# ATMOSPHERIC POP LEVELS AND TRENDS IN VARIOUS GEOGRAPHIC AND CLIMATIC CONDITIONS DERIVED FROM PASSIVE AIR SAMPLING

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## Introduction

There is a general lack of information on the levels and distribution of persistent organic pollutants (POPs) in developing countries.[1] Since high volume air samplers as expensive devices requiring reliable power supply and trained operators are not widely available, there is a need to obtain data in a cost-effective way. Global Monitoring Network designed with the objective of establishing baseline trends at global background sites for the purpose of the Stockholm Convention[2] adopted passive air samplers (PAS)[3-8] as a cheap and versatile alternative to the conventional high volume sampling. They have been currently recommended as one of the methods suitable for the purpose of new long-term monitoring projects.

Five years (2003-2007) of an intensive research in the field of passive air sampling techniques and many field studies performed in the Research Centre for Environmental Chemistry and Ecotoxicology proved the applicability of this tool in the long-term air quality monitoring including the assessment of the spatial and temporal trends. Following the first measurements estimating an impact of local pollution sources and based on the number of local studies, the first national PAS monitoring network was established in the Czech Republic in 2005.

The same approach was applied on the regional scale for all countries of the Central, Southern and Eastern European region. To develop a monitoring network, the local conditions were evaluated very carefully since only detail characterization of potential local effects for every sampling site can assure a successful selection of sites for larger (regional or global) scale monitoring. For this purpose, three screening studies have been designed in the Central and Eastern European countries between 2006 and 2008. At the same time, another two screening exercises were performed at two regions geographically climatically very different from Europe – Africa and the Pacific Island.

## Material and Methods

### Air sampling

Polyurethane foam based samplers were employed in this study as described elsewhere. [3-6] They consist of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm$^{-3}$, type N 3038; Gumotex Breclav, Czech Republic) housed in the protective chambers. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in freezer prior deployment. Exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported in cooling box at 5 °C to the laboratory where they were kept in freezer at –18 °C until the analysis. Field blanks were obtained by installing and removing the PUF disks at all sampling sites.

### Sample analysis

All samples were extracted with dichloromethane in Büchi System B-811 automatic extractor. One laboratory blank and one reference material were analyzed with each set of ten samples. Surrogate recovery standards (D8-naphthalene, D10-fenantrene, D12-perylene for PAHs analysis, PCB 30 and PCB 185 for PCBs analysis) were spiked on each filter prior to extraction. Terfenyl and PCB 121 were used as internal standards for PAHs and PCBs analyses, respectively. Volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on silica gel column; sulfuric acid modified silica gel column was used for PCB/OCP samples. Samples were analyzed using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, and OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p´*-DDE, *p,p´*-DDD, *p,p´*-DDT). 16 US EPA polycyclic aromatic hydrocarbons were determined in all samples using GC-MS instrument (HP 6890 - HP 5972) supplied with a J&W Scientific fused silica column DB-5MS.

## Results and Discussion

PAS have been used as a part of the regular EMEP background air monitoring program in the Kosetice observatory, Czech Republic since 2003. Simultaneous employment of PAS and high volume samplers at this site provided valuable information about the performance of the passive samplers. A network of fifty additional sites representing a gradient from local sources to rural and mountain sites has been monitored continuously since 2005 to assess the atmospheric distribution and transport of POPs in the Czech Republic.

This project was further extended in 2006 to cover most of the Central and Eastern Europe with the goal to investigate a feasibility of employing PAS as a tool for evaluation of the effectiveness of the international conventions with the special attention to the countries suffering the lack of air monitoring data. Sampling sites in Bosnia and Herzegovina, Estonia, Latvia, Lithuania, Romania, Serbia, and Slovakia (58 sites) were monitored in 2006, while Bulgaria, Croatia, Hungary, Macedonia, Moldavia, Poland, Russia, and Slovenia joined the project in 2007. Ukraine, Belarus, Armenia, Azerbaijan, Kazakhstan and Kyrgyzstan were screened in 2008.

For PCBs, highest atmospheric levels were found in Romania (Figure 1) where the amounts of PCBs (7 congeners) sequestered in PAS filters varied around 1 µg per filter (since the passive sampler of this design samples about 100 cubic meters per 28 days, those values roughly correspond to 10 ng $m^{-3}$). Levels were also higher in Serbia (Kragujevac) where the soil is known to be contaminated with PCBs, and other industrial sites. Highest atmospheric levels of HCHs (one to two orders of magnitude higher than in most other countries), DDT and its metabolites, and PAHs were also determined at Romanian sites.

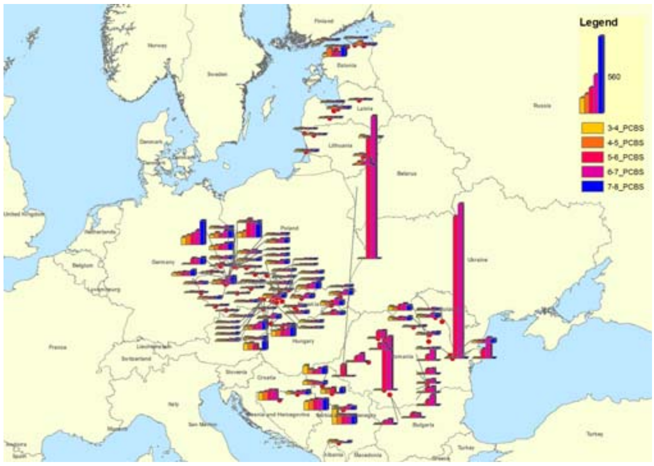

*Figure 1: PCB levels (7 indicators) in the ambient air (PAS, ng filter$^{-1}$) in Central, Eastern and Southern Europe, March - August, 2006*

The sites from MONET_CEEC network that qualify as backgrounds were selected in each participating country for future background monitoring network. Median PCB concentrations at all rural background sites in Baltic countries stayed bellow 5 ng filter$^{-1}$ and bellow 10 ng filter$^{-1}$ in Slovakia and Romania. In Serbia which probably still suffers the consequences of PCB spills the median level was almost 20 ng filter$^{-1}$. In the Czech Republic which offers a wide variety of background sampling sites, highest median value was found, as expected, at the urban background (13 ng filter$^{-1}$) while most of rural and mountain sites were bellow 5 ng filter$^{-1}$.

