

Passive air sampler as a tool for long-term air pollution monitoring: Part 1. Performance assessment for seasonal and spatial variations

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Passive air sampling techniques can indicate seasonal and spatial variations in the ambient concentrations of persistent organic compounds near point sources.

Abstract

The potential of passive air sampling devices (polyurethane foam disks) to assess the influence of local sources on the quality of the surrounding environment was investigated. DEZA Valasske Mezirici, 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. Levels of PCBs, OCPs and PAHs were determined for all sampling sites and sampling periods. The study brought useful data about the air concentrations of POPs in the investigated regions. 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. Very good capability of passive samplers to reflect temporal and spatial fluctuation in concentrations of persistent organic pollutants in the ambient air was confirmed which makes them applicable for monitoring on the local scale.

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Keywords: Passive air sampling; Monitoring; Pollution; POPs

1. Introduction

As the air pollution is an issue of great public health concern, new methods for air quality monitoring have been developed in recent years (Tremolada et al., 1996; Shahir et al., 1999; Peters et al., 2000; Wennrich et al., 2002; Harner et al., 2003). Persistent organic pollutants (POPs) due to their wide distribution, ability to bioaccumulate in the fatty tissues, and carcinogen, mutagen and endocrine disruption potentials, remain the center of our attention. They are emitted from various primary and secondary sources, and the atmosphere often plays a key role in their transport within the immediate vicinity of POPs sources as well as over great distances (Wania,

2003). Atmospheric transport is also the main route for delivery of POPs to the aquatic and terrestrial ecosystems (Hermanson et al., 1991; Harner et al., 1995; Simcik et al., 1996; Hafner and Hites, 2003). Current research on the global fate of POPs seeks new information on the sources of POPs (Hafner and Hites, 2003), but also on other factors controlling air concentrations, as the climate (Simcik et al., 1999; Ma et al., 2004), air-surface exchange or atmospheric transport influence greatly the spatial, and temporal variability of atmospheric POPs concentrations (Hillery et al., 1997; Cousins and Jones, 1998; Bidleman, 1999). From this point of view, frequent measurements of air concentrations in different locations as well as monitoring studies on various levels from around the local point sources up to the continental scale are a matter of a great importance.

The Stockholm Convention on Persistent Organic Pollutants was adopted in May 2001 with the objective of protecting

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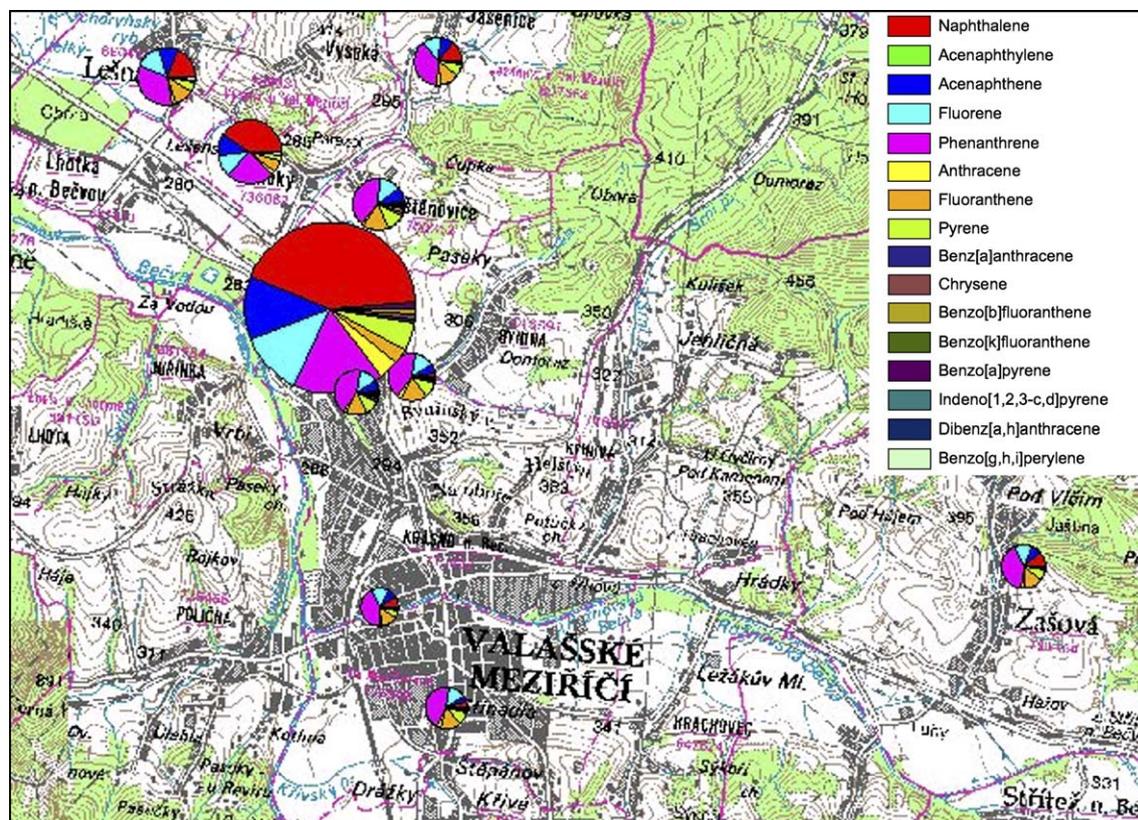


Fig. 1. Distribution of PAHs in DEZA vicinity, 19.3.2004–16.4.2004. Biggest circle represents the total amount of 0.533 mg of PAHs (a sum of EPA 16) sequestered on the filter.

human health and the environment from persistent organic pollutants and came into force in May 2004 (UNEP Stockholm Convention, 2001). It describes the problems of research, development and monitoring including data interpretation and evaluation as well as necessary effectiveness evaluation of Convention measures. 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 the Annexes and their regional and global environmental transport. Although a number of regional and global monitoring programs have been established to report on the presence of POPs in the

environment, there is very little previous experience of POPs monitoring designed to help evaluate the effectiveness 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. Passive air sampling 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 programs.

All these demands resulted in the development of a range of different passive air samplers (Bartkow et al., 2004a). These devices are capable of being deployed in many locations at the same time, which offers a new option for large scale monitoring projects. As it provides information about long-term

Table 1
Sampling sites in the vicinity of DEZA Valasske Mezirici

Sampling site	Description of the site
DEZA anthracene unit	Center of DEZA plant, next to the anthracene production unit
DEZA administration building	Southern border of DEZA grounds, direction towards Valasske Mezirici city center
Bynina	Edge of village, 500 m eastward from DEZA factory, no natural gas for domestic heating
VM Krizna	Residential district, 200 m north of Valasske Mezirici city center, south of DEZA
VM Observatory	Hilltop in the southern part of Valasske Mezirici, 50 m from the highway to Vsetin
Mstnovice	Small village 1 km NNE of DEZA, possible effect of traffic
Jasenice	Village 3 km NNE of DEZA, possible influence of domestic heating
Priluky	Edge of the small village 1.5 km NNW of DEZA, possible effect of traffic
Lesna	Rural site 3.5 km NW of DEZA, small effect of traffic, possible influence of domestic heating
Zasova	Background rural site 6 km east of DEZA, possible influence of domestic heating

