Persistent Organic Pollutants in the Environment

METEOROLOGICAL SYNTHESIZING CENTRE - EAST

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EXECUTIVE SUMMARY

In accordance with the EMEP work-plan for 2004 (ECE/EB.AIR/79/Add.2) Meteorological Synthesizing Centre - East (MSC-E) and Chemical Coordinating Centre (CCC) continued the investigations of the environmental pollution by persistent organic pollutants (POPs) on the basis of monitoring and emission data, and modelling results. In the current year the pollution of the environment by polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) was studied. The outcome of the studies is summarized below.

At present the measurements of POP concentrations in the atmosphere and precipitation are performed by 13 EMEP monitoring sites. Most of these sites are located in Northern Europe. There is only one site in Central Europe located in the Czech Republic. In the southern and eastern parts of Europe there are no POP monitoring sites. To improve the spatial distribution of monitoring sites in Europe the new EMEP monitoring strategy has been developed. In accordance with the strategy it is expected to have about 20 sites evenly distributed over the EMEP region to measure POPs in both the atmosphere and precipitation (“Core sites level 2" - supersites). The uncertainties in the measurement data are partially evaluated on the basis of the laboratory intercomparison. The detailed description of measurement results and methodology being applied can be found in the EMEP/CCC Report [Aas and Breivik, 2004].

The official data on POP emissions (PAHs, PCDD/Fs, PCBs, HCB and \(\gamma\)-HCH) for the period from 1990 to 2001 (at least for one year) were submitted by 32 Parties to the Convention. Data on other pollutants (Aldrin, Chlordane, Chlordecone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Mirex, Toxaphene, DDT, PCP and SCCP) were submitted by 16 countries. It should be pointed out that in recent years the number of countries that submit official information on POP emissions and their spatial distribution is increasing.

According to the official data and expert estimates the emissions of all the pollutants of concern tend to decrease from 1990 to 2001. For example, emissions of PAHs (B[a]P and B[b]F) decreased by 25% and emissions of PCDD/Fs - more than 2 times.

In the current year the model assessment of the environmental pollution levels was performed for the three indicator PAHs: benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F) and benzo[k]fluoranthene (B[k]F). For these PAHs spatial distribution of the air pollution in 2001 was obtained. The deposition flux mean value amounted to about 10 g/km²/y. For part of the territory of Poland, Germany, the Czech Republic, Lithuania and Latvia, higher deposition fluxes (50-100 g/km²/y) are typical. PAH concentrations in the air of most of European countries do not exceed 1 ng/m³, but in polluted areas they reach 2-3 ng/m³.

The transboundary transport of PAHs between European countries was assessed by the example of B[a]P. It is demonstrated that the contribution of the external sources to air concentrations is significant and varies typically from 30 to 60%. The detailed information for each European country is available on the Internet (www.emep.int и www.msceast.org).

The trends in the environmental pollution by PAHs were analyzed by the example of B[b]F and B[k]F. It is demonstrated that the rate of the decrease of PAH contents in all the environmental compartments except soil mostly correlates with that of PAH emission reduction. In soil PAH
concentrations decrease much more slowly due to the high persistence of PAHs in this compartment. As a consequence a significant fraction of the total PAH content in the environment is found in soil.

The assessment of the environmental pollution by dioxins/furans (PCDD/Fs) was based on simulation of each of 17 toxic congeners. The calculated levels of PCDD/F air concentrations (in TEQ units) in 2001 typical for most of European countries vary from 1 to 5 fg TEQ/m$^3$. In the most polluted regions of Central Europe (Poland, the Czech Republic, Slovakia, Belgium and some areas of Germany) PCDD/F air concentrations reach 10-30 fg TEQ/m$^3$ and more.

The calculations demonstrated that 60% of PCDD/F emissions deposit to the underlying surface. About 10% of the annual emissions deposit to the sea surface and about 50% to the land surface. Due to the high persistence of PCDD/Fs in soil about 95% of the total PCDD/F content in the environment were contained in this compartment due to long-term accumulation (1970-2001). Against the background of the total emission decrease the re-emission flux from soil becomes significant. In 2001 the re-emission from soil in Europe amounted to 20% of the total European emissions.

By the example of PCDD/Fs, a preliminary assessment of the transboundary transport of substances with a significant fraction of gaseous phase in the atmosphere was performed. Similar to PAHs the contribution of the PCDD/F transboundary transport to the total air concentrations for European countries varies typically from 30 to 60%. In the calculation the contribution of the re-emission process to air concentrations and depositions was also taken into account.

A possibility to use model calculations to evaluate the results of various scenarios of emission reduction is demonstrated by the example of two conventional scenarios for PCDD/Fs for the period from 2000 to 2010.

The parameterization of the PCB long-range transport model was further refined and air pollution in the EMEP region with account of emission sources of the Northern Hemisphere was assessed. Particular emphasis was given to PCB toxic congeners. At present expert estimates of emissions in the Northern Hemisphere are available for two toxic congeners: PCB-105 and PCB-118. In addition to the toxic congeners, PCB-28 ("light" congener with low chlorination degree) as well as PCB-153 and PCB-180 ("heavy" congener with high chlorination degree) were considered. The calculations were made for the period from 1970 to 2000 to take into account the impact of PCB long-term accumulation in environmental compartments on air pollution. Based on the calculations the trends of concentrations of various PCB congeners in the main environmental compartments (atmosphere, soil and seawater) as well as the spatial distribution of air pollution by PCB toxic congeners were evaluated.

The POP intercontinental transport was investigated by the example of HCB. Due to its high persistence in the air (typical atmospheric half-life is about 1 year) HCB has the maximum potential for the long-range transport among the POPs involved. It leads to the fact that about 80% of the HCB annual emissions in Europe are transported outside the European region. The calculations demonstrate that about 35% of air pollution in Europe are accounted for by external emission sources, and the contribution of Asian sources to pollution of the Arctic is about 30%. Therefore in assessing HCB air pollution in Europe its intercontinental transport should necessarily be taken into account.

For the pollutant being considered the main media-accumulators were identified (soil for PAHs, PCDD/Fs, PCBs and seawater for HCB). The trends of pollution of the main environmental compartments were analyzed. The obtained results may be of interest for the risk assessment. Currently a method is being developed to assess POP depositions to various types of the underlying surface.
In 2004, MSC-E took part in the two meetings of the Task Force on POPs aimed at the preparation of technical input for the reviewing the Protocol on POPs. At the first meeting (the Hague, 1-3 March) MSC-E has presented the information on the EMEP activities regarding the assessment of the environmental pollution by POPs and the results of model approach to the evaluation of new substances according to the criteria of long-range transport potential and overall persistence. At the second meeting the Task Force agreed that “a small team led by Canada, and including Norway and EMEP/MSC-E will carry out work on gathering best available scientific information on effects of deposition of POPs”. Besides, “the POPs Task Force requests EMEP to prepare a synthesis document on the best available country-submitted emissions data, including 1990 and more recent years”. According to the request MSC-E will present the information on emissions and atmospheric transport of selected POPs, depositions and contamination levels of the environmental media prepared under EMEP.

In the current year MSC-E continued to evaluate the long-range transport potential and overall persistence of some new substances in terms of their possible inclusion into the Protocol on POPs. In addition to the substances previously considered the long-range transport potential and overall persistence were evaluated for β-endosulfan and polybrominated diphenyl ethers (PDE-28 congener). The selected substances were ranked by the relevant criteria and compared with the “benchmark substance”. Benzo[a]pyrene being a regional-global boundary pollutant was selected as the “benchmark substance”.

In 2004, MSC-E continued the work on the intercomparison study of POP multicompartment models together with national experts from the Parties to the Convention. Experts from Canada, the Czech Republic, Denmark, France, Germany, Japan, the Netherlands, Switzerland, the United Kingdom, the USA, as well as the representatives of MSC-E and CCC took part in this work. In the current year the first stage of the intercomparison was completed and the calculations within the second stage were begun. The results of the first stage are presented in the MSC-E Technical Report [Shatalov et al., 2004b]. The report on the second stage will be published in 2005.

To refine model estimates of environmental pollution the MSCE-POP model was modified. In the current year model descriptions of the atmospheric removal and degradation processes were refined. The data on concentration of particles in seawater were prepared to refine model description of the sedimentation processes.

The assessment of environmental pollution by POPs was carried out in cooperation with international organizations and programmes (AMAP, HELCOM, UNEP, WMO).

The main results were presented for the discussion and examination at the fifth meeting of the Task Force on Measurements and Modelling (Prague, Czech Republic, April 2004).
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INTRODUCTION

In the current year the investigations of the environmental pollution by persistent organic pollutants (POPs) on the basis of measurements, emission data and modelling results were continued. The investigations were carried out in accordance with the EMEP work-plan for 2004 (ECE/EB.AIR/79/Add.2, Annex A).

At the previous stages the following activities were carried out: the estimation of the transboundary transport of polycyclic aromatic hydrocarbons (PAHs) within the European region by the example of benzo[a]pyrene (B[a]P), the initial estimation of the EMEP region pollution by benzo[b]fluoranthene (B[b]F), the calculation of the environmental pollution by polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) on the basis of 8 toxic congeners, the estimation of the intercontinental transport of pollutants by the examples of polychlorinated biphenyls (PCBs), γ-hexachlorocyclohexane (γ-HCH) and hexachlorobenzene (HCB). A start was made on the model estimation of long-range transport potential and overall persistence of new substances in terms of their possible inclusion into the Protocol on POPs. The results were published in the MSC-E Technical Report [Shatalov et al., 2003]. The outcomes of activities carried out in 2003 as well as preliminary results of 2004 were reported at the meeting of the EMEP Task Force on Measurements and Modelling in April 2004.

In the current year the following pollutants were investigated: polycyclic aromatic hydrocarbons (B[a]P, B[b]F, B[k]F), polychlorinated dibenzo-p-dioxins and dibenzofurans (all 17 toxic congeners), polychlorinated biphenyls (a set of 5 congeners, including toxic ones) and hexachlorobenzene. In addition the development of model approach for the assessment of new substances by criteria of their long-range transport potential and overall persistence was continued.

In the framework of the pollution investigation measurement data from the EMEP monitoring network (Section 1) were reviewed, emission data were prepared for model purposes on the basis of the official emission data and expert estimates (Section 2.1) and model calculations of the following were made (Sections 2.2 and 2.3):

- levels and long-term trends of pollution in the European region for B[b]F and B[k]F (Section 2.2.1) and PCDD/Fs (Section 2.2.2);
- transboundary transport between European countries for B[a]P (Section 2.2.1) and PCDD/Fs (Section 2.2.2);
- contribution of the intercontinental transport to the pollution of the European region and contribution of European emission sources to the pollution of remote regions (by the example of the Arctic) for PCBs and HCB (Section 2.3);

To carry out the model assessment of the environmental pollution the MSCE-POP model was modified. In particular the description of POP degradation in the atmosphere, deposition to the underlying surface and sedimentation in the marine environment was refined (Section 2.4).

The activities on the assessment of environmental pollution by POPs are carried out in close cooperation with other bodies to the Convention, international organizations and national experts. In
particular, to support the activities of the Task Force on POPs in the preparatory work for the review of the Protocol on POPs MSC-E has prepared the information on POP emissions, monitoring and modelling data available in the framework of EMEP. Besides, the estimation of long-range transport potential and overall persistence is continued for new substances (Section 3.1). MSC-E contributed to the UNEP Workshop on POP emission inventories and air pollution monitoring and modelling. Some preliminary estimates of POP transboundary transport for Kyrgyzstan were made. The intercomparison study of POP multicompartment models is carried out with the participation of experts from European countries, Japan, the USA and Canada (Section 3.2).

The detailed description of the results will be presented in the Technical Reports of the EMEP Centres ([Aas and Breivik, 2004] and [Shatalov et al., 2004a]), as well as on the Internet www.emep.int and www.msceast.org.

Acknowledgements

The authors are grateful to Prof. Dr. I. Holoubek, Dr. D. Kallweit and Dr. S. Gong for co-operation in the work on evaluation of POP contamination in the environment. We are grateful to Ms. M. Varygina and Dr. A. Gusev for great work on editing the text. A great contribution to the technical preparation of the report was made by Ms. I. Strizhkina and Ms. S. Yevdokimova.
1. MONITORING OF POPs

Measurement network

POPs were included in the EMEP’s monitoring program in 1999. However, earlier data has been available and collected, and the EMEP database thus also includes older measurements. A number of countries have been reporting POPs within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP and OSPAR.

The locations of the measurement sites, which have delivered POPs for 2002, are shown in Fig. 1. The different measurements programs are given in Table 1. Further details of the sites and the measurement methods are found in EMEP/CCC’s data report on heavy metals and POPs [Aas and Breivik, 2004]. The sites are divided in those measuring both in air and precipitation, and those measuring only in one media. In 2002 it was 5 sites measuring POPs in both compartments, and altogether it was 13 measurement sites.

