

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

Part II. Aquatic and terrestrial environments 1996–2005†‡

Ivan Holoubek,^{abc} Jana Klánová,^{*ac} Jiří Jarkovský,^a Vratislav Kubík^a and Jan Helešic^b

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A multimedia sampling of ambient air, wet deposition, surface water, sediment, soil and biota has been performed at Kosetice background observatory in the southern Czech Republic since 1988. An integrated monitoring approach was applied to assess the current state, anthropogenic impacts, and possible future changes of terrestrial and freshwater environments. Average PCB concentrations in the individual matrices calculated from ten years of sampling on multiple sites varied between 2 ng g⁻¹ in sediment and 7 ng g⁻¹ in soil or moss. DDT concentrations were lower in moss and needles (2 ng g⁻¹ and 4 ng g⁻¹, respectively) than in sediment (11 ng g⁻¹) and soil (20 ng g⁻¹), while the HCH level was higher in moss and needles (5 ng g⁻¹ and 6 ng g⁻¹, respectively) than in soil or sediment (1 ng g⁻¹ and 2 ng g⁻¹, respectively). The highest average level of PAHs was found in soil (600 ng g⁻¹), while it was lower in needles (230 ng g⁻¹), moss (210 ng g⁻¹) or sediment (210 ng g⁻¹). Time related trends of concentration levels of persistent organic pollutants in all matrices were investigated. Moss and needle trend patterns resembled those of the ambient air, showing a slight concentration decrease of all compounds, except for hexachlorobenzene. The soil, water and sediment concentrations showed a similar decrease of PAHs, PCBs, and HCHs, but there was no clear trend for DDTs and HCB.

Introduction

Persistent organic pollutants (POPs) remain in the center of scientific attention due to their slow rates of degradation, their toxicity, and potential for both long-range transport and bioaccumulation in living organisms. The accumulation of persistent organic pollutants in soils and sediments may present a significant risk for the future. In many regions, freshwater sediments were found to be a major reservoir of POP compounds, and under specific conditions they may turn into potential “chemical time bombs”—a significant source of the pollutants, posing a risk to the downstream sites.^{1–4} Polluted river sediments can be subject to remobilization and transport during certain environmental events such as bioturbation, floods or human activities (dredging and relocation of sediments).⁵ The remobilization processes also significantly affect the new distribution of contaminants throughout the aquatic

ecosystem as well as their bioavailability.^{6,7} The effects of major floods were examined from the continuous set of data for floodplain soils and sediments from an industrial area in the Czech Republic, where a 100 year flood event occurred in 1997.⁸ The changes in the distribution of pollutants have been assessed by multiple sampling of sediments and alluvial soils. Pollutant concentration and relative distribution in sediments and floodplain soils were significantly affected by the flooding. It resulted in a decrease of POP concentrations in sediments and a significant rise of pollution in the flooded soils.⁸ Therefore, any information on the levels of pollutants, as well as on their distribution, accumulation and mobility, is crucial for the evaluation of future fate and effects of those compounds in the terrestrial and aquatic ecosystems and the estimation of the risks connected with this contamination.

A long-term project of integrated monitoring including both aquatic and terrestrial environments has been carried out in the area of a background observatory in Kosetice, Czech Republic, since 1988.⁹ A small catchment of Anensky brook offers a diverse terrestrial ecosystem linked to the aquatic ecosystem of adjacent water bodies, and it includes all interacting components: atmosphere and depositions, plants and soils, brooks and ponds. While soils have a more stable long term environmental memory related to contamination level, pattern and distribution, sediments are more dynamic, as they provide information on the immediate situation within the watercourse. This article presents the second part of a work focused on the interpretation of the results from the Kosetice

^a RECETOX, Faculty of Science, Masaryk University, Kamenice 126/3, 625 00 Brno, Czech Republic. E-mail: klanova@recetox.muni.cz; Fax: +420 549492840; Tel: +420 549495149

^b TOCOEN, s.r.o., Kamenice 126/3, 625 00 Brno, Czech Republic. E-mail: klanova@recetox.muni.cz; Fax: +420 549492840; Tel: +420 549495149

^c National POPs Centre of the Czech Republic, Kamenice 126/3, 625 00 Brno, Czech Republic. E-mail: klanova@recetox.muni.cz; Fax: +420 549492840; Tel: +420 549495149

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Fig. 1 Map of the sampling sites.

monitoring project.⁹ Spatial and temporal trends in the background levels of persistent organic compounds in various matrices of terrestrial and aquatic environments are assessed here.