Table 2
Conditions of passive sampling campaigns in Valasske Mezirici

Sampling campaign no	Start	Termination	Mean temperature	Prevailing wind direction
1	23.01.2004	20.02.2004	4.5	SW-S-SE
2	20.02.2004	19.03.2004	2.7	SW-S-SE
3	19.03.2004	16.04.2004	7.8	SW-S-SE
4	16.04.2004	14.05.2004	13.7	SW-S-SE
5	14.05.2004	11.06.2004	15.2	SW-S-SE
6	11.06.2004	09.07.2004	17.9	SW-S-SE

contamination of the selected site, passive air sampling can be used as a screening method for semi-quantitative comparison of different sites contamination with the advantage of low sensitivity to accidental short-time changes in concentration of pollutants. Since the sampling rates and the relationship between the amount of POPs sequestered by the sampling devices and their concentrations in the sampled air have not been fully mathematically described yet, the interpretation of results is rather difficult and usually based on the field measurements (Peters et al., 2000; Bartkow et al., 2004b). Air concentration estimations are enabled either by calibration based on parallel active and passive samplings or an employment of the permeation reference compounds (Ockenden et al., 2001; Soderstrom and Bergqvist, 2004).

Most of the passive air sampling measurements have been performed using semi-permeable membrane devices (SPMDs) (Petty et al., 1993; Ockenden et al., 1998a; Meijer et al., 2003; Bartkow et al., 2004a; Jaward et al., 2004c), polyurethane foam disks (PUFs) (Wilford et al., 2004) and XAD resins (Wania et al., 2003) which can be exposed over the period of several weeks or months. They sample the variety of POPs at a similar rate of a few m³ of air per day. However, rapidly equilibrating samplers were developed also to sample low air volumes (Harner et al., 2003), and attempts have been made to do an intercalibration of different kinds of passive

samplers (Peters et al., 2000; Shoeib and Harner, 2002) in order to be able to compare the data. The ability of passive samplers to obtain data from the local (Lohmann et al., 2001) to the continental scale (Jaward et al., 2004a,b) and to conduct urban–rural (Harner et al., 2004) and latitudinal transects (Ockenden et al., 1998b; Meijer et al., 2003; Jaward et al., 2004c) was investigated but generally, passive samplers were mostly used for large scale monitoring projects, taking advantage of the possibility to collect data from remote regions or very large areas. 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 long-term monitoring programs may be necessary to assess the local point sources determination and their impact evaluation as well as to enhance our understanding of the contribution of primary and secondary sources and transport to the contamination of various regions. Feasibility of obtaining such data on seasonal variations in ambient air concentrations of persistent organic pollutants on the local scale using the passive air samplers was the main focus of this study.

2. Materials and methods

2.1. Air sampling

Passive air samplers consisting of 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 protective stainless steel chambers were employed in this study. The theory of passive sampling using similar devices was described elsewhere (Shoeib and Harner, 2002; Harner et al., 2004).

Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 h extraction in acetone and 8 h in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in a freezer prior deployment. Exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported in a cooling box at 5 °C to the laboratory where they were kept in a freezer at –18 °C until the analysis.

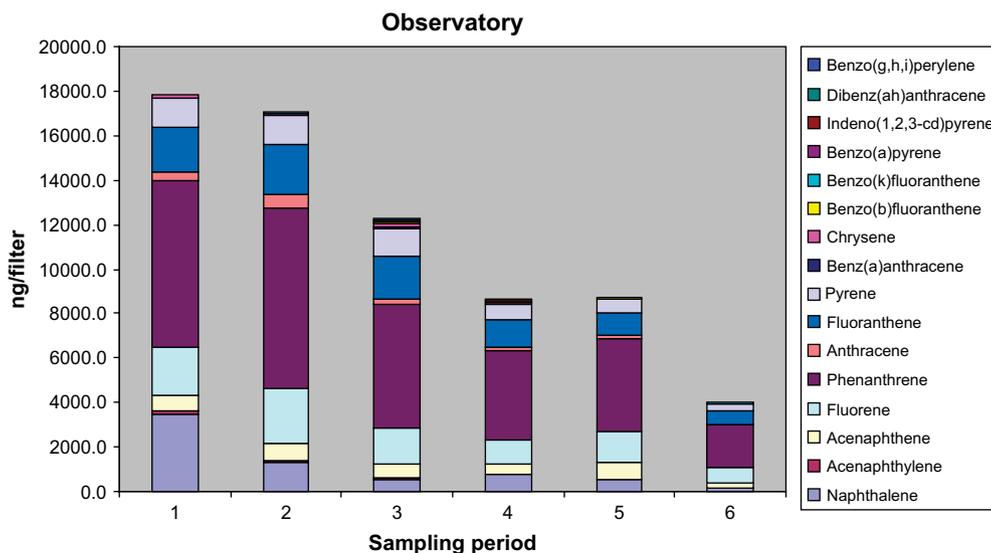


Fig. 2. Temporal variations of PAHs in DEZA vicinity, sampling site Observatory Valasske Mezirici.

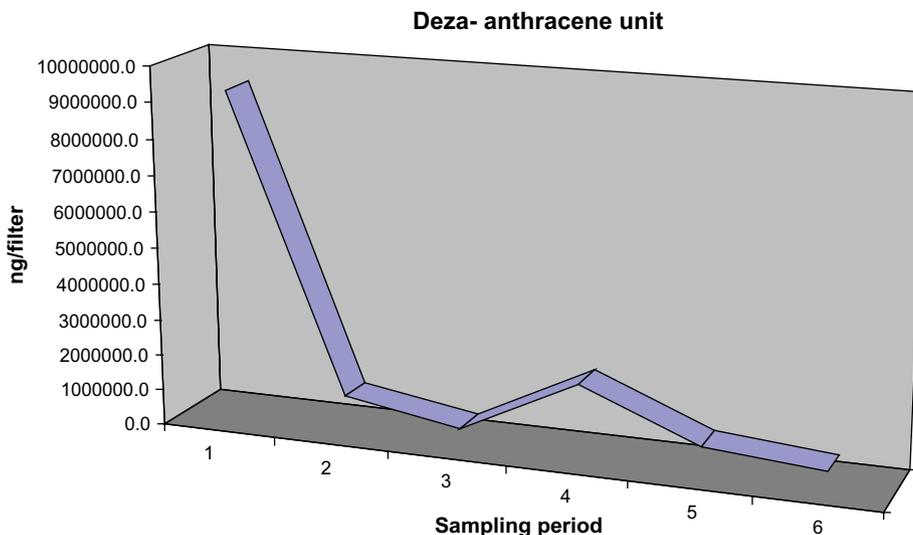


Fig. 3. Temporal variations of PAHs (a sum of 16 EPA) in DEZA, sampling site at anthracene production unit.

A field blank was obtained from each sampling site by installing and removing one clean PUF disk.

2.2. Sample analysis

All samples were extracted with dichloromethane in a 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-phenanthrene, D12-perylene for PAHs analysis, PCB 30 and PCB 185 for PCBs analysis, 10 ng per sample) 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; a 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.

