SPATIAL AND TEMPORAL TRENDS OF PERSISTENT ORGANIC POLLUTANTS IN AMBIENT AIR FROM THE AIR POLLUTION MONITORING NETWORK OF THE GERMAN FEDERAL ENVIRONMENT AGENCY

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Introduction

The 4th Daughter Directive (2004/107/EC)[1], relating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons (PAHs) in ambient air and deposition requests indicative measurements of Benzo[a]pyrene and other relevant PAHs, at least Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, and Dibenz(a,h)anthracene, at background sites. It also sets a target value of 1 ng/m³ for the total content of Benzo[a]pyrene in the PM10 fraction averaged over a calendar year. Member States shall take all necessary measures to ensure that, as from 31 December 2012, concentrations of Benzo(a)pyrene, do not exceed this target value.

In Germany these background measurements are performed by the German Federal Environment Agency (Umweltbundesamt, UBA) within their air pollution monitoring network. The sampling sites for these pollutants are selected in such a way that geographical variation and long-term trends can be identified. The monitoring of PAHs is coordinated with the European Monitoring and Evaluation Programme of the UN/ECE (EMEP).

EMEP is carried out in the scope of the international cooperation in the UN/ECE Convention on Long-range Transboundary Air Pollution (CLRTAP). The main objective of EMEP is to provide sound scientific support for the CLRTAP, inter alia by providing observational and modelling data on air pollutant concentrations, deposition rates, emissions and transboundary fluxes on the regional scale and identifying their temporal trends. Monitoring of atmospheric concentrations and deposition is one of the basic elements to achieve the objectives of EMEP.

The EMEP monitoring strategy for the time period 2004-2009[2] included the following persistent organic pollutants: PAHs, PCBs, HCB, gamma-Hexachlorocyclohexane (HCH), alpha-HCH, DDT/DDE, which have been incorporated into the UBA monitoring program. Additionally, a group of legacy pesticides (Heptachlor, Aldrin, Dieldrin, Endrin) is measured in ambient air and precipitation at the UBA monitoring sites Zingst, Westerland, Schmücke and Schauinsland, which are at the same time German EMEP sites. For a complete list of substances and results please see the latest report of the UBA[3].

In this paper we present selected results of the continuous measurements of POPs in ambient air in the UBA air pollution monitoring network in the time period 2006-2009 (in 2006 only for Benzo[a]pyrene). Benzo[a]pyrene is chosen as a lead substance for PAHs and marker for the carcinogenic risk of PAHs. Gamma-HCH is chosen as a typical semivolatile legacy pesticide and POP that occurs predominantly in the gaseous state in the atmosphere.

In order to enhance the spatial and temporal distribution and to compare the concentrations measured at the German sites, additional results for Benzo[a]pyrene and gamma-HCH from selected EMEP stations in the Czech Republic, Norway, Sweden and Finland for the time period 2005-2008 (if available) are included in this paper.

Materials and Methods

The sampling and analysis of selected POPs in the gas- and particulate phase within the air pollution monitoring network of the German Federal Environment Agency is based on the specifications in DIN ISO 12884[4] and DIN EN 15549[5].

Briefly it can be summarized as follows: For sampling, a combination of glass fibre filters, followed by pre-cleaned polyurethane foam (PUF) is used in a high volume sampler (modified Digitel DHA 80). The quality objectives and requirements of the 4th daughter directive (2004/107/EC) for PAHs are: twenty-four-hour sampling, 50% uncertainty (expressed at a 95% confidence interval), 90% minimum data capture and 14% minimum time coverage for

indicative measurements. Therefore, five daily samples (24h) are combined and extracted on a monthly basis. Samples were uniformly distributed over the weekdays and the year. Parallel measurements for a complete year were achieved in order to calculate the uncertainty in a direct approach according to DIN EN ISO 20988[6] (for results see below).
After sampling, the exposed filters and PUFs are sent to the laboratory and a mix of ^{13}C-labeled (PCB and pesticides) and deuterated (PAH) standards are added. After that the sampling material is Soxhlet extracted, using hexane/toluene 9:1. After pre-concentration to 50 ml, PAHs and pesticides/PCBs are separated. PAHs are cleaned using a silica column and eluted with hexane/toluene 7:3. Pesticides/PCBs are cleaned using a SPE column and eluted with hexane/toluol 65:35. The samples are further concentrated by applying a gentle stream of purified nitrogen. After volume reduction to approximately 0.1 ml, Benzo[e]pyrene d12 and ^{13}C-PCB 105 are added as a recovery standard. The detection and quantification are done using a combination of high resolution gas chromatography and high resolution mass spectrometry (resolution >10 000) with electron impact ionization.
The quality and reproducibility of air quality measurements is an important issue of the UBA monitoring program. Therefore, a complete quality assurance program is applied in this project, including the usage of mass labelled standards, certified reference materials, internal reference pools, continuous analysis of field and reagents blanks, nine point calibrations with routine recalibrations, recovery tests with control charts, test of the sampling efficiency of the filter/PUF system in the field (breakthrough experiments according to DIN ISO 12884) and participation in external lab intercomparison tests..
The uncertainty, obtained by parallel measurements (n=13) in a direct approach, is presented in this study, representative for the performance and quality of the complete procedure.
The standard uncertainty for Benzo[a]pyrene in ambient air in the concentration range of 0.005 – 0.5 ng/m³ accounts to u(y) = 0.019 ng/m³. The expanded 95% uncertainty in the range 0.005 – 0.5 ng/m³ accounts to $U_{0.95}(y)$ = 0.04 ng/m³. Relating to the mean value from the four German monitoring stations in the time period 2007-2009 of 0,11 ng/m³, the relative expanded measurement uncertainty is 37%. The relative expanded uncertainty complies with the quality objective of the 4th daughter directive (2004/107/EC) of 50% uncertainty.
The standard uncertainty for gamma-HCH in ambient air in the concentration range of 3.4 – 26 pg/m³ accounts to u(y) = 3.2 pg/m³. The expanded 95% uncertainty in the range 3.4 – 26 pg/m³ accounts to $U_{0.95}(y)$ = 6.5 pg/m³. Relating to the mean value from the four German monitoring stations in the time period 2007-2009 of 23 pg/m³, the relative expanded measurement uncertainty is 28%.