Methods and materials

Sampling sites

The long-term monitoring program at Kosetice observatory has been described in detail elsewhere.^{9,10} This station of the Czech Hydrometeorological Institute is a part of an European Monitoring and Evaluation Programme (EMEP) background network. The monitoring area consists of the Anensky Brook basin with 16 sampling sites, where the samples of various matrices are collected yearly, in late August. A list of the sites including an overview of sampled matrices is given in Fig. 1 and Table 1. There are four major sub-regions where the samples are taken. First (region I), is the stream area of the Anensky Brook. Water from the multiple sources (site 2) is

Table 1 List of the sampling sites

ID	Sampling site	Matrix ^a							
		A	R	W	SE	S	M	N	
1	Observatory	x	x			x			
2	Spring of Anensky Brook			x	x				
3	Meadow at the spring					x			
4	Old pond			x	x				
5	Slope above the spring					x	x	x	
6	Hydrological station (HS)			x	x				
7	HS, meadow under trees					x	x	x	
8	HS, open meadow					x	x	x	
9	HS, upper slope					x	x	x	
10	Right tributary (RT)			x	x				
11	RT, forest edge					x			
12a	Before the confluence			x	x				
12b	After the confluence			x	x				
13	RT, meadow					x	x	x	
14	New pond			x	x				
15	RT, hillside					x	x		

^a A—air, R—rain, W—surface water, SE—sediment, S—soil, M—moss, N—needles

drawn into the pond (site 4). A drain area includes the slopes of forested hills as well as the agricultural fields. Soil samples are collected from the meadow near the spring (site 3) and from the forested slope (site 5), which is also a source of the moss and pine needles. The original pond (site 4) was let out in 1990 because a new weir was constructed in the late 1980s only several hundred metres further down the stream. The bottom of the old pond was left as it was and it has gradually turned into a meadow in the last fifteen years. In wet years, however, the bottom still collected and held a variable amount of surface water. The old sediment, and eventually the surface water, were sampled here. In the spring of 2006, the old pond was filled again. The same matrices were also taken from the new pond (site 14). The second sub-region (II) is connected to the small right tributary (Forest Spring) of the Anensky Brook. Water and sediment samples from the tributary (site 10), and soil (sites 11, 13, and 15), moss (sites 13 and 15) and pine needle (site 13) samples were taken in this area. The third sub-region (III) is close to the junction of the Anensky Brook with the Martinicky Brook. Water and sediment samples (site 6) were collected near the old hydrological station, where the sediment tends to accumulate and creates thicker layers, and further down the stream: before (site 12A) and after (site 12B) the confluence with the tributary. Soils (sites 7–9), mosses (site 7–9), pine needles (site 7 and 9) and spruce needles (site 8) were sampled here. The sampling site no. 1 is the observatory (IV), where the samples of the ambient air (weekly), wet deposition (every event) and soil were collected on the regular basis.

Sampling procedures

A collection of surface water, sediment, soil, mosses, and needles is based on the recommendation of United Nations Economic Commission for Europe (UN ECE) integrated monitoring program.¹¹

Surface sediments (top 10 cm layer) were collected using a trowel from the sedimentation basis of the bed in zones of calm flow close to the bank. Representative samples were prepared by mixing 5–8 sub-samples from an area of about 4 m². Large pieces of wood, leaves and stones, greater than approximately 1 cm, were removed by hand and sediments were air-dried at the room temperature. Dry sediments were homogenized, ground with a pestle and mortar and sieved using a 2 mm sieve. Glass vessels (2 L) were used for surface water sampling. They were filled manually, closed, and transported to the laboratory immediately.

A soil profile was described and basic soil parameters were determined in all sampling sites in the beginning of the project. Soils were sampled at 25 × 25 m sampling plots as 5–10 sub-samples from the top 10 cm layer which were further homogenized. Soil samples were transported to the laboratory in polyethylene bags, air-dried at laboratory temperature, and sieved through a 2 mm mesh. The moss samples (*Hypnum cupressiforme*) were collected on the ground outside the crown projection of trees, and the 3 year-old pine and spruce needle samples (*Pinus silvestris*, *Picea abies*) were hand-picked. They were transported to the laboratory wrapped in aluminium foil, and air-dried at laboratory temperature.