Table 1. Measurements sites and programs for POPs in 2002

<table>
<thead>
<tr>
<th>Sites</th>
<th>POPs in air and aerosol</th>
<th>POPs in precipitation</th>
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<tbody>
<tr>
<td>BE04</td>
<td>PAHs, PCBs, pesticides, HCHs</td>
<td>Pesticides, HCHs</td>
</tr>
<tr>
<td>CZ03</td>
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<td>PAHs, PCBs, HCB</td>
</tr>
<tr>
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<td>PAHs, PCBs, pesticides, HCB</td>
<td>PAHs, PCBs, pesticides, HCB, HCHs</td>
</tr>
<tr>
<td>DE01</td>
<td>PAHs, PCBs, pesticides, HCB</td>
<td>PAHs, PCBs, pesticides, HCB, HCHs</td>
</tr>
<tr>
<td>DE09</td>
<td>PAHs, PCBs, pesticides, HCB, HCHs</td>
<td>PAHs, PCBs, pesticides, HCB, HCHs</td>
</tr>
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<td>IS91</td>
<td>PCBs, pesticides, HCB, HCHs</td>
<td>PCBs, pesticides, HCB, HCHs</td>
</tr>
<tr>
<td>IE02</td>
<td>PCBs, pesticides, HCB, HCHs</td>
<td>PCBs, pesticides, HCB, HCHs</td>
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<tr>
<td>LT15</td>
<td>PAHs, PCBs, pesticides HCHs</td>
<td>γ-HCH</td>
</tr>
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<td>NL91</td>
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<td>HCB, HCHs</td>
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<td>PCBs, pesticides, HCB, HCHs</td>
</tr>
<tr>
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<td>PAHs, PCBs, pesticides</td>
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</tr>
<tr>
<td>SE12</td>
<td>PAHs, PCBs, pesticides</td>
<td>PAHs, PCBs, HCHs</td>
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It is quite evident from Fig. 1 that the spatial distribution in Europe is unsatisfactory. Only sites in the northern Europe measure POPs. The new EMEP monitoring strategy for 2004-2009 aims to improve the current unsatisfactorily site distribution. At “Core sites level 2” (supersites), POPs in both air and precipitation should be measured at around 20 stations distributed over the domain.

Fig. 1 Measurement network of POPs in EMEP, 2002
**Measurement results of POPs in 2002**

Details of the measurements results and methodology are found in the EMEP/CCC data report on heavy metals and POPs [Aas and Breivik, 2004]. It is difficult to compare the results from the different sites since the measurement programs can vary and the methodology differs. E.g. much of the data from Ireland and Belgium, and to some extent from Iceland, are mainly below the detection limits and here one can only say something about the upper concentration limits. For precipitation it is difficult to compare the results in Europe due to different methodology, e.g. Finland and Sweden are measuring deposition while others are measuring concentration in precipitation.

**PCBs in air.** PCBs consist of various individual chemical species (congeners). Altogether, 209 different congeners are possible, although only a few are regularly monitored in environmental samples. The data presented herein includes seven individual PCB congeners (PCBs 28, 52, 101, 118, 138, 153, 180). During 2002, these PCBs were monitored in air at stations in the Czech Republic (CZ03), Sweden (SE12 and SE14), Finland (FI96), Iceland (IS91) and Norway (NO42). Fig. 2 shows the spatial pattern of the annual average air concentrations of the sum of the seven PCBs ($\Sigma_7$PCB).

Elevated levels of PCBs are observed at the station in the Czech Republic (86 pg/m³) as compared to the other stations, which are all below 17 pg/m³. The high levels in the stations in the Czech Republic is not surprising, considering that the high historical usage of PCBs in central Europe (Fig. 2; [Breivik et al., 2002]). It is also known that former Czechoslovakia were among the European countries where PCBs were produced in significant amounts until 1984 [Taniyasu et al., 2003]. Large differences in atmospheric PCB levels across Europe were also noted by Jaward et al. [2004]. They carried out a campaign during the summer of 2002, deploying 71 passive air samplers throughout Europe, and found that the atmospheric levels of PCBs vary by as much as two orders of magnitude. Elevated levels were found in urban areas, suggesting that densely populated regions tend to be key contemporary source regions of PCBs to the atmosphere. With the exception of the station in the Czech Republic and the southernmost station in Sweden, the concentrations of $\Sigma_7$PCB are generally low. Interestingly, the atmospheric levels of $\Sigma_7$PCB are indeed also virtually identical for the four northernmost stations (~5-6 pg/m³). However, the relative contribution of individual PCB congeners is rather different (Fig. 3).

![Fig. 2. Spatial pattern of $\Sigma_7$PCB in air in 2002 (red bars in pg/m³). Also shown is the estimated historical consumption of total PCBs in Europe [Breivik et al., 2002]](image)

![Fig. 3. Relative contribution of individual PCB congeners to $\Sigma_7$PCB in air at various stations. The stations are sorted from south (left) to north (right)](image)
Fig. 3 conveys the message that there is a tendency that the heavier congeners (PCBs 138, 153 and 180) are enriched in the southernmost stations (Czech Republic, Southern Sweden), whilst the lighter congeners (PCBs 28 and 52) are enriched at the northernmost sites (Iceland, Finland as well as Spitzbergen in Norway). This clearly confirms that there are marked differences in the long-range transport potential (LRTP) within the group of PCBs [Wania and Dugani, 2003]. LRTP is controlled by the competing processes of atmospheric degradation and net atmospheric deposition. The data in Fig. 3 suggest that it is net atmospheric deposition that tends to reduce the LRTP of the heavier PCBs as compared to the lighter PCBs. This is caused by a change in phase partitioning in the atmosphere for which the heavier PCBs get increasingly sorbed to atmospheric particles at decreasing temperatures. This again contributes to a depletion of heavier congeners due to atmospheric deposition, and thus an increased prevalence of lighter congeners in the northernmost air samples [Wania and Su, 2004].

**Data Quality.** The data quality of the POP measurements can to some extent be addressed by evaluating the results from the laboratory intercomparison in 2000-2002 [Manø and Schaug, 2003]. The comparison was a two-step exercise: Round 1: Analysis of a mixture of standards of known composition but with unknown concentrations. Round 2: Analysis of two raw-extracts from filter and gas phase adsorbents after high volume air sampling. Two groups of POPs were investigated during the exercise: Organochlorine compounds including pesticides, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The second round showed the importance of using an analytical method and instrumentation able to cope with possible interferences without loss of analyze even while working at low concentrations, while round 1 mainly was a calibration exercise. To assess the data quality of the EMEP sites, it is therefore looked at the second round. Not all countries reporting data to EMEP took part in the lab intercomparison, these are Finland, Sweden, and Netherlands. In principle the data quality from these countries are unknown. Ireland did only participate in round 1, but their results are very crude because of instrument problems. Those EMEP laboratories that did participate in round 2 did in general satisfactory and are mostly within 25% (green colour) of the average deviation from the median, Table 2. The Czech republic had some problems with insufficient cleaned silica during the comparison, which may explain the high deviation in the PCB analysis.

**Table 2.** Average of the absolute percent deviation from the median in the POP lab intercomparison, round 2

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| b) Organochlorine compounds | Lab | pp-DDT | pp’-DDE | 1-Chlorodane | α-Chlorodane | γ-ChH | HCB | PCB 28 | PCB 52 | PCB 101 | PCB 118 | PCB 138 | PCB 153 | PCB 180 |
|-----------------------------|-----|--------|---------|-------------|-------------|------|-----|--------|--------|---------|---------|---------|---------|---------|---------|
|                             | BE  | -      | 2       | 27          | 11          | -    | -   | -      | -      | -       | -       | -       | -       | -       | -       |
|                             | CZ  | 64     | 19      | 1           | 54          | 45   | 7   | 55     | 129    | 176     | 91      | 262     | 80      | 61      | -       |
|                             | DE  | 27     | 176     | 18          | 25          | 12   | 1   | 71     | 303    | 162     | 397     | 159     | 33      | -       | -       |
|                             | IS  | 17     | 2       | 8           | 22          | 5    | 1   | 1      | 12     | 5       | 7       | 8       | 6       | 23      | -       |
|                             | NO  | 19     | 13      | 9           | 13          | 15   | 5   | 24     | 17     | 10      | 7       | 10     | 6       | 7       | 33      |

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2. **AN EVALUATION OF POP TRANSPORT AND POLLUTION LEVELS IN THE ENVIRONMENT**

2.1. Emissions

Official data on emissions of PAHs, PCDD/Fs, PCBs, HCB and γ-HCH for the period from 1990 to 2001 (for at least one year) were reported by 32 countries. The emission data on other POPs (Aldrin, Chlordane, Chlorelcone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Mirex, Toxaphene, DDT, PCP and SCCP) for this period (for at least one year) were reported by 16 countries. It is worth noting that in recent years, the number of countries submitting data on POP emissions and their spatial distribution over the EMEP domain increased. For countries for which official emission data are not available, expert estimates were used.

Below we describe emission data available for selected POPs and evaluate emission reductions for two periods: from 1970 to 2001 (except for B[a]P) and from 1990 (the beginning of official submission of emission data) to 2001.

2.1.1. **Polycyclic aromatic hydrocarbons**

For the purposes of atmospheric emission inventories, the Protocol on POPs includes the following PAH indicator compounds: benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), and indeno[1,2,3-cd]pyrene (I_P) [Annex III, ECE/EB.AIR/60]. This year, model calculations have been performed for B[a]P, B[b]F and B[k]F.

Official data on emission totals of polycyclic aromatic hydrocarbons for 1990-2001 (for at least one year) were submitted by 27 European countries [EB.AIR/GE.1/2003/6 and Corr.1], and information about their spatial distribution was provided by 11 countries (Austria, Belgium, Bulgaria, Denmark, Finland, Hungary, the Netherlands, Norway, Poland, Spain and the United Kingdom).

**Benzo[a]pyrene**

Six countries - Belarus, Denmark, Estonia, Poland, Slovakia and the United Kingdom - reported official data on benzo[a]pyrene emissions for 2001. Since a number of countries that submitted official data on B[a]P emissions is limited, the B[a]P emissions for modelling were estimated on the basis of the fractions of B[a]P in officially submitted PAH emission totals. These fractions were calculated on the basis of the data from [Baart et al., 1995]. For the remaining countries, expert estimates were used [Pacyna et al., 1999; Tsibulsky et al., 2001; Berdowski et al., 1997]. According to the official data and expert estimates in the period from 1990 to 2001, European emissions of B[a]P decreased by 26% and amounted to 505 t in 2001. It is worth to note that due to inclusion of official data submitted in 2003, total European emissions for 2000 used in the calculations of the present year are about 1.5 times higher than that used in the calculations of the previous year.

The spatial distribution of B[a]P emissions in 2001 was prepared on the basis of official data on spatial distribution of PAH emissions reported by eleven countries. For other countries, expert estimates were used [Pacyna et al., 1999, Berdowski et al., 1997].
Official information on B[a]P sector emissions is available for 5 countries (Belarus, Denmark, Estonia, Poland and the United Kingdom). The contribution of the Nomenclature For Reporting (NFR) sectors to the total emissions of B[a]P in 2001 is presented in Fig.4. The maximum contribution to the total B[a]P emissions is made by the Residential sector (69%).

In the model computations, we took into consideration seasonal variations of B[a]P emissions (in winter it is 10% higher than in summer) [Baart et al., 1995].

**Benzo[b]fluoranthene**

Seven countries - Belarus, Denmark, Estonia, Lithuania, Poland, Slovakia and the United Kingdom - submitted official data on benzo[b]fluoranthene emissions for several years in the period from 1990 to 2001. At present, expert estimates of B[b]F emissions in the European region are available only for 1990 [Baart et al., 1995]. B[b]F emission values were estimated on the basis of the ratio of B[b]F and B[a]P emission values in European countries, calculated using official information and data available in [Baart et al., 1995]. The mean value of the B[b]F/B[a]P ratio in A.Baart et al. [1995] is close to 1.

Similarly to B[a]P, the spatial distribution of B[b]F emissions in the period from 1990 to 2001 was prepared on the basis of official data on spatial distribution of PAH emissions reported by eleven countries. For other countries, expert estimates were used [Pacyna et al., 1999; Berdowski et al., 1997].

The trend in B[b]F emissions in Europe for the period from 1970 to 2001 evaluated according to the official data and expert estimates is illustrated in Fig.5. The maximum emissions value was in 1970; during the following years, it decreased substantially. B[b]F emissions reduced 2.4 times during 1970-2001 and decreased by 24% during 1990-2001 and amounted 525 t in 2001.

Official information on B[b]F sector emissions is available for 4 countries (Belarus, Denmark, Poland and the United Kingdom). The contribution of the NFR sectors to the total emissions of B[b]F in 2001 is presented in Fig.6. Similarly to B[a]P, the maximum contribution to the total B[b]F emissions is made by the Residential sector (73%).

In the model computations, we took into consideration seasonal variations of B[b]F emissions (in winter it is 12% higher than in summer) [Baart et al., 1995].

1) NFR - Nomenclature For Reporting.
**Benzo[k]fluoranthene**

Official information about total B[k]F emissions for several years in the period from 1990 to 2001 was submitted by Belarus, Denmark, Estonia, Lithuania, Poland, Slovakia and the United Kingdom. At present, expert estimates of B[k]F emissions in the European region are available only for 1990 [Baart et al., 1995]. According to these estimates B[a]P, B[b]F, B[k]F and I_P emission values are rather close to one another (the mean value of ratios are B[b]F/B[a]P = 1; B[k]F/B[a]P = 0.7 and I_P/ B[a]P = 0.9). So, as a first approximation, B[k]F emissions were taken equal to B[a]P emissions estimated by [Pacyna et al., 1999] for a number of basic years from 1970 to 1995. In the period from 1996 to 2001, the annual values of emissions were accepted to be equal to those of 1995. It is a rather rough assumption and introduces a significant uncertainty to the estimates of B[k]F emissions. However, such assumption allows one to assess the impact of physical-chemical properties on the long-range transport of the 4 indicator PAHs by comparison of calculation results obtained with one and the same emission field [Pacyna et al., 1999].