2.3. 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 the quantities detected in samples for PCBs, 1% for OCPs, 3% for PAHs, indicating minimal contamination during transport, storage and analysis. Previous air sampling studies performed in our laboratory showed a good agreement between samples from duplicate passive air sampling, in which variability ranged from 5 to 20% for all analytes.

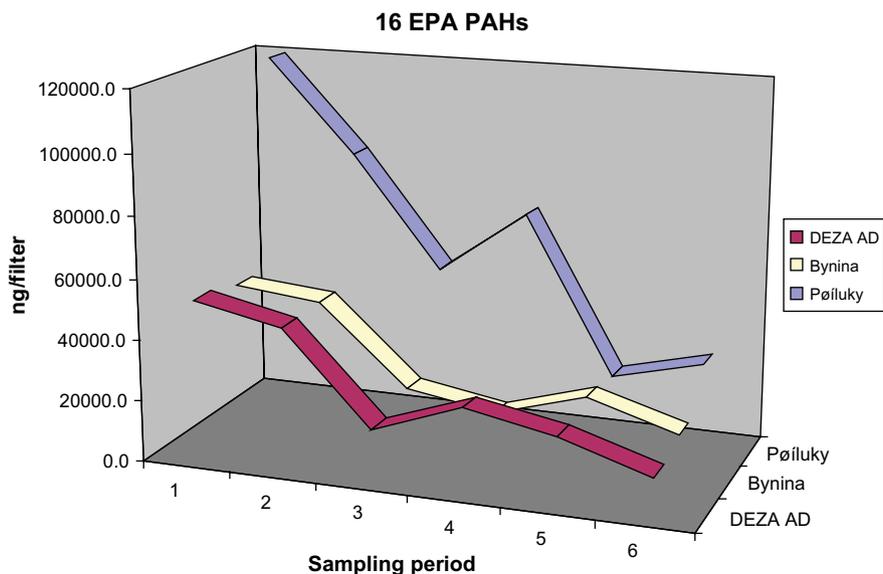


Fig. 4. Temporal variations of PAHs (a sum of 16 EPA) in DEZA vicinity, sampling sites within 1 km from the plant.

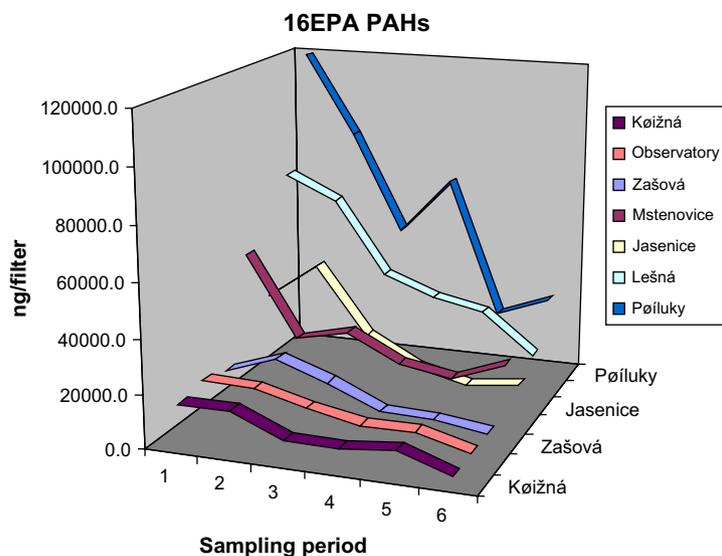


Fig. 5. Temporal variations of PAHs (a sum of 16 EPA) in DEZA vicinity, sampling sites within 6 km from the plant.

2.4. Design of the project

Two case studies were designed for this purpose, each region representing an area with a different history of extensive POPs emission. DEZA Valasske Mezirici, a tar and mixed oils processing plant, was selected as a primary point source of PAHs, while SPOLANA Neratovice, a chemical company with the history of production of organochlorinated pesticides, as a suspected secondary source of OCPs.

To gain information on the spatial distribution of pollutants and to assess the evaluation of the source impact, ten sampling sites were selected in the

vicinity of each point source, some inside the factory, the remaining sites in various directions and distances from the plant. Six sampling campaigns of 28 days were carried out starting January 2004 deploying polyurethane foam disks. Samples were analyzed for polychlorinated biphenyls (PCBs), organochlorinated pesticides (HCB, HCHs, DDT, DDE, DDD) and polyaromatic hydrocarbons (PAHs).

This set-up provided a basis to investigate the capability of polyurethane foam discs to assess the impact of local point sources, as well as spatial, seasonal and temporal variations in the ambient air concentrations of persistent organic pollutants in their vicinity.

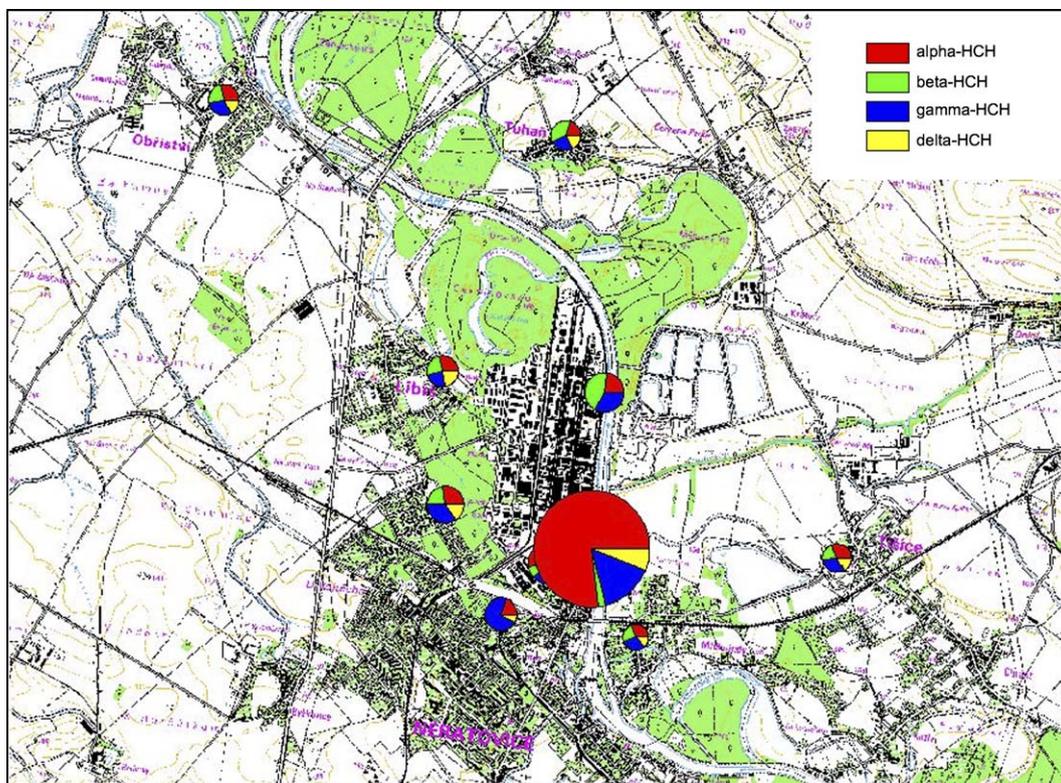


Fig. 6. Distribution of HCHs in Spolana vicinity, 16.2.2004–15.3.2004. Biggest circle represents the total amount of 445 ng of HCHs (a sum of α , β , γ , δ -HCH) sequestered on the filter.

