

Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic.

Part I. Ambient air and wet deposition 1996–2005†

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Kosetice observatory is a facility of the Czech Hydrometeorological Institute, which is a part of the European Monitoring and Evaluation Programme (EMEP) network. Persistent organic pollutants (POPs: PCBs, DDTs, HCHs, PAHs) have been monitored in all environmental matrices using the integrated monitoring approach. Generally, the atmospheric levels of POPs in this Central European background station (mean values: 0.115 ng m⁻³ for \sum PCBs, 0.040 ng m⁻³ for \sum DDTs, 0.077 ng m⁻³ for \sum HCHs, and 17 ng m⁻³ for \sum PAHs) are significantly higher than those in other EMEP stations localized mostly in Northern and Western Europe. Long-term trends of POP concentrations in the ambient air and wet deposition are presented in this article and they show a slow decline in the last decade for most of the investigated compounds. Temporally increased levels of certain chemicals were associated with some local climatic (floods) or socio-economic (fuel prices) factors.

Introduction

A risk of irreversible changes in the terrestrial and aquatic ecosystems as well as a danger of the global climate change caused by environmental pollution was first recognized in the early 1960s. However, detection of such changes in the natural environment at regional and global levels requires a coordinated monitoring effort based on broad international cooperation. First, international monitoring programs were introduced in the 1960s and 1970s by the international institutions (WMO, ECE, UNEP), and they focused on various environmental aspects, including effects of human activities on climate change, trans-boundary transport of pollutants and exchange of chemicals between environmental compartments. Persistent organic pollutants (POPs), as the substances prone to long-range atmospheric transport and deposition in distant regions,^{1,2} are the compounds of such concern. Their global impact has been apparent since the members of this group were detected in polar regions at levels posing risks to both wildlife³ and humans.⁴

In 1992, a newly established initiative of the United Nations Economic Commission for Europe (UN-ECE) had prepared a protocol on POPs² with the goal to control, reduce or elim-

inate their discharge, emission and release. A similar program of the United Nations Environment Program was introduced in cooperation with the International Forum for Chemical Safety (UNEP/IFCS).⁵ It has been recognized that an important step in establishment of effective control measures is the inventory of current POP concentrations in various environmental compartments, and assessment of their time trends. Determination of POP concentrations in the atmosphere, wet and dry deposition, surface water, sediment, soil and vegetation is desirable under various geographic and climatic conditions. Such information improves our understanding of the pathways and potential effects of chemical substances, and defines specific parameters for exposure assessment. At the same time, new data sets valuable for validation of regional and global models of atmospheric transport and environmental fate are generated. The number of sites where POPs are continuously monitored over extended time periods in several environmental compartments is, however, very limited.

One of the programs coordinating such a monitoring effort on multiple sites is the European Monitoring and Evaluation Programme (EMEP). It was established with the main goal of providing the governments and subsidiary bodies under the Convention on Long Range Trans-boundary Air Pollution with qualified scientific information supporting development and evaluation of the international protocols. The EMEP program was initially focused on the trans-boundary transport of acidification and eutrophication. Later, its scope broadened to address a formation of surface ozone, and more recently it also covers volatile organic compounds, persistent organic pollutants, and heavy metals. A map of the EMEP stations (including analyzed matrices) is presented in Fig. 1.⁶

Only six (out of fifteen) EMEP sites reported POPs in both air and wet deposition in 2004. Kosetice station (furthest to the right in Fig 1) was the only site where POPs were also

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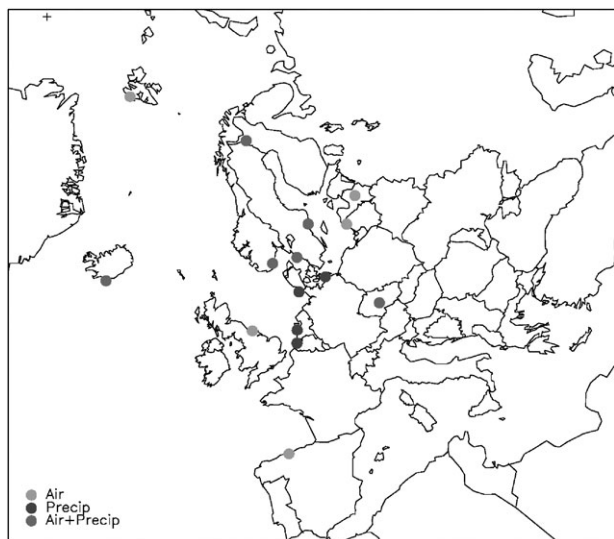


