source and thus, the imissions (viz. the ambient air concentrations in the area) rather than the emissions of the point sources were determined. The pollution situation and the environmental sampling conditions of each sampling location were described in detail by each country's research group (Table 1). In Poland, some of the sampling locations in 1999 and 2000 differed, but they were all located in a rather restricted area (Fig. 1). The average air temperatures were higher during summer 2000 than during autumn 1999 (16 vs. 7 °C). Hence, the temperature differences could have some influence on the results. The temperature differences between sites measured during each sampling campaign were generally small, suggesting that the air temperature had little influence on the results of each sampling campaign (Table 1). However, during the sampling in 1999, the average temperatures in Poland were considerably low (0.7 °C) and the average temperatures in Austria were high (13 °C) compared to the average temperature (7 °C) among countries.

2.3. Extraction, clean-up and analysis

The SPMD samples obtained from Austria, Poland and Sweden were analyzed by the Environmental Chemistry, Umeå University, Sweden, whereas the Department of Food Chemistry and Analysis, Prague Institute of Chemical Technology, Czech Republic, analyzed the SPMD samples obtained from the Czech Republic and Slovakia. The protocol used for the chemical analysis of SPMD samples at the Department of Food Chemistry and Analysis of the Prague Institute of Chemical Technology has been described by Setkova et al. (2004). In brief, the extraction, clean-up and analysis used at the Environmental Chemistry, Umeå University was as follows. SPMDs were mechanically washed in water, hexane and hydrochloride acid (1 M) to remove particles from the membrane surface. Organic contaminants were extracted from the SPMDs by dialysis of the two SPMDs from each site together in 100 mL of 95:5 (v:v) cyclopentane:dichloromethane for 24 h followed by dialysis for another 24 h in a fresh 180-mL batch of the same solvent mixture. The dialysates were pooled, and thereafter six deuterated PAHs (naphthalene, fluorene, anthracene, pyrene, chrysene and benzo(k)fluoranthene, all from Promochem, Kungsbacka, Sweden) and two deuterated nitro-PAHs (1-NP and 6-nitrochrysene from Larodan AB, Malmö, Sweden) were added as internal standards of the clean-up, and the pooled extracts were rotary evaporated to a volume of approximately 0.5 mL. The spiked extracts were cleaned on a high-resolution gel permeation chromatographic (GPC) column followed by further

clean-up on a mixed silica gel column with deactivated silica and potassium silicate. The volume of the samples was reduced to 100 μL by rotary evaporation followed by a gentle stream of nitrogen gas, ^{2}H-labeled dibenzofuran and ^{13}C-labeled PCB♯157 were added as recovery standards and the samples were transferred to GC/MS-vials. During and after the clean-up, samples were covered with aluminum foil and stored in the dark at −18 °C. Each sample was analyzed for 15 of EPA PAHs (excluding acenaphthylene), and the six nitro-PAHs 1-NN, 2-NN, 2-nitrofluorene (2-NF), 9-NA, 3-nitrofluoranthene (3-NF), and 1-NP. However, interferences in the GC/MS analysis of fluoranthene and pyrene were detected in a number of samples. Thus, to limit the analytical cost, the analytical method was not further developed, and instead, these compounds were excluded from the analysis of both sampling campaigns. In addition, in 2000, all SPMDs were spiked with native fluorene, so this compound was not analyzed in these samples. The SPMD samples were analyzed for PAHs by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS) operated in electron ionization mode monitoring selected ions. For details on the quality of the chemicals, their sources, and the analytical method used at the Environmental Chemistry, Umeå University, Sweden, see Söderström and Bergqvist, (2003). All SPMD samples were analyzed for the nitro-PAHs by HRGC/LRMS operated in negative ion chemical ionization mode, monitoring selected ions, at the Department of Food Chemistry and Analysis, Prague Institute of Chemical Technology, using an analytical method described in detail elsewhere (Dusek et al., 2002).

2.4. Quality control/quality assurance

The respective clean-up protocols used by the Environmental Chemistry, Umeå University and the Department of Food Chemistry and Analysis, Prague Institute of Chemical Technology, were compared. The inter-calibration study showed differences of less than 10% in the amounts found in replicate SPMD samples (Bergqvist, 2004).