In accordance with the assumptions made, B[k]F emissions in the EMEP region reduced twice during 1970-2001 and 1.8 times during 1990-2001 and amounted 597 t in 2001. In the model computations, seasonal variations in B[k]F emissions were taken from [Baart et al., 1995].

### 2.1.2. Dioxins and furans

Official data on total emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) for the period from 1990 to 2001 (for at least one year) were reported by 26 European countries [EB.AIR/GE.1/2003/6 and Corr.1]. PCDD/F emission data in Austria, the Czech Republic, Finland, France, Hungary, Italy, Monaco, Norway, Poland, Spain, Sweden, the United Kingdom are available for each year of the period from 1990 to 2001. According to the official data, the maximum relative decrease of the PCDD/F emissions (100x(E_{1990}-E_{2001})/E_{1990}) took place in the Netherlands (by 95%), whereas the maximum absolute decrease of the emissions (E_{1990}-E_{2001}) was registered in France (by 1.4 kg TEQ). The information about the spatial distribution of PCDD/F emissions was submitted by 12 countries (Austria, Belarus, Belgium, Bulgaria, Finland, France, Hungary, the Netherlands, Norway, Poland, Spain, Sweden). For the remaining countries, we used expert estimates of PCDD/F total emissions and their spatial distribution in 1970-1995 [Pacyna et al., 1999].

Variations in PCDD/F emissions in Europe for the period from 1970 to 2001 are illustrated in Fig.7. The maximum emissions value was in 1980; during the following years, it decreased substantially. PCDD/F emissions reduced 4.5 times during 1970-2001 and 2.3 times during 1990-2001 and amounted to 5.5 kg TEQ in 2001.

Official information on PCDD/F sector emissions is available for 18 countries. The contribution of the NFR sectors to the total emissions of PCDD/F in 2001 is presented in Fig.8. The maximum contribution to the total PCDD/F emissions is made by the Residential sector (32%).

Due to essential differences in the properties of toxic PCDD/F congeners affecting their environmental
behaviour, modelling was performed for each congener separately. For these calculations splitting of the overall toxicity of PCDD/F mixture between different congeners was performed and spatial distributions of emissions for each congener were prepared for each year from 1970 to 2001. The splitting was done on the basis of the data from [Pacyna et al., 1999]

### 2.1.3. Polychlorinated biphenyls

Official information about total emissions of polychlorinated biphenyls for the period from 1990 to 2001 (for at least one year) was submitted by 16 countries [EB.AIR/GE.1/2003/6]. PCB emission data in the Czech Republic, France, Monaco, Poland and the United Kingdom are available for each year of the period from 1990 to 2001. According to the official data, the PCB emissions combined for Bulgaria, the Czech Republic, France, Monaco, Poland, Slovakia and the United Kingdom (for which official information for 1990 and 2001 is available) decreased 2.3 times. The maximum decrease of the PCB emissions took place in the United Kingdom (4.5 times).

The modelling of PCB long-range transport for the period from 1970 to 2000 was performed for the set of 5 individual PCB congeners (PCB-28, PCB-105, PCB-118, PCB-153, and PCB-180). The set includes all PCB congeners having dioxin-type toxicity for which emission data are available (PCB-105 and PCB-118). The sources located over the whole Northern Hemisphere were taken into account in the computations. PCB emissions data required were prepared with the use of a global emission inventory of 22 PCB congeners [Breivik et al., 2002]. For the evaluation of the emissions distribution over the 2.5°x2.5° calculation grid, data on the population density available in the Canadian Global Emissions Interpretation Centre (http://www.ortech.ca/cgeic) were used.

According to the data by [Breivik et al., 2002], total emissions of the 22 PCB congeners in the Northern Hemisphere decreased 7.2 times during 1970-2000 and 2.6 times during 1990-2000 and amounted to 464 t in 2000 (Fig.9). According to the expert estimates, total PCB emissions in the European region reduced 3.1 times and 2.3 times in the same periods, respectively, and amounted to 281 t in 2000.

![Fig. 9. PCB emissions in the Northern Hemisphere in the period from 1970 to 2000](image)

### 2.1.4. Hexachlorobenzene

Official information about total emissions of hexachlorobenzene for the period from 1990 to 2001 (for at least one year) was reported by 18 countries [EB.AIR/GE.1/2003/6]. HCB emission data in Austria, France, Hungary, Poland, Spain and the United Kingdom are available for each year of the period from 1990 to 2001. According to the official data, the HCB emissions combined for Austria, Bulgaria, France, Hungary, Poland, Spain and the United Kingdom (for which official information for 1990 and 2001 is available) decreased by 17% during the period indicated. The maximum relative decrease of the HCB emissions took place in Bulgaria (by 96%), whereas the maximum absolute decrease of the emissions was registered in the United Kingdom (by 817 kg).
For modelling of HCB long-range transport within the Northern Hemisphere an emission scenario was prepared with the use of different expert estimates.

HCB emission values in the USA, Canada and emissions of the whole Northern Hemisphere are taken from expert estimates by R. Bailey [2001] for the middle of 90th. For European countries and European part of Russia HCB expert estimates by [Pacyna et al., 1999] were used. HCB emission values in China, Pakistan, Republic of Korea, Russia (Asian part of Russia) and Japan were estimated on the basis of the relationships of gross domestic product and official HCB emission data for countries with similar economic indexes. HCB emission values in India are estimated as the difference between hemispheric emissions and sum of emissions from North-American continent, Europe and Asian countries mentioned above.

For the evaluation of transcontinental transport HCB sources of the Northern Hemisphere were split into 5 groups. The spatial distribution of emissions for each group was prepared (Fig. 10).

In accordance with the above emission scenario, HCB emissions in the Northern Hemisphere amounted to 92 t, including 12.5 t in North America, 36.4 t in Central Asia, 16.7 t in South-eastern Asia, 12.5 t in Europe and 14 t in Russia in 2000.

2.2. Pollution levels in the EMEP domain

This section is aimed at the evaluation of contamination of the EMEP region by PAHs and PCDD/Fs. Here we present evaluation of pollution levels of three indicator PAHs (B[a]P, B[b]F and B[k]F) and of 17 PCDD/F toxic congeners in 2001. For B[a]P and PCDD/Fs the evaluation of transboundary transport (country-to-country matrices) was done. The possibility of model evaluation of different scenarios of emission reduction is exemplified by two conventional scenarios for PCDD/Fs.

2.2.1. Polycyclic aromatic hydrocarbons

In the current year the model computations of the environmental pollution were made for three compounds from the group of indicator polycyclic aromatic hydrocarbons (PAHs): benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F) and benzo[k]fluoranthene (B[k]F). In the previous studies the spatial distribution of B[a]P concentrations in the main environmental compartments was calculated, and its accumulation trends in the last 30 years were studied. In addition the development of the model approach to the evaluation of B[a]P transboundary fluxes on the "country-to-country" basis in the EMEP domain [Shatalov et al., 2000, 2001, 2002, 2003] was started. Last year tentative calculations of the B[b]F atmospheric transport and accumulation in different environmental media were performed for the first time. The trends of its accumulation in the environment were studied for the period from 1970 to 2000.
In 2004 the calculations of B[a]P concentrations in the atmosphere and depositions to the underlying surface were continued. Much attention was given to the assessment of transboundary transport of B[a]P and its impact on the pollution levels in European countries in 2001. The concentrations of B[b]F in different environmental compartments in 2001 have been calculated. In contrast to the last year, the initial data on emissions along with the expert estimates [Pacyna et al., 1999] included the available official information submitted by the Parties to the Convention. Finally, in the current year tentative calculations of the B[k]F transport and accumulation in the environment have been performed. The main aim of these calculations is to evaluate the B[k]F pollution levels (deposition and concentrations in different environmental compartments) in 2001 and to study the trends of pollution in the environment for the period from 1970 to 2001.

**Benzo[a]pyrene**

Calculations of the benzo[a]pyrene pollution levels in the EMEP region were performed with the 50x50 km² model and meteorological information for 2001. The emission data used in the calculations are based on official data and include expert estimates if official information is not available [Pacyna et al., 1999] (see Section 2.1.1). The assessment of air pollution by B[a]P and contribution of the transboundary transport is given below.

**The spatial distribution of pollution.** The mean value of B[a]P deposition flux to European countries in 2001 amounts to 11 g/km²/y. The B[a]P deposition field estimated for the EMEP domain is shown in Fig.11a. High values of deposition fluxes (exceeding 100 g/km²/y) were obtained for the northern regions of Poland and Germany; significant levels (50-100 g/km²/y) are typical for the major part of Poland, Germany, the Czech Republic, Lithuania and Latvia.

Mean annual air concentrations of B[a]P are shown in Fig. 11b. In regions with a high level of emissions - in the western part of Germany and Poland - mean annual concentrations exceed 3 ng/m³. In the rest of the European countries concentrations vary within 0.1-1 ng/m³.

*Fig.11. Spatial distribution of B[a]P depositions (a) and concentrations (b) in the air surface layer in 2001*

**Transboundary transport.** The half-life of B[a]P in the atmosphere is rather long (about 6 days). Therefore it can be transported with air masses over long distances. In particular it can be pointed out that over 20% of B[a]P emitted in Europe are transported outside the EMEP region. The model approach allows to evaluate both the contribution of each particular country to B[a]P air pollution in
different European regions and the contribution of the transboundary transport to pollution in each particular European country.

In most of the European countries the contribution of external sources to B[a]P air pollution varies from 30 to 60% (Fig. 12). However the contribution of external sources depends significantly on the levels of internal B[a]P emissions in the country under consideration as well as its geographic position. For instance in such countries as Luxembourg and Monaco external sources are almost entirely responsible for the surface air contamination by B[a]P. The effect of transboundary transport on air concentrations is more significant than that of domestic emission flux in such countries as Albania (88% of the total concentration), Portugal (74%) and Armenia (72%). At the same time, the contribution of transboundary transport to the total concentrations in Spain does not exceed 5%.

The absolute contribution of external sources to the B[a]P mean annual air concentrations over the territory of some countries is also of interest. The countries, where this contribution exceeds the average annual European concentration (0.3 ng/m^3), are shown in Fig. 13. The most significant effect of transboundary transport is observed for Monaco (1.1 ng/m^3), Luxembourg (0.7 ng/m^3) and Belgium (0.5 ng/m^3).

The outcomes of the calculations also make it possible to identify the highest B[a]P exporters, i.e. the main contributors to the total B[a]P depositions to the territory of other countries. Fig. 14 shows a diagram illustrating contributions of a number of countries to transboundary transport. As is seen the...
highest exporters of B[a]P are France (8.3 t/y), Poland (5.8 t/y) and Spain (5.2 t/y).

Finally, it is possible to rank the countries by the contribution of external sources to B[a]P total depositions (Fig. 15). The greatest external-source impacts on the total depositions are typical for the Russian Federation (8 t/y), Germany (4 t/y), Ukraine and Poland (about 3 t/y in each countries), i.e., for the countries with vast territories. Data on the contribution of transboundary transport to B[a]P depositions to each European country are available on the Internet (www.emep.int or www.msceast.org).

![Fig 14. Contributions of some countries to B[a]P transboundary depositions](image)

![Fig 15. Contributions of external emission sources to B[a]P depositions to the territories of some countries](image)

The computations made allow us to analyze the effect of transboundary transport on each country. In this report the analysis is made on the example of Germany.

**Country-specific information (on the example of Germany).** According to the official data, the total B[a]P emissions in Germany in 2001 were about 30 t, of which more than 13 t degraded in the air, 6 t were transported beyond the calculation grid, and more than 11 t deposited over the EMEP domain. Depositions are distributed in the following way: 7.6 t (68% of the total deposition) deposited to the territory of Germany; 0.6 t (5%) - to Poland; the Czech Republic, France and the Russian Federation received 0.4 t (3%) each; depositions to the rest of EMEP countries were 2 t (18%) (Fig. 16).

The estimated field of B[a]P depositions from German sources is shown in Fig. 17. For most of the German territory B[a]P deposition exceeds the mean value for Europe (11 g/km²/y). Depositions of B[a]P from German sources to the larger part of France and Belgium vary from 5 to 20 g/km²/y. In most of the other European countries, depositions of B[a]P from German sources vary from 0.2 to 5 g/km²/y. The same range is also typical for the areas located rather far from Germany, i.e., for the southern parts of Norway and Sweden.
Fig. 16. Distribution of B[a]P depositions from German sources over the territory’s of European countries

Fig. 17. B[a]P depositions from German sources in 2001, g/km²/y
The spatial distribution of the input from external sources is given in Fig. 18. Over the major part of the territory of Germany the pollution import varies from 30 to 70%; however, in some regions near the boundaries the contribution of the neighbouring countries may be as high as 80% and more. The contribution of France to the total deposition of B[a]P to Germany is approximately 1600 kg/y (14% of the total deposition to the country, Fig. 19). Noticeable contributions to the contamination of Germany are also made by Belgium - 1077 kg/y (9%), the Czech Republic - 353 kg/y (3%) and Poland - 326 kg/y (3%). The integral contribution from the remaining European countries is 741 kg/y (6%). Approximately the same values of contributions from external sources are typical for air concentrations of this pollutant in Germany.

![Fig. 18. Contribution of external sources to B[a]P depositions to the territory of Germany, %](image)

The assessment of the transboundary transport for other European countries can be found on the Internet: http://www.msceast.org/countries/index.html.