Chemical analysis

A full set of US EPA 16 PAHs, seven indicator PCB congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180), *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE, α -, β -, γ -, δ -hexachlorocyclohexanes, hexachlorobenzene and pentachlorobenzene were analyzed in all matrices.

All solid samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. Two techniques were used for the analysis of water samples. Liquid–liquid (L–L) extraction was employed until 2004, and solid phase extraction (SPE) has been applied in 2005. All analytical procedures and quality assurance/quality control measures were described in detail in the first part of this article.⁹

Data processing and statistical methods

The analysis can be divided into two parts: spatial variation of data in the sampling sites and analysis of the time related trends. Prior to statistical analysis of the time trends, the spatial aggregation was adopted and samples from all sites in a given year and matrix were aggregated by taking the median values. This approach gives stable estimates of the measured values for analyses of the general time trends, not influenced by the local fluctuations.

Standard parametric and non-parametric statistical methods were applied for data presentation (mean, median, minimum, maximum). A Pearson correlation was used for the trend analysis of species; positive correlations mean a increasing trend, negative correlations indicate a decreasing trend. $\alpha = 0.05$ 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

Levels

Minimum, maximum, mean and median levels of selected groups of compounds found in environmental matrices in Kosetice between 1996 and 2005 are listed in Table 2. Regarding the individual compounds, phenanthrene, fluoranthene, pyrene and benzo[*b*]fluoranthene were found to be the most abundant PAHs in the soil and sediment samples, phenanthrene and naphthalene most abundant in surface waters, and phenanthrene, fluoranthene and pyrene most abundant in the moss and needle samples. PCB congeners 153 and 138 were dominant in the soils and sediments, while there was no such pattern in the mosses and needles. The measured concentrations of γ -HCH were higher than those of α -HCH in all moss, needle, and soil samples, but in sediments α -HCH occasionally prevailed. There were several soil and sediment samples with a significant fraction of β -HCH as well. The *p,p'*-DDE levels were higher than those of *p,p'*-DDT in most of the soil samples, however there were sampling sites with *p,p'*-DDT dominating the pattern. In some sites a significant change of the DDT/DDE ratio in the last ten years can be observed. In contrast, *p,p'*-DDE dominated in all moss, needle, and sediment samples.

POP levels measured in Kosetice can be compared to data from other monitoring programs summarized in the National POPs Inventory of the Czech Republic.¹² Monitoring of Czech agricultural soils, for instance, has been carried out since 1994

Table 2 Minimum, maximum, mean and median POP concentrations in surface water, sediment, soil, mosses and needles, Kosetice 1996–2005^a

Matrix (units)	Species	Mean	Median	Min.	Max.
Water (ng L ⁻¹)	Σ PAHs	23	13	2.3	170
	Σ PCBs	2.1	0.50	BQL	20
	Σ HCHs	6.1	2.10	BQL	69
	Σ DDTs	1.2	0.20	BQL	14
	HCB	0.51	0.30	0.10	1.8
Sediment (ng g ⁻¹)	Σ PAHs	210	160	13	1100
	Σ PCBs	2.2	2.1	0.23	7.1
	Σ HCHs	0.47	0.27	BQL	4.1
	Σ DDTs	11	4.8	0.28	68
	HCB	3.3	0.39	0.04	78
Soil (ng g ⁻¹)	Σ PAHs	600	280	41	5400
	Σ PCBs	7.3	3.7	BQL	40
	Σ HCHs	1.1	0.43	BQL	20
	Σ DDTs	20	5.1	BQL	190
	HCB	1.5	0.86	BQL	9.2
Mosses (ng g ⁻¹)	Σ PAHs	210	170	83	690
	Σ PCBs	7.1	4.8	0.87	20
	Σ HCHs	4.6	0.89	BQL	150
	Σ DDTs	2.2	2.0	BQL	7.2
	HCB	2.7	0.76	BQL	47
Needles (ng g ⁻¹)	Σ PAHs	230	200	66	1000
	Σ PCBs	5.6	5.3	BQL	12
	Σ HCHs	6.4	2.6	BQL	37
	Σ DDTs	4.2	2.7	BQL	25
	HCB	4.8	2.8	BQL	51

^a BQL = below quantification limit. Quantification limit is 10 pg g⁻¹ for the individual compounds in the solid matrices, and 50 pg L⁻¹ in the surface water.