Fig. 1 POP monitoring EMEP network, 2000.

determined in other environmental matrices. Kosetice observatory of the Czech Hydrometeorological Institute is located in the southern Czech Republic (N49°35'; E15°05'). The climatic classification of the region is a moderately warm and moderately humid upland zone with a mean annual temperature of 7.1 °C, mean annual total precipitation of 621 mm, between 60 and 100 days with snow-cover per year, 1800 hours of sunshine per year, and prevailing westerly winds. The observatory was established as a regional station of an integrated background monitoring network in the late 1970s.

All measurements assigned to EMEP stations (including VOCs, POPs and heavy metals) are currently implemented in Kosetice,^{7–13} and monitoring design is based on the EMEP POP monitoring strategy.¹⁴ Samples of the ambient air, wet deposition, surface water, sediment, soil and biota, as the key components of the environmental system, are collected. The ecosystem indicators are further applied to determine the current state, anthropogenic impacts and influences, and to predict the future changes of terrestrial and freshwater ecosystems in a long-term perspective.¹⁴ A dataset generated over ten years of integrated monitoring in Kosetice was used in this study to assess the Central European trends in background levels of persistent organic pollutants.

Methods and materials

Selection of compounds and matrices

16 US EPA polycyclic aromatic hydrocarbons (PAHs), 7 indicator polychlorinated biphenyls (PCBs: IUPAC congener numbers 28, 52, 101, 118, 153, 138, 180), organochlorine pesticides (OCPs: *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE), α -, β -, γ -, δ -hexachlorocyclohexane (HCH), hexachlorobenzene (HCB) and pentachlorobenzene are being analyzed on a regular basis.

Ambient air sampling has been carried out in Kosetice since September 1988 which makes it a unique achievement of 18 years of continuous monitoring. One sample per three months was the sampling frequency between 1988 and 1993. Since 1994, the air samples have been collected once a week (every Wednesday, from 08:00 h to Thursday, 08:00 h) resulting in 52 samples per year.^{7–12} Wet deposition samples were collected during each rain event.

Sampling techniques

High volume ambient air samplers PS-1 (Graseby-Andersen, USA, flow: 12–18 m³ h⁻¹, volume: 250–400 m³ per 24 h) and two types of adsorbents were used: a Whatmann quartz filter (QF) (fraction $d_{ae} < 50 \mu\text{m}$) for collection of particles, and a polyurethane foam (PUF) filter (Gumotex Břeclav, Czech Republic, density 0.03 g cm⁻³) for collection of the gaseous phase. PUF filters were cleaned before the campaign by extraction with acetone and dichloromethane in a Soxtec extractor. The duration of sampling was 24 hours; quartz filter field blanks and PUF field blanks were collected each month.

Precipitation samples were collected using manually operated stainless steel collection vessels (total sampling area of 0.5 m²). They were opened at the beginning of each rain event to make sure that only wet deposition is collected. The samplers were closed when the rain stopped, wet deposition samples were removed immediately or after 24 hours in the case of continuing precipitation, and containers were cleaned. The sample was analyzed whenever more than 250 mL of water was collected.

Chemical analysis

Quartz filters and polyurethane foam filters were extracted and analyzed separately in order to determine the gas–particle partitioning of all compounds. Surrogate recovery standards (*d*₈-naphthalene, *d*₁₀-phenanthrene, *d*₁₂-perylene for PAH analysis; PCB 30 and PCB 185 for PCB analysis) were spiked on each sample prior to extraction. All filters were extracted with dichloromethane in a Büchi System B-811 automatic extractor.