Laboratory blanks (LBs) and field controls (FCs), respectively, consisting of solvent and SPMDs exposed to air during the deployment and retrieval of the samples, were analyzed in the same way as described above. In each country, one SPMD per sampling period was used as a FC. The amounts of nitro-PAHs found in the LBs and FBs analyzed by the Environmental Chemistry, Umeå University, were 2% and 5% on average, respectively, of the amounts found in the samples. The PAH amounts found in the LBs and FCs (excluding the Swedish FC in 1999, due to problems with contamination, principally of benzo[a]anthracene) were 2% and 15% on average, respectively, of the amounts found in the samples. Thus, contamination of

nitro-PAHs and PAHs introduced in the sampling and analysis procedures had limited effects on the results (and no correction was made for it). The reported data were corrected for recovery values.

2.5. SPMD data calculations

To allow quantitative data interpretation (converting amounts sequestered by the SPMDs to air concentrations) the relevant R_S or SPMD-air partition coefficient, K_{SA}, has to be known. To our knowledge, available calibration data for SPMDs in air are limited to field-calibrated R_S values for PCBs reported by Ockenden et al. (1998a, 2001) and Shoeib and Harner (2002). In the absence of calibration data, SPMD air data have mostly been interpreted by comparing differences in sequestered amounts and profiles. This semi-quantitative approach was adopted here, and the data were expressed in $ng\,SPMD^{-1}\,day^{-1}$. The site effects of environmental factors such as UV radiation and wind speeds/turbulence were assumed to be similar since protective sampling devices were used.

2.6. Principal component analysis (PCA)

PCA is a method used to project the variations in a multivariate data matrix X with n rows (objects) and k columns (variables) into a few uncorrelated (orthogonal) principal components (PCs) (Jackson, 1991). Basically, the systematic variation of the X matrix is extracted into the smaller matrices, the score T and the loading P' matrices. The first PC is oriented to explain as much variation in the data as possible and presents the best linear summary of X. The second PC is orthogonal to the first, and explains the next largest variation in the data, and so forth. The PCs of the T matrix can be plotted in two-dimensional space to produce score plots. In a score plot, the relationship between objects is visualized, hence, two objects close to each other in the score plot are similar and vice versa. The loading plots of the P' matrix are produced in the same way and visualize how the variables are related to each other. Comparing the score and loading plots reveals the relationship between the objects and the variables, e.g. which individual PAHs are present in high or low concentrations at the sampling sites positioned in different parts of the score plot.

In this study, two PCA calculations were performed on the data set, which consisted of 10 columns (variables) and 79 rows (objects) with the unit $ng\,SPMD^{-1}\,day^{-1}$. The object AU2-99 and the two variables dibenz[a,h]anthracene and fluorene were excluded from the two models since more than 50% of the corresponding values in the data set were missing. Furthermore, the two variables benzo[b]fluoranthene

and benzo[*k*]fluoranthene were analyzed together, since they co-eluted in the GC/MS-analysis. The variables (the individual PAH concentrations in the data matrix) showed a positive skewness for the objects (sampling sites) when plotted in a histogram. The data were therefore log-transformed to obtain an approximately normal distribution. The number of significant PCs in the PCA was determined by cross-validation (Wold, 1978). The first PCA calculation aimed to visualize the spatial differences in atmospheric PAH-levels between countries and all variables were mean-centered and scaled to unit variance. In the second calculation, the aim was to visualize the PAH patterns of different potential sources. Data were therefore mean-centered and normalized to the total PAH amount sampled at each sampling location, to avoid the results being affected by the spatial differences in PAH concentrations. The Soft Independent Modelling of Class Analogy (SIMCA) software package SIMCA-P 9.0 obtained from Umetrics Inc., Umeå, Sweden, was used to perform the PCA calculations.

3. Results and discussion

3.1. PAH-levels, -patterns and -profiles in SPMDs

The total amounts of 13 EPA PAHs (1999) and 12 EPA PAHs (2000) sequestered by the SPMDs ranged between $6.3-1.2 \times 10^3$ and $5.0-1.0 \times 10^3$ ng SPMD^{-1} day^{-1}, respectively (Fig. 2). The PAH-profiles in the SPMDs dominated by 3-ring PAHs followed by 4-ring PAHs, showing that SPMDs mainly sampled PAHs associated with the gas phase, as expected (Fig. 2). In the PAH-patterns, phenanthrene was the most abundant individual PAH, with amounts found in the SPMDs ranging from 3.1 to 9.0×10^2 ng SPMD^{-1} day^{-1}. These SPMD air data are in a wider range as those reported by Lohmann et al. (2001) who deployed SPMDs at 11 sites in northwest England to measure vapor phase PAHs.