Table 3 Minimum and maximum POP concentrations in sediment, soil, moss and needles, Kosetice 2006, Central and Eastern Europe (CEE)

Matrix	Species	Kosetice 2006	CEE 2005–2006
Sediment (ng g ⁻¹)	∑PAHs	39–302	19–30 232
	∑PCBs	0.1–0.7	1–143
	∑HCHs	0.1–0.7	0.1–4
	∑DDTs	0.6–38	0.3–58
	HCB	0.1–112	0.1–78
Soil (ng g ⁻¹)	∑PAHs	78–2193	68–58 384
	∑PCBs	1–7	0.3–3309
	∑HCHs	0.5–2	0.2–4893
	∑DDTs	0.6–29	0.2–1283
	HCB	0.3–2	0.5–2140
Moss (ng g ⁻¹)	∑PAHs	47–112	74–4500
	∑PCBs	0.9–2.4	0.9–15
	∑HCHs	2–4	1–58
	∑DDTs	2–4	0.4–109
	HCB	2–4	0.4–2
Needles (ng g ⁻¹)	∑PAHs	33–79	23–250
	∑PCBs	0.6–2	0.5–5
	∑HCHs	1–10	1–56
	∑DDTs	0.8–14	0.4–7
	HCB	0.3–0.7	0.1–3

on more than two hundred soils. In 2002, the mean concentration in the soil matrix was 1264 ng g⁻¹ for PAHs, 5.7 ng g⁻¹ for PCBs, 25 ng g⁻¹ for DDTs, and 7.3 ng g⁻¹ for HCHs, which means that mean levels in the background soils are generally lower than the levels in agricultural soils included in the study. However there was no clear time trend observed for these compounds in agricultural soils over a period of ten years.

Table 3 compares the ranges of POP concentrations found in various matrices in Kosetice (2006) to data from other studies performed in this region. The National POPs Inventory of the Czech Republic¹² is a source of sediment data. Soil samples (50 sites from the Czech Republic and 50 from the Central and Eastern European countries) were collected in 2005 and 2006 in frames of the international project focused on the development of the passive air monitoring network in the Central and Eastern European countries. Background, rural, urban, and industrial sites were included. Moss and needle concentrations were measured in 2005 and 2006 as a part of the screening study covering 50 sampling sites in the Czech Republic (unpublished results).

Distribution

PAHs showed a very uneven distribution in the soil, water and sediment, and uniform distribution in space and time in moss and needles (Fig. 2). PAH concentrations decreased in sediments from the Anensky Brook spring (area I) over the period of ten years but did not change in the old and new ponds. Originally, very low sediment concentration in the forest spring (area II) increased significantly in the last years (half to one order of magnitude). This sudden increase was connected to the reconstruction of the forest road located just up the hill in 1999. Unfortunately, the old surface layer scraped off the neighboring highway was used as a construction material for the forest road. This fine grit was sampled and analyzed in 1999, and a PAH concentration more than 5 µg g⁻¹ was determined. A repeated sampling and analysis