Liquid–liquid (L–L) extraction was employed for the analysis of wet deposition samples until 2004, and solid phase extraction (SPE) has been applied since 2005. Both techniques have been co-employed for one year to ensure a consistency of results. For L–L, the sample (250–1000 ml) was extracted by 5 mL of dichloromethane in 15 mL of hexane in the separation funnel. For SPE, solid phase extraction disks (Envi-Disk C₁₈, 47 mm diameter, Supelco) conditioned by methanol were used. After the sorption, all analytes were re-eluted with a mixture of dichloromethane–hexane 1 : 1. The extracts were dried using Na₂SO₄.

The volume of samples was reduced after the extraction under a gentle nitrogen stream at ambient temperature, and divided in two halves for PCB/OCP and PAH analyses. Fractionation was achieved on a silica gel column; a sulfuric acid modified silica gel column was used for PCB/OCP samples. Terphenyl and PCB 121 were used as internal standards for PAH and PCB analyses, respectively. Air samples

Table 1 POP concentration, Kosetice observatory, 1996–2005^a

Matrix (media) unit	Species	Mean	Median	Min.	Max.
Air (PUF)/ng m ⁻³	∑PAHs	12.0	7.9	0.360	208
	∑PCBs	0.084	0.070	BQL	0.390
	∑HCHs	0.068	0.044	BQL	0.771
	∑DDTs	0.036	0.030	0.001	0.207
	HCB	0.145	0.115	BQL	0.831
Air (QF)/ng m ⁻³	∑PAHs	5.4	2.2	0.060	359
	∑PCBs	0.031	0.024	BQL	0.215
	∑HCHs	0.009	0.004	BQL	0.104
	∑DDTs	0.004	0.003	BQL	0.050
	HCB	0.004	0.002	0.001	0.134
Rain water/ng L ⁻¹	∑PAHs	239	120	2.4	6310
	∑PCBs	2.8	0.5	BQL	459
	∑HCHs	32.3	5.2	BQL	2256
	∑DDTs	2.50	0.20	BQL	96
	HCB	0.14	0.05	BQL	2.5

^a BQL = below quantification limit. Quantification limit is 1 pg m⁻³ for the individual compounds in the ambient air, and 50 pg L⁻¹ in the rain water.

were analyzed using a GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs and OCPs, a GC-MS (HP 6890—HP 5975) with a J&W Scientific fused silica column DB-5MS was used for confirmation. 16 US EPA PAHs were determined in all air samples using a GC-MS instrument (HP 6890—HP 5972 and 5973) supplied with a J&W Scientific fused silica column DB-5MS. GC-MS technique (HP 6890—HP 5972) was also used for the analysis of all samples of wet deposition (PCBs/OCPs and PAHs).

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 75% and 70% for all air 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 100% for PCBs, from 75 to 98% for OCPs, from 72 to 102% for PAHs. Field blanks were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 1% of the quantities detected in samples for PCBs, 1% for OCPs, 3% for PAHs, indicating a minimal contamination during the transport, storage and analysis. Laboratory blanks were always lower than 1% of the amount found in the samples.

Data processing and statistical methods

Standard parametric and non-parametric statistical methods were applied for data presentation (mean, standard deviation, median, minimum and maximum). A Pearson correlation was used for the trend analysis of species; positive correlations mean increasing trends, negative correlations indicate decreasing trends. $\alpha = 0.05$ was defined as the critical level of statistical significance for all analyses. The analyses were performed using Statistica for Windows 7.1 (StatSoft Inc., 2005) and SPSS 12.0.1 (SPSS Inc., 2003).

Results and discussion

Although the ambient air and wet deposition measurements have been carried out since 1988 at Kosetice observatory, only POP data from the last ten years (1996–2005) were used for the evaluation of the long-term trends mainly due to the comparability of the sampling and analytical techniques.