The spatial distribution of B[a]P depositions allows to evaluate the contribution of emission sources from different countries to depositions over specific regions of the country under consideration. As an example, Fig. 20 illustrates the contribution of emission sources from European countries to depositions over particular Lands of Germany.

The contribution of domestic sources varies from 50 to 88%. Significant contributions to depositions to particular Lands of Germany are made by France, Belgium, Poland and the Czech Republic. For instance the major input to B[a]P depositions to the territory of Saarland (73 kg/y, or 58%) is made by France.

![Fig. 19. Contributions of European countries to B[a]P depositions to the territory of Germany](image)
Fig. 20. Contribution of emission sources in European countries to B[a]P deposition to different Lands of Germany
**Benzo[b]fluoranthene**

Calculations of B[b]F pollution levels covered the period from 1970 to 2001. The main objective of these calculations was to estimate B[b]F pollution levels in the main environmental compartments, analyze their long-term trends and compare the outcomes with measurements. Expert estimates [Pacyna et al., 1999] as well as official data were used as emission data (see Section 2.1.1).

The analysis of B[b]F accumulation in the main environmental compartments. Let us analyze the distribution of B[b]F annual emissions between the main environmental compartments in 2001 (Fig. 21). About 40% of the annual emissions deposit to soil and vegetation; 8% - to marine environment; 6% degrade and about 1% remain in the atmosphere. Almost a half (46%) of the emitted pollutant is transported outside the EMEP region. The same picture is typical for other years covered by calculations.

The trends of B[b]F accumulation in various environmental compartments are different due to the peculiarities of B[b]F behaviour in them. Fig.22 shows the plots of B[b]F emission reduction (Fig.22a) and variations of B[b]F concentrations in the main environmental compartments (atmosphere, soil and seawater, (Fig.22b,c,d) in the period from 1970 to 2001. B[b]F emissions reduce significantly (1.7 times) in the period from 1985 to 1990. The trend of B[b]F content in the air (Fig. 22b) is basically similar to that of emissions. Different persistence of B[b]F in soil and seawater (half-lives are 700 and 70 days, respectively) causes the differences in the character of B[b]F accumulation in these media. Whereas the trend of B[b]F accumulation in seawater (Fig. 22c) actually follows emissions, the trend of accumulation in soil differs from that observed in other media significantly. B[b]F content in soil increases reaching the maximum in 1982. Then it decreases smoothly and the rate of the decrease is lower compared with other media.

**Fig. 21. Distribution of B[b]F annual emissions in 2001**

**Fig. 22. B[b]F emission variation (a) and accumulation trends in the main environmental compartments of the EMEP domain (air (b), seawater (c) and soil (d)) during 1970-2001**
The above trends result in the fact that by the end of the calculation period the greater part (more than 96%) of B[b]F is accumulated in soil (Fig. 23).

**Fig. 23.** Distribution of B[b]F between different environmental compartments in 2001

**Spatial distribution of the pollutant.** Now we consider the spatial distribution of B[b]F depositions and concentrations in the main environmental compartments (air and soil) at the end of the calculation period (2001).

The average value of B[b]F deposition flux for Europe is 13 g/km²/y. High deposition fluxes (>50 g/km²/y) are noted for Poland, France, the Czech Republic, Germany, Belgium, Lithuania and Latvia (Fig. 25). For these countries, as well as for Spain and Georgia the most intensive fluxes of emissions are typical (>200 g/km²/y) (Fig. 24).

**Fig. 24.** Spatial distribution of B[b]F emissions in 2001

**Fig. 25.** Spatial distribution of B[b]F depositions in 2001

**Fig. 26.** Air concentrations of B[b]F in 2001

**Fig. 27.** Soil concentrations of B[b]F in 2001
In polluted regions of Poland, France and Belgium the mean annual B[b]F concentrations in the air exceed 2 ng/m\(^3\) (Fig. 26) and the average value for Europe is 0.2 ng/m\(^3\). Rather high B[b]F concentrations in the air (1-2 ng/m\(^3\)) are also typical for Spain, the Netherlands, Lithuania, the Czech Republic, Hungary, Belarus and Georgia. In the rest of European countries the mean annual concentration of B[b]F in the air does not exceed 1 ng/m\(^3\).

For Europe the average value of B[b]F concentration in soil is 1.5 ng/g. High levels of soil concentrations (10 ng/g and higher) are typical for polluted regions of Poland (Fig. 27). B[b]F soil concentration in France, Belgium, Germany and Baltic States varies from 5 to 10 ng/g. It is well to point out that the spatial distribution of B[b]F concentration in soil differs from that of B[b]F emissions, since to a large extent it is dictated by the B[b]F long-term accumulation in the previous years.

**Benzo[k]fluoranthene**

Preliminary calculations of the B[k]F pollution levels covered the period from 1970 to 2001. The main objective of these calculations was to make a provisional estimation of B[k]F pollution levels in the main environmental compartments, analyze their long-term trends and compare the calculation results with measurements. Expert estimates [Pacyna et al., 1999] were used as emission data. As was mentioned above (see Section 2.1.1) B[k]F emissions were assumed to be equal to those of B[a]P. The same approach was used in 2003 to estimate B[b]F emissions [Shatalov et al., 2003]. The results obtained make it possible to compare the effect of peculiarities of physical-chemical properties of these two compounds on their behaviour in different environmental compartments within the EMEP region.

**The analysis of B[k]F accumulation trends in the main environmental compartments.** Fig.28 shows the plots of B[k]F emission reduction (Fig.28 a) and variations of B[k]F concentrations in the main environmental compartments (atmosphere, soil and seawater) (Fig.28 b,c,d) in the period from 1970 to 2001. In addition similar plots for B[b]F based on the same emission data are given. B[k]F emissions reduce significantly (1.5 times) in 1990-95. The trend of B[k]F accumulation in air and sea (Fig. 28b,c) actually follows the emission variation.

![Fig. 28. The trends of (a) emissions and content of B[k]F and B[b]F in the (b) air, (c) seawater and (d) soil within the EMEP region in 1970 - 2001](image-url)
The trend of B(k)F accumulation in soil (Fig. 28d) differs from that observed in other media significantly. In spite of emission reduction from 1970 to 1980, B(k)F concentration in soils increases reaching the maximum in 1982. Then it smoothly decreases. Such behaviour of B(k)F in soil is dictated by its high persistence in this media (B(k)F half-life in soil is 700 days).

The above trends result in the fact that by the end of the calculation period the greater part (more than 96%) of B(k)F is accumulated in soil (Fig. 29).

The plots in Fig. 28 (b, c, d) show that in all the compartments concentration of B(k)F is lower than that of B(b)F. On the average over 30 years the difference varies from 9% in vegetation to 25% in the air. Mainly it is due to the fact that B(k)F and B(b)F have different rates of degradation in the atmosphere. Fig. 30 shows distribution of B(b)F and B(k)F annual emissions in 2000. As is seen the amount of B(k)F degraded in the atmosphere is 4 times higher than that of B(b)F. Therefore we can state that B(b)F has a higher long-range transport potential compared with B(k)F. For example, in 2000 nearly 48% of the annual B(b)F emissions was transported outside the EMEP region, whereas for B(k)F this value did not exceed 36% (Fig. 30a,b).

Spatial distribution of the pollution. We proceed with consideration of the spatial distribution of B(k)F depositions and concentrations in the main environmental compartments (air and soil) at the end of the calculation period (2001).

The average value of B(k)F deposition flux for Europe is 13.5 g/km²/y. High deposition fluxes (>50 g/km²/y) are noted for Poland and the Russian Federation (Fig. 32). According to the emission scenario these countries also have the most intensive fluxes of emissions (>200 g/km²/y) (Fig. 21).

The average value of B(k)F air concentrations for Europe is 0.25 ng/m³ (Fig. 33). In polluted regions of Poland and the Russian Federation the mean annual B(b)F concentrations in the air exceed 2 ng/m³. Rather high B(k)F concentrations in the air (1-2 ng/m³) are also typical for Georgia, the Czech Republic and Hungary. In the rest of European countries the mean annual concentration of B(k)F in the air surface layer is within the range of 0.4-1 ng/m³.

![Fig. 29. Distribution of B(k)F between different environmental compartments in 2001](image)

![Fig. 30. Annual budgets of (a) B(b)F and (b) B(k)F in the atmosphere for 2000](image)
For Europe the average value of B[k]F concentration in soil is 1.5 ng/g. High levels of B[k]F soil concentrations (10 ng/g and higher) are typical for polluted regions of Poland, Germany and central Russia (Fig. 34). In most of the countries of Central and Eastern Europe B[k]F soil concentration are in the range of 5-10 ng/g. The same level is in the United Kingdom, France and the southern part of Sweden. As in the case with B[b]F the spatial distribution of B[k]F concentration in soil differs from that of B[k]F emissions, since to a large extent it is dictated by the B[k]F long-term accumulation in the previous years.

**Fig. 31. Spatial distribution of B[k]F emissions in 2001**

**Fig. 32. Spatial distribution of B[k]F depositions in 2001**

**Fig. 33. Air concentrations of B[k]F in 2001**

**Fig. 34. Soil concentrations of B[k]F in 2001**

**Comparison with measurements.** For B[a]P the comparison of measurement data with modelling results is complicated due to the limited amount of measurements on concentrations in the air and precipitation in 2001 (for concentrations in the air data from 5 EMEP sites, for concentrations in precipitation from 2 EMEP sites and for deposition fluxes from 3 EMEP sites are available) and wide spread of mean monthly values measured within a year. The ratio between measured maximum and minimum mean monthly air concentrations at one and the same site varies from 20 to 70 times for different sites. For concentrations in precipitation and deposition fluxes at some sites this ratio is as large as two orders of magnitude. At that the outcomes of various measurements performed at EMEP sites demonstrate that basically measured and calculated mean annual concentrations agree within a factor of 3. For most stations calculated concentrations are within the spread of measurement data. Calculated concentrations slightly increased as compared with the last year due to the fact that the
official data on emissions reported by some countries had been revised (the total B[a]P emissions of Europe in 2001 increased by a factor of 1.5 as compared with the previously submitted data).

For the comparison with modelling results mean annual values of B[b]F concentrations in the environmental media and deposition fluxes in the period from 1991 to 2001 were used. About 60% of calculated air concentrations are within a factor of 2 relative to measurements, the remaining 40% are within a factor of 5. All calculated concentrations in precipitation are within a factor of 3 and all calculated deposition fluxes are within a factor 2 relative to measurements. In case of deposition fluxes it should be pointed out that a number of measurements is limited (only 8 records are available). It is noteworthy that by and large the agreement between calculations and measurements is reasonable.

For the comparison with modelling results mean annual values of B[k]F concentrations in the environmental media and deposition fluxes in the period from 1988 to 2001 were used. About 70% of calculated air concentrations are within a factor of 2 relative to measurements, the remaining values are within a factor of 5. All calculated concentrations in precipitation are within a factor of 3. Three fourths of calculated deposition fluxes are within a factor of 2 relative to measurements but it should be pointed out that in this case a number of measurements is limited (only 8 records).

To make the agreement between measurements and calculation better it is necessary to further improve parameterization of models, refine emission data and enlarge the measurement base for comparison.

### 2.2.2. Dioxins and furans

The group of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) contains 210 congeners. To 17 of them International Toxic Equivalency Factors are assigned. The objective of this stage of investigations is to assess the atmospheric transport of PCDD/Fs in the EMEP region in 2001 for each of the 17 toxic congeners on the basis of the model calculations. Data on the model parameterization for all 17 toxic congeners can be found in [Shatalov et al., 2004a]. To take into account the effect of accumulation of PCDD/Fs’ congeners in different environmental compartments (soil, seawater and vegetation) the modelling of their long-range transport was performed for the period from 1970 to 2001. The investigations were undertaken along the following lines:

- behaviour of different PCDD/F congeners in the environment;
- pollution of the EMEP region by dioxins/furans in the period from 1970 to 2001;
- transboundary transport of PCDD/Fs in the EMEP region in 2001 ("country-to-country" basis);
- model evaluation of the effectiveness of different emission reduction scenarios;
- agreement between calculated and measured data and the analysis of discrepancies revealed.

All estimates of pollution levels are given in NATO toxic equivalency units (TEQ).

**Behaviour of PCDD/Fs in the environment.** The transport and accumulation of PCDD/F congeners in the environment were assessed for each of 17 toxic congeners separately, taking into account the differences in their behaviour in the environment. According to the calculations toxic PCDD/F congeners differ in the distance of their airborne transport. To assess it we have calculated the length of the distance in the atmosphere at which the congener concentration decreases twice ($L_{1/2}$). The
values of $L_{1/2}$ for different PCDD/F congeners vary from 700 to 1500 km. The distribution of PCDD/F congeners' annual emissions in the environment is also different. Namely from 1 to 14% of PCDD/F annual emissions degrade; from 46 to 52% deposit to land; from 6 to 9% deposit to sea and from 30 to 41% are transported outside the EMEP region.

Overall toxicity of PCDD/Fs was estimated as a sum of contributions of toxic congeners. The distribution of the annual PCDD/F mixture emissions in the environment of the EMEP region is shown in Fig. 35.

![Annual budget of the mixture of toxic PCDD/F congeners in the atmosphere over Europe](image)

Ultimately, only about 1% of the annual PCDD/F emissions remain in the atmosphere, about 5% degrade, 38% are transported outside the EMEP region. The remaining part deposits to other media: about 47% - to soil and vegetation and about 9% - to sea.

