POLYCYCLIC AROMATIC HYDROCARBONS AND NITRATED DERIVATES IN AIR OF FIVE EUROPEAN COUNTRIES.

Hanna S. Söderström and Per-Anders Bergqvist

Environmental Chemistry, Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden.

Introduction

In spatial studies, passive samplers are favoured for their low-cost, long-term operation and the fact that they need no electricity. E.g. Kylin et al collected pine needle wax from the central and northern parts of Europe to monitor air concentrations of polychlorinated biphenyls[1]. Semipermeable membrane device (SPMD) is a passive air sampler used to measure gaseous lipophilic organic pollutants[2-4]. Standard SPMDs are 91.4 cm long and 2.5 cm wide tubes of low-density polyethylene (pore size ~10 Å) filled with 1 mL (0.915 g) of > 95 % pure triolein. The membrane controls the uptake resulting in a linear and integrative sampling for several weeks up to years depending on compound sampled. Another advantage of SPMDs is that the samples are reproducible with no variance due to different species or biological variations.

Polycyclic aromatic hydrocarbons (PAHs) are a class of lipophilic organic pollutants that are widely distributed in the environment. Some of them have reported carcinogenic effects. Although PAHs are emitted to the atmosphere from natural combustion, anthropogenic sources are the major emissions of PAHs to the atmosphere. The major anthropogenic sources of PAHs in the atmosphere are traffic emissions from both gasoline and diesel powered vehicles, municipal and commercial incinerations, residential heating such as combustion of coal, wood, gas and oil, and a variety of industrial processes. In the atmosphere PAHs display a wide range of gas-particle partitioning characteristics where PAHs with three or four rings, which have relatively low log K_{oa} values, are mainly associated with the vapor phase[2].

This study used SPMDs to perform a simultaneous integrative sampling of the gas-phase PAHs and nitro-PAHs in the atmosphere of five European countries. The aims of this study were to 1) quantify if there were spatial differences in the gas-phase PAHs and nitro-PAHs within and between countries, and 2) decide the contribution of different sources to gaseous concentrations of PAHs. The multivariate projection method, principal component analysis (PCA) was used to evaluate the results. PCA is a method that visualized the dominating patterns and major trends in a multivariate data matrix X with n rows (observations) and k columns (variables) by project the variations in the data into uncorrelated (orthogonal) principal components (PC)[5]. The first PC presents the best linear summary of X. The second PC is orthogonal to the first, and explains the next largest variations in the data, and so forth. The PCs can be plotted in two-dimensional spaces producing score and loading plots, respectively, visualizing the relation between objectives and variables, respectively. Comparing score plots and loading plots, the relation between observations and variables can be found. This study used PCA to find the trends in detected PAH amounts (variables) and the locations studied (observations), and to decide the relation between gaseous PAHs detected and the exposure situation at each site.

Methods and Materials

Each country received samplers and solvent cleaned tin cans together with sampling instructions from the department of Environmental Chemistry, Umeå University, Sweden. The SPMDs, obtained from ExposMeter AB (Trehörningen, Sweden), were delivered in sealed solvent-cleaned tin cans and stored at -18 °C. During the sampling, each SPMD was mounted between seven steel rods attached to a 150×140 mm steel disc. The steel device holding the SPMD during sampling was called spider. Two SPMDs, mounted on separate spiders, were placed horizontally on top of each other inside a metal umbrella (320 mm diam.). After about 21 days of exposure, all SPMD were retrieved and stored in separate solvent-cleaned tin cans at -18 °C until analyzed. To control the contribution of the sampling procedures to amounts found in the SPMDs, each country received one extra SPMD (referred to as field control) which was exposed to air only during deployment and retrieval.

Simultaneous integrative SPMD sampling was performed for three weeks at eight locations in Sweden (SE), Austria (AU), Czech Republic (CZ), Poland (PL) and Slovakia (SK), respectively (Figure 1). Each country performed sampling during both autumn/winter 1999 and summer 2000, respectively. In Poland, different locations were used during the sampling in winter 1999 (W-PL) and summer 2000 (S-PL), respectively (Figure 1). If possible, the average temperature and wind-speed of each sampling site was measured. The sampling sites ranged from rural to industrial areas, with sampling of the air in the vicinity of minimum three different potential sources of PAHs. Each sampling site was classified as a rural, urban or industrial area, respectively.