The ranges of measured air and wet deposition concentrations for all POP groups, their means, medians, minima, and maxima in the period of ten years are presented in Table 1. The maximum PAH air concentrations reached as high as hundreds of nanograms per cubic metre for the sum of 16 PAHs in each, gas and particulate phase (median 8 ng m⁻³, and 2 ng m⁻³ for gas and particulate phase, respectively). In contrast, all groups of chlorinated compounds stayed at the maximum levels of hundreds of picograms per cubic metre. While a significant portion (up to 50%) of PAHs was associated with the particles and captured on the quartz filter, almost the entire amount of chlorinated compounds was present in the gas phase. We are, however, aware that particle phase constituents can be slightly underestimated due to the common high volume sampling artifact. Regarding the individual compounds, phenanthrene (median: 4 ng m⁻³, maximum: 31 ng m⁻³) and fluorene (median: 2 ng m⁻³, maximum: 23 ng m⁻³), were found to be the most abundant PAHs in the gas phase, fluoranthene (median: 0.5 ng m⁻³, maximum: 19 ng m⁻³), pyrene (median: 0.5 ng m⁻³, maximum: 13 ng m⁻³), and phenanthrene (median: 0.3 ng m⁻³, maximum: 15 ng m⁻³) reached the highest levels on the particles. There was no significant predominance of any PCB congener in the air; the measured concentrations of γ -HCHs were approximately two times higher than those of α -HCH, and the p,p' -DDE levels were almost a half order of magnitude higher than those of p,p' -DDT. Prevalence of DDT metabolites in the ambient air (observed also in the samples of other environmental matrices)^{12,13,15–19} suggests that old burdens rather than a long-range transport are responsible for the levels of DDT compounds in the air.

A typical seasonality in the atmospheric POP concentrations can be seen in Fig. 2–5. The PAH levels show a characteristic pattern (Fig. 2) prompted by higher occurrence of these compounds in the cold seasons when they are produced by various combustion processes. The highest atmospheric PAH levels found in January and February were as much as three orders of magnitude higher than the lowest ones measured in July and August. January monthly means varied between 22 and 86 ng m⁻³, while those of July stayed between 1 and 4 ng m⁻³.

PCB and OCP concentrations displayed a very different profile (Fig. 3–5). Most of these compounds were banned in Europe and their maxima are not connected to their production or seasonal application. They are present in the atmosphere due to their volatilization from the old deposits (soils, sediments, wastes) or possibly due to a long-range atmospheric transport from regions where they are still applied. In agreement with this hypothesis, elevated levels of chlorinated compounds can be observed during the summer when increasing temperatures enhance the evaporation of these chemicals from the old burdens. Even though this seasonality is not as

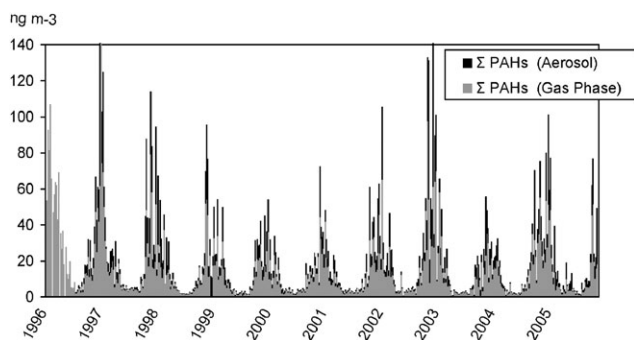


Fig. 2 Σ PAHs in the ambient air, Kosetice observatory, 1996–2005.

well pronounced as it is in the case of PAHs, it can still be detected for PCBs in Fig. 3, and for pesticides in Fig. 4 and 5.

POP concentrations in wet deposition reflect the air concentrations. Phenanthrene, fluorene, and pyrene were the most abundant compounds in all wet deposition samples; γ -HCH was detected in the highest concentrations of all chlorinated compounds. While the mean concentration of PAHs (EPA 16) was 120 ng L^{-1} , the mean concentrations of chlorinated compounds were lower: 0.5 ng L^{-1} for the sum of 7 PCBs, 5 ng L^{-1} for the sum of HCHs, 0.2 ng L^{-1} for the sum of DDT, DDD, and DDE, and 0.05 ng L^{-1} for HCB. A seasonality in the PAH rain water concentrations similar to the atmospheric concentrations can be seen in Fig. 6.