Results and Discussion

Figures 1 and 2 show the monthly averaged concentrations of the four German EMEP stations Zingst, Westerland, Schmücke and Schauinsland for gamma-HCH and Benzo[a]pyrene in the years 2006-2009. The results from Germany are complemented by ambient air concentrations from the EMEP stations Aspvreten (Sweden), Birkenes (Norway), Pallas/Särkijärvi (Finland), Råö (Sweden), Spitzbergen (Norway) and Košetice (Czech Republic) in the time period 2005-2008 (if available). For site information, see Table 1.

Table 1: Site information

Station Name	Country	EMEP Code	Geographical Coordinates		Altitude m a.s.l.	Station Type
Schauinsland	Germany	DE03	47º 55'N	07º 54'E	1205	rural background, midrange mountain site
Schmücke	Germany	DE08	50º 39'N	10º 46'E	937	rural background, midrange mountain site
Zingst	Germany	DE09	54º 26'N	12º 44'E	1	rural background, coastal site
Westerland	Germany	DE01	54º 54'N	08º 20'E	10	rural background, coastal site
Košetice	Czech Republic	CZ03	49º 35'N	15º 05'E	534	rural background, midrange mountain site
Råö	Sweden	SE14	57º 24'N	11º 55'E	10	rural background
Birkenes	Norway	NO01	58º 23'N	08º 15'E	190	rural background

Aspvreten	Sweden	SE12	58º 48'N	17º 23'E	20	rural background
Pallas	Finland	FI96	67° 58'N	24° 07'E	566	remote, arctic site
Spitzbergen	Norway	NO42	78º 54'N	11º 53'E	474	remote, arctic site

Figure 1 indicates a clear seasonal pattern for gamma-HCH at most of the stations with a maximum during summer. This pattern is most distinct at the four German stations and the Czech site with a more temperate climate and higher temperatures during summertime than at the Scandinavian stations. Gamma-HCH occurs predominantly in the gaseous state. Therefore emissions and re-emission are higher during summer. Schauinsland reveals the highest concentrations during summer with maximum concentrations above 100 pg/m³ and an overall mean value for the three consecutive years 2007-2009 of 53 pg/m³ (n=35). The clear South to North gradient confirms the latest results from Eckhardt et al.[7]. They have used the model FLEXPART to estimate the main source regions for gamma-HCH concentrations measured at Birkenes (Norway) in the period 2004-2007. The main estimated source region for this site is Western Europe, which contributes approximately 50% to the measured concentrations at Birkenes, followed by Central Europe and America which both contribute by 10%. Emission fluxes are also available from the inventories of Li et al.[8], in which Gamma-HCH has its main European source regions in France and Spain.

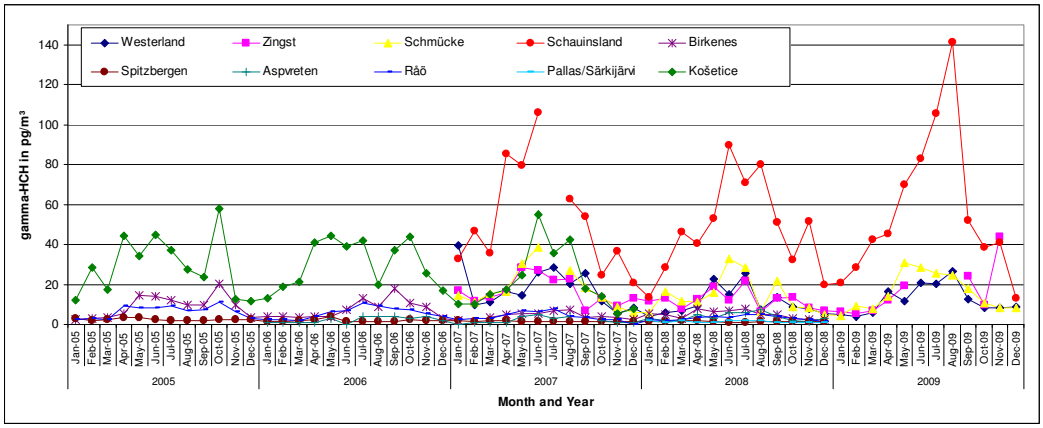

Figure 1: monthly averaged concentrations of gamma-HCH in ambient air from 10 European monitoring stations between 2005 and 2009.