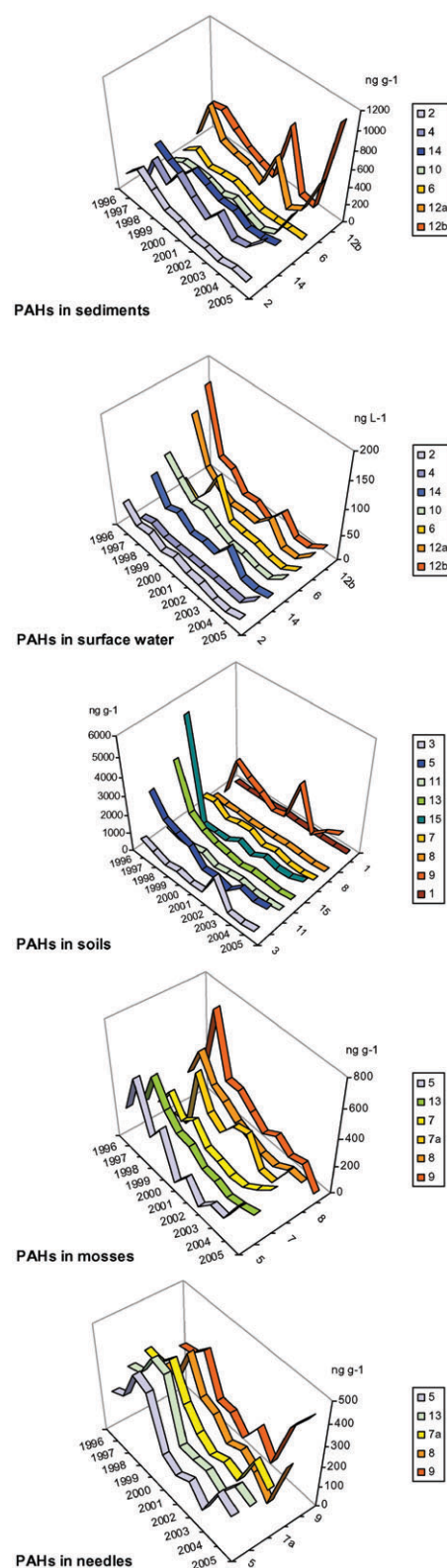


Fig. 2 Spatial and temporal variations of PAH concentrations in sediment, surface water, soil, moss and needles, Kosetice observatory, 1996–2005.

two years later revealed a concentration of $1.5 \mu\text{g g}^{-1}$. This suggests that PAHs from the construction material were slowly washed away and transported to the surrounding forest soils, where they were retained or transported further down the hill to the forest spring. This can explain PAH concentrations in the forest soil steadily rising since 2001 as well as elevated levels in the sediment.

The PAH levels in the soil varied in space, while the variability in time was low. High correlation of the soil contamination with the soil type should be noticed. While the forest soils with high organic carbon content stored high PAH loads, meadow soils with low organic carbon content from the same sub-regions showed concentrations one order of magnitude lower. The PAH distribution in soils corresponded very well to that in sediments. The highest PAH concentrations in the Anensky spring area and at the junction with Martinicky Brook suggest that the forest soils can be a source of PAH contamination of the sediments.

PAH concentration in moss and needles were very uniform for all the sampling sites. Temporal variations show a gradual decrease of concentration between 1998 and 2002, followed by an ongoing increase since 2002. This corresponds very well with the results of the air monitoring,⁹ where the same trend was observed and assigned to enhanced coal combustion in the local heating systems.

All moss and needle samples from the same sampling period also had a very low spatial variability in the PCB concentrations, while contamination of soil was more heterogeneous (Fig. 3). As in the case of PAHs, there were significantly higher levels of PCBs in the forest soils than in the meadows, as the influence of the soil type is apparently much stronger than site-to-site variability.

Sediments in the spring area (area I) were more PCB contaminated than in regions II and III, and the PCB concentrations in ponds were higher than those in the spring of Anensky Brook—probably due to accumulation over time. However in 2005, the PCB concentrations increased significantly in all sampling sites.

The highest concentrations of DDTs were also associated with the spring area (I). The elevated levels in both pond sediments as well as in the spring itself suggest that the surrounding agricultural fields supply the spring with this pesticide. This hypothesis is supported by the high levels of DDTs in the soil from the forested slope above the spring as well as from the meadow surrounding the spring. Analysis of the surface waters suggests the same conclusions. Although the DDT concentrations in water are generally very low, elevated concentrations can be seen in the spring and new pond. The new pond is the most interesting sediment sampling site. Unlike the sediments from the brooks, it has a lower mobility and a higher potential to accumulate POPs from the spring area. Since it was only constructed in the late 1980s, we can observe this accumulation in the monitoring data. It is most pronounced for DDTs: while the initial sediment concentration for the sum of DDT, DDD and DDE was below 0.02 ng g^{-1} , it grew to 29 ng g^{-1} in 2005. DDT levels seemed to be growing also in some other sediments, moss and needles. A contamination of the spruce needles from region III (the only site where the spruce needles are collected) was 2–3 times