3.2. Nitro-PAH-levels, -patterns and -profiles in SPMDs

The total amounts of the six nitro-PAHs sequestered by the SPMDs in 1999 and 2000 ranged between $3.6 \times 10^{-2}-4.0$ and $1.1 \times 10^{-3}-2.7$ ng SPMD^{-1} day^{-1}, respectively (Fig. 3). Of the six nitro-PAHs analyzed in the SPMDs, the nitro-PAH-profiles were dominated by 2-ring nitro-PAHs. The three nitro-PAHs 1-NN, 2-NN and 2-NF dominated the nitro-PAH-patterns found in the SPMDs. In SPMDs obtained from the Czech Republic and Slovakia 9-NA and 3-NF were also found. 1-NN and 2-NN are nitro-PAHs that mainly occur in the gas phase, whereas 9-NA and 3-NF are mostly bound to particles (Dimashki et al., 2000). Thus, the SPMDs predominantly sequestered gas phase nitro-

PAHs, although particle-associated nitro-PAHs were also sequestered to a lesser extent. To our knowledge, passive sampling of nitro-PAHs using SPMDs has not previously been reported. However, the levels detected in this study were about a tenth of the gas phase concentrations of 1-NN and 2-NN measured with an active high-volume sampler system by Dimashki et al. (2000).

Feilberg et al. (1999) analyzed diesel exhaust for 1-NN and 2-NN and found only 1-NN, whereas Atkinson et al. (1987) found that gas phase reactions between naphthalene initiated by OH radicals produced 1-NN and 2-NN in nearly equal abundance. Thus, the 1-NN to 2-NN concentration ratio can be used to assess whether direct emissions or gas phase reactions produced these nitro-PAHs in the atmosphere. Generally, the ratio between 1-NN and 2-NN found in the SPMDs were close to unity, or between one and two, indicating that these nitro-PAHs mainly originated from formation in the gas phase. However, in the SPMD samples of Austria, Poland and Sweden from the sampling campaign in 1999, the ratios between 1-NN and 2-NN were generally around 0.4. These samples were stored for considerably longer periods than the other samples before being analyzed for nitro-PAHs, and since Feilberg et al. (1999) have reported that photo degradation proceeds more rapidly for 1-NN than for 2-NN, the lower ratios found in these samples could have been caused by higher degradation of 1-NN. These results demonstrate the importance of using corresponding labeled standards for each of the native nitro-PAHs being analyzed to assure the quality of the data.