Figure 2 shows a seasonal pattern for Benzo[a]pyrene at most of the stations as well. However, this time series is dominated by a maximum during winter. The German stations Zingst, Schmücke, Schauinsland and Westerland reveal the highest concentrations during winter. PAHs are produced during pyrolysis or because of incomplete combustion of carbon compounds (fossil fuels). Motor vehicles and, especially in fall and winter, domestic heating contribute to Benzo[a]pyrene emissions. Because of its physical and chemical properties, Benzo[a]pyrene is mostly particle-associated in the atmosphere. Generally lower heights of the mixing layer and stationary temperature inversions during cold seasons can enhance the concentrations in the boundary layer as well. Except one month (Dec. 08 for Zingst), all measured monthly concentrations at the German EMEP sites stay below the target value of 1 ng/m³. The yearly averages in Figure 4 at 10 European background stations are 2-20 times lower than the target value of the 4th Daughter Directive (2004/107/EC).

There is no significant trend for the two selected pollutants at one of the EMEP background stations during the time period 2005-2009 (Figures 3 and 4). It is intended to continue the monitoring program in order to have a more comprehensive time series for further investigations in the near future.

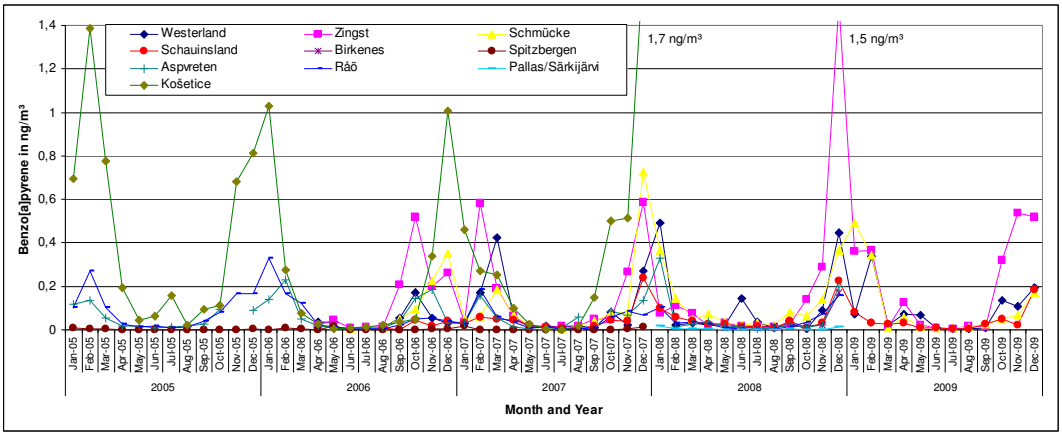

Figure 2: monthly averaged concentrations of Benzo[a]pyrene in ambient air from 10 European monitoring stations between 2005 and 2009.

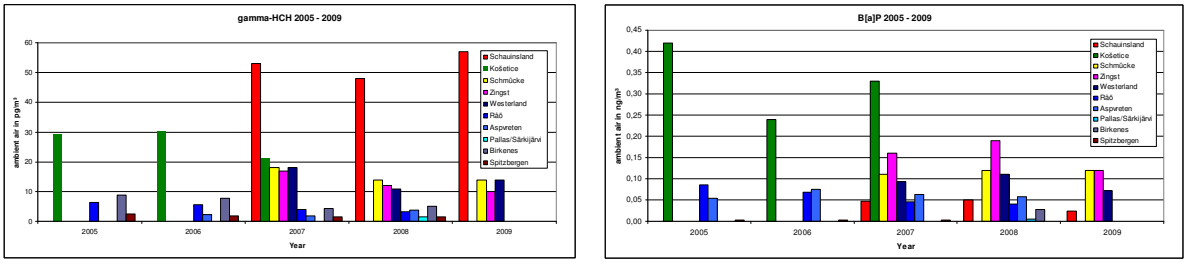

Figure 3 and 4: yearly averaged concentrations of gamma-HCH and Benzo[a]pyrene in ambient air from different European monitoring stations between 2005 and 2009.

Acknowledgements

This work was funded by the German Federal Environment Agency.

We thank EMEP for providing the concentration and deposition data for the stations Aspvreten, Birkenes, Pallas/Särkijärvi, Råö, Spitzbergen and Košetice. Thanks also go to Dr. Axel Eggert from UBA and the technical personnel at the UBA monitoring stations for their support and management of the sampling processes.

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