Results of this continuous monitoring are used not only to fill the gaps in data about the ambient air contamination in the Central and Eastern European region but also for identification of the sources of pollution, and estimation of their impact on the air quality. PAS samples were, for instance, used for radiocarbon-based source apportionment project, and the results of this study clearly indicated that combustion of non-fossil fuels has a significant impact on the amount of PAHs emitted into the southern European atmosphere.[7]

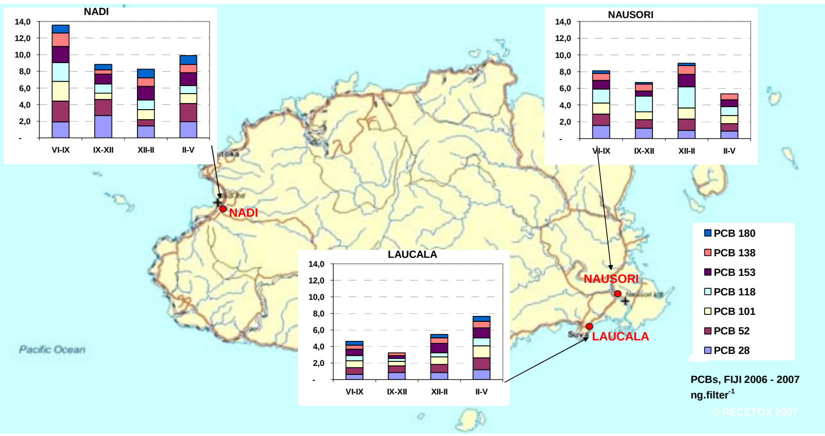

*Figure 2: Concentrations (ng filter$^{-1}$) of PCBs in ambient air at three sampling sites and four sampling periods in Fiji*

Application of PAS in the next two regions (Africa and Pacific Islands) opened up a question of a PAS performance under various climatic conditions. A combination of a 28-days and 3-months sampling periods were applied in these countries. All results were compared to the European PAS levels. Concentrations of PCBs and HCHs found at the individual sampling sites in Fiji were at the similar level. Concentration of DDT was higher than in the Baltic countries, closer to the levels measured at backgrounds in Bosnia or Romania. On the contrary, level of hexachlorobenzene was extremely low in Fiji, one order of magnitude lower than any place in Europe. Also for PAHs the median air concentrations at three sampling sites in Fiji were the same as the cleanest background sites in the Central Europe (Czech or Slovak Republic). Comparison of the same data with the high volume derived concentrations indicated that atmospheric levels of POPs at Fiji are also close to the ones measured in the backgrounds in Scandinavia or the Great Lakes area in case of PCB 101 or phenanthrene. They are higher than those backgrounds in *p,p'*-DDE concentrations, while they are much lower for α-HCH.

Extended exposition times are desirable to overcome the POP detection limits when the background sites are being monitored. Since the background monitoring is a goal of the Global monitoring plan, three months exposition period was, for instance, selected for the Global air passive sampling project (GAPS) [2] performed on many background site all over the word by the Environment Canada. In the other hand, we need to be aware that operating the passive sampler close to the equilibrium conditions causes lowering of the sampling rates and consequently also the underestimation of the atmospheric levels of POPs. Previous experiments proved that an equilibrium conditions are not reached when PAS is exposed for the period of 4 weeks but the most volatile compounds may reach the equilibrium when a 12 week exposition period is applied. Degradation of the compounds in the PUF filter can be another reason for a decrease of the sampling efficiency. To evaluate an extent of such errors; one passive sampler with the 4-week exposition period was co-employed beside the regular 12-week exposition sampler.

For PCBs, the amount in the 12-week filter sometimes exceeded the sum of three filters because the longer exposure period gives better chance to overcome the detection limits of the analytical instruments – some compounds were identified in the long exposition samples which were not found in the filters exposed for 4 weeks only due to the detection limit. Similar situation was with HCHs and DDTs. On the other hand, the most volatile compounds apparently approached the equilibrium: for hexachlorobenzene or pentachlorobenzene, up to 50 % of the sum of three samples was lost in the 12-week filter. Longer exposition times also resulted in the reduced amounts of PCB 28 or α-HCH. This effect was even more pronounced for PAHs, levels of which were sufficiently high. Total amounts of EPA 16 PAHs sequestered in 12-week samples were some 30% lower when compared to the sum of three 4-week samples. Another problem possibly affecting sampling efficiency of PAHs in the tropical conditions is a degradation of PAHs in the PUF filter.

## Conclusion

The absence of information on concentrations of persistent organic pollutants in the environmental matrices in developing regions is preventing the local authorities from taking the adequate actions to protect the people and environment. A potential of passive air sampling technique to serve as a cost-effective monitoring tool and provide seasonally and spatially resolved information about the local sources and levels of contamination was confirmed in this study.

## Acknowledgements

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