3.3. Factors affecting R_S values and gas phase concentrations

3.3.1. PAHs and nitro-PAHs

The ranges of PAH-amounts found in the SPMDs from autumn 1999 and summer 2000 were similar, indicated that the imissions of the gas phase PAHs were similar during the two sampling campaigns, except in Poland. The higher amounts of nitro-PAHs found in SPMDs from 1999 than in SPMDs from 2000 indicated that the imissions of gaseous nitro-PAH were higher in 1999. However, the average air temperatures differed somewhat between the 1999 ($7\,^{\circ}$C) and 2000 ($16\,^{\circ}$C) campaigns. These differences had probably no effect on the R_S values of the PAHs and the nitro-PAHs, but could have affected their gas phase concentrations during the two sampling campaigns. The higher temperature in summer 2000 probably increased the gas partitioning of the PAHs with four rings or more, and the nitro-PAHs with three rings or more. Furthermore, the higher temperature in the summer of 2000 could have increased the volatilization of PAHs from polluted soil, and the influence of short-range transport
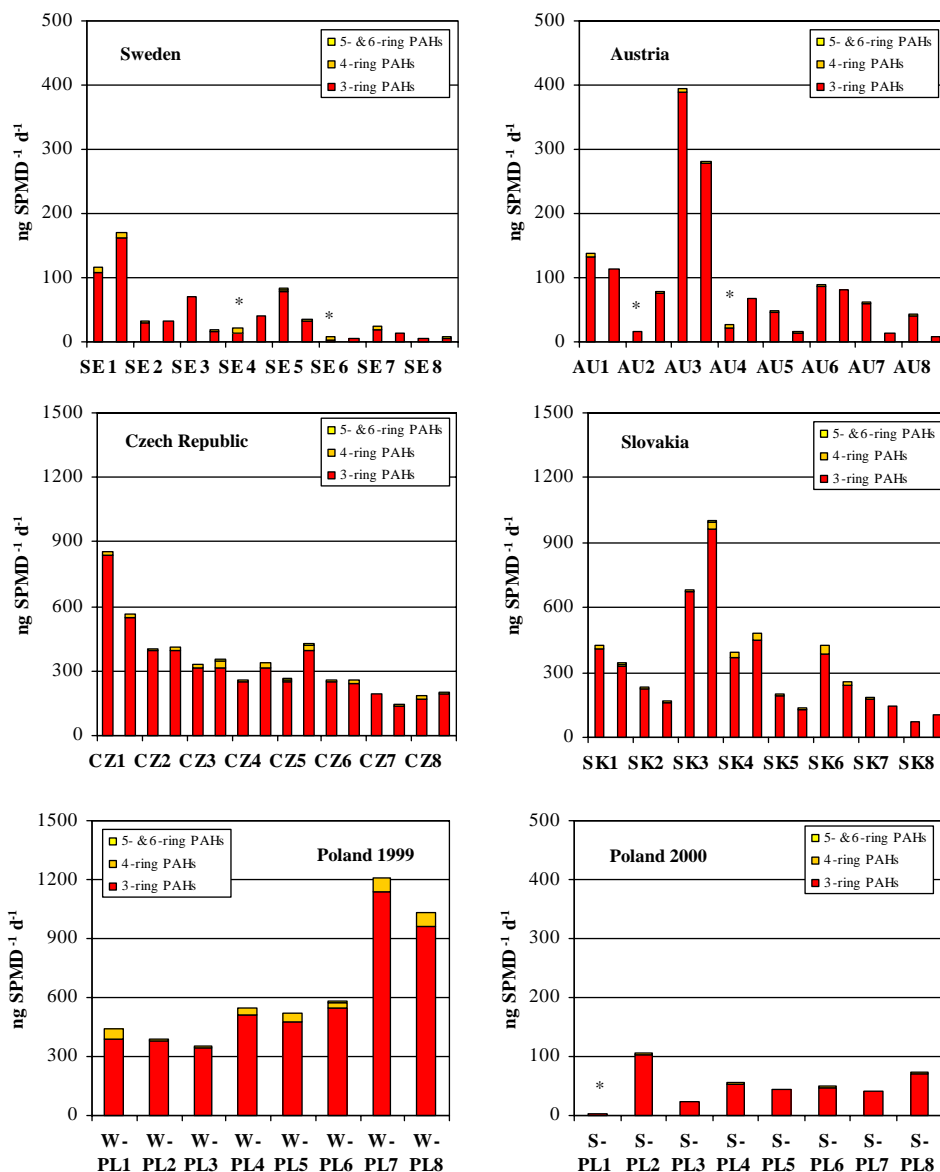
Fig. 2. Amounts (ng SPMD^{-1} day^{-1}) of 3-, 4-, 5- and 6-ring PAHs found in SPMDs exposed to air in the 1999 (left bar) and 2000 (right bar) sampling campaigns in Sweden (SE), Austria (AU), the Czech Republic (CZ) and Slovakia (SK), and in the Polish sampling campaigns in 1999 (W) and 2000 (S). *Phenanthrene not analyzed due to interferences.

of volatile PAHs and nitro-PAHs, as have been suggested for PAHs by Sofuoglu et al. (2001). Therefore, the higher sampling temperature in 2000 could have a slight increasing effect on the gas phase concentrations of PAHs and nitro-PAHs and, hence, the amounts sequestered by the SPMDs. The UV-radiation was probably also higher in summer 2000 than in autumn 1999. However, the SPMDs were protected by metal umbrellas from direct sunlight and, thus, the UV-degradation during sampling was restricted. In conclusion, the differences in nitro-PAH- and

PAH-amounts sequestered by the SPMDs due to site effects of temperature and UV-radiation were probably minor between the two sampling campaigns. Thus, the PAH-imissions were similar in the two sampling campaigns, and the imissions of nitro-PAHs were higher in autumn 1999 than in summer 2000.

