Research Articles

Regional Background Monitoring of PBT Compounds

The Comparison of the Results from Measurements and Modelling

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Abstract. A comparison of the modelling results of persistent, bioaccumulative and toxic (PBT) chemicals is presented with measurements. Contribution will present mean annual concentrations calculated and observed at EMEP stations and their ratios. The comparison of the calculated results with older results indicates that the model modification improved the agreement with measurement data. PBT compounds in ambient air are monitored in the area of Košetice observatory (professional observatory of the Czech Hydrometeorological Institute located in south Bohemia). Calculated and measured mean annual concentrations of PBTs in precipitation, soil, vegetation and their ratios are presented. It should be mentioned that the number of measurements in such compartments as seawater, soil and vegetation is insufficient for model verification at present. The agreement between results from MSC-East models and results from long-term regional air background monitoring in Central Europe is good.

Keywords: Long-range transport; measurements vs. modeling; PBT compounds; persistent organic pollutants (POPs); POPs; regional background monitoring

Introduction

Organic substances that are persistent, bioaccumulative and possess toxic characteristics which are likely to cause adverse human health or environmental effects are called PBTs (Persistent, Bioaccumulative, and Toxic substances). In this context, 'substance' means a single chemical species, or a number of chemical species, which form a specific group by virtue of (a) having similar properties and being emitted together into the environment or (b) forming a mixture normally marketed as a single product. Depending on their mobility in the environment, PBTs could be of local, regional or global concern (Vallack et al. 1998).

A subclass of PBTs, the so-called POPs (persistent organic pollutants), is a group of compounds which are prone to long-range atmospheric transport and deposition (Vallack et al. 1998, UN-ECE 1998). The global extent of POP pollution became apparent with their detection in areas such as the Arctic, where they have never been used or produced, at levels posing risks to both wildlife (Barrie et al. 1992) and humans (Mulvad et al. 1996).

The regional and global nature of the processes make international efforts to generate comparable measurements the only basis on which further knowledge on the pools and fluxes can rest. Only a few POPs have been measured at a few sites. For persistent organic pollutants, the reversibility of deposition processes and the consequent re-emission make soils and vegetation relevant sinks, and resources as well as receptors are at risk so that the assessment of existing concentrations in different media based on an improved understanding of the current status of the relevant pathways and potential effects of the different substances under consideration in different environments is an important step for developing effective control measures.

Originally, the overall aim of integrated monitoring was to determine and predict the state and change of terrestrial and freshwater ecosystems in a long-term perspective with respect to the impact of air pollutants including persistent organics (IM EMEP 1998).

Integrated monitoring of ecosystems means simultaneous physical, chemical and biological measurements of different ecosystem compartments over time at the same location. A small catchment (or other hydrologically well defined area), such as in an integrated monitoring site, is large enough to encompass all the interacting components: atmosphere and vegetation, plants and soils, bedrock and groundwater, brook or lake, and surrounding land. A small catchment comprises a terrestrial ecosystem usually with a linked aquatic ecosystem of an adjacent brook. Some basins contain one or more ponds or lakes. A terrestrial ecosystem is conventionally viewed as an assemblage of living organisms interacting in a complex way with one another and with their environment, air, soil and water.

The contribution of integrated monitoring programmes in the future could be very significant if comparable and simultaneous measurements of atmospheric concentrations, wet, bulk and dry deposition, concentration in soils, sediments, water and vegetation (lichens, mosses, needles, leafs, bark) could be obtained for a range of different ecosystems in different regions such as the ICP IM network. Such information would be of great value to: a) enhance the precision of vegetation samples as indicators, b) improve the estimates of local pools and fluxes and of uncertain, substance and

site-specific parameters on which exposure estimates can be developed and c) by reporting the information to the modelling community to improve the accuracy of extensive regional modelling of the long-range atmospheric transport of POPs.

International scientific workshops make a significant contribution to the development of EMEP policies and strategies in the field of POP transboundary pollution. Recently, the following workshops were held: Workshop on POPs and HMs (US EPA, October 1999); AMAP Workshop on techniques and associated uncertainties in quantifying the origin and long-range transport of contaminants in the Arctic (Bergen, Norway, June 1999); WMO/EMEP/UNEP Workshop on modelling of atmospheric transport and deposition of persistent organic pollutants and heavy metals (Geneva, Switzerland, November 1999).

The discussions and conclusions of these workshops were focused on investigations of POP accumulation in compartments along with their spatial distribution; trend analysis of accumulation in compartments; monitoring and the comparison of calculation results versus measurements not only for air but for other environmental compartments (soil, sea water, vegetation); assessment of emission data uncertainties; assessment of uncertainty of model results related to input information (sensitivity study) as a routine part of modelling studies; a comprehensive assessment of dry deposition, in particular to a forest; studies of pollutant behaviour in the marine environment including the transport by sea currents; investigations of the impact of pollutant distribution with particle sizes on deposition and concentration levels in different compartments; and the refinement of intercompartment exchange processes including re-emission.

Based on these topics, the co-operation between RECETOX-TOCOEN & Associates, Brnoand EMEP MSC_East, Moscow is now focused on the six main parts:

- The modification and further development of the POP long-range transport model for the European region
- Investigations of physical-chemical properties and parametrization for some new POPs (four congeners of dioxins/furans and HCB) and its refinement for previously considered pollutants (PCB, B[a]P, γ-HCH)
- Preparation of input data for modelling
- Collection and processing of measurement data
- Long-range modelling of selected POPs (first of all PCB, B[a]P, γ-HCH) and the analysis of the results obtained
- Model validation: the comparison of calculated and observed values, model sensitivity analysis in regard to integration of new processes as well as to parametrization modifications

According to the POP Protocol, B[a]P, PCB-153, and γ-HCH were selected for the top-priority modelling. These substances can be characterized as chemicals which are persistent, toxic, and able to withstand the long-range transport. From the viewpoint of model development, these substances are interesting since they are distributed differently between the gaseous and aerosol phase in the air. Namely, the largest fraction of B[a]P settles on particles, γ-HCH mainly exists in the gaseous phase of the atmosphere, and PCB is an intermediate substance.

In this paper, the analysis of calculated spatial distribution of selected POPs in 1997 and comparisons with the results from long-term monitoring project, are presented.

1 Methods

1.1 Project TOCOEN: regional background monitoring of POPs

The regional background monitoring of POPs as a part of the TOCOEN (Toxic Organic Compounds in the Environment) research Project is performed in the area of the Košetice observatory from 1988. This monitoring is part of a long-term co-operation between the Czech Hydrometeorological Institute and RECETOX-TOCOEN & Associates. The philosophy of this part of the TOCOEN Project is based on the main approaches of EMEP strategy in the field of POP measurements (Holoubek et al. 1990, Holoubek 1993, Holoubek et al. 1996a, Holoubek et al. 2000a).

