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Persistent Organic Pollutants in the Environment

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EXECUTIVE SUMMARY

In accordance with the EMEP work-plan for 2003 [ECE/EB.AIR/77/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). The prime object is the assessment of pollution levels in Europe (hereinafter – EMEP region) by polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), γ -hexachlorocyclohexane (γ -HCH) and by hexachlorobenzene (HCB) with the use of monitoring data from the EMEP network stations and mathematical modelling.

The outcome of studies of the environmental pollution by POPs under EMEP is discussed below:

The official data on POP emissions (PAHs, PCDD/Fs, PCBs, γ -HCH, HCB) for 1980-2000 were submitted by 30 countries. During recent years the number of countries providing the data on POP emission totals and their spatial distribution increased. According to the official data and expert estimates, total POP emissions in the EMEP region on the whole tend to cut down. For example, emissions of PAHs (benzo[a]pyrene and benzo[b]fluoranthene), PCDD/Fs and PCBs in Europe decreased from 2 to 5 times in the period from 1980 to 2000.

Thirteen measurement sites have reported POP data to CCC for 2001. Six of these were measuring POPs in both precipitation and air. The number of sites is still unsatisfactory in EMEP and especially in south and east of Europe.

On the basis of measurements, it is estimated that the general trends in concentrations of atmospheric α - and γ -HCH and HCB are decreasing since 1991. The concentration of benzo[a]pyrene (and other PAHs) shows a clear seasonal variation, with peak concentrations during winter. The concentration level is decreasing towards the north of Europe.

The trend analysis of POP accumulation in the main environmental compartments shows that the rate of POP soil content variation lags emission reduction rate. For instance, PCDD/F emission decrease

4.5 times from 1980 to 2000 results in a moderate (by 4%) reduction of soil concentration. The concentration decrease of the considered POPs in air and seawater also lags the emission reduction rate.

Calculations covering a long period of time allowed evaluating the levels of pollution by POPs in Europe in 2000. Substantial levels of PCDD/F pollution are specified for the Czech Republic, Belgium, Switzerland, Luxembourg, Slovakia and Italy. High concentrations of benzo[b]fluoranthene in the main environmental media are characteristic of polluted territories of Central Europe and Russia. In some regions of Poland, Germany, and the Czech Republic mean annual air concentrations of benzo[a]pyrene (B[a]P) are higher than 1 ng/m³. B[a]P mean diurnal concentrations can exceed mean annual ones as much as 5 times (and more). The assessment of B[a]P and PCDD/F depositions to regional seas is also available. The most intensive fluxes are over the Baltic Sea and least intensive – over the Mediterranean Sea.

POP transboundary transport significantly affects the level of pollution in the European region. On the example of B[a]P, it is demonstrated that in the majority of countries the contribution of transboundary transport to air concentration and deposition levels is from 30 to 70%. B[a]P transboundary transport is analyzed in detail for all Parties to the Convention and its input to the pollution in different parts of a country is estimated.

Along with the evaluation of POP levels in Europe the long-range transport potential of PCDD/Fs, PCBs, γ -HCH and HCB is investigated. The transport distance of these POPs is from 5000 km (some congeners of PCDD/Fs) to 10000 km (HCB). An essential fraction of POP emissions from European sources can be transported beyond the EMEP domain. Pollution levels in the Northern Hemisphere are evaluated (on the example of PCBs and γ -HCH). High levels of PCB pollution are found in some regions of West Europe and the US eastern coast. High γ -HCH concentrations and depositions are estimated in some regions of West Europe and southeastern Asia.

POP intercontinental transport can make a noticeable contribution to the contamination of the Northern Hemisphere, in particular to the Arctic. On the example of PCB-153, it is shown that the main contribution to the Arctic contamination (approximately 60%) is made by European emission sources. The combined input of African and Asian sources is about 10% of PCB-153 total depositions to the Arctic area.

This year at the meeting of Expert Group on POPs (the Working Group on Strategies and Review) a model approach for the evaluation of the long-range transport potential and overall persistence in the environment of new substances (potential candidates to the Protocol on POPs) was presented. This approach has been tested for a number of new species (hexachlorobutadiene, pentachlorobenzene, polychlorinated naphthalenes, α -endosulfan and dicofol). Among the considered compounds hexachlorobutadiene and pentachlorobenzene are mostly apt to the long-range transport. PCN-47 (congener from the group of polychlorinated naphthalenes) is most persistent in the environment. The investigation results can be used for making a decision whether it is reasonable to incorporate new substances to the Protocol on POPs.

Studies, which could be beneficial for the development of the effect-based approach for the evaluation of POP impact upon the environment, are underway. The POP contamination and accumulation dynamics in different environmental compartments are estimated. The calculation results make it possible to identify the main medium

accumulating the bulk of this or that pollutant mass in the environment. According to model estimates, 90% of PCDD/F overall toxicity accumulated in soil. High concentrations in soil are found in the majority of European countries. A model approach to the evaluation of POP deposition fluxes to various types of underlying surfaces is under development.