3.3.2. Poland

In Poland, the levels of PAHs and nitro-PAHs were one and two magnitudes higher, respectively, in winter 1999 than in summer 2000, indicating that the imissions
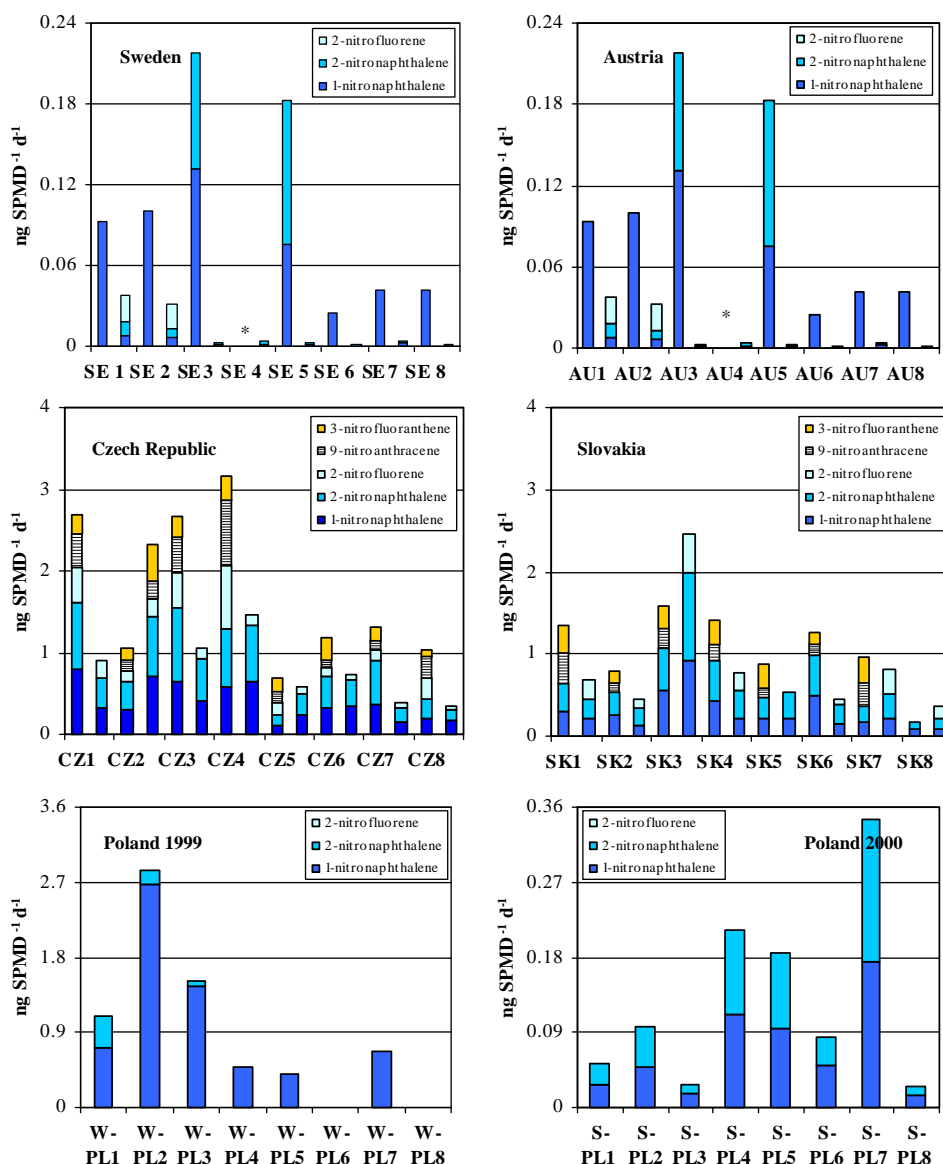
Fig. 3. Amounts (ng SPMD^{-1} day^{-1}) of individual nitro-PAHs found in SPMDs exposed to air in the 1999 (left bar) and 2000 (right bar) sampling campaigns in Sweden (SE), Austria (AU), the Czech Republic (CZ) and Slovakia (SK), and in the 1999 (W) and 2000 (S) sampling campaigns in Poland (PL). *Nitro-naphthalenes not analyzed due to interferences.

were considerably higher during 1999. The average temporal differences could not have been the site effect of temperatures since this would have caused higher PAH- and nitro-PAHs levels in summer 2000. One possible reason to these results is that the emissions and/ or the sources varied with temperature. In Poland, the emissions of nitro-PAHs and PAHs were probably higher in winter 1999 than in summer 2000 because of increasing emissions from coal combustion for residential heating. In addition, Ockenden et al. (1998a) have suggested that the R_S of PCBs can increase at cold temperatures. However, we consider the additional

emissions from coal combustions to be the main reason for the higher levels of PAHs and nitro-PAHs found in SPMDs obtained from winter 1999, and the SPMD data reflected the higher emissions in Poland during the winter of 1999 than in the summer of 2000.