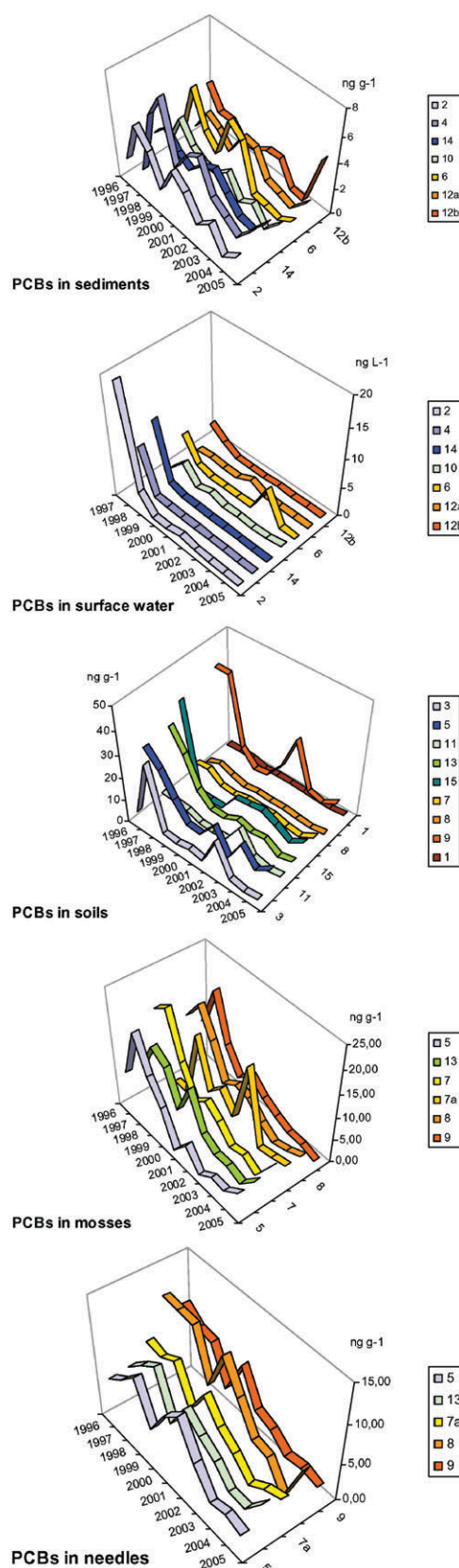


Fig. 3 Spatial and temporal variations of PCB concentrations in sediment, surface water, soil, moss and needles, Kosetice observatory, 1996–2005.

higher than contamination of the pine needles from any site, even though the soil level of DDTs in this region was low. Since this is a consistent finding over ten years, it seems that certain compounds have higher affinity to the wax on the surface of the spruce needle than to the pine needles.

The same discrepancy between the concentrations in the spruce and pine needles was observed for the group of HCHs. Otherwise, the spatial distribution of the HCH compounds was very homogeneous in the moss, soil, sediment and surface water samples. On the other hand, the HCB contamination is once again associated with the spring area (I). The HCB levels have been found elevated and still growing not only in the forest but also in the meadow soil. However, the concentration in the sediment/soil from the bottom of the former old pond is gradually decreasing, probably due to evaporation from exposed sediments.

Time related trends

As a next step, the temporal trends were assessed. Moss and needle trend patterns for all investigated POPs resembled those of the ambient air, showing a slight concentration decrease of all compounds,⁹ except for hexachlorobenzene.

Time trends of the POP concentrations in the soil, water and sediments showed similar decreasing trends for PAHs, PCBs and HCHs, but the pattern for DDTs and HCB is not clear. Comparison of the time related trends of investigated groups of POPs in the individual matrices is presented in Fig. 4–8.

A statistically significant decline of the PAH concentrations can be detected in the wet deposition, soil and surface water (Fig. 4). A weaker declining trend is also in the air, moss and needle concentrations. On the other hand, PAH concentrations in sediments did not decrease.

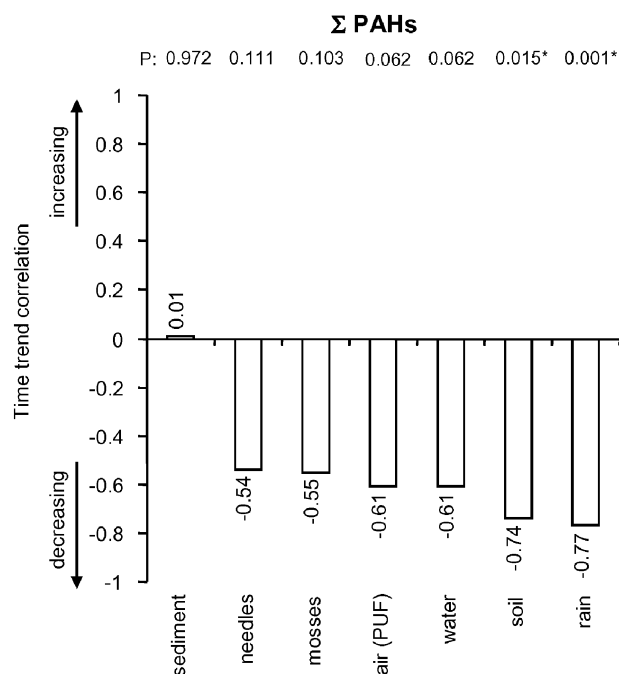


Fig. 4 Time related trend of PAHs; trends range from –1 (decreasing trend) to 1 (increasing trend).