Table 3
Sampling sites in the vicinity of Spolana Neratovice

Sampling site	Description of the site
Spolana archive	Archive building in southern part of Spolana chemical factory
Spolana gate	Gatehouse no. 1, southern border of Spolana grounds, besides Labe river (high probability of soil contamination)
Spolana WWTP	Eastern part of Spolana grounds, behind the waste water treatment plant, close to Labe river
Neratovice	Area of nursery school on Hamplova street, to the south from Spolana factory, 100 m from the railway station, 200 m from the city center
Libis woods	Edge of village, 1 km to the SW from Spolana factory (behind the woods), small effect of traffic and domestic heating
Libis	Village 1 km to the NW from Spolana factory, small effect of traffic and domestic heating, contaminated water-gang
Obřístvi	Background site 5 km to the NW from Spolana factory, village with possible influence of traffic and domestic heating
Tuhan	Nursery school in the center of village, 3 km northward from Spolana factory, possible effect of traffic and domestic heating
Tisice	Village 3 km eastward from Spolana factory, small effect of traffic, possible influence of domestic heating
Mlekojedy	Small village 1.5 km to the SSE from Spolana factory, no effect of traffic, possible influence of domestic heating

3. Results

3.1. DEZA Valasske Mezirici

DEZA activities comprise of processing of coal tar, mixed pitch oils and crude benzol, production of basic aromatic compounds including benzene, toluene, xylene, production of anthraquinone, anthracene, carbazole, acenaphthene, naphthalene, phthalic anhydride, phthalate plasticizers, impregnating oils, indene-coumarone resins, phenol, cresols, xylenols, and coal tar pitches, production of auxiliary compounds and by-products relating to the industry, electricity and heat generation, industrial wastes incineration with the annual capacity of 10 000 tons, and decontamination of soils polluted with polyaromatic hydrocarbons. With its history reaching back to 1960 and a capacity of 150 000 tones of raw benzol and 400 000 tones of raw tar processed annually, DEZA is among the largest enterprises in its business area.

DEZA plant is located to the north from Valasske Mezirici city center. The sampling site inside the factory next to the anthracene production unit was supposed to monitor the source itself; the remaining nine sites were chosen within a radius of 6 km from this point (Fig. 1). Since prevailing wind directions in this vicinity are SW-S-SE, the majority of samplers were positioned to the north of the plant. A list of the sampling sites including a short description is given in Table 1; Table 2 summarizes the sampling periods and conditions.

Six consecutive passive air samples collected on each site between January and July 2004 were analyzed for PAHs, PCBs, OCPs. A sum of 16 EPA PAHs collected on individual filters varied from 0.533 to 9.272 mg close to the anthracene production unit, and from 0.003 to 0.120 mg in the vicinity. On the background site (Zasova) the amount of PAHs varied between 0.003 and 0.015 mg, similar to both sites located to

Table 4
Conditions of passive sampling campaigns in Neratovice

Sampling campaign no	Start	End	Temperature	Prevailing wind direction
1	16.02.2004	15.03.2004	2.7	W-SW
2	15.03.2004	13.04.2004	7.8	SE-W
3	13.04.2004	11.05.2004	13.7	SE-W
4	11.05.2004	08.06.2004	15.2	SW-W-NW
5	08.06.2004	07.07.2004	17.9	SW-W-NW

the south of DEZA (Krizna 0.003–0.015 mg, Observatory 0.004–0.017 mg). Samplers positioned on the southern edges of the plant (administration building and Bynina) collected 0.011–0.052 mg and 0.015–0.049 mg, respectively. Two samplers placed 1 km to the NW (Priluky) and NE (Mstenovice) from DEZA collected 0.022–0.120 mg and 0.014–0.054 mg, respectively, Lesna (3.5 km NW) and Jasenice (3 km NE) 0.013–0.076 mg and 0.006–0.046 mg, respectively. The spatial pattern of contamination remained the same for 6 months (example for the sampling period 19.3.2004–16.4.2004 is given in Fig. 1); PAHs levels on all sites outside the plant had a declining tendency from January to July (example for the Observatory sampling site is in Fig. 2). Seasonal variations of the amounts of PAHs in all sampling sites are demonstrated in Figs. 3–5.

For PCBs and OCPs, the amounts collected on PUF filters were distributed more evenly; higher variability was observed among the consecutive samples from the same site than among the sampling sites. For PCBs, the sum of seven indicator congeners varied between 5 and 91 ng, the sum of HCHs between 2 and 16 ng, and the sum of *p,p'*-DDT, DDD, DDE between 1 and 20 ng in one sample. The pattern of spatial distribution for all three groups of POPs stayed the same for all 6 months; the highest levels of PCBs were measured on the grounds of DEZA and were declining toward the rural sites while the highest levels of DDTs were found in the rural sites Lesna and Priluky. Seasonal variations of all three groups were clearly visible. While winter maxima never exceeded 19 ng (PCBs), 7 ng (HCHs), and 4 ng (DDTs), summer maxima reached 91 ng (PCBs), 16 ng (HCHs), 20 ng (DDTs).

3.2. Spolana Neratovice

Spolana is one of the leading chemical companies active in the Czech industry as a member of the Unipetrol Group. Spolana volume of revenues makes the company the fourth largest chemical plant in the Czech Republic. The primary scope of business involves the petrochemical and chemical production of suspension polyvinyl chloride and PVC granulates (both softened and hard types), linear alpha olefins (LAO) and LAO based products, caprolactam as an intermediate for polyamide fibers and engineering plastics, and inorganic compounds such as sodium hydroxide, liquid chlorine,

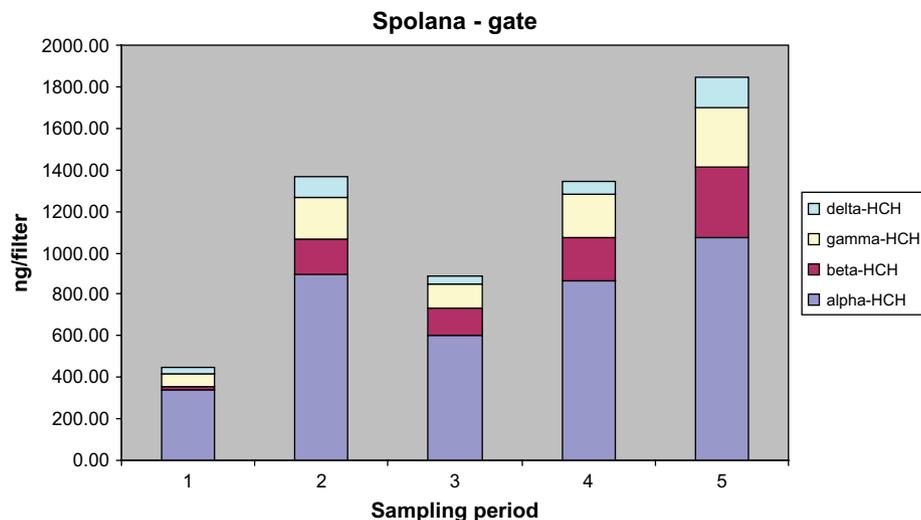


Fig. 7. Temporal variations of HCHs in Spolana, sampling site Spolana-gate.

hydrochloric acid, sulfuric acid, sodium hypochlorite, or ammonium sulfate. However, between 1952 and 1975 Spolana was one of two largest producers of pesticides in former Czechoslovakia. Pesticides containing DDT were produced between 1958 and 1969, lindane preparations until 1975. Technical HCH was produced from 1961 with a total of 60 000 tons (more than 3000 tons of pure lindane).