The Czech Ministry of the Environment and RECETOX Brno have performed the System of Monitoring of Organic Compounds in the Ambient Air (SYMOS), a preliminary monitoring system of PBT compounds in ambient air in the Czech Republic. During the SYMOS pilot study in 1994–1995, PAHs, PCBs, chlorinated pesticides and PCDDs/Fs were monitored in the area of the Košetice observatory (professional observatory of Czech Hydrometeorological Institute located in south Bohemia). Košetice observatory was established as a regional background station of international monitoring (EMEP, GAW, GEMS) and national monitoring programmes (monitoring of Czech MOE, Project TOCOEN, GEOMON) (Holoubek et al. 1992, Holoubek et al. 1996b, Vana et al. 1997).

In the pilot study of the SYMOS Project, samples were taken in the area of Košetice observatory from July to December 1995. The 24-hour samples were collected weekly; starting on Wednesdays at 8 a.m., PCDDs/Fs were sampled at four-week intervals. High volume samplers equipped with a quartz filter and polyurethane foam adsorbents for the sampling of POPs were used.

From 1996, the regular monitoring of semi-volatile PBTs was continued at the Košetice observatory under a co-operation scheme between the Czech Hydrometeorological Institute Prague and RECETOX-TOCOEN & Associates, Brno. The Košetice Observatory is included among regional background stations under both international (GAW, EMEP) and national (TOCOEN) programmes. At the present time, the TOCOEN monitoring programme of PBTs at Košetice observatory has been carried out on a regular basis already for 14 years – a unique achievement globally. The sampling procedure (one sample per week for the determination of PAHs, PCBs and OCPs) and analytical determination is based on conclusions of the EMEP co-ordinating meeting which took place in Norway in November 1997. Pollutants mentioned above are monitored in the gaseous state as well as in atmospheric particulates.

1.2 Model description

This part of the paper describes the results of co-operation between the modellers from EMEP MSC-East, Moscow, Russia and RECETOX-TOCOEN & Associates in the field

validation and experimental validation of POP transport models (Shatalov et al. 2000a,b). For this comparison, the data of POP transport and accumulation in the European region for 1997 were used. For an adequate description of the environmental contamination, the calculations of POP transport and accumulation should be performed for decades. Consequently, to assess the contamination in 1997, the calculations were to be carried out for the period from 1970 to 1997.

The 3-D Eulerian multicompartment model (MSCE-POP) operates with the EMEP grid with a spatial resolution of 150x150 km. Along with the pollution transport in the atmosphere and ocean, the model includes the description of exchange processes between different environmental compartments. **Fig. 1** (Appendix) shows a scheme of the model structure with an indication of the considered compartments and processes of exchange between them, and of the POP redistribution between different phases. The dashed arrows represent processes which we plan to integrate to the model at future stages of its development.

The model considers the following compartments: air, soil, sea, vegetation and litter fall. It is assumed that initially emitted POP enters the atmospheric air. Then, in the course of dry and wet depositions of the gaseous and aerosol phase, a pollutant enters the soil, sea and vegetation. Dry deposition of the gas-phase pollutant is considered to be reversible, thus allowing us to consider the re-emission process important for some pollutants directly in the course of the modelling. From vegetation with fallen leaves, a pollutant enters the litter fall which, after some time, finds its way to the soil. The accumulation in compartments decreases due to POP degradation in the course of chemical, biochemical and photochemical reactions.

Due to advection and diffusion in the atmosphere and sea, pollutants are transported at long distances from the emission source and are partially exported outside the calculation domain. The pollutant fraction transported outside the EMEP grid can be used as an estimate of the considered pollutant capability for the long-range transport.

The input information on POP modelling is emission fields, meteorological data, land use, properties of soil, vegetation and marine environment, including sea currents and physical chemical properties of a specific pollutant in question.

B[a]P, PCB-153, and γ-HCH were selected for the top-priority modelling. These substances can be characterized as chemicals which are persistent, toxic, and able to withstand the long-range transport (Shatalov et al. 2000b). From the viewpoint of model development, these substances are interesting since they are differently distributed between the gaseous and aerosol phase in the air. Namely, the largest fraction of B[a]P settles on particles, γ-HCH mainly exists in the gaseous phase of the atmosphere, and PCB-153 is an intermediate substance.

2 Results and Discussion

2.1 The results from the regional background observatory Košetice

The mean observed concentrations of PAHs (minimum, maximum, arithmetic and geometric mean, median) for the year 1997 are shown in **Table 1**. The same values for PCBs and

Table 1: Observed concentrations of PAHs, Košetice observatory, 1997, gas phase + aerosol [ng·m^{-3}]

PAHs	Gas phase + aerosol				
	Minimum	Maximum	Arithmetic mean	Geometric Mean	Median
Naphthalene	0.0400	56.6900	2.0909	0.5381	0.3500
Acenaphthylene	0.0025	38.1700	1.6962	0.1862	0.1800
Acenaphthene	0.0200	6.9300	0.4683	0.2027	0.1500
Fluorene	0.5000	56.0600	5.3347	2.4794	2.3500
Phenanthrene	1.3900	117.5000	11.1826	6.2419	6.5400
Anthracene	0.0300	8.9200	0.5409	0.2187	0.2100
Fluoranthene	0.3300	77.3300	4.5130	1.9048	2.1600
Pyrene	0.1600	54.7300	2.9713	1.1407	1.3700
Benz(a)anthracene	0.0050	23.7800	0.9918	0.1371	0.1200
Chrysene	0.0200	32.3700	1.6502	0.4558	0.4800
Benzo(b)fluoranthene	0.0050	34.4500	1.4298	0.2504	0.2000
Benzo(k)fluoranthene	0.0050	9.7100	0.8624	0.2676	0.3700
Benzo(a)pyrene	**0.0050**	**13.7700**	**0.6970**	**0.0991**	**0.0800**
Indeno(123-cd)pyrene	0.0050	20.4200	1.0498	0.1712	0.2100
Dibenz(ah)anthracene	0.0050	2.8400	0.1317	0.0240	0.0200
Benzo(ghi)perylene	0.0050	14.0000	0.7129	0.1239	0.1300
Sum of PAHs	**3.15**	**567.67**	**36.32**	**15.62**	**13.94**

Table 2: Observed concentrations of PCBs and OCPs, Košetice observatory, 1997, gas phase + aerosol [ng.m^{-3}]

Compounds observed	Gas phase + aerosol				
	Minimum	Maximum	Arithmetic mean	Geometric mean	Median
PCB 28	0.0007	0.0840	0.0254	0.0200	0.0240
PCB 52	0.0010	0.0720	0.0205	0.0160	0.0190
PCB 101	0.0007	0.0790	0.0238	0.0184	0.0230
PCB 118	0.0006	0.0130	0.0037	0.0029	0.0030
PCB 153	**0.0090**	**0.1010**	**0.0428**	**0.0378**	**0.0390**
PCB 138	0.0070	0.1120	0.0334	0.0273	0.0270
PCB 180	0.0040	0.1170	0.0267	0.0200	0.0180
Σ PCBs	**0.0340**	**0.4670**	**0.1762**	**0.1530**	**0.1550**
α-HCH	0.0006	0.2130	0.0341	0.0196	0.0270
β-HCH	0.0005	0.0110	0.0008	0.0006	0.0005
γ-HCH	**0.0008**	**0.3470**	**0.0335**	**0.0079**	**0.0060**
δ-HCH	0.0005	0.0005	0.0005	0.0005	0.0005
Σ-HCHs	**0.0020**	**0.5650**	**0.0678**	**0.0323**	**0.0340**
p,p´-DDE	0.0060	0.1150	0.0434	0.0368	0.0380
p,p´-DDD	0.0012	0.0220	0.0043	0.0030	0.0030
p,p´-DDT	0.0030	0.0780	0.0060	0.0040	0.0033
Σ DDTs	**0.0060**	**0.1650**	**0.0506**	**0.0413**	**0.0420**
HCB	0.0290	0.2770	0.1354	0.1226	0.1280

OCPs are presented in **Table 2.** The long-term trends in ambient air concentrations of PAHs and PCBs on the middle European background level are shown in **Fig. 2** and 3 (Appendix).