The Institute of Chemical Technology, Prague, Czech Republic, performed the chemical analysis of the SPMD samples collected in Czech Republic and Slovakia. SPMD samples collected in Poland, Sweden and Austria, respectively, were analysed as follows. Each SPMD was mechanically washed in n-hexane followed by hydrochloric acid (1 M). The organic contaminants were recovered by dialytical extraction with a solvent mixture of 95/5 (v/v) cyclopentane/dichloromethane. The two SPMDs from each site were dialysed together while the field controls were dialysed separately. ^{2}H-1-nitropyrene, ^{2}H-6-nitrochrysen and a mixture of ^{2}H-PAH standards were added to the extracts as internal standards of the clean up. Spiked extractes were cleaned with high-resolution gel permeation chromatography (HRGPC) using a mixture 35/65 (v/v) of dichloromethane/n-hexane as mobile phase followed by a mixed silica gel column of deactivated silica and potassium silicate, elution by 60 ml 1/1 (v/v) hexane/dichloromethane. The samples were analysed for 13 EPA priority PAHs and six nitro-PAHs by high-resolution gas chromatography /low-resolution mass spectrometry (HRGC/LRMS). Before the GC/MS-analysis, ^{2}H-labelled dibenzofuran was added as recovery standard. For more details on the materials, chemicals and analytical methods used during the SPMD clean up, see Söderström and Bergqvist[3]. The Simca-P v 9.0 computer soft ware, obtained from Umetrics Inc., Umeå, Sweden, was used to perform the PCA calculations.
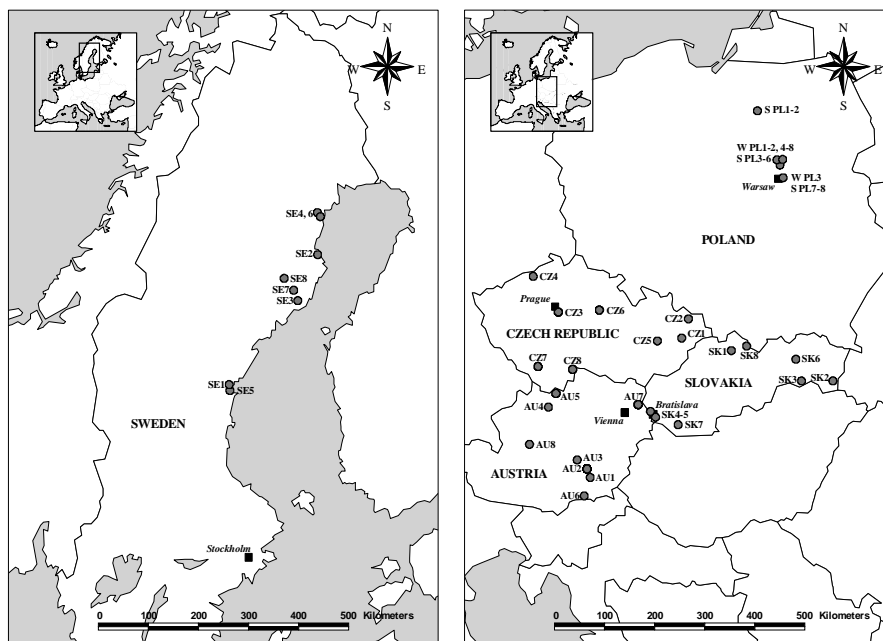
Figure 1. Locations of the sampling sites in Sweden (SE), Austria (AU), Czech Republic (CZ), Slovakia (SK) and Poland (W-PL and S-PL) respectively.

Results and Discussion

The two EPA PAHs, fluoranthene and pyrene, were not analysed in the samples due to specific interferences. Phenanthrene was the most abundant individual PAH compound measured, and the amounts found in the SPMDs were $3.1\text{-}9.8 \times 10^2$ ng · SPMD^{-1} · day^{-1}. The total amount of 13 EPA PAHs found in the SPMDs ranged from 5.6 ng · SPMD^{-1} · day^{-1} to 1.3×10^3 ng · SPMD^{-1} · day^{-1}. The highest total amounts of PAHs were detected during summer 2000 at the third location in Slovakia (SK 3). Ten times higher levels were detected in Slovakia, Czech Republic and Poland (W-PL), respectively, compared to those levels found in Sweden. The levels in Austria ranged between these two groups. Within each country, the levels of gas-phase PAHs differed about five to 20 times. The highest levels where detected in urban and industrial areas. Traffic and the metal industry, respectively, were the two major sources of gas-phase PAHs.