The Spolana factory is located to the northeast of Neratovice city center. Three sampling sites were on Spolana grounds

(gate, archive, WWTP), and the remaining sites were within 5 km from the factory (Fig. 6). A list of the sampling sites including a short description is given in Table 3; the sampling periods and conditions are summarized in Table 4.

Five consecutive passive air samples collected on each site were analyzed for PAHs, PCBs, OCPs. Amounts of POPs sequestered on PUF filters during the winter varied for the sum of α , β , γ , δ -HCHs between 5 and 26 ng outside the factory, while reaching 445 ng at the factory gate; in the case

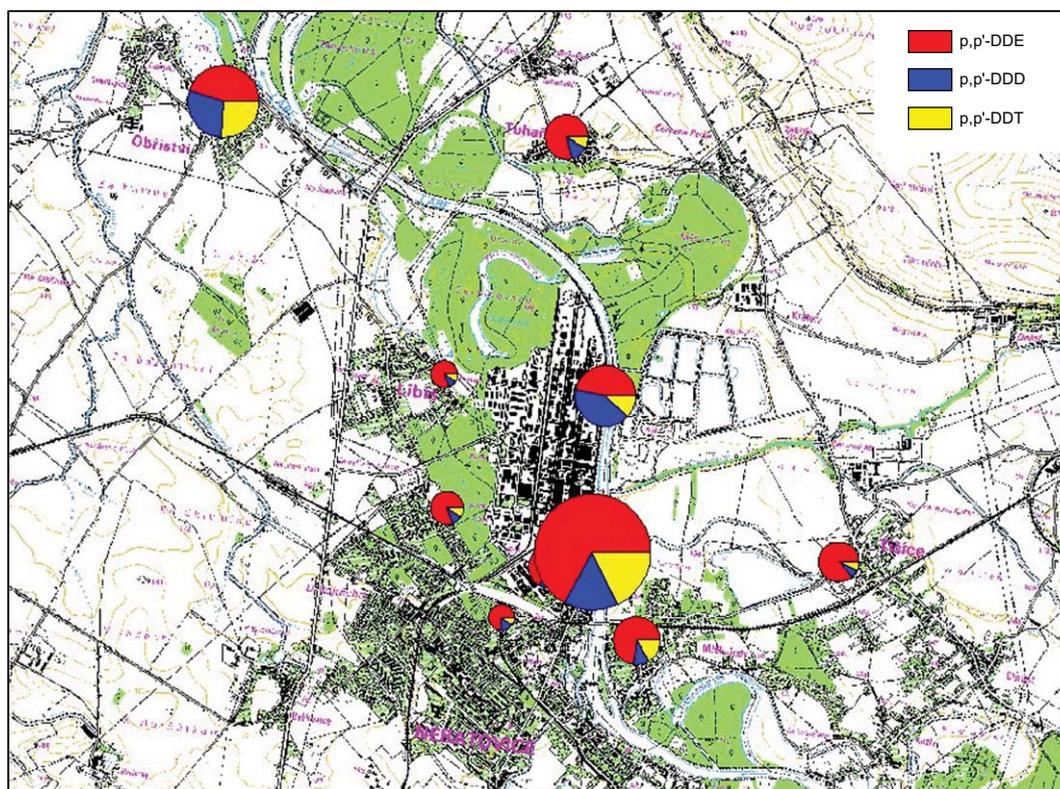


Fig. 8. Distribution of DDTs in Spolana vicinity, 11.5.2004–8.6.2004. Biggest circle represents the total amount of 108 ng of DDTs (a sum of p,p' -DDT, DDE, DDD) sequestered on the filter.

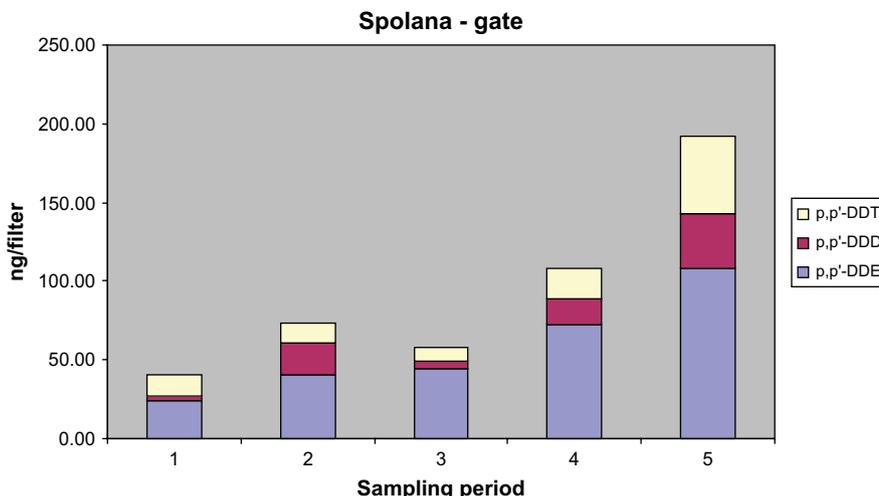


Fig. 9. Temporal variations of DDTs in Spolana, sampling site Spolana gate.

of DDTs they stayed between 6 and 16 ng outside and reached 40 ng at the gate, while those of PCBs were between 12 and 26 ng outside and up to 40 ng at the gate. The summer maxima for HCHs reached 62 ng per filter outside the factory and 1875 ng at the factory gate, those of DDTs were 51 ng outside and 192 ng at the gate, while those of PCBs were 66 ng outside and 90 ng at the gate. The spatial patterns of contamination remained the same for 5 months (example for HCHs, sampling period 16.2.2004–15.3.2004 is given in Fig. 6, for DDTs, sampling period 11.5.2004–8.6.2004 in Fig. 8, for PCBs, sampling

period 13.4.2004–11.5.2004 in Fig. 11). Again, the seasonal variations were pronounced as the levels of PCBs and OCPs were increasing from February to July (examples for the sampling site at Spolana gate are given in Figs. 7, 9, 12). Temporal variations of the amounts of PCBs and OCPs in all sampling sites are demonstrated in Figs. 10 and 13.