The PAH concentrations identified follow a characteristic course prompted by the higher occurrence of these compounds in winter when they are produced by various combustion processes. The seasonal trends of PAHs in ambient air in relation to average temperature are shown in **Fig. 4** (Appendix). The high level of PAHs during the New Year 1997 sampling time was probably the result of an episodic input from local heating systems.

PCB and OCP concentrations display a totally different profile in which no such 'seasonality' has been identified. This tendency is also shown in **Fig. 5** and 6 (Appendix), where the relationships between the ambient air levels of OCPs and PCBs, and average temperatures, is shown. These compounds are present in the atmosphere today due to their volatilisation from the soil and sediments, i.e. as secondary inputs from old deposits, and also due to the long-range atmospheric transport from regions in which they are still used. These results reflect the global trends. PCB occurrence remains at the level of the European background. From the PCB pictures, we can see the decreasing tendency during this period. A predominance showing the degradation of metabolites of DDT (DDE and DDD) was observed (the same trend exists in all environmental samples from this observatory) (Holoubek et al. 2000b). This predominance reflected old loads – input from old usage and environmental accumulation of DDT rather than the long-range transport from regions where the compound is still in use.

The important part of the long-term, ambient-air monitoring programme of PBTs is to focus on the identification of their sources. The main sector of air masses, which are transported to the Košetice observatory location, is between 220 and 320°. In this sector, wind collects the PBTs from industrial and urban sources such as Prague, Pilsen or Budweis (in the case of the nearest sources in the Czech Republic). Of course, this is only the end of wind trajectories of air masses and we can determine the other sources which are located in these air masses. For this reason, the more detailed study of main contributors to the air-mass contamination will be based on the comparison of air-mass trajectories from NOAA with the results from the measurements.

2.2 Examples from the comparison of measurement/ modelling results

The results from the modelling of three model compounds (PCB-153, B[a]P, γ-HCH) with a comparison to the results from EMEP measurements at Košetice observatory, are described in the EMEP MSC-East Reports (Shatalov et al. 2000a,b). In this paper, we have used some results from these comparative studies concerning the Košetice observatory, but only data for the year 1997 are presented in this paper together with some general comments for the whole EMEP network.

2.2.1 Polychlorinated biphenyls

Modelling of PCB emissions transported within the European region covered the period of 1970–97. To take into account PCB accumulation in soil and other media, and to determine initial concentrations, a preliminary calculation for 1940-69 has been carried out. According to the results obtained in (Pekar et al. 1999), properties of the *indicator congener*, PCB-153, are used for physical-chemical proper-

ties of PCB mixture. For the comparison, we use measurements of PCB-153 concentrations in different media (remember that the PCB transport was calculated using properties of this congener). To recalculate PCB-153 concentrations from that for a mixture of all PCBs, it was assumed that PCB-153 emission is 4% of the total PCB emissions (Pekar et al. 1999).

The ratio between measured and calculated air concentrations at the EMEP measurement sites varies from 1.0 to 5.8. The correlation between calculated and measured values is rather high.

As far as calculated and measured mean annual concentration in precipitation and their ratio, in spite of the large underestimation of concentration in precipitation, the correlation between measured and calculated data is rather high. The influence of emission sources located outside the EMEP domain can increase the calculated concentrations, especially at stations near the grid boundary. In fact, according to modelling results, about 65% of the ejected PCB is transported outside the EMEP domain and, hence, a considerable amount can be imported from other regions. Such influence is to be examined by hemispheric modelling.

Besides, the difference in ratios of measured and calculated data on concentrations in air (2.2) and precipitation (7.4) indicates that the washout ratio used in the model seems to be underestimated.

The ratios of measured to calculated concentrations in soils vary from 0.25 to 4.45 for the whole EMEP Net. In the case of soil levels, the Czech observatory had the highest value of this ratio in 1997. On the average, the calculated concentrations in soil are 1.6 times lower than those measured.

The ratios of measured to calculated values in the case of coniferous trees are within 0.38–9.1. The average measured values are about 1.8 times larger than those calculated.

PCB-153 air, soil and vegetation (spruce needles) concentration from Košetice observatory (minimum, maximum and median) for measurements from 1997 are compared with the model calculation and are shown in Fig. 7 (Appendix).

It is generally difficult to give full credit to the information content in the POP data (Berg et al. 2000). Different sampling and analysis techniques make it difficult to compare data. For example, the Icelandic station generally has lower concentrations than the high Arctic NO0042G, which is reasonable considering the geographical location in relation to known source areas, although the differences are also due to different data handling and analysis techniques. Iceland subtracts blanks, whereas Norway does not.

Conclusions

Preliminary estimates of PCBs emitted within each country and deposited in other European countries were obtained (here we indicate countries with large enough export values only). A primary analysis was also made of the relationship between emission levels in the individual countries and their air concentrations. In order to verify the model, measured and calculated values are compared.

The comparison of measured and calculated values pointed out that calculation results for all studied compartments, on the average, are lower than the available measurement data. First of all, it can be explained by the fact that the impact of emission sources outside the EMEP domain was neglected in the model. The mean ratio of measured to calculated air concentrations is 2.2. Most underestimated are concentrations found in the precipitation.

2.2.2 Benzo[a]pyrene

The ratio of measured to calculate values of BaP air concentration were within the limits of 0.33–1.5 (except for a single value of 18.7). On the average, the calculated values were 1.2 times higher than those measured.

The comparison of the calculated results with the data obtained in Pekar et al. (1999) indicates that the model modification improved the agreement with measurement data. Note that, in contrast to the findings with PCBs, the calculated air concentrations of B[a]P exceed measurements on the average. This is in agreement with the fact that the transport outside the EMEP grid amounts to about 30% for this pollutant and the influence of external sources with respect to the EMEP grid seems to be less significant.

The comparison of the calculated results with the data obtained by Pekar et al. (1999) indicates that the model modification improved the agreement with measurement data. Similar to PCB-153, the washout ratio seems to be underestimated.

Measured and calculated concentrations in the topsoil layer at Košetice are shown again together with the results from other compartments and the results from model calculations in Fig. 8 (Appendix). Calculations underestimate soil concentrations 1.7 times on the average. In the comparison with PCB-153 results, the value of this ratio for B[a]P was in extremely good agreement in the case of this station.