3.4. Spatial variation between countries

The 40 sampling sites, located from northern to central and eastern Europe showed a wide range of gas phase concentrations of PAHs and nitro-PAHs. Comparisons between countries showed that the levels

measured were not always comparable with the subjectively defined pollution situations of the respective sampling locations (compare Table 1 with Figs. 2 and 3). For example, levels measured in the areas of the Czech Republic and Slovakia that were defined as rural were comparable with levels measured in areas of Sweden that were defined as urban. These results were expected since each country defined the pollution situation at each location in relation to the pollution situation of their country rather than in relation to the situations in the other participating countries.

The PAH-levels measured in East Europe (Poland, Slovakia, and the Czech Republic) were about 10 times higher than the lowest measured values found in the areas of northern Europe (Sweden) and more than two times higher than the levels found in central Europe (Austria) (Fig. 2). The most heavily PAH-polluted site found was in Slovakia during summer 2000, where PAH concentrations were two orders of magnitude higher than the lowest measured values in Sweden during summer 2000 (Fig. 2). The measured levels of nitro-PAHs were more than 10 times higher in East Europe than the levels measured in northern (Sweden) and central (Austria) Europe (Fig. 3). The highest measured levels of nitro-PAHs $(2.17 \, \text{ng} \, \text{SPMD}^{-1} \, \text{day}^{-1})$ were found in a site located in the Czech Republic during the sampling campaign in 1999. This area was three orders of magnitude more heavily nitro-PAH polluted than the least polluted area found in Sweden during 2000. Thus, the differences in atmospheric PAH and nitro-PAH concentrations between countries were high, and the continental distribution in nitro-PAHs and PAHs were similar. The spatial variations in both PAH- and nitro-PAH concentrations found in this study are similar to the variations in atmospheric PAH concentrations measured across Europe by Jaward et al. (2004a) using other types of passive samplers than SPMDs.

3.5. Spatial variation within countries

The within-country spatial differences were also high, with about 5–20-fold differences between the lowest and highest PAH-levels and 6–30-fold differences in nitro-PAH-levels. The highest levels were detected at sites defined as urban, while the lowest levels occurred at remote/rural sites. Hence, the variation in PAH- and nitro-PAHs concentrations within each country followed their subjectively defined pollution situations (compare Table 1 with Figs. 2 and 3). The highest within-country spatial variations were found in Poland, where levels of PAHs and nitro-PAHs were one and two orders of magnitude, respectively, higher in winter 1999 than in summer 2000. The high variation in PAH- and nitro-PAH-levels detected between the Polish sampling sites in 1999 and 2000, which were all located in a relatively restricted area, demonstrates the high seasonal variations in the atmospheric PAH- and nitro-PAHs concentrations in this area of Poland. In Austria, the measured PAH-levels were in a similar range to the PAH-levels previously measured in northwest England using SPMDs (Lohmann et al., 2001). Furthermore, the PAH-levels measured in the remote site of the Czech Republic (CZ8) were similar to the maximum levels measured with active volume samplers at background sites in the Czech Republic from 1996 to 1998 (Holoubek et al., 2000). Furthermore, the levels of the two nitro-naphthalenes, 1-NN and 2-NN, measured in this study were lower than the gas phase concentrations measured in a road tunnel in Birmingham, UK, whereas the levels found in the Czech Republic, Slovakia and Poland in 1999 were higher, and the levels in Sweden, Austria and Poland in 2000 were similar to those measured in the city center of Birmingham, UK, with active volume samplers (Dimashki et al., 2000).