While the minimum summer concentration was only 2 ng L^{-1} , the maximum winter concentration reached as high as 6310 ng L^{-1} .

The annual median concentrations were calculated for all POP subgroups (PAHs, PCBs, DDTs, HCHs and HCB) in the air and wet deposition, and the resulting ten annual values for the period of 1996–2005 were compared to evaluate the long-term trends for each group of compounds and each matrix (Fig. 7 and 8). The analysis revealed time related changes in the amounts of chemical species. An interesting time development can be seen for the sum of 16 PAHs in the atmospheric gas phase (Fig. 7): a very pronounced decrease between 1996 and 2000 was followed by an increase in 2001–2002. This effect probably reflects the local economic situation in the Czech Republic where growing prices of gas in 2001 brought back the coal and wood combustion in local heating systems. A similar trend can be identified for the particulate phase as well as the wet deposition. In the case of wet deposition, the annual

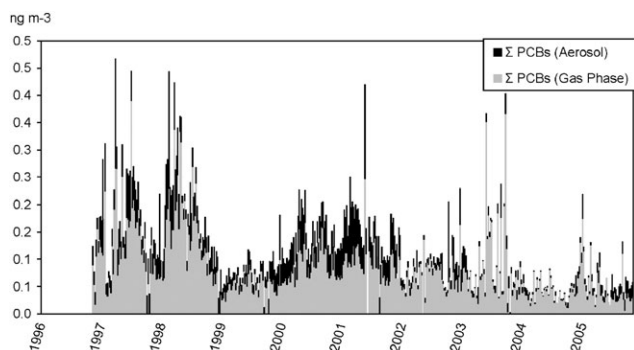


Fig. 3 Σ PCBs in the ambient air, Kosetice observatory, 1996–2005.

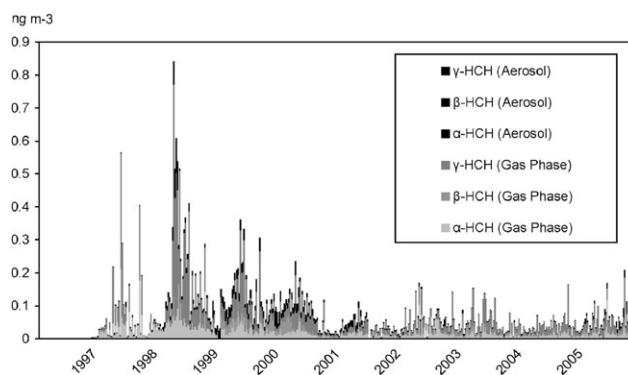


Fig. 4 Σ HCHs in the ambient air, Kosetice observatory, 1996–2005.

medians of PAH concentrations do not show any increase in 2001 (Fig. 8), however, elevated winter maxima can be identified in 2002 (Fig. 6).

The annual medians of PCBs also indicate a general decreasing trend interrupted by two periods of higher concentrations (Fig. 7): 1997–1998 and 2000–2001. As can be seen from Fig. 3, there are significantly elevated summer maxima of PCB concentrations in 1997 and 1998 (maxima 390 pg m^{-3} and 337 pg m^{-3} for the sum of 7 PCB congeners in 1997 and 1998, respectively). In contrast, summer maxima between 2000 and 2001 were lower (167 pg m^{-3} and 246 pg m^{-3}) but due to the higher winter minima (52 pg m^{-3} —same as in 1998), the annual medians remained quite high. Interestingly, in the 2000–2001 period there was also a significant fraction of particle associated PCBs (Fig. 3). In contrast, high summer maxima were observed in 2002 and 2003 (366 pg m^{-3} for the sum of 7 congeners) but due to the low winter levels, it was not reflected in the annual medians. These fluctuations in the annual medians of PCBs may reflect the major flood events in the Czech Republic in 1997 and 2002. A large area of central and southern Moravia (to the east from Kosetice) was flooded in 1997, including industrial and agricultural facilities where various chemicals were stored. The floods were followed by extremely hot summer, therefore those chemicals could evaporate from impacted areas and be a subject of atmospheric transport. Similarly, the central part of Bohemia (to the west from Kosetice, Prague included) was flooded in 2002. Several large chemical enterprises located to the north of Prague were severely damaged, and a variety of chemicals escaped to the surface waters and was distributed with the flood. According