A sum of 16 EPA PAHs collected on individual filters from various sampling sites varied from 0.001 to 0.024 mg with higher variability observed among the consecutive samples from the same site than among the sampling sites during the

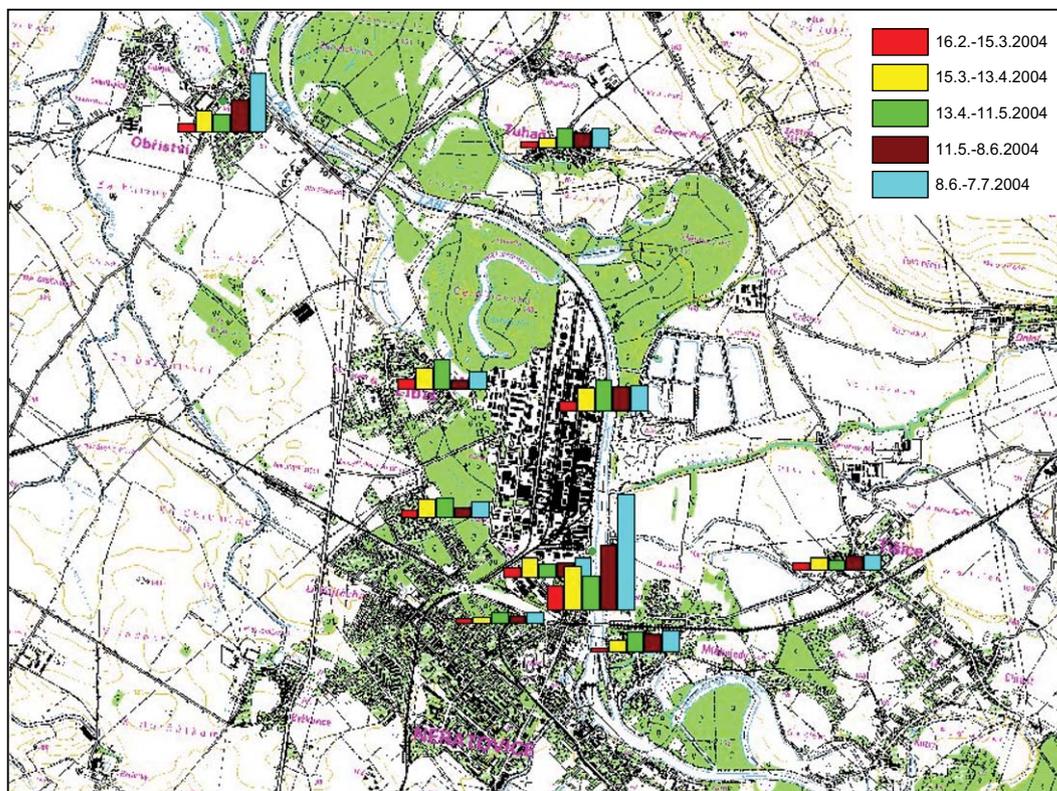


Fig. 10. Temporal variations of DDTs (a sum of *p,p'*-DDT, DDE, DDD) in Spolana vicinity, all sampling sites. Highest bar represents the total amount of 192 ng of DDTs sequestered on the filter.

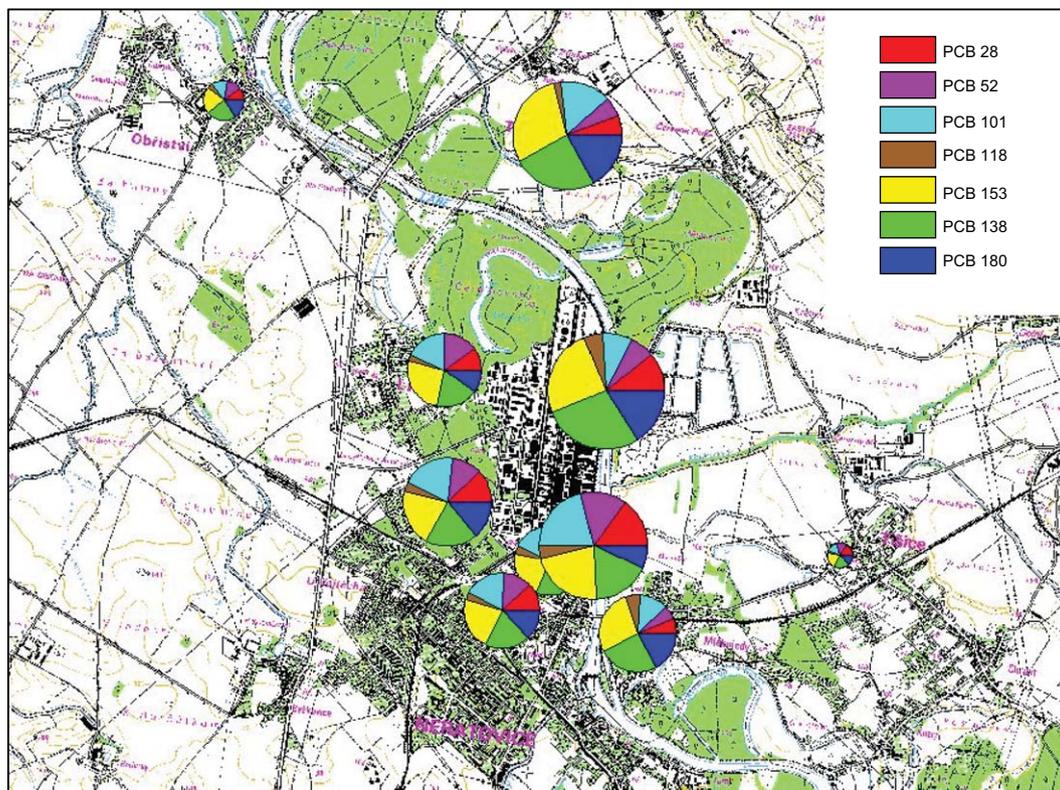


Fig. 11. Distribution of PCBs in Spolana vicinity, 13.4.2004–11.5.2004. Biggest circle represents the total amount of 66 ng of PCBs (a sum of 7 indicator PCBs) sequestered on the filter.

same period. The influence of the local combustion sources responsible for elevated levels in the rural sites is visible in Fig. 14 while the declining winter–summer trend is demonstrated in Fig. 15.

4. Discussion

When the PUF disks are deployed in the sampling chambers they were estimated to give typical sampling rates of 3–4 m³ of air per day (Shoeib and Harner, 2002). The ambient

concentrations represented by the measured amounts of POPs per sample values can therefore be derived. Previous work has also shown that characterization of the uptake profiles of various POPs based on their octanol–air partition coefficients gives satisfactory results and equivalent air sample volumes can be calculated (Harner et al., 2004).

Since the goal of this study was to assess the sensitivity of polyurethane foam based passive air samplers deployed for spatial and seasonal studies, the total amounts of POPs sequestered on the PUF filters were used for comparison rather than

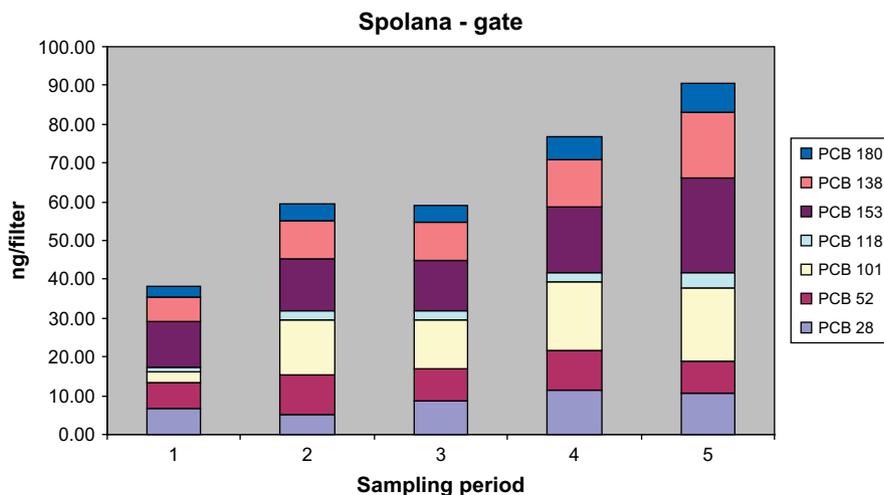


Fig. 12. Temporal variations of PCBs in Spolana, sampling site Spolana gate.