The co-operation with national experts of Parties to the Convention is keeping on. MSC-E started the intercomparison study of POP models describing the behavior of POP in the environment. Experts from Canada, the Czech Republic, Denmark, France, Germany, Japan, Norway, Switzerland, the United Kingdom, and the USA are taking part in the comparison of models.

The assessment of environment pollution by POPs was carried out in close co-operation with international organizations and programmes (UNEP, AMAP, HELCOM, WMO). The main results were presented for the discussion and examination at a number of international conferences, workshops, and expert meetings.

CONTENTS

Introduction	5
1. Monitoring of POPs	7
2. An evaluation of POP transport and pollution levels in the environment	9
2.1. Emissions	9
2.2. Pollution levels in the EMEP domain	12
2.3. Pollution levels in the Northern Hemisphere	23
3. Co-operation	33
3.1. Co-operation with subsidiary bodies to the Convention	33
3.2. Co-operation with national experts and programmes	35
3.3. Co-operation with international organizations	35
Conclusions	37
References	39
Annex A EMEP work-plan for 2003	41
Annex B Model modification	44

INTRODUCTION

Persistent organic pollutants (POPs) are very toxic and inflict mutagenic, teratogenic and carcinogenic impact. These substances can be transported over long distances, can be deposited to and accumulated in soil, marine environment, plants and in tissues of living organisms. Persistent organic pollutants can be found actually everywhere on the Earth even in regions located far away from emission sources (for example in the Arctic) [AMAP, 1998].

The activity connected with the examination and prevention of the environmental pollution by these substances is in the spotlight of many international programmes and organizations: the United Nation Environment Programme (UNEP), the Organization for Economic Co-operation and Development (OECD), the World Health Organization (WHO), the World Meteorological Organization (WMO), the Arctic Monitoring and Assessment Programme (AMAP), the Baltic Marine Environment Protection Commission (HELCOM), The Oslo-Paris Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and others.

Thirty six Parties to the Convention on Long-range Transboundary Air Pollution (hereinafter Convention) signed the Protocol on Persistent Organic Pollutants (hereinafter the Protocol on POPs) in 1998. In compliance with the Protocol "in good time before each annual session of the Executive Body, EMEP shall provide information on the long-range transport and deposition of persistent organic pollutants" (Article 9) [ECE/EB.AIR/66].

This Status Report describes the progress in the investigation of environmental pollution by POPs made by Meteorological Synthesizing Centre - East (MSC-E) and Chemical Coordinating Centre (CCC) in 2003. This work was fulfilled in accordance with the work-plan of EMEP for 2003 (Annex A) approved by the Executive Body for the Convention [ECE/EB.AIR/77/Add.2]. The basic activity was aimed at monitoring and modelling of the environmental contamination by: polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs),

γ -hexachlorocyclohexane (γ -HCH), hexachlorobenzene (HCB). Rather much consideration is given to the investigation of the effect of emission intensity of different regions in the Northern Hemisphere on the environmental pollution of Europe as well as to the transport of pollution from European sources outside European domain (hereinafter EMEP domain). This Report provides the following information on the evaluation of environmental pollution by POPs obtained by the EMEP Centres in 2003.

- Assessment of POP air pollution levels on evidence of measurements (Chapter 1) namely:
 - measurement program and site distribution in EMEP in 2001;
 - seasonal variations of benzo[a]pyrene and HCB;
 - long-term trends (1991-2001) of α - and γ -HCH and HCB.
- Evaluation of environmental pollution levels with the use of mathematical models (Chapter 2) including:
 - assessment of PAH and PCDD/F dispersion in the natural environment and analysis of pollution trends during 1970-2000;
 - assessment of PAH transboundary transport between European countries in 2000 (exemplified by benzo[a]pyrene);
 - assessment of PCDD/F, PCB, γ -HCH and HCB transport and accumulation in the Northern Hemisphere;
 - evaluation of the long-range transport potential of a number of new substances and their persistence in the environment;
 - evaluation of PCDD/F and PAH depositions to regional seas.

The model estimation of POP pollution levels in the EMEP domain was made by the modified versions (hemispheric and regional) of the MSCE-POP model. In particular, the model description of POP behavior in soil and sea was improved (Annex B). A

special attention was given to POP transport processes in soil, to turbulent diffusion in the ocean, to the effect of dynamics of ice cover and sea currents on POP transport within the Northern Hemisphere.

The activity of the EMEP Centres in 2003 was carried out in close collaboration with subsidiary bodies to the Convention, international organizations, and national experts. Progress in the

POP assessment was discussed at a number of conferences and workshops as well at the meeting of the Task Force on Measurements and Modelling of EMEP (TFMM) in April 2003.