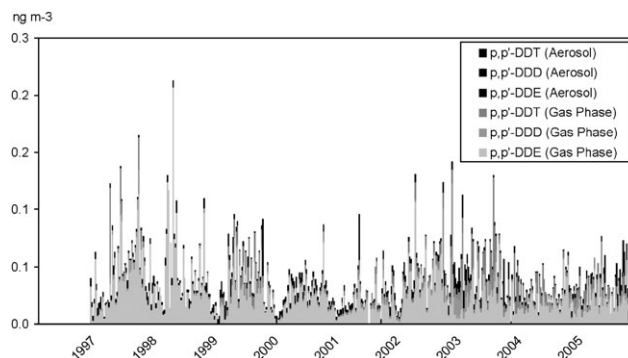


Fig. 5 Σ DDTs in the ambient air, Kosetice observatory, 1996–2005.

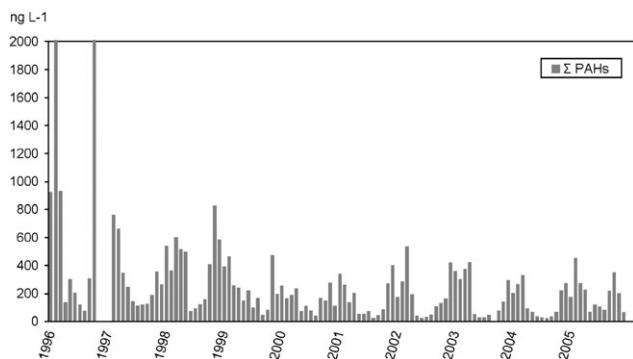


Fig. 6 Σ PAHs in rain (monthly means), Kosetice observatory, 1996–2005.

to the results of our previous research, which focused on the impact of these flood events on aquatic and terrestrial environments,²⁰ one of the effects of floods is a re-distribution of the old burdens from the river sediments to the surface layers of the soils that were flooded. Semi-volatile persistent organic compounds can easily re-evaporate from these top soil levels during the warm season. This is probably the source of elevated atmospheric concentration of chlorinated POPs in the years following these disasters. The reason why the floods

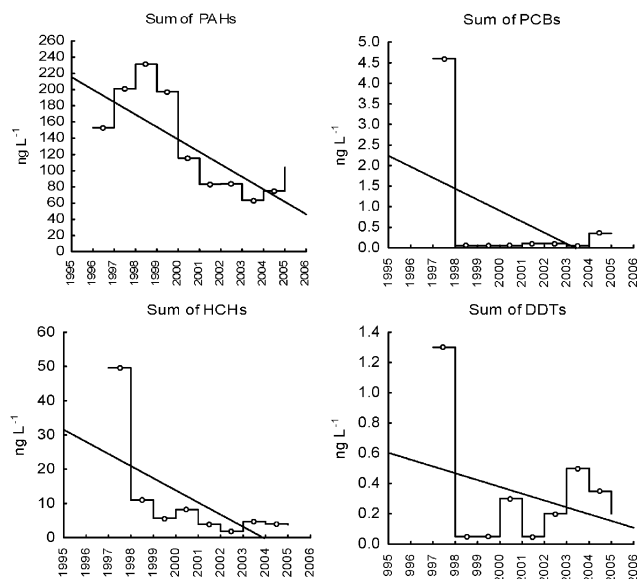


Fig. 8 Time related trends of POPs in the wet deposition. The line represents an estimated trend.