Calculated values of concentrations in vegetation are both overestimated (6 times).

Conclusions

Preliminary estimates of B[a]P emitted in each country and deposited in other European countries were estimated and a primary analysis of the relationship between emission and concentration levels was made in individual countries. The measured and calculated data were compared for 1991–97.

The comparison of calculation and measurement results indicates that calculated air concentrations exceed measured ones by an average of 20% and measured concentrations in precipitation exceed calculated ones 2-fold. For concentrations in soil, vegetation and sea water, the agreement of measured and calculated values is within a factor of 5. The number of measurement data for these media, however, is not quite sufficient for model verification. For all the compartments but air, the calculated results are somewhat underestimated.

2.2.3 γ-Hexachlorocyclohexane

Modelling of γ-HCH transport in the European region was carried out for the period of 1970–97. Since it is important to take into account γ-HCH long-term accumulation in environmental compartments, a preliminary calculation run

covering a 15-year period with emission and meteorological data for 1970 has been carried out. As for other studied pollutants, emission estimates obtained under the POPCYCLING-Baltic project (Breivik et al. 1999) are used.

The ratio of mean annual concentrations calculated and observed at EMEP stations and their ratios vary from 0.11 to 20.5. However, if we exclude station NO42 located near the EMEP grid boundary from the comparison, the mean ratios will vary from 0.11 to 1.3. The underestimation of the calculated concentration at station NO42 can result from the fact that the calculation is made on a European scale and real concentrations can be affected by sources located outside the EMEP region. The considerations of these sources can be made by means of hemispherical modelling.

The comparison of the calculated results with that obtained in Pekar et al. (1999) indicates that the model modification improved the agreement with measurement data excluding station NO42. On the other hand, the modelling of γ-HCH transport on the hemispherical scale can result in some increase of calculated concentrations, since the export outside the EMEP grid for this pollutant is 60%.

Measured (at Košetice) and calculated mean annual concentrations in soil were 0.16. The overestimation of soil concentrations can be conditioned by the fact that the model does not consider the run-off by melting and rainwater, and the γ-HCH transport by river currents while describing processes in the soil. Measured and calculated mean annual concentrations in needles of coniferous trees were about 1.

At present the number of measurements in the EMEP net in such compartments as seawater, soil and vegetation is insufficient for model validation.

γ-HCH air, soil and vegetation (spruce needles) concentrations from Košetice observatory (minimum, maximum and median) for measurements from 1997 are compared with the model calculation and are shown in **Fig. 9** (Appendix).

Fig. 10 (Appendix) shows temporal trends for γ-HCH in air at 5 stations (Berg et al. 1999). The concentration level of α-HCH at the Norwegian stations is relatively high compared to the other stations, but decreasing. This is probably due to a higher input of technical HCH at high latitudes. Almost 80% of the remaining use of α-HCH in Europe in 1996 was assigned to the new states of the former Soviet Union (422 t of technical HCH) (Breivik et al. 1999). The other 20% were attributed as usage in some former eastern European countries (Breivik et al. 1999). Iceland is influenced by westerly air masses, which explains the lower concentrations seen at IS0091R.

Lista (NO0099R) at the southern coast of Norway, shows the highest concentrations of γ-HCH in the air, which may be due to long range transport from southern parts of Europe. According to the Centre International d'Etudes du Lindane, the average annual lindane consumption in Europe was 2,130 t during the period from 1992 to 1997. France was the major user of lindane in Europe during this period, with an annual average consumption of 1,600 t.

Conclusions

Using the MSCE-POP model, the simulation of γ-HCH transport within European region was carried out for the period of 1970–97. Emission estimates obtained under the POPCYCLING-Baltic project for the indicated time period were used in modelling (Pacyna et al. 1999). On the basis of calculations, the mean deposition and concentration values were determined in environmental compartments (air, soil, sea water, vegetation) in the European countries for 1997. Preliminary estimates of γ-HCH emitted in each country and deposited in other European countries are estimated and the primary analysis of the relationship between emission and air concentration levels in individual countries is made (here we only indicate countries with sufficiently large export values). Measured and calculated data for 1991–97 are compared (**Fig. 11**).

This comparison indicates that concentrations in the marine environment coincide within a factor of 2, and within a factor of 6 in soil. The calculated content in air and precipitation is underestimated by a factor of 5 and 2, respectively. As to the other compartments, the calculations give overestimated results. On the whole, the consistency between calculations and measurements has improved compared to the results of the previous year. The comparison base for soil, sea and vegetation is still insufficient for the reliable model validation.

3 Conclusion

For validation of modelling results for soil, vegetation, (and sea water also), additional measurements are still needed. Collection and analysis of POP concentration measurements in different media obtained both at the EMEP monitoring network and in the framework of national measurement campaigns and programmes was performed and the more detailed comparison of all EMEP networks will be prepared.

At further stages of the investigation, intentions are made:

- To carry out model assessment of the transport and contamination levels for HCB and selected congeners of PCDD/Fs.
- To refine the model block describing exchange processes between the atmosphere, soil, and vegetation taking into account the POP degradation in vegetation.
- To develop an operational version for the B[a]P long-range transport model with a spatial resolution of 50x50 km and to assess transboundary fluxes (using a 'country-to-country' scheme).
- To clarify the influence of different emission scenarios on the contamination level considering the dynamics for different media in the European region.
- To assess the influence of external sources of semi-volatile POPs upon the European contamination level.

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References

Barrie LA, Gregor D, Hargrave B, Lake R, Muir D, Shearer R, Tracey B, Bidleman TF (1992): Arctic Contaminants: Sources, Occurrence And Pathways. Sci Total Environ **122**, 1-74

Berg T, Hjellbrekke A-G, Larssen R (2000): Heavy Metals and POPs within the ECE Region 1998. Kjeller, Norwegian Institute for Air Research (NILU EMEP/CCC-Report 7/98)

Breivik K, Pacyna JM, Munch J (1999): Use of α-, β- and γ-hexachlorocyclohexane in Europe, 1970-1996. Sci Total Environ **239**, 151-163

EMEP (1998): Expert Meeting on Measurements of Persistent Organic Pollutants (POP) in Air and Precipitation. Lillehamer, Norway, 11-14 November 1997. EMEP/CCC-Report 8/98, O-92016, October 1998, NILU Norway

Holoubek I, Houšková L, Šeda Z, Holoubková I, Kott F, Korínek P, Bohácek Z, Cáslavský J, Bezacinský M, Mikeš C, Horák M, Kocan A, Petrik J (1990): Project TOCOEN. The Fate of Selected Organic Compounds in the Environment. I. Introduction. Toxicol Environ Chem **29**, 9-17

Holoubek I, Kocan J, Petrik J, Chovancová J, Biliková K, Korínek P, Holoubková I, Pekárek J, Kott F, Pacl A, Bezacinský M, Neubauerová L (1992): Project TOCOEN – The Fate of Selected Organic Compounds in the Environment. Part XI. The PAHs, PCBs, PCDDs/Fs in Ambient Air at Area of background GEMS Station. Seasonal Variations. Toxicol Environ Chem **36**, 115-123