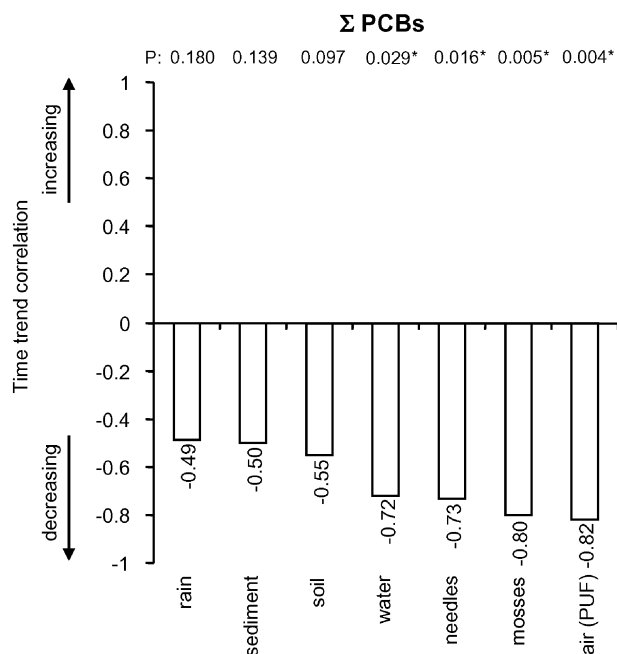


Fig. 5 Time related trend of PCBs; trends range from –1 (decreasing trend) to 1 (increasing trend).

As can be seen in Fig. 5, PCBs manifested a significant decrease in the air, moss, needles and surface water. Decreasing trend measures above 0.5 were, however, also achieved for sediment and soil. Since PCBs were banned in Europe and there are no fresh inputs, the overall decreasing trend is expected. Although the detailed temporal analysis revealed some short periods of increased concentrations (often

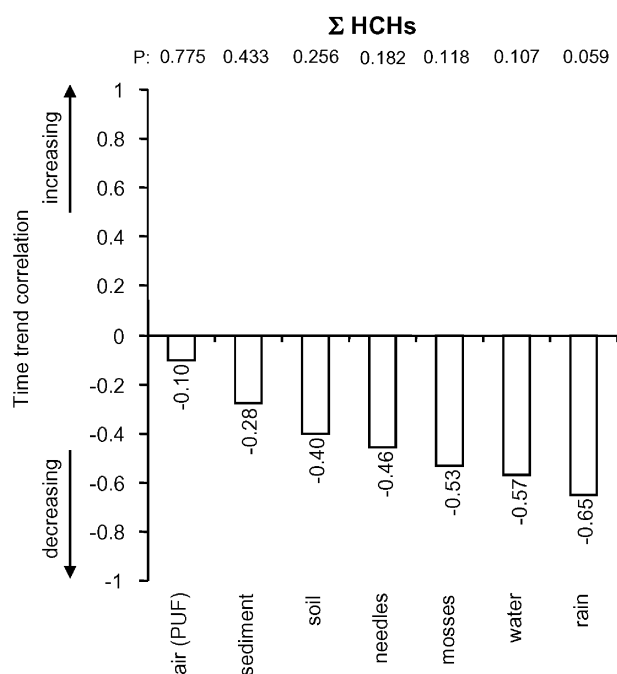


Fig. 6 Time related trend of HCHs; trends range from –1 (decreasing trend) to 1 (increasing trend).