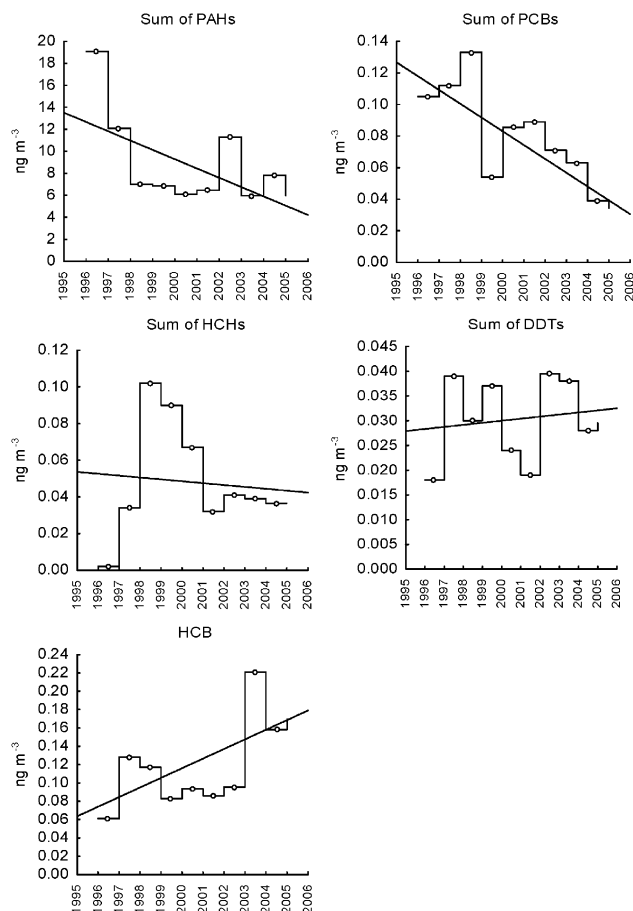


Fig. 7 Temporal trends of POPs in the air, gas phase. The line represents a linear trend estimate.

in 1997 so significantly affected the background levels of PCBs, and the flood events in 2002 had a much smaller impact, can be a character of the flooded regions. In 1997, the region with highest PCB levels in environmental matrices (including mother milk) in the Czech Republic was impacted. A paint factory located in this area (Colorlak) was the major consumer of PCB mixtures produced in the former Czechoslovakia (Chemko Strazske)²¹ under the commercial name Delor, and PCB-containing paints were heavily used in this region.

The same reasoning can be applied to explain the elevated levels of organochlorine pesticides over the same periods (Fig. 4 and 5). HCHs exhibited extremely high levels in the summer of 1998, and gradually decreased in 1999 and 2000 (Fig. 4 and 7). An elevated fraction of β -HCH was observed in 1999 and 2000 (Fig. 4) suggesting that some old deposits of HCH technical mixtures or ballast HCH congeners were newly exposed. The levels have been stabilizing since 2001, showing only a typical seasonal variability.

DDTs followed the same pattern with very high summer maxima in 1997 and 1998 and a gradual decrease until 2001 (Fig. 5 and 7). However, since the second increase in 2002–2003, the concentrations of DDT and its metabolites have stabilized at elevated levels. This is probably again connected to the flood events in 2002, when the chemical factories which earlier produced pesticides, agricultural enterprises and pesticide storage facilities were affected and large amounts of pesticides escaped to the environment. However, the influence of the local sources (evaporation from the soils or ponds) cannot be excluded. A new DDT fingerprint is typical with a less pronounced seasonal variability and the enhanced fraction of *p,p'*-DDD.

HCB is the only analyte which shows a statistically significant increasing trend in its air concentrations. We can still detect high summer air concentrations of HCB following the floods in 1997 but—similarly to DDT—the floods in 2002 seem to have had a more lasting impact. The very high

concentrations from 2002 and 2003 have only declined very slowly in the next few years. Thus, what seems to be an increasing trend in the statistical analysis of annual medians is most probably only a very slow recovery of the ecosystem from the severe impact of the natural disaster. At the same time, an extreme level of pentachlorobenzene as a degradation product of HCB was detected in 2002.