Holoubek I (1993): TOCOEN Project – Goals, State and Prospects. Centr Eur J Publ Hlth **1** (2) 107-109

Holoubek I, Cáslavský J, Helešic J, Kocan A, Petrik J, Chovancová J, Drobná B, Korínek P, Bohácek Z, Holoubková I, Kalácková L, Kalácek J, Vancura R, Šeda Z, Dušek L, Mátlová L, Kohoutek J, Štaffová K, Zemek A (1996a): Project TOCOEN. Arch Environ Protect, Poland, 3-4, 9-34

Holoubek I, Caslavský J, Korínek P, Štaffová K, Kohoutek J, Hrdlicka A (1996b): Polycyclic Aromatic Compounds **9**, 159-167

Holoubek I, Ansorgová A, Kohoutek J, Korínek P, Holoubková I (2000a): The regional background monitoring of POPs (PAHs, PCBs, OCPs) in the Czech Republic. Organohalogen Compounds **46**, 387-390

Holoubek I, Kocan A, Holoubkova I, Hilscherova K, Kohoutek J, Falandysz J, Roots O (2000b): Persistent, Bioaccumulative and Toxic Chemicals in the Central and Eastern European Countries – State-of-the-Art Report. The 2nd version. TOCOEN REPORT No 150a, May 2000. RECETOX - TOCOEN & Associates, Brno, Czech Republic. Internet: http://recetox.chemi.muni.cz/

IM EMEP (1998): Manual for Integrated Monitoring, UN ECE CLRTAP, International Cooperative programme on Integrated Monitoring of Air Pollution Effects on Ecosystems. Finish Environment Institute, Helsinki, Finland

Mulvad G, Pederson HS, Hansen JC, Dewailly E, Jul E, Pedersen MB, Bjerregaard P, Malcom GT, Deguchi Y, Middaugh JP (1996): Exposure of Greenlandic Inuit to Organochlorines and Heavy Metals Through the Marine Food-Chain: An International Study. Sci Total Environ **186**, 137-139

Nordic Council of Ministers (2000): Assessment of the Sources, Atmospheric Fluxes, Environmental Cycling, Effects and Sinks of Persistent Organic Pollutants (POPs). International Workshop held in Preston UK, April 30-May 01, 1998. TemaNord 2000:514, Copenhagen, Denmark

Pacyna JM et al. (1999): Technical Report. Appendix 1 to Executive Final Summary Report. Environmental Cycling of Selected Persistent Organic Pollutants (POPs) in the Baltic Region (Popcycling-Baltic project). Contract No ENV4-CT96-0214. CD-Rom

Pekar M, Pavlova N, Gusev A, Shatalov V, Vulykh N, Ioannisian D, Dutchak S, Berg T, Hjellbrekke A-G (1999): Long-Range Transport of Selected Persistent Organic Pollutants, EMEP-MSC-E Report 4/99

Shatalov V, Malenichev A, Berg T, Larsen R, Holoubek I, Milukaité A-R, Afinogenova O, Rozovskaya O (2000): Investigation and Assessment of POP Transboundary Transport and Accumulation in Different Media. Part I. EMEP Report 4/2000, June 2000, MSC-EAST, Moscow, Russia, 90 pp

Shatalov V, Malenichev A, Erdman L, Vulykh N, Strukov B (2000): Investigation and Assessment of POP Transboundary Transport and Accumulation in Different Media. Part II. EMEP Report 4/2000, June 2000, MSC-EAST, Moscow, Russia, 79 pp

UN-ECE (1998): Draft Protocol to the Convention on Long-range Air Pollution on Persistent Organic Pollutants (EB.AIR/1998/2), The Convention on Long-range Transboundary Air Pollution. United Nations Economic and Social Council, Economic Commission for Europe, 1998

UNEP (1996): UNEP Survey on Sources of POPs. A Report Prepared for an IFCS Expert Meeting on POPs. Manila, Philippines, 17-19 June 1996, UNEP, Geneva

Vana M, Pacl A, Pekarek J, Smitka M, Holoubek I, Honzak J, Hruska J (1997): Quality of the Natural Environment in the Czech Republic at the Regional Level. Results of the Košetice Observatory. CHI Prague, 102 pp

Vallack HW, Bakker DJ, Brandt I, Brostrom-Lundén E, Brouwer A, Bull KR, Gough C, Guardans R, Holoubek I, Jansson B, Koch R, Kuylenstirna J, Lecloux A, Mackay D, McCutcheon P, Mocarelli P, Taalman RDF (1998): Controlling Persistent Organic Pollutants – What Next? Environ Toxicol Pharmacol **6**, 143-175

WMO/EMEP/UNEP (1999): Workshop on Modelling of Atmospheric Transport and deposition of Persistent Organic Pollutants and Heavy Metals. WMO GAW Report No 136/EMEP/MSC-E Report 1/2000. WMO/TD No 1008, Geneva, Switzerland

