STUDY OF THE EUROEPAN REGIONAL AND LOCAL TRENDS OF PERSISTENT ORGANIC POLLUTANTS IN THE AMBIENT AIR USING ACTIVE AND PASSIVE SAMPLING

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Introduction

Long-term monitoring effort, and the collection of the broad information at the scale of global and regional pollution is required to detect the change in the natural environment, and to assess its contribution to climate change and other environmental issues[1,2].

The Stockholm Convention on Persistent Organic Pollutants also describes the problems of research, development and monitoring including data interpretation and evaluation as well as necessary effectiveness evaluation of Convention measures[3]. Parties to the Stockholm Convention are required to develop National Implementation Plans to demonstrate how the obligations of the Convention will be implemented and therefore they will need the establishment of arrangements to provide themselves with comparable monitoring data on the presence of the chemicals listed in Annexes, and their regional and global environmental transport.

Although a number of regional and global monitoring programmes have been established to report on the presence of POPs in the environment, there is a very little previous experience with the POPs monitoring designed to help with the effectiveness evaluation of a legally binding international agreement. Moreover, the establishment of an appropriate monitoring capacity in areas where it does not exist yet will take several years to become operational.

Air monitoring for POPs has conventionally been conducted at a very limited number of sites using 'active' or high volume air samplers. These are expensive; require electricity and a trained operator. Regulatory and other developments mean there will be a pressing need to obtain more POPs data for the air, in a much more routine and cost-effective way, to ensure compliance. This provides the incentive to develop new and cheaper air sampling options.

Passive air sampling (PAS) as a cheap and versatile alternative to the conventional high volume air sampling is one of the methods currently considered as suitable for the purpose of such monitoring programmes.

Materials and Methods

Few of the sites have reported data for POPs to date. The monitoring stations are generally located distant from the local emission sources in order to be representative for a larger region.

The Košetice Observatory located in the southern part of the Czech Republic has been registered as a regional station in the co-operative programme for monitoring and evaluation of the long-range transmissions of the air pollutants in Europe (EMEP). Košetice Observatory currently implements all measurements prescribed for EMEP stations (including VOCs, POPs, and heavy metals). Persistent organic pollutants (POPs) in all environmental matrices are monitored in the area of Košetice observatory since the 1988[1,2].

Besides the ambient air, the concentrations of POPs in the samples of wet deposition, surface water, sediment, soil, spruce and pine needles, and mosses are analyzed on the regular basis. New methods of sampling (PUF based passive air samplers, passive water samplers) were employed in the recent years for comparative studies.

The national and regional monitoring, and measurements of POPs is a part of two research projects of the RECETOX, Masaryk University, Brno, CR. The first is a TOCOEN Project (Toxic Organic Compounds in the Environment) (since 1988), the second is an INCHEMBIOL Project (Interactions among the chemicals, environment and biological systems and their consequences on the global, regional and local scales) (since 2004).

Subregional and Local Monitoring and Research Projects (Czech Republic, Balkan countries) (1993-2005) - Active Air Sampling Campaigns[1,5]

RECETOX performed several other active sampling campaigns in the few regions in the Czech Republic, and in the countries of former Yugoslavia.

Czech Republic:

- RECETOX study area - region Zlin, eastern Moravia, measurements of POPs (PAHs, PCBs, OCPs, PCDDs/Fs) + VOCs + HMs, 1993-2005 – at least one week of the sampling campaign per year, 5-8 sampling sites for the air + soils (10-30 sampling sites) + sediments (around 15 sites)
- Episodic campaigns – Beroun, small industrial town near Prague, in 2002 - 3 one week sampling campaigns - PAHs, PCBs, OCPs, PCDDs/Fs
- National monitoring of PAHs performed by Czech Hydrometeorological Institute - 20 sampling sites sampled every week + similar activity of the State Institute of Health

Former Yugoslavia:

RECETOX has participated on the 5th EU Framework Programme - project APOPSBAL (EU Project ICA2-CT2002-10007 "Assessment of the selected POPs in the atmosphere and water ecosystems from the waste generated by warfare in the area of former Yugoslavia"), and performed 3 sampling campaigns using the high volume samplers:

- 2002 - Zadar (Croatia) - 4 sampling sites in Zadar + 1 in Zavizan - 1 700 m a.s.l. - background observatory, one week campaign, 24 hrs sampling period
- 2002, 2003 - Kragujevac, Pancevo, Novi Sad (Serbia) - 9 sampling sites in total, 3 days of sampling campaign on every site, 24 hrs sampling period
- 2004 - Sarajevo, Tuzla (Bosnia and Herzegovina) – 5 sampling sites in each town, one week sampling campaigns, 24 hrs sampling period

Subregional and Local Monitoring and Research Projects (Czech Republic, Balkan countries) (2002-2005) - Pasive Air Sampling Campaigns[1,5]

In contrast to other groups, RECETOX has a very broad set of data from the PAS applications (around 120 sampling sites with the sampling duration between 5 and 30 months, sampling frequency of 28 days).

In 2004, passive air samplers were employed for the purpose of two case studies in the Czech Republic. DEZA Valašske Meziříčí, a coal tar and mixed tar oils processing plant, and Spolana Neratovice, a chemical factory with the history of high production of organochlorinated pesticides (OCPs), were selected as the point sources of PAHs, and OCPs, respectively.