Between 1987 and 2004, there have been ten reports published by EMEP presenting data on POPs and heavy metals from national and international monitoring programs.^{6,22,23} POPs were included in the EMEP's monitoring program in 1999; however, data for POPs have been reported only from countries around the North and Baltic Seas, in the Arctic and from the Czech Republic. In general the concentrations decrease from south to north, except for α -HCH where the highest concentration was seen in 2004 in Svalbard, Norway (Zeppelin, 17 pg m^{-3}) and Finland (Pallas, 18 pg m^{-3}), followed by lower concentrations in Sweden (Råö, 13 pg m^{-3}), Czech Republic (Kosetice, 12 pg m^{-3}) and Iceland (Storhovdi, 5 pg m^{-3}).⁶ The presence of HCH in environments far away from the sources is due to long-range atmospheric transport. Preferential deposition and accumulation in polar latitudes are expected according to the hypothesis of global fractionation and cold condensation.²⁴ Iceland, on the other hand, is influenced by westerly air masses, which may explain the lower concentrations. A similar monitoring study performed in the Great Lakes area (Integrated Atmospheric Deposition Network—IADN)²⁵ found the α -HCH concentration in Chicago area (Lake Michigan, 45 pg m^{-3}) lower than the one in Eagle Harbor (Lake Superior, 52 pg m^{-3}).

Concentrations of other POPs are much higher in the Czech Republic than those observed in the Nordic countries. For PCBs it is explained by the high historical usage in central Europe²⁶ and production of PCBs in the former Czechoslovakia in significant amounts until 1984.²¹ The concentration of, for instance, PCB 101 in Kosetice was 7 pg m^{-3} in 2004, while it is only 1–2 pg m^{-3} in all the other stations. In the Great Lakes area, for comparison, a concentration of 33 pg m^{-3} was measured for PCB 101 in Chicago, while it was only 2 pg m^{-3} in Eagle Harbor.²⁵

A similar situation was observed for DDTs. A DDE concentration as high as 21 pg m^{-3} was observed in Kosetice, while it was only 3 pg m^{-3} in Sweden, 1 pg m^{-3} in Finland and Svalbard, and below the detection limit in Iceland. The IADN program reported 20 pg m^{-3} of DDE in Chicago and 1 pg m^{-3} in Eagle Harbor.²⁵

Determination of PAHs in the air samples showed the levels of 5.9 ng m^{-3} for phenanthrene and 279 pg m^{-3} for benzo(a)pyrene in Kosetice, 1.1 ng m^{-3} and 29 pg m^{-3} in Sweden, 470 pg m^{-3} and 33 pg m^{-3} in Finland, and 7 pg m^{-3} and 3 pg m^{-3} in Svalbard. At the Great Lakes, a concentration of 27.8 ng m^{-3} was measured for phenanthrene and 230 pg m^{-3} for benzo(a)pyrene in Chicago, while it was only 480 pg m^{-3} and less than 1 pg m^{-3} in Eagle Harbor.²⁵

A significant effort connected to the long-term ambient air monitoring program in the Kosetice observatory is also focused on source identification. Due to the prevailing westerly wind direction and the main sector of incoming air masses between 220° and 320°, major industrial and urban centers in

the Czech Republic, *i.e.* Prague, Plzen, and Ceske Budejovice may act as source areas for Kosetice observatory. These sources, of course, only contributed towards the end of air parcels' traveling to the site. A detailed analysis of the wind trajectories and the origin of air masses is needed in order to identify other, more remote sources, and the main contributors to the atmospheric pollution at the background station. Those tasks are currently being addressed.

Conclusions

Data from ten years of integrated monitoring at Kosetice observatory were used in this project to assess long-term trends of POPs in the ambient air and wet deposition in the European continental background. Most of the selected compounds exhibited decreasing trends in the last decade. This is consistent with data reported from other European sites.⁶

The results of our project demonstrated that the long-term background monitoring is not only an excellent way to study the regional levels and trends, but also a powerful tool for evaluation of the impact of various local and regional events—from industrial accidents to natural disasters. As such, this approach has the potential to play a crucial role in the implementation of regional and global measures and conventions on persistent toxic substances.

Monitoring data from Kosetice are currently being used for the assessments of the sources and distribution processes, and for the validation of long-range transport and environmental fate models. This study was carried out as a contribution to the ongoing national POPs inventory in the Czech Republic.

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