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Appendix

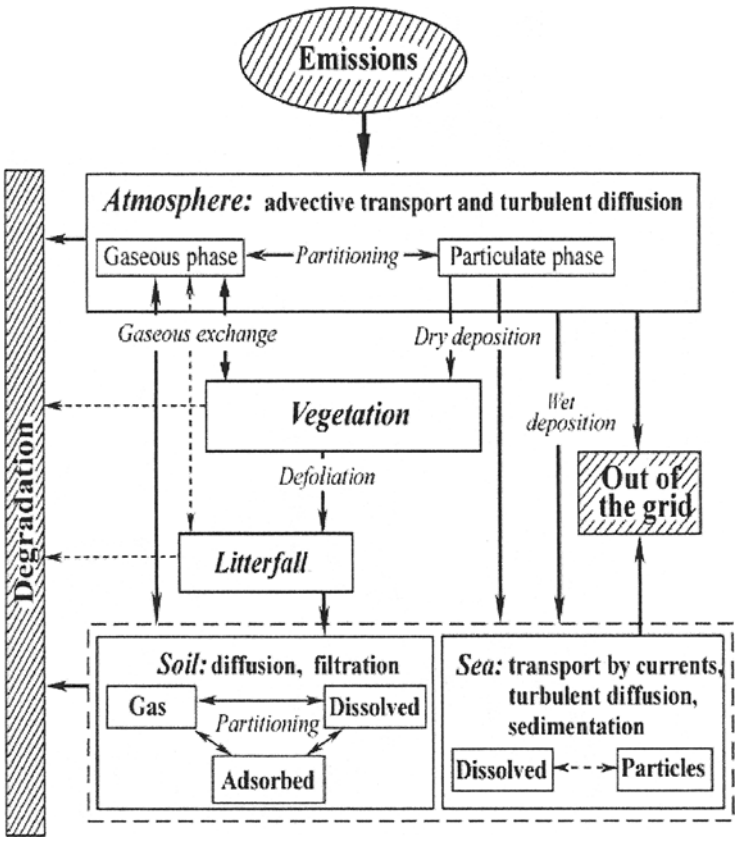

Fig. 1: Structural model scheme

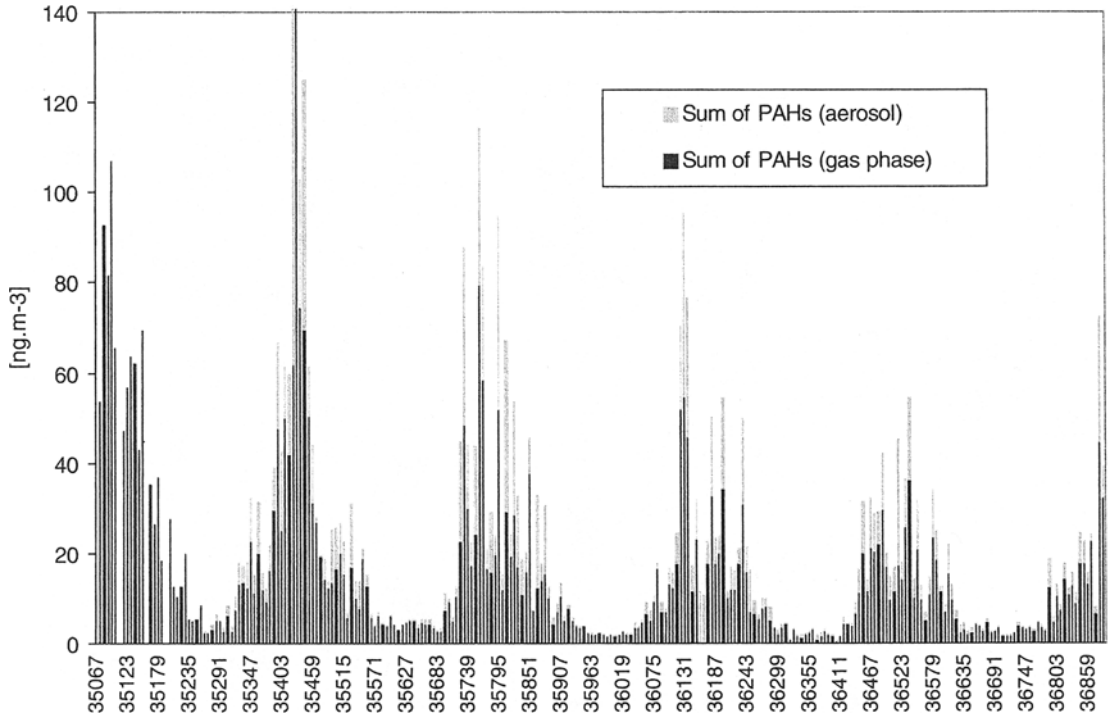

Fig. 2: PAHs in ambient air – Košetice 1996-2000

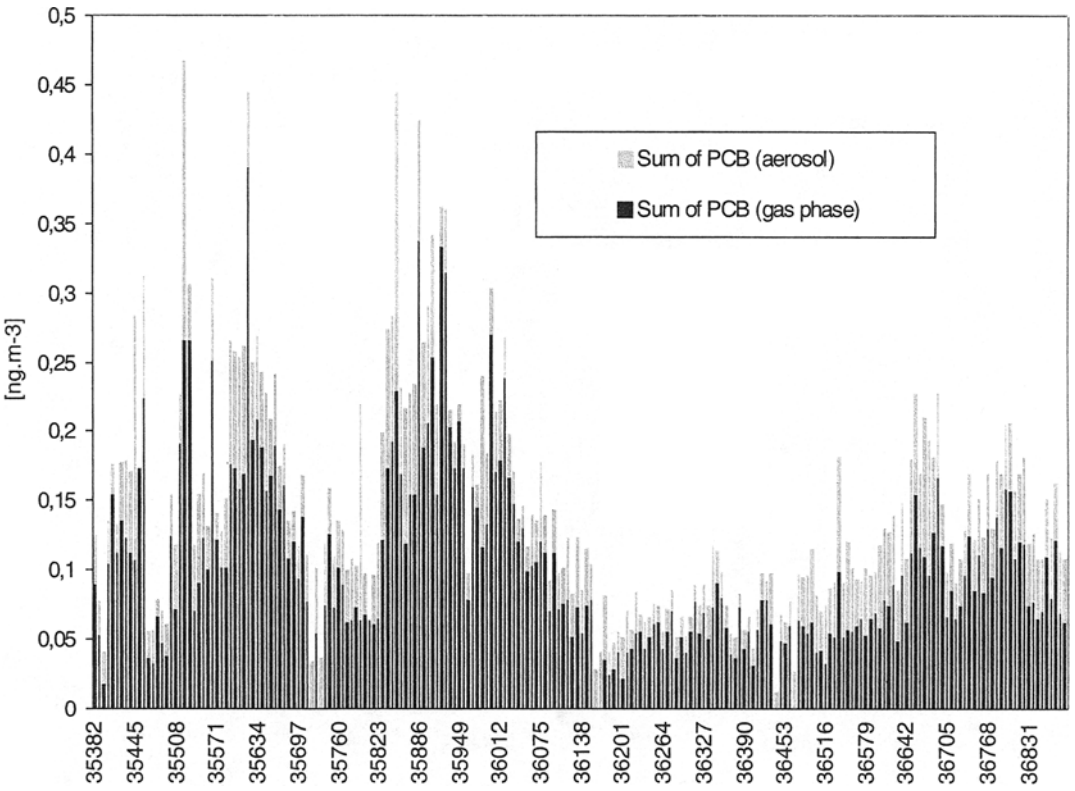

Fig. 3: PCBs in ambient air – Košetice 1996-2000