Table 5
Comparison of the air concentrations of POPs in the vicinity of DEZA Valasske Mezirici obtained by high volume sampling in 2004 and the air concentrations estimated from the results of a passive sampling campaign in 2004 (based on the sampling volume 100 m³/28 days)

Sampling site	PAHs/HV (ng m ⁻³)	PAHs/PAS (ng m ⁻³)	PCBs/HV (pg m ⁻³)	PCBs/PAS (pg m ⁻³)	DDTs/HV (pg m ⁻³)	DDTs/PAS (pg m ⁻³)	HCHs/HV (pg m ⁻³)	HCHs/PAS (pg m ⁻³)
Observatory	68–207	33–157	32–84	90–130	13–32	40–70	25–117	30–60
VM-Krizna	73–204	40–178	53–131	60–140	30–70	30–70	39–148	20–70
Bynina	377–591	155–492	38–70	78–200	15–38	50–120	31–83	40–80
Mstenovice	213–730	148–538	31–70	70–140	23–58	30–80	28–102	20–90

estimated air concentrations. However, providing the sampled air volumes were around 100 m³ per 28 days, estimated air concentrations of POPs in both industrial and rural sites were well within the range measured in this area using conventional high volume samplers. Comparison of the air concentration estimations based on the passive air sampling campaign described in this study, and the air concentrations measured during two high volume campaigns (1 week each) in the same region in 2004 (unpublished results) is given in Table 5.

PAHs, PCBs and OCPs enter the environment by different routes. PAHs are associated with combustion processes, PCBs originate from either primary (former production, disposal or release of products and wastes containing PCBs) or secondary (volatilization from the soil or water reservoirs) anthropogenic sources, OCPs are released by application and post-application volatilization. Emissions as well as further transport and fate are influenced by many physical and chemical factors. The

data obtained from two case studies presented here demonstrate this contrasting behavior of different groups of POPs.

Spatial distribution of PAHs in the vicinity of DEZA Valasske Mezirici is shown in Fig. 1. It is clear that the plant acts as a primary local point source of PAH contamination having larger impact on the sites to the north of the factory due to the prevailing wind direction from the south. Influence of the local combustion sources is evident in most of the rural places as is the declining seasonal trend (Fig. 2). For the sampling sites within 1 km from the plant, the amount of PAHs sequestered by PUF filters each month corresponded well with the amounts emitted at the anthracene unit (Figs. 3 and 4), northern sites getting the load of PAHs 2–4 times higher than the southern ones. The same trend is visible in Fig. 5, where the amounts of PAHs on the southern sites within 6 km from the plant (Krizna, Observatory, Zasova) were lower by a factor of 2–10 compared with the northern sites.

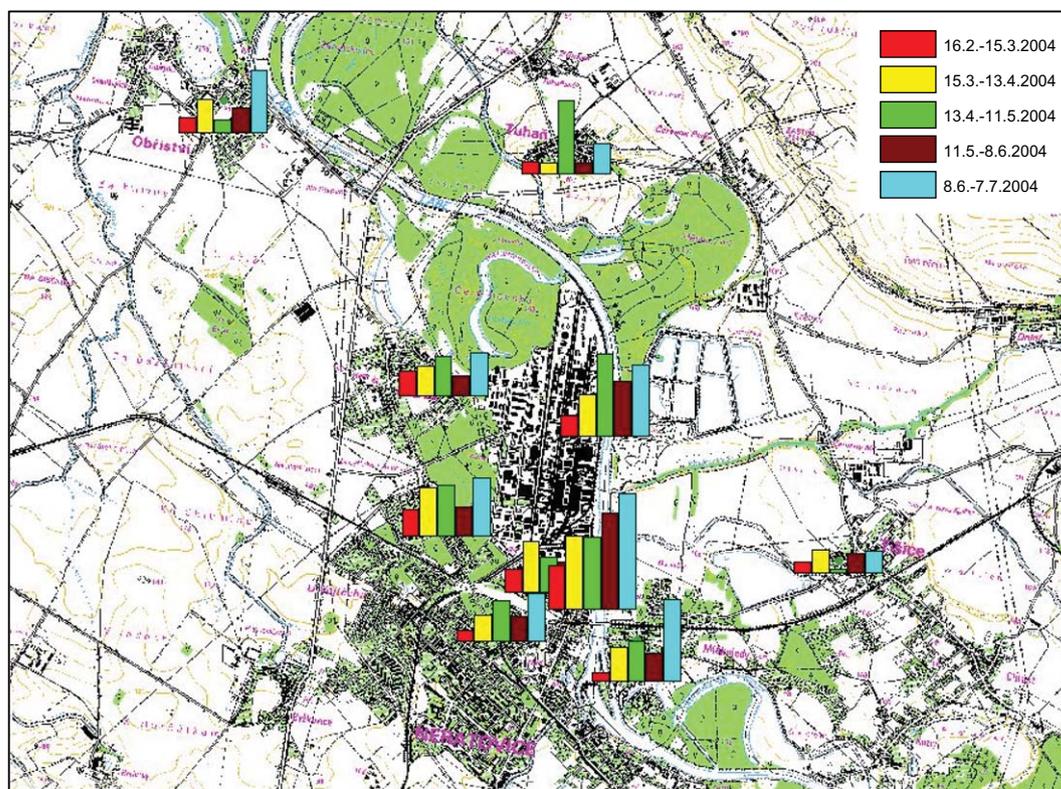


Fig. 13. Temporal variations of PCBs (the sum of 7 indicator PCBs) in Spolana vicinity, all sampling sites. Highest bar represents the total amount of 91 ng of PCBs sequestered on the filter.