Besides, twenty sampling sites were selected in Brno city on the area of approximately 20x20 km in October and November 2004 to investigate the option of PAS employment for toxicological studies.

In the last two years RECETOX performed a lot of research work in the field of PAS application focused on determination of the conditions influencing the sampling process (variability of a sampling volume, wind effect, temperature effect, construction of the sampler), and several studies of temporal and spatial variations of POPs in selected sites of the Czech Republic and countries of former Yugoslavia (Croatia, Serbia, Bosnia).

New project "Determination of trends in the ambient air POPs concentrations in the Central and Eastern European Region using the polyurethane foam based passive air samplers (PAS_CEECs)" organized by RECETOX and Central and Eastern European POPs Centre started in March 2006.

Project goals:

1) Application of the polyurethane foam based passive air samplers as a tool for determination of the effectiveness of the measures of international POPs conventions (POPs under the Stockholm Convention and POPs Protocol of CRLTAP).
2) Filling the informational gap about the POPs ambient air levels in the CEE countries where the regular monitoring programs are missing.
3) Evaluation of the temporal and spatial trends in the POPs ambient air concentrations in the countries of the Central and Eastern European region.
4) Establishment of the long-term PAS monitoring programme in this region.
5) Dissemination of the knowledge about newly developed techniques for the sampling, chemical analysis, toxicological screening, and risk assessment.

6) Presentation of the activities of the Regional POPs Centre of the Czech Republic, and Research Centre for Environmental Chemistry and Ecotoxicology RECETOX, Masaryk university, Brno, Czech Republic.

Project duration: February 2006 – December 2007
Countries and number of sampling sites:

1) 2006 – Czech Republic (60), Slovakia (11), Latvia (5), Estonia (5), Lithuania (5), Romania (18), Serbia (7), Bosnia and Herzegovina (5)
2) Armenia, Georgia, Poland, Belarus, Ukraine, Moldavia, Macedonia, Hungary, Slovenia

Results and Discussion

Passive samplers were mostly used for the large scale monitoring projects, taking advantage of possibility to collect data from remote regions or very large areas[4,5].
However, since the sampling campaigns were usually restricted to the small number of sites and very limited time periods, reliable information on the spatial and temporal variations of POPs atmospheric concentrations is still sparse.
Establishment of the long-term monitoring programmes may be necessary to assess the local point sources determination and their impact evaluation as well as to enhance our understanding to contribution of primary and secondary sources and transport to the contamination of various regions.
Feasibility of obtaining such data on seasonal variations in the ambient air concentrations of persistent organic pollutants on the local scale using the passive air samplers was the main focus of the RECETOX activities.
It was demonstrated previously[6-8] that passive air samplers using PUF filters are suitable to study vapour-phase air concentrations of some types of POPs, particularly more volatile compounds from the group of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorinated pesticides, and they were successfully applied as a tool for POPs monitoring on the global and regional levels. RECETOX studies confirmed that they are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring of spatial, seasonal and temporal variations. Passive samplers can be used for point sources evaluation in the scale of several square kilometers or even less - from the local plants to diffusive emissions from transportations or household incinerators - as well as for evaluation of diffusive emissions from secondary sources. While not being sensitive to short time accidental releases passive air samplers are suitable for measurements of long-term average concentrations at various levels.
On the other hand, this sensitivity to local effects can lead to some limitations toward its application in large-scale monitoring. Sampling site selection seems to be crucial for the success of such projects since small-scale variability in each region can exceed the continental variability. To develop a monitoring network, the local conditions must be evaluated very carefully since only detail characterization of potential local effects for every sampling site can assure the successful selection of sites for larger (regional or global) scale monitoring.
Results of the PAS screening study focused on the ambient air contamination of Brno city proved the feasibility of using this method for the direct genotoxic potential assessment. Very good agreement between the analytical and toxicological data obtained from this study was found.
Application of the passive air sampling method in Balkan countries was the main task in the third year of APOPSBAL project [12-14]. The aim of the APOPSBAL was to map the situation with the POPs contamination of former Yugoslavian countries, find possible hotspots, evaluate the risks, and suggest suitable remediation activities. The application of passive samplers was a suitable tool serving this goal. Determination of the polychlorinated biphenyls, organochlorinated pesticides, and polyaromatic hydrocarbons in the atmosphere using the conventional high volume samplers was performed in the first years of the project.
In order to better compare data from different sampling events, to collect the samples from remote places, as well as to gain more information about the spatial and temporal distribution of POPs, additional passive air sampling (PAS) campaign was organized in Croatia, Serbia, Bosnia, Herzegovina, and Kosovo in 2004. Passive samplers were employed at 34 sampling sites for 5 consecutive periods of 28 days. The network was based on the results of previous high volume ambient air sampling campaigns. Industrial, residential, as well as background areas were included. Some background sites were added to the list of locations to learn more about spatial variations, as well as several sites where active air sampling proved to be difficult to organize (Kosovo, Western Slavonia).

Results of the passive air sampling campaign were in very good agreement with the previous high volume measurements. The samples of the top soil layer were taken close to all passive air sampling sites. Decreasing trend in the levels of PCB and OCP contamination from July to December corresponds with decreasing temperature and indicates enhanced evaporation from secondary sources during the warm season.
Very good capability of passive air samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air was confirmed by our studies. It makes them capable of employment in the monitoring projects at various levels.

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