3.6. PCA of spatial PAH variations

In order to visualize the spatial differences between the 40 sampling sites located in the five European countries, a PCA model with three significant PCs, explaining 89.2% of the variation in the data, was calculated. The first component (PC1) was mainly influenced by the differences in PAH-levels between sampling locations and explained 74% of the variance, whereas the second (PC2) and third (PC3) components explained 9.6% and 5.6%, respectively, and were influenced by the PAH pattern of each sampling site. A score plot of the first two PCs visualizes the differences in the levels of gas phase PAHs between northern, central and east Europe (Fig. 4a). On the left-hand side of the score plot sampling sites of Sweden and Austria were predominantly found, whereas sampling sites of the Czech Republic and Slovakia were found on the right-hand side of the score plot. The Polish sampling sites were located to the right-hand side of the score plot for summer 2000 and to the left for winter 1999, visualizing the temporal differences in gas phase PAHs between the winter of 1999 and the summer of 2000 (Fig. 4a). The corresponding loading plot revealed that at the sampling sites to the right in the score plot viz. East Europe (the Czech Republic (CZ), Slovakia (SK) and Poland 1999 (PL-W)) the levels of e.g. phenanthrene, chrysene and the total amounts of PAHs found in the SPMDs were higher than the levels of these compounds found in Sweden, Austria and Poland 2000 (PL-S). The corresponding loading plot also shows that at the sampling sites in the upper part of the score plot, the levels of the gas phase PAH acenaphthene were high and the levels of the particle-associated PAH benzo[g,h,i]perylene were low, and vice versa for the sampling sites in the lower part of the score plot.
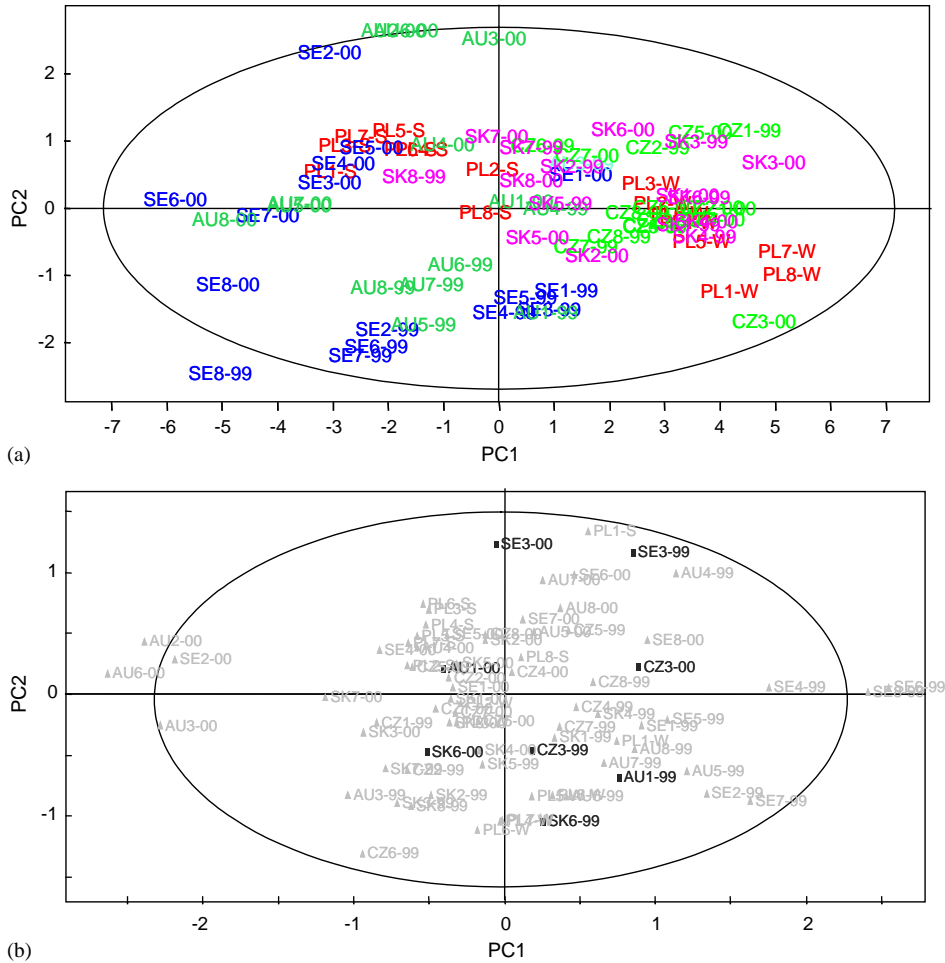
Fig. 4. Score plots of the first two PCs of two PCA models. (a) Visualizing the relationship between the sampling sites in Sweden (SW), Austria (AU), Poland (PL-W and PL-S), Slovakia (SK) and the Czech Republic (CZ) during the 1999 and 2000 sampling campaigns. Each point in the score plot represents the individual and total PAH-amounts found in the SPMDs at respective sites. Hence, sampling sites close to each other have similar atmospheric PAH-levels and vice versa. (b) Visualizes the relationship between the sampling sites in Sweden (SW), Austria (AU), Poland (PL-W and PL-S), Slovakia (SK) and the Czech Republic (CZ) during the 1999 and 2000 sampling campaigns. Each point represents a specific PAH-pattern and sites close to each other have similar PAH-patterns and vice versa. Note that the Polish sampling sites differed in winter 1999 (PL-W) and summer 2000 (PL-S).