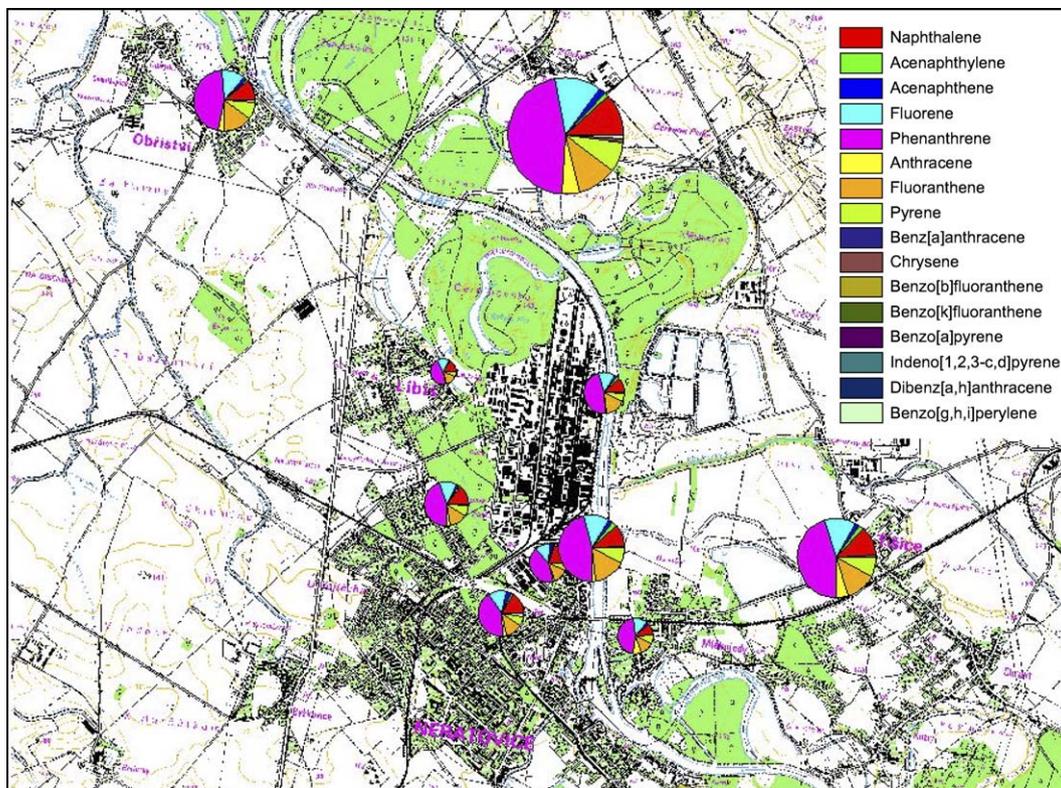


Fig. 14. Distribution of PAHs in Spolana vicinity, 16.2.2004–15.3.2004. Biggest circle represents the total amount of 0.024 mg of PAHs (a sum of EPA 16) sequestered on the filter.

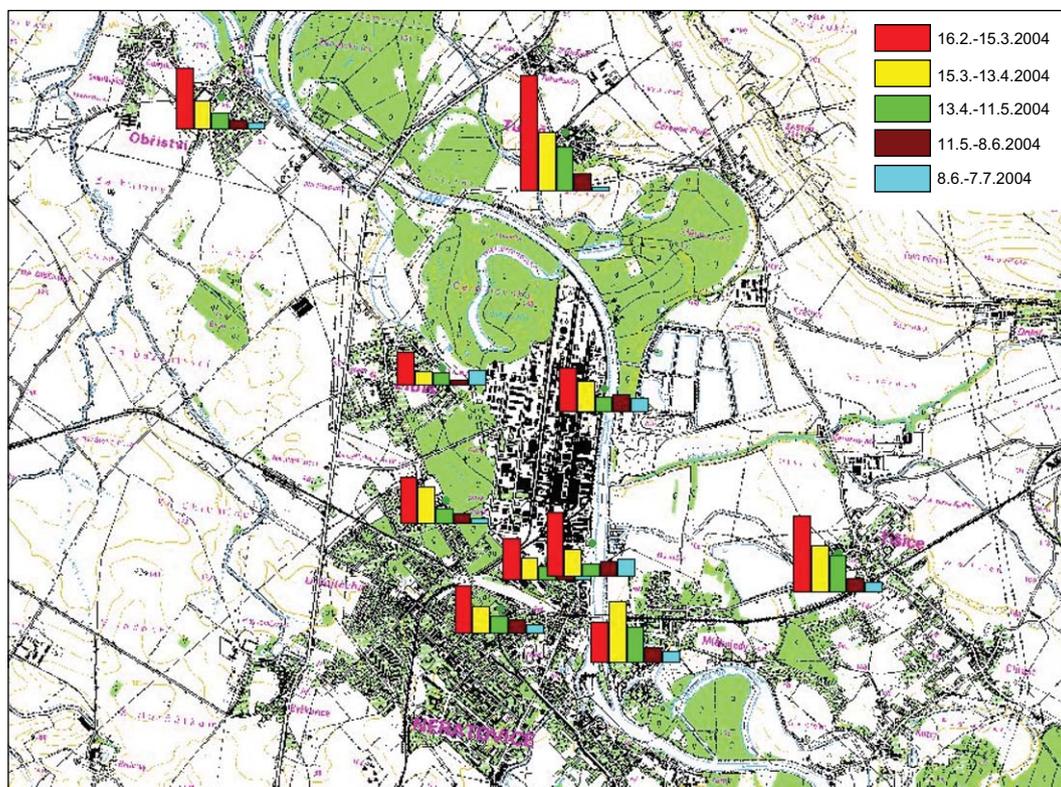


Fig. 15. Temporal variations of PAHs (the sum of 16 EPA PAHs) in Spolana vicinity, all sampling sites. Highest bar represents the total amount of 0.024 mg of PAHs sequestered on the filter.

PCB and OCP contamination kept the same spatial pattern during the whole study indicating diffusive sources and good reproducibility of the method. Increasing trend in the levels of PCB and OCP contamination from January to July corresponds with increasing temperature and indicates enhanced evaporation from secondary sources.

On the contrary, Spolana Neratovice clearly is a point source of secondary air pollution by OCPs probably due to the volatilization from contaminated soils and contaminated buildings. Fig. 6 shows the spatial distribution of HCHs around the factory, while Fig. 7 demonstrates the increasing trend for HCH contamination from February to July. Similarly, Figs 8–10 show spatial and temporal variation in DDTs. In Fig. 10, rising levels can be seen on most sampling sites for the sum of *p,p*-DDT, DDE, DDD. Since the wind direction is more variable here and changes from W-NW to SE, it is more difficult to follow the air transport from more contaminated sites within the factory to various directions. However, in Fig. 10 the drops in DDT concentrations in the SE sites during the third period, and in the DDT concentrations in the NW sites during the fourth period could be assigned to the change in prevailing wind directions from SE to NW between those two time periods.

Uniform levels of PCBs (Fig. 11) with the same pattern throughout the sampling campaigns indicate diffusive sources. Increasing seasonal trend corresponding with the increasing temperature is well demonstrated in Figs. 12 and 13.

On the other hand it is apparent from Fig. 14 that Spolana is not a considerable source of PAH pollution in the region. Contamination of the rural sites to the north and west of the plant is linked with the local combustion sources and follows typical declining seasonal trend during the period considered in this study (Fig. 15).

It was demonstrated previously (Harner et al., 2004; Jaward et al., 2004a,b) that passive air samplers using PUF filters are suitable to study vapor-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. This study suggests they are sensitive enough to mirror even small-scale differences, which makes them capable of monitoring spatial, seasonal and temporal variations. Passive samplers can be used for point source 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 detailed characterization of potential local effects for every sampling site can assure the successful selection of sites for larger (regional or global) scale monitoring.

5. Conclusions

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 in this study. While this sensitivity makes them suitable for the monitoring of local sources, it also needs to be considered when designing large scale monitoring networks.

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