**Behaviour of PCDD/Fs in different environmental compartments.** In soil PCDD/Fs are mainly sorbed on the organic matter: the coefficient $K_{oc}$ characterising the distribution of PCDD/Fs between the soil organic matter and the soil solution varies from several thousands to tens of thousands. Therefore the mobility of dioxins and furans in soil is low. The rate of their degradation is also low: the half-life of PCDD/Fs in soil varies from 10 to 150 years. Hence a continuous input of new portions to soil over a period of several decades results in the accumulation of the significant amount of PCDD/Fs in this environmental compartment.

Equilibrium concentrations of PCDD/Fs in the atmosphere and vegetation are established within relatively short periods (several weeks). High values of the partitioning coefficient in the octanol/air system ($10^{10} - 10^{13}$) predetermine relatively high concentrations of PCDD/Fs in vegetation.

In water the mobility of PCDD/F congeners is significantly higher due to the fact that they are transported with sea currents and sedimentation. Besides, the rate of PCDD/Fs degradation in seawater is also higher compared with soil: the half-life varies from about 4 months to 20 years depending on a congener. As a result, the long-term accumulation of PCDD/Fs in seawater is much lower than that in soil.

**The trends of PCDD/Fs accumulation in the main environmental compartments** (air, seawater and soil) as compared with that of emissions throughout the calculation period (1970 - 2001) is shown in Fig. 36.

According to the emission data used in the calculations, the total PCDD/F emissions in Europe decreased five-fold in the period from 1980 to 2001. In general the trends of PCDD/F content in air and seawater follow the emission variation. The trend of PCDD/F soil accumulation is different from that of emissions. Emissions began to reduce in 1980, whereas the decrease in soil contamination started in 1990. The rate of the soil content decrease is much lower. This causes the substantial PCDD/F re-emission flux from soil (Fig. 37) amounting in 2001 to about 20% of the annual emissions.
In its turn re-emission slows down the tendency for a decrease in PCDD/F content in the atmosphere (Fig. 36).

![PCDD/F emissions and air content](image1.png)

**Fig. 36. Trend of PCDD/Fs content in the main environmental compartments as compared with that of emissions in Europe for a period from 1970 to 2001**

The redistribution of PCDD/Fs between different environmental compartments resulting from the long-term (1970 - 2001) accumulation in the environment is shown in Fig. 38. The greater part of PCDD/Fs accumulated in the environment is in soil (about 95%). PCDD/F content in vegetation and seawater amounts to 3 and 2% of the total PCDD/F content in the environment respectively.

This pattern of PCDD/Fs distribution in different environmental compartments is not directly determined by depositions. The annual contribution of PCDD/Fs to soil is about 47% of the total emissions. However, relatively low rates of PCDD/Fs degradation in soil results in the fact that about 95% of the total PCDD/F amount in the environment are accumulated in soil after a long time period (1970-2001). At the same time deposition of about 9% of the annual PCDD/F emissions to seawater does not lead to the long-term accumulation in this compartment. Only 2% of PCDD/F total environmental content are accumulated in seawater. So, we can conclude that soil is the main “accumulator” of PCDD/Fs. Re-emission of toxic congeners from soil to the atmosphere affects the PCDD/F air pollution. Below we shall focus our attention on contamination of air and soil by PCDD/F toxic congeners.

Significant variations are observed in the spatial distribution of PCDD/Fs air concentrations during the calculation period. Due to the decrease in emissions of PCDD/Fs started in 1980, air concentrations have decreased significantly by 2001. PCDD/F concentrations in the surface air layer in 1980 and 2001 are given in Fig. 39.
More detailed analysis can be made on the basis of data on the average concentrations of toxic congeners in the surface air layer of European countries as well as the emission trends in particular countries (Fig. 40).

As is seen the ratio of PCDD/Fs air concentrations in 1980 to those in 2001 varies from 0.9 to 9.4 depending on a country. It should be noted that a significant reduction in emissions of toxic congeners in some countries does not necessarily lead to the respective decrease in air concentrations. For example, the emissions of PCDD/Fs in Luxembourg and Austria in the period from 1980 to 2001 reduced 46 and 11 times respectively, whereas air concentrations decreased only 3.5 - 4 times. The disagreement between the reduction of emissions and air concentrations is explained by PCDD/F transboundary transport.

The long-term accumulation of PCDD/Fs in soil in combination with the changes in the emissions also leads to significant differences in the spatial distribution of toxic congeners in the air and soil of European countries. The air and soil spatial distribution patterns for 2001 are shown in Fig. 41.

For example, high concentrations of PCDD/Fs in soil (> 1 pg TEQ/g) are observed in the northern part of Germany, whereas air concentrations are relatively low there (2-3 fg TEQ/m³). High concentrations of PCDD/Fs in soil in the northern part of Germany are caused by the PCDD/F long-term
accumulation in this media and high levels of emissions in Germany before 1980 (Fig. 42a). PCDD/Fs were accumulated in soil in Germany by this time. Further reduction in emissions led to the relevant decrease in air concentrations, whereas concentrations in soil decreased much slower resulting in the residual accumulation of PCDD/Fs in this environmental compartment (Fig. 42b).

Fig. 41. Spatial distribution patterns of concentrations of PCDD/Fs in the air (a) and soils (b) of Europe in 2001

Fig. 42. PCDD/F emissions from the territory of Germany (a) and air and soil concentrations (b) in Germany from 1970 to 2001

Pollution levels of PCDD/Fs in the air over the EMEP region. The calculations of the environmental pollution by 17 PCDD/F toxic congeners allow to assess the spatial distribution of these substances in the main environmental compartments (air, soil, vegetation and sea water). The total concentration of all 17 toxic congeners in a particular environmental compartment was estimated as sums of concentrations of individual congeners. The data obtained allow us to estimate the environmental pollution by PCDD/Fs in different countries and identify “hot spots” with the highest contamination levels, which is of importance for further risk assessment.

In 2001 the typical levels of air contamination by dioxins and furans in Europe vary from 1 to 5 fg TEQ/m³ with the maximum of 10 - 30 fg TEQ/m³ and higher in the most polluted regions of Central Europe (Poland, Czech Republic, Slovakia, Belgium and some regions of Germany). PCDD/F concentrations in soil in Europe vary from 0.1 to 1.8 pg TEQ/g. The highest concentrations (> 0.5 pg TEQ/g soil) are typical for Central European countries (Austria, Belgium, Germany, Luxembourg, Poland, France and Czech Republic). Typical levels for vegetation contamination vary from 10 to 50 fg TEQ/g reaching 100 fg TEQ/g and higher in the most polluted regions. Due to the filtering
properties of forests, PCDD/Fs concentrations in vegetation may appear significant even against the background of low air concentrations (e.g. in Scandinavia). Concentrations of toxic congeners in seawater of the Atlantic Ocean (within the EMEP region) vary from 0 to 5 fg TEQ/L.

Transboundary transport. At the first stage of the study, 18 countries with the highest contribution to the overall toxicity of atmospheric emissions in Europe (Belgium, Bulgaria, Hungary, Germany, Greece, Spain, Italy, Poland, Romania, Russian Federation, Slovakia, the United Kingdom, Ukraine, France, Croatia, Czech Republic, and Switzerland) have been selected for model calculations. The contributions of PCDD/F emissions and re-emission in these countries (conditioned by the historical emissions from all European countries in a period from 1970 to 2000) to the total pollution of the atmosphere in 2001 have been assessed.

![Fig. 43. Contributions of the transboundary transport (a) and historical emissions (b) to the air pollution in particular European countries in 2001](https://example.com/fig43.png)

The contribution of transboundary transport (i.e., the contribution of all emission sources in 2001, except for the sources in country under consideration) to the total air pollution in European countries varies from 7 to 60% (Fig. 43a). The contribution of historical emissions (due to re-emission process) is also significant and varies from 2 to 18% (Fig. 43b).

Diagrams illustrating transboundary transport of pollutants between European countries (with respect to air concentrations and depositions) can be found in the Internet: [www.emep.int](http://www.emep.int) and [www.msceast.org](http://www.msceast.org).

Scenarios of emission reduction. To illustrate the possibility of model assessments of different scenarios of the PCDD/F atmospheric emission reduction in Europe two conventional scenarios have been considered.

The first scenario suggests that PCDD/F emissions of all European countries, except for the Czech Republic, Poland and Germany, (i.e., except for Central European countries with significant emissions in 2001) would remain constant throughout the calculation period (2001 - 2010). The mean annual emission reduction in Poland and the Czech Republic amounts to 5% per year. The mean annual emission reduction in Germany for the same period is taken at 2% per year. The second scenario suggests that the emission reduction would take place only in the eastern part of the EMEP region, i.e., in the Russian Federation and Ukraine, and would be equal to 5% per year. The emissions of rest of European countries are assumed to remain constant. According to both of the scenarios the decrease in the total PCDD/F emissions in Europe for the calculation period is about 8%.
The results of the calculations show that with the first scenario a significant reduction in the level of air pollution (exceeding 8% - the mean reduction of European emissions) is observed in 11 countries (Austria, Belarus, Germany, Lithuania, Poland, Slovakia, Latvia, Slovenia, Czech Republic, Sweden and Hungary). With the second scenario the relevant decrease is observed in 7 countries (Belarus, Kazakhstan, Moldova, Russian Federation, Turkey, Finland and Ukraine) (Fig. 44).

As is seen the implementation of the first scenario would bring a significant reduction in the level of air pollution by PCDD/Fs in a larger number of European countries than that of the second scenario.

Model calculations also allow to obtain more detailed estimates of changes in air pollution levels with the implementation of one of the two scenarios. As an example, the results of modelling for the first scenario are shown in Fig. 45. More detailed analysis of the considered scenarios will be given in MSC-E Technical Report.

Therefore, the model calculations make it possible to estimate the decrease in air concentrations for each European country in line with the selected scenario and identify the countries where air pollution would be most strongly affected. This information might be useful for developing different scenarios of the PCDD/F emission reduction in the European region.
Comparison against measurements. The validation of the model describing the behaviour of PCDD/Fs in the environment is complicated due to the insufficient amount of measurement data.

The database for the comparison study includes the results of 30 measurements made in different years at several EMEP monitoring sites and under various national measurement campaigns. The comparison of measurements and calculations shows that over 40% of measured data agree with modelling results within a factor of two; over 60% - within a factor of three. Normally the calculated values are slightly lower than measured values. The analysis of the most significant discrepancies between measured and calculated data on air concentrations of toxic congeners shows that they are caused not only by the model uncertainties but also by the uncertainty and incompleteness of official emission data introduced into the model.

The absence of measurements of PCDD/F concentrations in seawater complicates the model validation with respect to this parameter. However, the range of concentrations of toxic congeners in seawater of the Atlantic Ocean as obtained by the model (0-5 fg TEQ/L) is of the same order of magnitude as that of the Baltic Sea (2-9 fg TEQ/L).

More detailed analysis of calculated and measured PCDD/F concentrations in different environmental compartments of the EMEP region is given in MSC-E Technical Report [Shatalov et al., 2004a].

In general, we can state that taking into account the existing uncertainty in official emission data on PCDD/Fs (within an order of magnitude) and probable discrepancies between concentrations of these pollutants measured in different environmental compartments in different years and under various measuring campaigns, the agreement between measurement and calculations seems to be reasonable. To verify the model more completely additional measurements are required. It is also important to take into account the model uncertainties together with those of official emission data and measurement data on the PCDD/F concentration in different environmental compartments.

The use of a limited number of congeners for modelling. On the previous stage of investigations the assessment of the environmental contamination by PCDD/Fs was performed on the basis of 2,3,4,7,8-PeCDF as an “indicator congener” [Shatalov et al., 2002] or of a group of eight congeners with the highest contribution to the total PCDD/F emissions [Shatalov et al., 2003]. The use of all 17 PCDD/F toxic congeners allowed to estimate the uncertainty of calculations related to the limited number of congeners. For instance, if the properties of the indicator congener (2,3,4,7,8-PeCDF) are used for modelling the transport of the entire PCDD/F mixture, the error in the spatial distribution of PCDD/F air concentrations is about 30%. For the calculation on "country-to-country" matrix the error is about 5%. The error in the spatial distribution of PCDD/Fs in soil is about 60%.

To improve the accuracy of calculations it is possible to enlarge the group of congeners distributing the total emission data between them. In this case a group of four congeners (1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,4,7,8-PCDF and 1,2,3,4,6,7,8-HpCDF) will reduce the error in the spatial distribution of PCDD/F concentrations in air, soil and seawater to 20%. With certain eight congeners the error will be less than 10%.

Therefore we can conclude that taking into account the existing uncertainties of emission data, it is feasible to use the "indicator congener" to calculate the "country-to-country" matrix and the group of four congeners (see above) to calculate the spatial distribution of PCDD/Fs in different environmental compartments within the European region. If the emission data are refined, it might be reasonable to make model calculations with a group of eight congeners or even all 17 toxic congeners of PCDD/Fs.
2.2.3. Pollution of European marginal seas by POPs

In 2001 the pollution of the European marginal seas (Baltic, North, Black and Mediterranean) was assessed for PAHs (B[a]P) and PCDD/Fs. For that the official data submitted by countries to the UNECE Secretariat in 2003 complemented by expert estimates [Pacyna et al., 1999] were used. The calculation of pollution by dioxins/furans was made with account of properties of each of 17 toxic congeners.

The values of B[a]P and PCDD/Fs deposition fluxes to the marginal seas are given in Table 3.