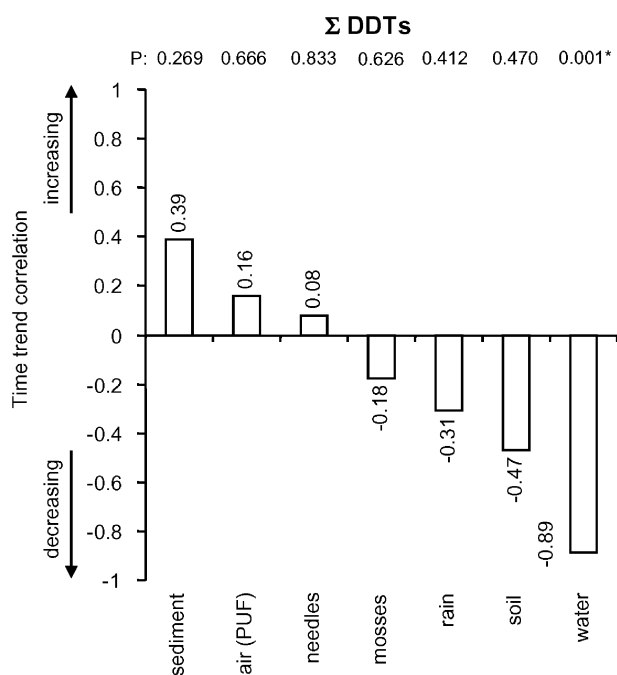


Fig. 7 Time related trend of DDTs; trends range from -1 (decreasing trend) to 1 (increasing trend).

connected to flood events),⁹ those did not affect the overall trend.

Even though there was no significant downtrend of HCHs in the air concentrations, a weak decreasing trend was detected in moss and needles, and especially in both rain and surface water (Fig. 6). Similarly, while there is a significant decrease of DDT concentrations in surface water, the concentrations in

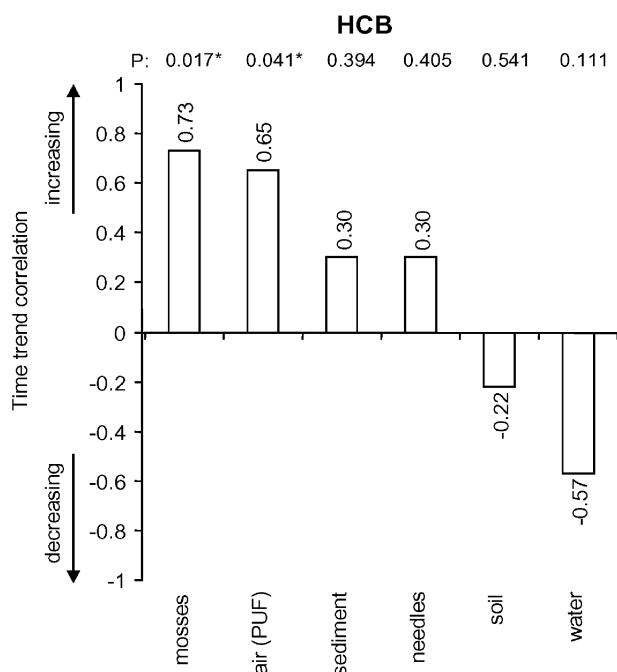


Fig. 8 Time related trend of HCB; trends range from -1 (decreasing trend) 1 (increasing trend).

sediments slightly increased (Fig. 7). The most significant rising tendency was, however, detected for the HCB concentrations, especially in the air and moss.

Conclusions

The POP concentrations in sediment, surface water, soil, moss and needle samples have been monitored in 16 sampling sites over a period of eighteen years. There was a significant variability in occurrence and distribution of selected groups of persistent pollutants in the environmental matrices. PAHs are emitted from a variety of primary sources, and the influence of the local heating systems, for instance, can be easily detected even in the background station—both in the typical seasonal fluctuations of the ambient air concentrations, and in the long-term trends.

The atmospheric concentrations of PCBs and OCPs are more homogeneous in time and space since they are more influenced by diffusive sources, such as evaporation from contaminated soils. However, even here we can detect events with high environmental impact (floods, industrial disasters and constructions) transporting significant amounts of persistent compounds from their primary sources, storage places or contaminated sites to the surface waters and soils, where they are a subject of evaporation in the following years. The moss or needle samples precisely reflect the current contamination of the atmosphere, while the sediment and soil samples (especially the organic carbon rich forest soils which can act as an efficient sink of the POP pollution) provide us with a long-term record of the regional pollution. At the same time, we need to be aware that the matrices with high accumulation potential can turn from sinks to local sources of POPs. Such complex background monitoring data can be used not only to evaluate the long-term trends in the environmental pollution or the impact of various short-term events. They are also very valuable for the assessment of the fate of persistent compounds in the environment—their cycling between compartments, long-range transport or accumulation in various matrices—as well as for the validation of various distribution and transport models. Results of our project presented in this article strongly support the argument that long-term monitoring programs are of high importance for decision making and legislation, as well as for the effective evaluation of various measures.

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