3.7. PCA of PAH source patterns

The high spatial differences measured both within and between the five European countries indicate that there were local point sources of both the gas phase nitro-PAHs and PAHs in each country. Furthermore, the high levels at areas defined as rural indicated an influence of both short- and long-range transport of these compounds. According to the site descriptions, sources likely to be responsible for the high PAH- and nitro-PAH-levels detected at urban and industrial sites were traffic, metal, chemical, and petrochemical industries, tar production, coal-fired systems for residential heating and other types of local combustion systems. The site

descriptions also showed that at many sampling locations, the nitro-PAHs and PAHs appeared to be emitted to the atmosphere by a number of confounding sources. The SPMD samplers were located in the vicinity of potential sources, but actual emissions of the sources were not measured at any of the sites.

To visualize the PAH-patterns of each sampling site, and thus attempt to correlate PAH-patterns with specific sources, a PCA model on the data set, normalized to the total amount of PAHs at each respective site, was calculated. The PCA resulted in a model with two significant PCs, which explained 65.7% of the variation in the data, the first (PC1) explaining 43.9% of the variance and the second (PC2) 21.8%. In a score plot of

the two PCs, the differences in PAH-patterns amongst sampling sites were visualized (Fig. 4b). The corresponding loading plot showed that both the first and second PCs were influenced by the levels of acenaphthene, benzo[g,h,i]perylene and benzo[a]anthracene. The sampling sites in the left and upper parts of the score plot had high levels of acenaphthene, sites in the right and upper parts had high levels of benzo[g,h,i]perylene, while those in the right and lower parts had high levels of benzo[a]anthracene. Thus, there were differences in the PAH-patterns of each site. However, no correlation between PAH-patterns and the specific sources was detected. For example, the highlighted sites in the score plot visualize the differences in PAH-patterns of sites described as highly influenced by traffic (Fig. 4b). The reasons for these results are several. Imissions (the ambient air concentrations) rather than emissions were measured in this study and thus, the gas phase PAHs found at many sites originated from multiple sources. Furthermore, it was difficult to control the environmental and pollution situations during sampling, and although the intention was to take measurements upwind of described sources, additional sources could also have influenced the PAH-levels of each site. Finally, volatilization of PAHs from soil could have affected the results since the sampler were deployed at 1.5 m height. Thus, there are many diffusive sources that can affect the atmospheric PAH concentrations which make specific source-patterns of PAHs very difficult to discern.

4. Conclusions

Wide ranges of PAH and nitro-PAH amounts were taken up by the SPMDs in this study. The environmental sampling conditions, such as air temperatures, were generally similar between sampling locations. Consequently, the site effects on the R_S values of the SPMDs were limited. Therefore, variations in the SPMD data reflected the spatial differences in gas phase concentrations of PAHs and nitro-PAHs within and between the five European countries Austria, the Czech Republic, Poland, Slovakia and Sweden. The highest gas phase concentrations of PAHs and nitro-PAHs were measured in East Europe (Poland, Slovakia, and the Czech Republic) where the levels were about 10 times higher than the lowest measured values found in the areas of northern Europe (Sweden) and central (Austria) Europe (the PAH-levels in Austria were only two times lower than those found in East Europe). The highest within-country spatial differences were found in Poland, where measured levels of PAHs and nitro-PAHs were one and two magnitudes higher, respectively, in the winter than in the summer, probably due to additional emissions from residential coal combustion. Further-

more, the high spatial differences found both within and between the five countries, ranging from North to East Europe, demonstrate that SPMDs are suitable for integrative sampling of the atmospheric distribution of POPs at both local and continental scales. This study also demonstrated the user-friendliness, time- and cost-effectiveness of SPMDs since the sampling campaigns were accomplished by sending the SPMDs to the laboratory of each country and the SPMD samplers were set up, deployed and retrieved by the participating research group of each country. The SPMD air data were interpreted by comparing the differences in the sequestered amounts and profiles. If "performance reference compounds (PRCs)" had been used as sampling standards in the sampling protocols, or calibration data for the sampled compounds in air had been available, reliable gas phase concentrations could also have been calculated for each site. Calibration methods and R_S values for PAH, alkyl-PAHs and PCBs in air are currently being developed and determined, respectively, in our laboratory.

The PCA analysis visualized differences in the PAH-patterns between sites. However, no correlation between PAH-patterns and specific sources were found, probably because imission rather than emissions were measured. The chosen sampling strategy probably resulted in multiple sources to be confounded at many sites, which made it difficult to completely describe all sources that influenced the atmospheric PAH-concentrations at each site. Furthermore, the PCA detected no significant differences in PAH-patterns between countries or laboratories, showing that both the sampling and the clean-up protocols of the participating research groups were comparable.

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