Table 3. Deposition fluxes of the selected POP to the marginal seas in 2000

<table>
<thead>
<tr>
<th>Sea</th>
<th>B[a]P, g/km²/y</th>
<th>PCDD/Fs, μg TEQ/km²/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baltic</td>
<td>4.7</td>
<td>108</td>
</tr>
<tr>
<td>North</td>
<td>2.1</td>
<td>86</td>
</tr>
<tr>
<td>Black</td>
<td>1.4</td>
<td>83</td>
</tr>
<tr>
<td>Mediterranean</td>
<td>1.6</td>
<td>48</td>
</tr>
</tbody>
</table>

The most intensive deposition fluxes were obtained for the Baltic Sea. It should be pointed out that only European sources of emissions were taken into account. The levels of pollution of the marginal seas can be refined by taking account of emissions from other sources of the Northern Hemisphere.

The contribution of European countries to the B[a]P depositions to the marginal seas was also evaluated. By way of example Fig.46 provides the diagram illustrating the contribution of European countries to depositions to the Baltic Sea. Five main contributors are pointed out.

More detailed information on pollution of the marginal seas, including the assessment of pollution of different areas of the Baltic and Mediterranean Seas will be given in the MSC-E Technical Report [Shatalov et al., 2004a].

Fig. 46. The contribution of European countries to B[a]P depositions to the Baltic Sea basin
2.3. Pollution levels in the Northern Hemisphere

2.3.1. Polychlorinated biphenyls

This stage of the study aims to further refine parameterization of the PCB long-range transport and accumulation model and to assess air pollution within the EMEP region with respect to sources of the Northern Hemisphere. In assessing air pollution a special emphasis was laid on PCB toxic congeners. At present the emission expert estimates are available for two toxic congeners: PCB-105 and PCB-118. In addition, PCB-28 (“light” congener with low chlorination degree) as well as PCB-153 and PCB-180 (“heavy” congeners with high chlorination degree) were considered. The calculations were made for the period from 1970 to 2000 to take into account the impact of PCB long-term accumulation in environmental compartments on air pollution.

The model was refined through the input of the spatial distribution and temporal variations of OH-radical concentrations and atmospheric aerosol specific surface in the atmosphere.

To achieve the above aim the following was performed:

- assessment of spatial distributions of air surface layer concentrations within the EMEP region for toxic congeners (PCB-105 and 118);
- analysis of the differences in the behaviour of PCB congeners caused by the peculiarities in their physical-chemical properties to assess the impact of re-emission fluxes on atmosphere pollution;
- comparison of calculated and measured pollution levels.

Spatial distribution of the atmosphere pollution with PCB toxic congeners. Based on the calculations of long-range transport and accumulation of PCB toxic congeners (PCB-105 and PCB-118), the spatial distribution of air pollution by these congeners in 2000 was assessed. Spatial distributions of PCB-105 emissions, air concentrations and direct depositions (not including gas exchange) in 2000 are shown in Fig.47.

![Fig. 47. Spatial distribution of PCB-105 emissions (a), concentrations in the air (b) and direct depositions (c) in 2000](image)

The levels of PCB-105 air concentrations for Europe basically range from 1 to 10 pg/m³. Lower concentrations (<1 pg/m³) are typical for the Scandinavian Peninsula. The comparison of spatial distributions of emissions and concentrations in the air surface layer demonstrates the long-range transport potential of PCBs. The typical levels of pollution in the Atlantic area are 0.5 - 1 pg/m³. They
are comparable with those in some regions of Europe. The difference in the spatial distribution of
emissions and air concentrations shows that air pollution in European countries is determined to a
large extent by the transboundary transport. For instance, in some countries located in the south-west
of Europe (Bulgaria, Bosnia and Herzegovina, Serbia and Montenegro, Romania and Croatia) the
emission flux is low (less than 0.05 g/km²/y), at the same time the level of air concentrations in these
countries is fairly high (up to 3 pg/m³).

The levels of depositions in Europe range from 0.2 to 0.5 g/km²/y. Rather high levels of depositions
(up to 0.5 g/km²/y) observed in some regions of the Scandinavian Peninsula can be explained by the
filtration ability of forests performed in the formation of the deposition flux.

Similar situation is observed for PCB-118 congener (Fig. 48).

In line with the levels of emissions the levels of air concentrations and depositions for this congener
are somewhat higher (air concentrations are up to 30 pg/m³ and depositions are up to 1.5 g/km²/y).

Assessment of the impact of peculiarities of physical-chemical properties of various congeners on
their behavior in the environment. The impact of differences in physical-chemical properties of
congeners on their behavior in the atmosphere is clearly seen on the diagram of removal processes
(Fig.49, where the annual emissions of each of the five congeners under consideration were
supposed to be equal to 100 t/y). The impact of
the degradation process appears to be most significant for the light PCB-28 congener and least
significant for the heavy PCB-153 and PCB-180
congeners.

Accordingly depositions to soil and seawater are
higher for heavy than for light congeners. Depositions to soil are somewhat higher than
those to seawater due to the fact that major
emission sources are located on the land.

Annual depositions of PCB congeners to soil and
seawater result in their accumulation in these environmental compartments. PCB accumulation is
most significant in soil due to high persistence of the pollutant in this compartment (typical half-life
varies from 3 to 40 years depending on a congener). The trends of PCB content in the main
compartments (atmosphere, soil, and seawater) given in comparison with the emission trend are
presented for the light (PCB-128) and heavy (PCB-153) congeners in Fig. 50 and 51 respectively.

For the light PCB-28 emissions reduced eight times beginning from 1975. In the same period PCB
concentration in the air reduced 7 times, in seawater - 2 times and in soil - by 16%. For the heavy
PCB-153 congener emissions reduced more than 9 times, concentration in the air - 5 times, in
seawater - by 40% and in soil - only by 6%. Therefore the reduction of emissions leads to the fairly
rapid decrease of the atmospheric content and comparatively slow decrease of seawater and
(particularly) soil contents. The reduction rate of soil and seawater contents lags behind that of
emissions. This is most noticeable for heavy PCB congeners.

Stable levels of soil and seawater content against the background of the atmosphere content
reduction cause re-emission from these compartments most pronounced for heavy congeners. For
PCB-153 the gas flux from soil in 2000 appears to be comparable in amount with the anthropogenic
emission flux (it is estimated that the emission flux density in Europe amounts to 1.4 g/km²/day, and
the density of gas flux from soil - to 0.9 g/km²/day). This partly explains a comparatively low rate of the
reduction of PCB-153 content in the atmosphere (5 times) compared with the rate of emission
decrease (9 times).

Therefore while a significant reduction of emissions is observed, the levels of the atmospheric
content of polychlorinated biphenyls may be strongly supported for the long-term period due
to heavy congeners accumulated in soil and seawater in the previous time.
Comparison against measurements. The comparison of the calculated and measured deposition fluxes and air concentrations of the considered PCB congeners demonstrated that the model overestimates both parameters. The ratio of measured/calculated values ranges from 0.7 to 2 for air concentration and from 0.4 to 1.4 for deposition fluxes. For all congeners 50-60% of the measured and calculated air concentrations agree within a factor of 4.

2.3.2. Hexachlorobenzene

This stage of the study aims to assess the HCB intercontinental transport. Hexachlorobenzene is a POP with the maximum long-range transport potential. For HCB the typical atmospheric half-life is about 1 year, whereas for PCB it ranges from 9 to 95 days depending on a congener, and for B[a]P it is about 6 days. So it might be expected that HCB emissions in remote regions can significantly affect Europe’s pollution and vice versa emissions from European sources can contribute to air pollution in the remote regions. In this section model evaluation of the impact of HCB emissions from the sources of some remote regions (America, Central Asia and South-eastern Asia) on European pollution and the contribution of European sources to air pollution in the remote regions including the Arctic Region is presented.

To perform the study a special emission scenario was developed. The Northern Hemisphere was divided into five regions: Europe, Russia, North America, Central Asia and South-eastern Asia (Fig. 52). For each region the emission totals are given and appropriate spatial distributions are constructed. Emission data are described in Section 2.1.4. It is pertinent to note that due to the incompleteness of the HCB emission data the scenario developed should be taken as tentative.

To assess HCB intercontinental transport the following calculations were performed:

1. Simulation of HCB atmospheric transport from the sources of each selected region on the assumption that originally there were no HCB accumulation in environmental media. The outcomes were used to assess the impact of each region on air pollution in various parts of the Northern Hemisphere.

2. Simulation of HCB transport and accumulation in the main environmental media for the period from 1970 to 2000. The outcomes were used to assess the impact of the re-emission processes on air pollution.

On the basis of the above calculations it was made possible to:

1. Describe the pathways of HCB atmospheric transport.

2. Assess the impact of various atmospheric processes on HCB transport within the Northern Hemisphere

3. Assess the contribution of HCB emission sources located in Europe to air pollution of different regions of the Northern Hemisphere, as well as the contribution of emissions of different regions to air pollution in Europe.

4. Provide a preliminary assessment of the contribution of re-emission processes to air pollution over different regions of the Northern Hemisphere.
**Long-range transport potential.** According to the simulation outcomes about 80% of annual emissions are transported outside Europe. HCB transported outside Europe partly remains in the atmosphere over other regions of the Northern Hemisphere and partly deposits on the territory of these regions. For sources of the other regions the fraction of emissions transported outside the relevant territory varies from 60% for Russia to 85% for South-eastern Asia. The outcomes demonstrate that HCB has a fairly high long-range transport potential in the atmosphere.

**Atmospheric HCB pathways.** Spatial distribution of HCB pollution from different sources can be used to describe the pathways of HCB atmospheric transport. By way of example we consider the maps of mean annual concentrations caused by emission sources in Europe, America and South-eastern Asia (Fig.53). Pollution from European sources moves mainly to the east and south-west and partly to the north (to the Arctic). Pollution from sources in America for the greater part is transported eastward. Finally, pollution from sources in South-eastern Asia moves almost exclusively to the east.

![Fig. 53. Spatial distribution of HCB air pollution in Northern Hemisphere from sources located in Europe, North America and South-eastern Asia](image)

Below the contribution of each group of sources to pollution of different regions of the Northern Hemisphere is assessed.

**Accumulation in environmental compartments.** To assess the impact of the re-emission process on air pollution, the estimation of HCB distribution between the main environmental compartments (atmosphere, soil and seawater) is of importance. The most important atmospheric processes, which affect HCB distribution between the above compartments, are degradation in the atmosphere, exchange with the underlying surface (land and water) and export beyond the calculation grid. Distribution of the HCB annual emissions between these processes for sources in Europe and South-eastern Asia is given in Fig.54. The diagrams of emission distribution show that the relative impact of different processes of HCB removal from the atmosphere depends significantly on the routes of HCB transport.

The impact of degradation in the air is more significant for HCB emitted from Europe. For European sources the fraction of HCB degraded in the air is about 11%, and for sources of South-eastern Asia it is 8%. This fact is explained by higher temperatures in the regions covered with pollution from European sources.
The fraction of annual HCB emissions from Europe deposited to the land is about 19% and to the sea is about 15%, whereas only 7% of emissions from South-eastern Asia are deposited to the land and 12% - to the sea. The difference in HCB emissions deposited on the land and sea is dictated by the fact that pollution from European sources is transported mainly over the land and from sources of South-eastern Asia - over the sea.

**Fig. 54. Distribution of HCB annual emissions from different sources between the processes of removal from the atmosphere for sources of Europe and South-eastern Asia**

The total HCB deposition from all the sources to the sea surface is somewhat higher than to the land. Since the persistence of HCB in these media is fairly high (the typical half-life in these media is about 4 years), it leads to a considerable difference in the HCB accumulation in soil and seawater over a long period of time. Distribution of HCB between environmental compartments resulted from the calculation for the period from 1970 to 2000 is given in Fig. 55.

**Fig. 55. Distribution of the HCB total content by different environmental compartments in 2000**

Consequently, seawater appears to be the main media-accumulator for HCB.

**Intercontinental transport assessment.** The calculation performed allow to assess the distribution of pollution from various groups of sources between different regions (export) and contribution of various groups of sources to pollution in these regions (import).

**Import.** We consider HCB depositions and air concentrations by the example of two regions: Europe and the Arctic (Fig. 56).
64% of HCB depositions to Europe (Fig. 56) are accounted for by European sources. The rest 36% are deposited from remote sources. The contribution of sources of Russia to HCB depositions to Europe is 19%, sources of North America - 7%, sources of Asia - about 10%.

The Arctic does not have its own sources, therefore 100% of HCB depositions to the Arctic are accounted for external sources (Fig. 56b). The total value of HCB depositions to the Arctic is 4 tonnes which is approximately the same as depositions to the EMEP region. Most of HCB deposition to the Arctic is contributed by Russia (31%) and Europe (22%). Contributions of America, Central Asia and South-eastern Asia are about the same amounting to 15-17%.

We now turn to the contribution of various sources to HCB air concentrations. The calculations show that a significant contribution to HCB air concentrations is made by the re-emission process caused by HCB accumulation in soil and seawater during a number of preceding years (Fig.57).

The contribution of re-emission to HCB air concentrations for Europe, Russia, America, Central Asia and South-eastern Asia varies from 15 to 40%. For the Arctic it is much higher and amounts to 55%. It is due to the more intensive accumulation of HCB in environmental compartments at lower temperatures typical for the Arctic.