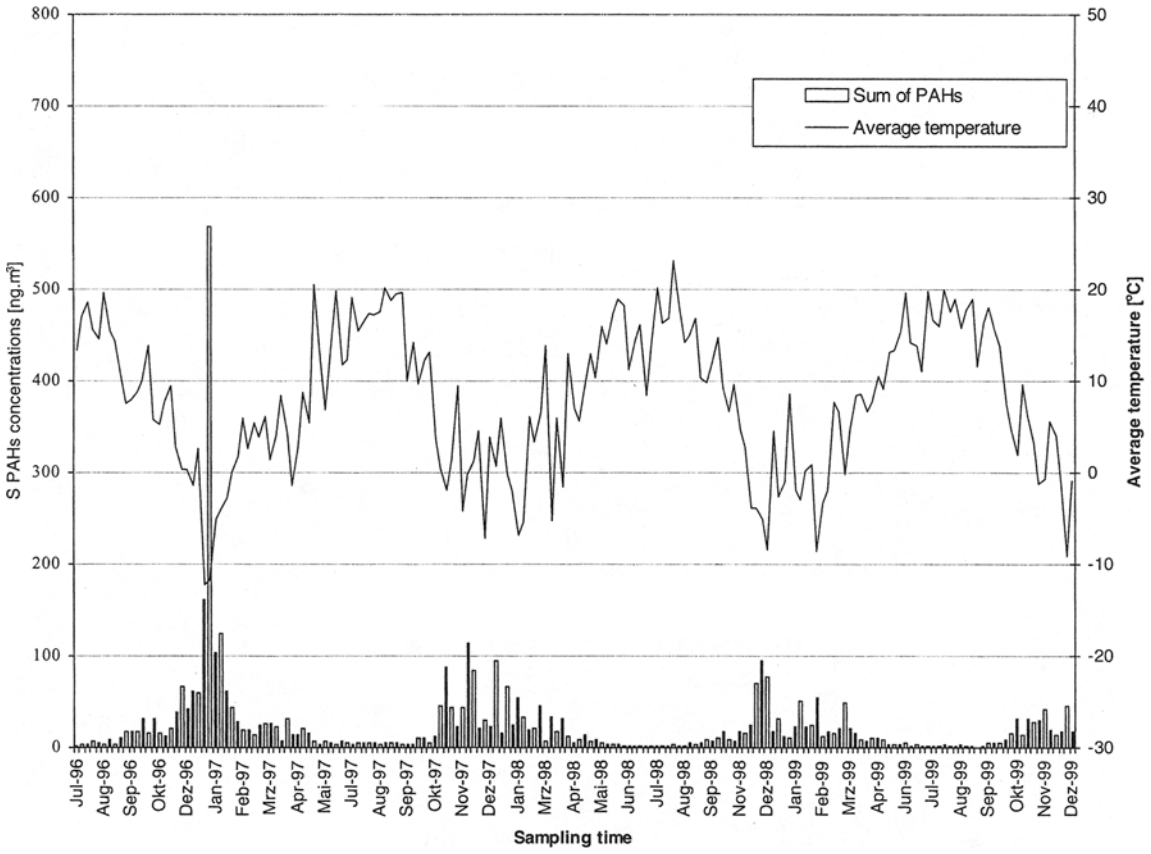

Fig. 4: Concentrations of S PAHs in ambient air in relation to average temperature (1996-1999)

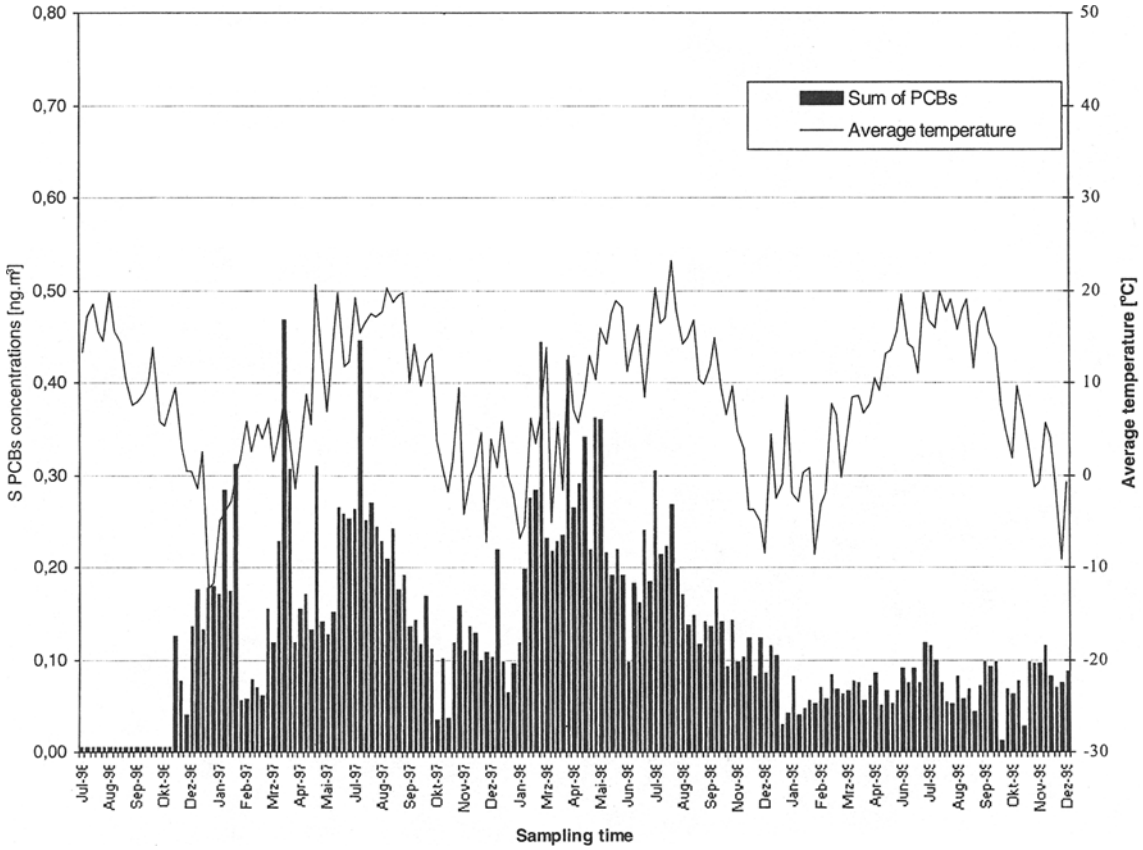

Fig. 5: Concentrations of S PCBs in ambient air in relation to average temperature (1996-1999)

