POPs contamination of Balkan countries as a consequence of war damages: passive air sampling network.

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Introduction

Damaging of industrial and military targets, natural resources, infrastructure, and homes in the Former Republic of Yugoslavia during the Balkan wars resulted in the release of the large quantities of chemicals, including persistent organic pollutants (POPs), into the environment. The results of few investigations of the PCB contamination in the vicinity of damaged industrial and military objects indicated serious pollution problems in Croatia and Serbia [1-6]; however there are hardly any data available from Bosnia, Herzegovina, and Kosovo. The information on the levels of these compounds in the atmosphere is even more limited. Under suitable meteorological conditions these chemicals could be transported across the borders over the large distances. This hypothesis was confirmed by some measurements of POPs levels in neighboring countries after wars [7]. However, difficulties and high costs associated with conventional high-volume air sampling as a standard method for monitoring of semi-volatile organic compounds in the air are partly responsible for the general lack of air quality measurements in this region. Passive air samplers were employed in this study as a technically feasible and cost-effective alternative for investigating chemical signatures in the air, capable of semi-quantitative measurements of the air pollution as well as relative comparisons of the individual sampling sites.

Materials and methods:

Air sampling

Passive air samplers consisting of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm^{-3}, type N 3038; GumotexBreclav, Czech Republic) housed in the protective chambers were employed in this study. Theory of passive sampling using similar devices was described elsewhere [8, 9].

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; sulphuric 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.

Quality Assurance / Quality Control

Recoveries were determined for all samples by spiking with the surrogate standards prior to extraction. Amounts were similar to detected quantities of analytes in the samples. Recoveries were higher than 71 % and 69 % for all samples for PCBs and PAHs, respectively. Recovery factors were not applied to any of the data. Recovery of native analytes measured for the reference material varied from 88 to 103 % for PCBs, from 75 to 98 % for OCPs, from 72 to 102 % for PAHs. Laboratory blanks were very low. Field blanks consisted of pre-extracted PUF disks and were taken on each sampling site. They were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 5 % of quantities detected in samples for PCBs, 1% for OCPs, 3% for PAHs, indicating minimal contamination during the transport, storage and analysis.

Results and discussion

The aim of the APOPSBAL project was to map the situation with the POPs contamination of former Yugoslavian countries, find possible hotspots, evaluate the risks, and suggest suitable remediation activities. As a part of this project high volume ambient air sampling was performed at 25 sampling sites (both industrial and background) in Croatia, Serbia, Bosnia and Herzegovina during 2003-2004 period, and the levels of PCBs, organochlorinated pesticides and polyaromatic hydrocarbons were determined. As expected, considerable PCBs contamination of several sites was confirmed. Levels of PCBs in Zastava factory in Kragujevac reached as high as 40 ng m^{-3} for the sum of 7 indicator PCBs, for instance (concentration of individual congeners PCB 52 and PCB 101 reached 12 ng m^{-3}), while the levels in other industrial objects and the storage places were bellow 10 ng m^{-3}, and concentrations in residential and background areas never exceeded 200 pg m^{-3} for the sum of 7 indicator congeners.

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. PUF based 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). Additional twenty sampling sites in the Czech Republic served as a reference region, including the background sampling station Kosetice serving as EMEP observatory [10].

Results of the passive air sampling campaign were in very good agreement with the previous high volume measurements. Amounts of PCBs sequestered by PAS filters reached as high as 7 µg of the sum of 7 indicator congeners (2 µg for the individual congeners) in Zastava factory sampling site, while staying in the range of hundreds of nanograms for most of the other industrial sites, and in the range of tens of nanograms for residential areas. These results also support the assumption that PUF based samplers give the typical sampling rates of 3-4 m^3 of air per day [9]. 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.

PCB congener pattern was investigated as well. While in Zadar transformer station, PCB 28 was most abundant in both, active and passive sampling results, PCB 52 and PCB 101 were most abundant in highly contaminated sites in Tuzla fire station and Zastava factory in Kragujevac, indicating different sources of contamination. Again, passive and active samplings gained very similar information about the congener distribution.

The samples of the soil top layer were taken close to all passive air sampling sites. Significant correlation between both, the PCBs levels in the atmosphere and in the soil surface, and between the congener distribution in the air and soil, was found. The PCB concentration in the soil from Zastava factory in Kragujevac was 1.3µg g^{-1} for 7 congeners, in Tuzla fire station 0.9 µg g^{-1}, and in Zadar transformer station 0.2 µg g^{-1}, while it never exceeded 80 ng g^{-1} for remaining sampling sites.

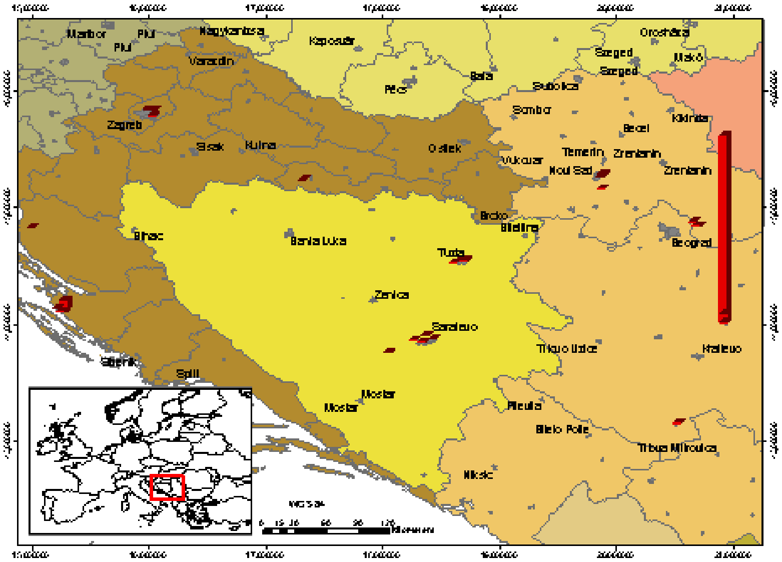

Fig.1: Amounts of PCBs (sum of 7 indicators) sequestered by the passive samplers (28 days sampling period).

Highest bar corresponds to 6.3 µg per filter.

Results of the study show highly uneven distribution of PCBs and other POPs in the atmosphere of former Yugoslavian countries (Fig.1), which indicates the presence of the strong point sources of pollution. All sites originally suggested for investigation due to the war damages were confirmed to be a source of considerable air pollution. On the contrary, PCBs levels in residential and background areas are comparable with levels in the Czech republic as a reference region. In the Czech republic, the average amount of PCBs sequestered in the PUF filter of the passive sampler was 50-130 ng for the sum of 7 indicator congeners for the industrial sites, 10-40 ng for residential and rural sites, and 7 ng for background observatory.

The study brought useful data about the air concentrations of POPs in the investigated region. More important, it provided information on the transport and fate of POPs in the vicinity of local sources of contamination useful for the estimation of their influence. Results of the study suggest, that passive samplers are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring of spatial, seasonal and temporal variations. They can be used for point sources evaluation in the scale of several square kilometers or even less - from the local plants to emissions from transportations or household incinerators - as well as for evaluation of diffusive emissions from secondary sources. While not being sensitive to accidental releases, passive air samplers are suitable for measurements of long-term average concentrations at various levels. Very good capability of passive air samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air indicates, that they can be successfully applied as a tool for POPs monitoring on the global and regional levels.

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