The contributions of emissions of 2000 to air pollution over Europe and the Arctic are shown in Fig. 58a and Fig. 58b, respectively. As might be expected these contributions basically correspond to the contribution of various sources to HCB deposition over the regions under consideration.
**Export.** Here distribution of HCB depositions from various groups of sources between the regions of the Northern Hemisphere is considered by the example of Europe and South-eastern Asia (Fig. 59).

The calculations show that only 33% of the total depositions caused by HCB emissions from European sources fall on the territory of Europe. The rest 67% are distributed in the following way: Russia - 42%, Asia - about 12%, North America - about 13%. The fraction of depositions caused by HCB emissions from sources in South-eastern Asia to its own territory amounts to 31%, whereas HCB export from this region to America amounts to 32%. As is seen from the map of HCB mean annual concentrations caused by this source (Fig. 53) HCB pollution is transported from South-eastern Asia to North America via the Pacific Ocean.

So, the study of HCB intercontinental transport shows that it can make a significant contribution to depositions, particularly for remote regions of the Northern Hemisphere such as the Arctic.

**Comparison against measurements.** The comparison of the calculated and measured data on HCB concentrations in the lower atmosphere shows that the calculations underestimate the measured values. For the most part the calculated concentrations are consistent with the measurements within an order of magnitude. The situation with concentrations in precipitation is similar. Since the emission scenario used for the calculations is tentative it is possible to conclude that the agreement between the calculations and measurements is satisfactory. The refinement of the emission scenario will enable this agreement to be improved.
2.4. Model modification

To refine the assessment of pollution of the environment by POPs the work on the POP long-range transport model was performed in the current year along the following lines:

1. Taking into account spatial and temporal variations of OH radical in the atmosphere to refine the model description of POP degradation in the atmosphere.

2. Taking into account spatial and temporal variations of atmospheric aerosol specific surface to refine the model description of POP redistribution in the atmosphere between gas and particle phases.

3. Preparation of mean monthly fields of organic carbon (OC) concentration on particles in seawater and its vertical flux at different depths to refine the model description of sedimentation.

The first two modifications have been introduced to the hemispheric version of the model and are currently used to assess the long-range transport of HCB (Section 2.3.2) and various PCB congeners (Section 2.3.1). The last modification (preparation of fields of OC fluxes and concentration in the marine environment) is to be introduced in the future.

The detailed description of the model modification will be given in the MSC-E Technical Report (see [Shatalov et al., 2004a] and Annex B below).
3. CO-OPERATION

In the framework of MSC-E and CCC activities on the assessment of the environmental pollution in 2004 special attention was given to cooperation with subsidiary bodies to the Convention and international organizations and programmes as well as with national experts. The outcomes of the EMEP Centres’ activities were reported at the fifth TFMM meeting (Prague, 31 March - 4 April 2004) and have been submitted for discussion at various international conferences, seminars and expert meetings.

3.1. Task Force on POPs

In 2004 MSC-E operated in close cooperation with the Task Force on POPs set up under the Working Group on Strategies and Review. According to the 2004 Work-Plan on the Implementation of the Convention [ECE/EB.AIR/79/Add.2] “EMEP will support the preparatory work on the review of the Protocol on POPs, in particular the work of the proposed Task Force on POPs”.

In the current year MSC-E participated in two meetings of the Task Force on POPs aimed at preparing the technical input for the reviewing the Protocol on POPs. At the first meeting (the Hague, 1-3 March) MSC-E presented the information on the EMEP activities on the assessment of the environmental pollution by POPs and the outcomes of the model-based approach to evaluating new substances on the basis of their long-range transport potential and overall persistence.

Important issues addressed by the second meeting (Prague, 31 May - 3 June) were the preparation of annotated chapter headings for the technical components of the sufficiency and effectiveness review of the Protocol on POPs and preparation of the generic guidelines and/or procedures for the technical review of dossiers of new substances that may be proposed by Parties for inclusion into annexes to the Protocol. The Task Force agreed that “a small team led by Canada, and including Norway and EMEP/MSC-E will carry out the work on gathering best available scientific information on effects of deposition of POPs”. Besides, “the POPs Task Force requests EMEP to prepare a synthesis document on the best available country-submitted emissions data, including 1990 and more recent years”. To support the activities of the Task Force on POPs MSC-E has prepared the draft Information Note “EMEP contribution to the review of the CLRTAP Protocol on Persistent Organic Pollutants”. This note summarizes the available monitoring and modelling data on POP atmospheric transport, deposition, and levels in the environmental media and information on emissions, prepared under EMEP.

In 2004 MSC-E continued the activities on evaluating new substances by criteria of the long-range transport potential and overall persistence in terms of their possible inclusion into the Protocol on POPs. In addition to the substances discussed previously: hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), polychlorinated naphthalenes (PCN-47 congener), α-endosulfan and dicofol (see [Shatalov et al., 2003]), model assessments of the long-range transport potential and overall persistence were made for β- endosulfan and polybrominated diphenyl ethers (BDE-28 congener). The detailed information on this work will be presented in the MSC-E Technical Report [Shatalov et al., 2004a] and be available on the MSC-E home page www.msceast.org.
Ranking the substances by their long-range transport potential and overall persistence. The substances mentioned above have been ranked by their long-range transport potential (Fig. 60a) and overall persistence (Fig. 60b). To make this assessment the calculations of long-range transport from a point emission source (1 t/y) located in Europe (France) were used with the help of the modified model taking into account spatial distributions of OH-radical and atmospheric aerosol specific surface. For these calculations physical-chemical properties of the considered substances were refined.

Fig. 60. Transport distance and overall persistence calculated for new substances

Differences in the geographical location of an emission source used for the calculation have a significant effect on the calculated values of transport distance (TD) and typical environmental half-life (T1/2). One of the possible ways to minimize uncertainties in evaluating new substances proposed by the OECD/UNEP Workshop on the use of Multimedia Models (Ottawa, Canada, 2001) was to use a “benchmark” substance. This way suggests that modelling results are used to compare the pollutants under study with some adequately studied “benchmark substance”. Benzo[a]pyrene (B[a]P), which is a regional/global boundary pollutant, was chosen as such substance.

Ranking the substances by various criteria produces close results. However, there are some differences. For instance BDE-28 and PCN-47 have lower long-range transport potential than B[a]P but are more persistent in the environment.

Spatial distribution of pollution from point sources. The calculated spatial distributions of air pollution by new substances under consideration provide complementary information on the regions most affected by pollution from emission sources of different geographical location. By way of example the spatial distribution of PCN-47 and HCBD air concentrations calculated for three different locations of a source (Europe, America and China) are given in Fig. 61 and 62 respectively. The analysis of the maps in these Figures shows that for PCN-47 air pollution from a source located in America can reach some regions in Europe. As for HCBD it is seen that this pollutant is of a global character.

Besides, the spatial distribution of air pollution shows the difference between TD estimates dictated by the geographical location of a source. For both pollutants under consideration the area covered by pollution from emission sources in Europe and America is larger than that from a source in China. According to the calculation the TD value may vary 1.5-2 times depending on the source location.

Therefore the model calculations allow the substances to be ranked by their long-range transport potential and overall persistence. The spatial distribution of concentrations in the atmosphere provides
complementary information on pollution of various regions from sources of different geographical location.

Fig. 61. The spatial distribution of air pollution by PCN-47 from sources (1 t/y) located in Europe, America, and China

Fig. 62. The spatial distribution of air pollution by HCBD from sources (1 t/y) located in Europe, America, and China

3.2. Working Group on Effects

The model calculations made in 2004 enabled MSC-E to obtain the information on the environmental pollution by the following POPs: PAHs PCDD/Fs, PCBs, HCB. The long-term accumulation of these POPs in different environmental media has been studied and the main media-accumulators have been identified (soil for PAHs, PCDD/Fs, and PCBs and seawater for HCB). The rate of the PAH and PCDD/F content decrease in the air and seawater is basically in line with that of the emission reduction. In contrast, the content of these pollutants in soil decreases much slower due to their high persistence in this media.

In addition the spatial distribution of the considered POP depositions and concentrations in different media with a resolution of 50x50/150x150 km has been obtained to allow the “hot spots” to be identified. The development of the model approach to evaluating POP depositions on various types of the underlying surface is currently under way.

This information may be helpful for the development of the risk-assessment approach to evaluate the impact of POPs on the human health and the environment.
3.3. United Nations Environment Programme

In accordance with [ECE/EB.AIR/79/Add.2] in 2004 MSC-E and CCC continued cooperation with the United Nations Environmental Programme (UNEP) with the aim “to harmonize the global monitoring strategy with the one of EMEP”.

Besides, MSC-E contributed to the UNEP Workshop on POP emission inventories and air pollution monitoring and modelling held in Bishkek, Kyrgyzstan in January 2004. The main objective of the meeting was to prepare recommendations for the development of national plan of actions on monitoring, modelling and emission inventories in Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan and Uzbekistan). The meeting was informed on the progress in the investigations of POP air pollution under EMEP and on some preliminary estimates of POP transboundary transport for Kyrgyzstan.

3.4. Co-operation with national experts

In 2004 MSC-E in cooperation with national experts of the Parties to the Convention continued the work on the intercomparison study of POP multi-compartment models. Experts from Canada, the Czech Republic, Denmark, France, Germany, Japan, the Netherlands, Switzerland, the United Kingdom, the USA as well as representatives of MSC-E and CCC took an active part in this study. In the current year the first stage of the intercomparison has been completed. It was aimed to compare model descriptions of basic processes determining the behavior of POPs in the environment. The second stage aimed to compare model assessments of pollutant contents in different media of European region, fields of POP depositions and concentrations and to analyze model sensitivity to the change of parameterization was started.

The first stage has resulted in the EMEP/MSC-E Technical Report [Shatalov et al., 2004b]. The report on the second stage is expected to be available in 2005.

MSC-E also continued cooperation with national experts from the Czech Republic, Germany, Canada and the Netherlands on the exchange of data on POP measurements in various environmental media and spatial distribution of particles and OH-radical in the atmosphere.
CONCLUSIONS

In the current year the EMEP Centres continued the investigations of the environmental pollution in the European region by persistent organic pollutants (PAHs, PCDD/Fs, PCBs and HCB) on the basis of measurements and modelling. The investigations include estimation of air pollution levels, calculation of the spatial distribution of air concentrations and depositions, assessment of the POP transboundary transport within the EMEP region on the “country-to-country” basis and evaluation of the impact of the intercontinental transport on pollution of Europe and remote regions (the Arctic). A possibility to use model calculations to evaluate the results of possible scenarios of emission reduction was demonstrated by the example of two conventional scenarios of PCDD/F emission reduction. The estimation of depositions of PAHs and PCDD/Fs to the marginal seas was performed. The development of the model approach to the assessment of long-range transport potential and overall persistence for new substances that may be proposed for inclusion into the Protocol on POPs is under way. To take the re-emission processes into account the redistribution of pollutants between various environmental media (atmosphere, soil, seawater and vegetation) is studied. Spatial and temporal trends of POP contents in various compartments of the environment are analyzed.

The main outcomes of the investigations are summarized below.

**Measurements**

- For 2002 13 monitoring sites of EMEP submitted to CCC the measurement data on POP concentrations either in the air or in precipitation. 5 of them submitted data on POP concentration in both media. Most of the monitoring sites are located in the northern part of the EMEP region. To improve the spatial coverage of the territory of Europe by monitoring sites the new EMEP monitoring strategy for 2004-2009 has been developed.

- Measurement data show a tendency that the heavier congeners (PCBs 138, 153 and 180) are enriched in the southernmost stations (Czech Republic, Southern Sweden), whilst the lighter congeners (PCBs 28 and 52) are enriched at the northernmost sites (Iceland, Finland as well as Spitzbergen in Norway).

- The outcomes of Round 2 of the laboratory intercomparison demonstrate that for most of the laboratories the deviation from the median is within 25% though for some laboratories it may reach 3-4 times.

**Emissions**

- Official data on emissions of PAHs, PCDD/Fs, PCBs, HCB and γ-HCH for the period from 1990 to 2001 were reported by 32 countries. Emission data for other POPs (Aldrin, Chlordane, Chlorodecone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Mirex, Toxaphene, DDT, PCP and SCCP) for the period from 1990 to 2001 were submitted by 16 countries. In recent years, the number of countries submitting data on POP emissions and their spatial distribution over the EMEP domain increased.

- According to the official data and expert estimates in the period from 1990 to 2001 emissions of pollutants under consideration reduced. Emissions of PAHs (B[a]P and B[b]F) in the EMEP domain reduced by 25% and emissions of PCDD/Fs - more than twice. In the Northern Hemisphere according to the expert estimates emissions of PCBs also reduced more than twice.
Modelling

Polycyclic aromatic hydrocarbons

- The mean value of deposition flux in the EMEP region for PAHs under consideration (B[a]P, B[b]F and B[k]F) amounted to about 10 g/km²/y. For some territories in Belgium, Poland, Germany, the Czech Republic, Lithuania and Latvia higher deposition fluxes (50-100 g/km²/y) are typical. PAH concentrations in the air over most parts of territories of Europe do not exceed 1 ng/m³, but in some regions of the above listed countries they reach 2-3 ng/m³.

- About 10% of the annual PAH emissions in Europe deposit to the sea surface and about 40% - to the land surface. Due to the long-term accumulation (1970 - 2001) at the end of the calculation period (2001) about 90% of the total PAH content in the environment were accumulated in soil.

- In 2001 in European countries the contribution of the B[a]P transboundary transport to air concentrations and depositions is significant, varying typically from 30 to 60%.