The total amounts of the nitro-PAHs found in the SPMDs were $9.5 \times 10^{-3} - 2.9$ ng · SPMD^{-1} · day^{-1}. In general, 1-nitronaphthalene, 2-nitronaphthalene and 2-nitrofluorene, respectively, were found in the SPMD samples. In SPMD samples from Czech Republic and Slovakia, also 9-nitroantracene and 3-nitrofluoranthene were detected. Nitro-PAHs have not been sampled with SPMDs previous to this study, but the atmospheric levels of 1-nitronaphthalene sampled (with the exception of the Swedish samples) were in the same range as the atmospheric levels in Birmingham, measured with a high volume sampler[6].

A PCA model with three significant PCs was calculated, explaining 88.3 % of the variation in the data. The object AU2-99 and the variable dibenz[a,h]antracene, respectively, were excluded from

the model due to > 50 % missing values for this object and variable, respectively. The score plot of the first two PCs showed the spatial differences in gas-phase PAHs between northern and central Europe (Figure 2). Corresponding loading plot showed that the spatial differences depended on e.g higher amounts of phenanthrene in the SPMDs from Slovakia compared to Sweden.
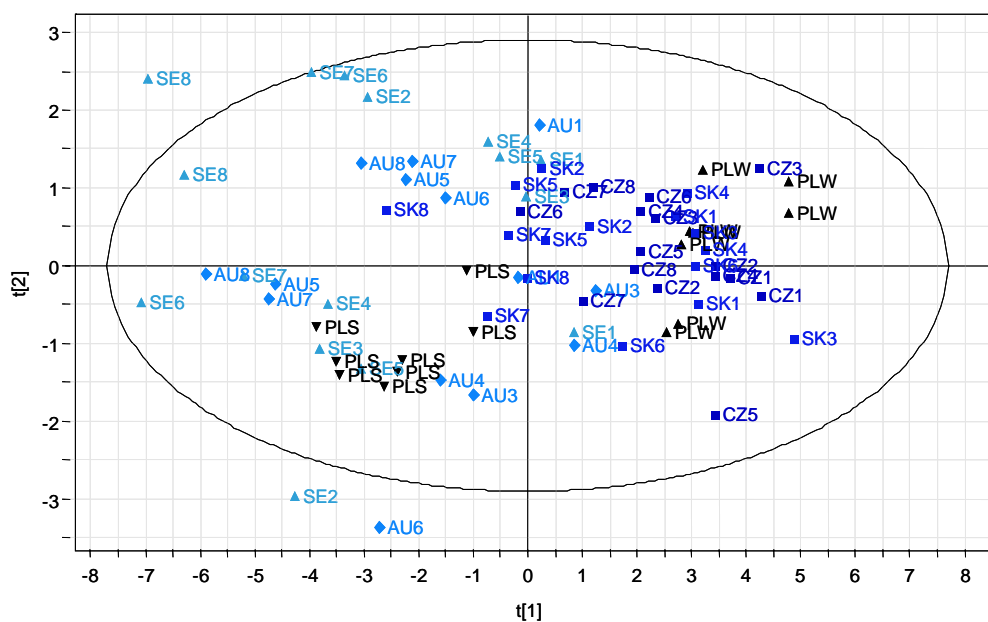

Figure 2. PCA score plot of the first two principal components (PCs) showing the spatial differences in gas-phase PAHs between northern and central Europe.

References
1. Kylin, H., Grimvall, E., Ostman, C.; (1994) Environmental Science & Technology, 28, 1320.
2. Lohmann, R., Corrigan, B. P., Howsam, M., Jones, K. C., Ockenden, W. A.; (2001) Environmental Science & Technology, 35, 2576.
3. Söderström H.S, Bergqvist P.-A.; (2003) Environmental Science & Technology, 1, 47.
4. Ockenden, W. A., Sweetman, A. J., Prest, H. F., Steinnes, E., Jones, K. C.; (1998) Environmental Science & Technology, 32, 2795.
5. Jackson, J. E.; (1991) A users guide to principal components, John Wiley & Sons.
6. Dimashki, M., Harrad, S., Harrison, R. M.; (2000) Atmospheric Environment, 34, 2459.