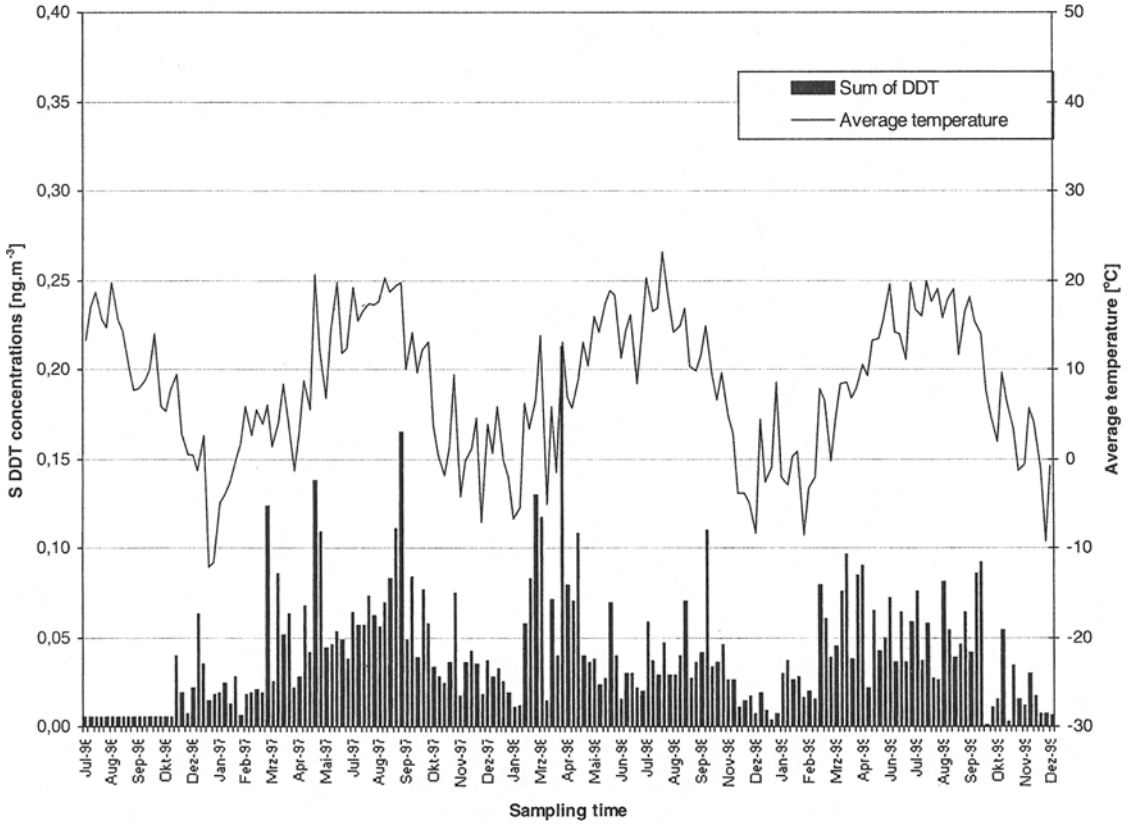

Fig. 6: Concentrations of S DDT in ambient air in relation to average temperature (1996-1999)

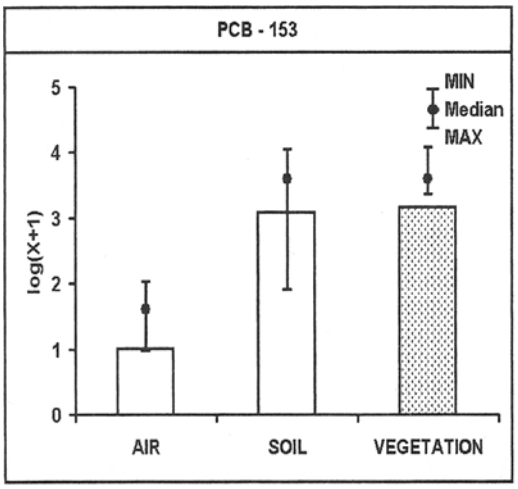

Fig. 7: The comparison of PCB-153 air, soil and vegetation (spruce needles) concentration from Kosetice observatory (minimum, maximum and median) for measurements from 1997 with the results from model calculation

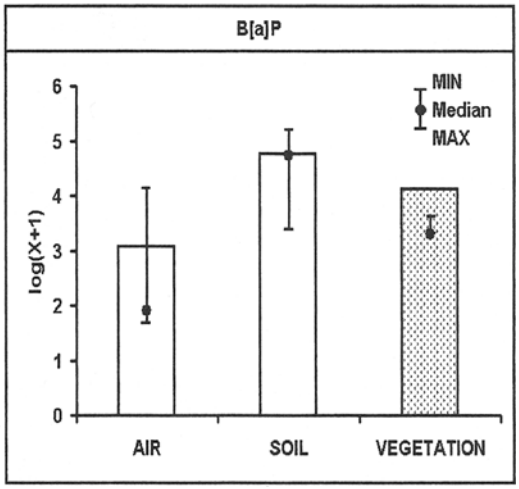

Fig. 8: The comparison of BaP air, soil and vegetation (spruce needles) concentration from Kosetice observatory (minimum, maximum and median) for measurements from 1997 with the results from model calculation

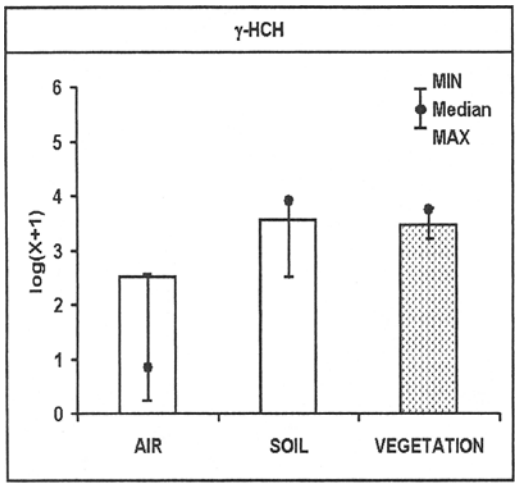

Fig. 9: The comparison of δ-HCH air, soil and vegetation (spruce needles) concentration from Kosetice observatory (minimum, maximum and median) for measurements from 1997 with the results from model calculation

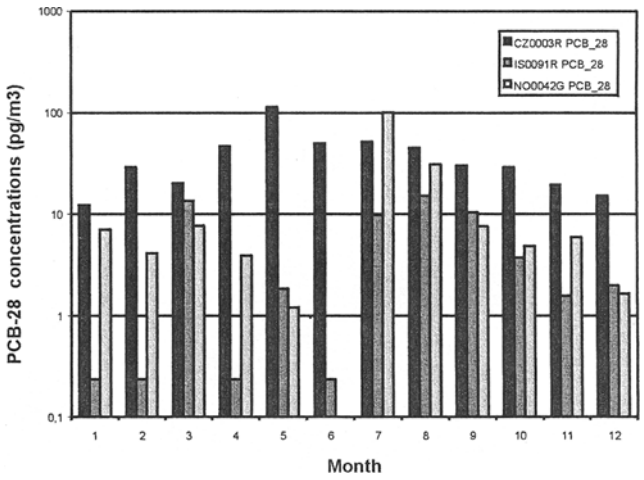

Fig. 10: Concentrations of PCB-28 in air+aerosol at three EMEP stations in the Czech Republic, Iceland and Norway

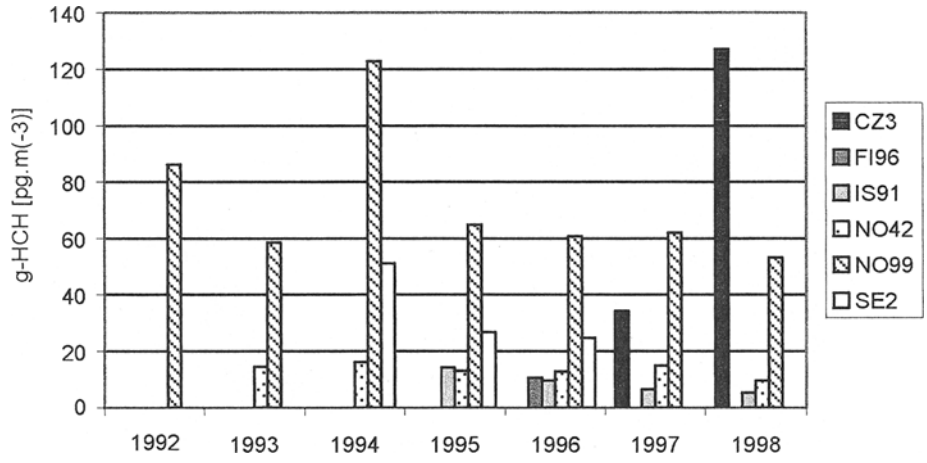

Fig. 11: Annual weighted means for δ-HCH during 1992-1998 at six monitoring stations in the Czech Republic, Finland, Norway and Swede