Polychlorinated dibenzo-p-dioxins and dibenzofurans

- The calculated levels of PCDD/F air concentrations (in TEQ units adopted by NATO) typical for most of European countries in 2001 vary from 1 to 5 fg TEQ/m³. In the most polluted regions of Central Europe (Poland, the Czech Republic, Slovakia, Belgium and some areas of Germany) PCDD/F air concentrations reach 10-30 fg TEQ/m³ and more.

- About 10% of the annual PCDD/F emissions deposit to the sea surface and about 50% - to the land surface. Due to the long-term accumulation (1970 - 2001) at the end of the calculation period (2001) 90% of the total PCDD/F content in the environment were accumulated in soil. The re-emission flux from soil in Europe was significant in 2001 amounting to about 20% of the total anthropogenic emissions of Europe.

- In 2001 in European countries the contribution of the PCDD/F transboundary transport to air concentrations and depositions is significant, varying typically from 20 to 60%.

Polychlorinated biphenyls

- Concentrations of PCB toxic congeners in Europe calculated with account of emission sources of the whole Northern Hemisphere amount to 1-10 pg/m³ for PCB-105 and 1-30 pg/m³ for PCB-118. The levels of depositions are 0.2 - 0.5 g/km²/y for PCB-105 and 0.2-1.5 g/km²/y for PCB-118.

- The levels of PCB-105 air concentration over the Atlantic Ocean (0.5 - 1 pg/m³) are comparable with those over the European region. It demonstrates a high long-range transport potential of PCB toxic congeners.

- About 20% of the annual PCB emission deposit to the sea surface and about 40% - to the land. Due to the long-term accumulation (1970 - 2000) at the end of the calculation period (2000) 15-20% of the total PCB content in the environment were accumulated in seawater and 80% - in soil. Whereas emissions decrease, air concentration can be supported for a long time (decades) due to re-emission.
Hexachlorobenzene

- HCB has high long-range transport potential. In particular about 80% of the HCB annual emissions in Europe are transported outside the European region. About 35% of HCB air pollution in Europe were accounted for by external sources.

- At the end of the calculation period (1970-2000) 60% of the total HCB content in the environment were accumulated in seawater and about 20% - in soil.

Model modification

- The influence of spatial and temporal variation of OH-radical and atmospheric aerosol specific surface on POP removal and degradation processes was taken into account. The input of these modifications has a significant impact on the calculated values of air concentrations and depositions.

- Spatial distribution of organic carbon content in seawater particles at different depths was prepared with monthly resolution. The prepared estimates are in a reasonable qualitative agreement with the data on measurements and will be used at the next stages of investigations to refine the model description of the sedimentation process.

Model validation

- The comparison of the modelling data with the available data on measurements for the pollutants under consideration demonstrates that most of them agree within a factor 3. For more comprehensive model validation by measurement data it is required to enhance the database used for comparison. In particular, more uniform spatial coverage of the EMEP domain by monitoring sites and availability of measurements in different compartments of the environment are required.

- In cooperation with national experts MSC-E performs the intercomparison study of the POP multicompartiment models. The first stage of the intercomparison was completed (model descriptions of the main processes affecting the POP behavior in the environment were compared) and the second stage was begun (calculated POP concentrations in the environmental compartments and pollution space distributions are compared). On the basis of the outcomes of the first stage the EMEP/MSC-E Technical report [Shatalov et al., 2004b] was prepared.

CCC and MSC-E activity in the field of environmental pollution assessment was carried out in cooperation with subsidiary bodies to the Convention and international organizations (AMAP, HELCOM, UNEP, WMO) and national experts.
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Pacyna J.M. et al. [1999] Final report for Project POPCYCLING-Baltic. EU DGXII, Environment and Climate Program ENV4-CT96-0214. Available on CD-rom including technical report, the emission and environmental databases as well as the POPCYCLING-Baltic model. NILU, P.O. Box 100, N-2027 Kjeller, Norway.
EMEP work-plan on POPs for 2004

**EMEP work-plan elements in 2004 [ECE/EB.AIR/79/Add.2]**

*Description/objectives:* Improve the monitoring and modelling data on concentrations, depositions and transboundary fluxes of selected POPs. Study further the physico-chemical processes of POPs in different environmental compartments, taking into account their transboundary transport within the EMEP region and on the hemispheric scale. Develop reliable emission data for the POPs listed in the Protocol, as well as a preliminary data set for other substances. Support preparatory work for the review of the Protocol on POPs, in particular the work of the proposed Task Force on POPs.

**Main activities and time schedule:**

(a) MSC-E will prepare information for 2001 on: source-receptor relationships for benzo[a]pyrene (B[a]P), deposition and concentration fields for benzo[b]fluoranthene (B[b]F) and benzo[k]fluoranthene (B[k]F); transboundary transport and accumulation of all toxic congeners of PCDD/Fs (back to 1970), the spatial variability, including hemispheric transport, and pollution levels of PCBs and HCB; and transport of selected POPs to the marginal seas. It will contribute to work to explore a possible effects-based approach under the Working Group on Effects;

(b) MSC-E will further develop its models with respect to: the redistribution between different phases and sedimentation in the marine environment; the gas/aerosol partitioning process in the atmosphere; and the distribution in the atmosphere taking into account spatial and temporal variations of OH radical concentrations. It will complete the first stage of the model intercomparisons and prepare the second phase;

(c) In cooperation with Parties, CCC will enhance the establishment of new sites to meet the requirements of the draft monitoring strategy. In cooperation with MSC-E, it will complement EMEP monitoring data with data from other international and national programmes for comparison with model results. Both centres will cooperate with UNEP to harmonize the global monitoring strategy with the one of EMEP;

(d) CCC and MSC-E, in consultation with the Task Force on Emission Inventories and Projections and with Parties, will improve the POPs emission data quality with specific emphasis on PAHs, PCDD/Fs, PCBs and HCB. They will adjust European emission inventories for POPs to the modelling requirements. CCC will develop profiles of chemical species of the selected POPs and collate information on the height of major point sources.
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### Table A.2. Northern Hemisphere

<table>
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<tr>
<td>PCBs</td>
<td>1. For PCBs and HCB - refinement of physical-chemical properties and collection of available measurement obtained for the countries of the Northern Hemisphere under different international and national programmes.</td>
<td>Modelling PCB long-range transport within the hemispherical scale for 1996 from emission sources of the Northern Hemisphere (expert estimates) for a group of selected congeners including toxic congeners PCB-105 and PCB-118.</td>
<td>Assessment of pollution of the Northern Hemisphere and the EMEP region from emission sources of the Northern Hemisphere for 2001.</td>
<td>Comparison of measured and calculated pollution levels in the Northern Hemisphere.</td>
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<td>HCB</td>
<td>2. Refinement of model description of POP degradation in the atmosphere taking into account spatial and temporal variations of OH-radical concentrations. 3. Refinement of model description of gas/particle partitioning with allowance of spatial and temporal variations of concentrations of atmospheric aerosol. 4. Refinement of the description of POP redistribution between different phases in the marine environment</td>
<td>Modelling of HCB long-range transport within the Northern Hemisphere from 5 source groups (Northern America, Central Asia, South-Eastern Asia, Europe and Russia).</td>
<td>Preliminary assessment of intercontinental transport of HCB within the hemispherical scale for 2000.</td>
<td>Provisional comparison of calculated and measured levels of pollution levels in the Northern Hemisphere.</td>
</tr>
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</table>
Model modification

This Annex contains the description of model modifications made in the current year. As was previously mentioned, these modifications concern the refinement of atmospheric degradation by taking into account spatial and temporal distribution of OH-radical and the refinement of gas/aerosol partitioning in the atmosphere (affecting POP removal from this media) by including the spatial and temporal distribution of aerosol specific surface, and calculation of fields of organic concentration in seawater suspended particles.

Below we present the analysis of model sensitivity to the spatial distribution of OH-radical concentrations and atmospheric aerosol specific surface performed by the example of the “indicator” congener PCB-153. In the analysis the OH-radical spatial distribution of monthly resolution from [Spivakovski et al., 2000] was used. The spatial distribution of atmospheric aerosol specific surface was kindly provided by Dr. Sunling Gong (Canada). The last subsection briefly describes the work on the modification of the model description of POP behavior in seawater.

Sensitivity of the model to the OH-radical spatial distribution. The following calculations were performed to assess the model sensitivity:

1. Calculation of PCB-153 transport and accumulation for the period from 1970 to 2000 with the uniform spatial distributions of OH-radical concentrations (the previous model version).

2. Calculation of PCB-153 transport and accumulation taking into account the OH-radical spatial distribution and seasonal variations with monthly resolution.

In both cases emissions and meteorological data for 2000 were used.

The impact of OH-radical on the main removal processes (degradation, direct depositions and export beyond the calculation grid) is shown in Fig.B1. The input of the OH-radical spatial distribution led to the increase of PCB-153 degraded in the atmosphere, significant decrease of PCB-153 transported outside the calculation grid (across equator and to the upper atmosphere), and insignificant decrease of PCB-153 content in the atmosphere and deposition to the land and sea.

The spatial distribution of concentrations in the air surface layer changes considerably (Fig.B2).
Within the Northern Hemisphere the decrease in atmospheric concentration due to taking account of the OH-radical spatial distribution may reach 40%. In most of the EMEP region this decrease ranges from 0% to 5% and in southern and southwestern areas - from 5% to 10%.

**Therefore the input of the spatial distribution and seasonal variations of OH-radical atmospheric concentration leads to the significant change in the spatial distribution of atmospheric pollution (up to 40% in some regions) with insignificant variation in the PCB-153 total content in the atmosphere. OH-radical virtually has no impact on the trends of the main environmental media content in the period from 1970 to 2000 as well as on PCB-153 distribution between the media obtained by the end of the calculation period. In both calculations a major fraction of the pollutant is in soil (about 82%), 12% are in seawater and 6% - in vegetation.**

**Model sensitivity to the spatial distribution of atmospheric aerosol.** Sensitivity of the model to the spatial distribution and seasonal variations of aerosol specific surface was assessed with account of the OH-radical spatial distribution. Two calculations were performed:

1. Calculation of PCB-153 transport and accumulation on the assumption that distribution of atmospheric aerosol specific surface is uniform (equal to the background value 1.5·10^{-4} \text{m}^2/\text{m}^3 as in the previous version of the model, see MSC-E Technical Report [Shatalov et al., 2003]);
2. Calculation using the aerosol spatial distribution of 1980 with the specified 5-day spatial resolution provided by Dr. Sunling Gong (Canada).

The input of the spatial distribution of atmospheric aerosol specific surface led in particular to the decrease of PCB-153...
degraded in the air (Fig.B3). It is explained by the increase of the fraction of the particulate phase that is much more resistant to the atmosphere degradation processes.

Furthermore the values of direct depositions to the land and sea obtained with account of the atmospheric aerosol spatial distribution appeared to be significantly higher than those in the previous calculations. It leads in particular to the increase of PCB-153 content in soil and seawater and consequently to the increase of the re-emission flux from these environmental compartments. In the calculation made with account of the aerosol spatial distribution the gas flux from soil becomes comparable with the emission value both in Europe and America.

Hence, the input of the spatial distribution of atmospheric aerosol specific surface has a significant impact on PCB-153 distribution between media as well as on exchange processes.

Significant changes are also observed in the spatial distribution of concentrations in the air surface layer (Fig. B4).

![Fig. B4. Differences in the spatial distribution of PCB-153 concentration in the air surface layer caused by the input of the spatial distribution of atmospheric aerosol specific surface, %: a - throughout the Northern Hemisphere, b - in the EMEP region](image)

The input of the spatial distribution of atmospheric aerosol specific surface leads to the changes of PCB-153 concentrations in the air surface layer, and significant changes are observed specifically in the EMEP region (up to 120%).

The input of the spatial distribution of atmospheric aerosol specific surface leads to the changes of PCB-153 concentrations in the air surface layer, and significant changes are observed specifically in the EMEP region (up to 120%).

**Therefore the input of the spatial distributions of atmospheric aerosol specific surface has a considerable impact on distribution of concentrations in the air surface layer as well as on deposition values. In the future it is required to refine data on the spatial distribution of aerosol specific surface for all the years of the modelling period.**

**Model description of POP behavior in the marine environment.** To describe the process of sedimentation in seawater it is essential to take into account concentrations of suspended particles and the content of organic carbon (OC) in these particles. To calculate the spatial distribution of OC fluxes and concentration on particles in seawater a simplified model of dynamics of various types of particles has been developed. Mean monthly fields of primary products for the Northern Hemisphere derived from satellite data are input data of the model (Institute of Marine and Coastal Sciences, http://marine.rutgers.edu/opp/Database/DB.html). Mean monthly fields of OC concentrations at
various depths of mid-ocean within the Northern Hemisphere and fields of OC vertical fluxes of monthly resolution are output data of the model. In Fig. B5 the spatial distribution of the mean annual OC flux to the ocean bottom is given as an example.

The calculations show that OC maximum fluxes to the ocean bottom are observed mainly in the coastal zones. This is supported by a lot of research [Ittekkot, 1996; Usbeck, 1999]. Low levels of the flux observed in the Arctic region are attributed to the input data inaccuracy. By and large it is possible to point out that the qualitative agreement between calculations and measurements is reasonable. This allows to use the calculated OC concentrations and fluxes in suspended particles for the POP global transport simulation as a first approximation.

The description of sedimentation in seawater based on calculated fields is to be refined at the next stages of the study.

Fig. B5. Calculated mean annual OC flux to the ocean bottom, mMol/m²/y