The detailed description of monitoring and modelling results can be found in Technical Reports of MSC-E [*Shatalov et al., 2003*] and CCC [*Aas and Hjellbrekke, 2003*].

1. MONITORING OF POPs

Measurement network

POP_s 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, Table 1. A number of countries have been reporting POP_s 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 POP_s for 2001, 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 POP_s [Aas and Hjellbrekke, 2003]. The sites are divided in those measuring both air and precipitation, and those measuring only one of them. In 2001 it was 6 sites measuring POP_s in both compartments, and altogether it was 13 measurement sites.

It is quite evident from Fig. 1 that the spatial distribution in Europe is unsatisfactory. Only sites in the northern Europe measure POP_s. In the new EMEP monitoring strategy for 2004-2009 new monitoring requirements are given which among others aim to improve the current unsatisfactorily site distribution. The sites will now be differentiated into three levels where a "Core site level 1" is a basic EMEP site. Since POP measurements are very demanding, such measurements are not

expected at this level. At "Core sites level 2" (supersites), POP_s in both air and precipitation should be measured at around 20 stations distributed over the domain. The following are considered to be priority compounds: PAHs PCBs HCB, chlordane, HCHs and DDTs. "Level 3" sites are for more specialized measurements and these are voluntary under the EMEP program. These may be used for campaign studies and more detailed studies on e.g. congener specific measurements of compounds such as PCDDs and PCDFs.

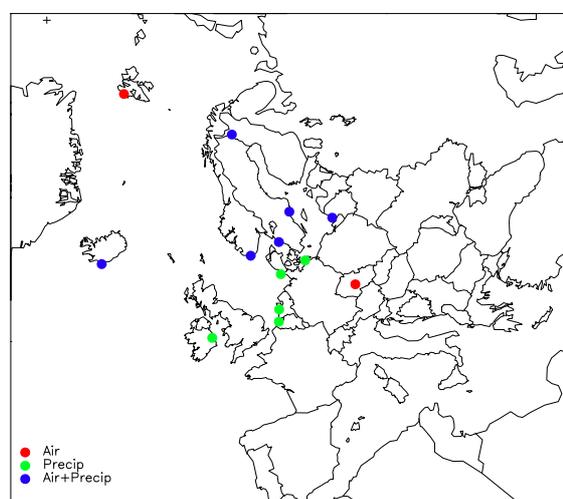


Fig. 1. Measurement network of POP_s in EMEP, 2001

Table 1. Measurements sites and programs for POP_s in 2001

Sites	From	POP _s in air and aerosol	POP _s in precipitation
BE04	1996		Pesticides, HCHs
CZ03	1999	PAHs, PCBs, pesticides, HCHs	
FI06	1996	PAHs, PCBs	PAHs, PCBs
DE01	1996		PAHs, PCBs, pesticides, HCB, HCHs
DE09	1996		PAHs, PCBs, pesticides, HCB, HCHs
IS91	1995	PCBs, pesticides, HCB, HCHs	PCBs, pesticides, HCB, HCHs
IE02	1994		PCBs, pesticides, HCHs,
LT15	2000	Benzo[a]pyrene	Benzo[a]pyrene
NL91	1996		γ-HCH
NO99	1991	HCB, HCHs	HCB, HCHs
NO42	1993	PAHs, pesticides, HCHs, HCB, PCBs	
SE02	1994	PAHs, PCBs	PAHs, PCBs
SE12	1995	PAHs, PCBs	PAHs, PCBs

Measurement results of POPs in 2001 and trends from 1991

Details of the measurements results and methodology are found in the EMEP/CCC data report on heavy metals and POPs [Aas and Hjelbrekke, 2003]. 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.

Fig. 2 shows the seasonal variation of Benzo[a]pyrene (B[a]P) at 6 EMEP sites in 2001. B[a]P (and other PAHs) is destroyed by UV radiation. In addition the emission of B[a]P is lowest during summer, and in absence of local sources, a seasonal variation therefore is expected. This is also what was observed at all sites, which is shown in Fig. 2. The concentration is decreasing towards the north of Europe.

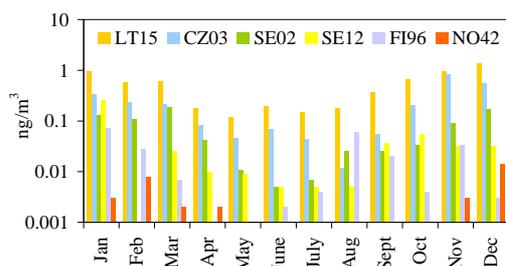


Fig. 2. Seasonal variation in benzo[a]pyrene in aerosols in 2001

The source of γ -HCH is use of the pesticide lindane, which consists of at least 99% of the γ -HCH isomer. The trend in atmospheric γ -HCH levels is decreasing (Fig. 3). In 1994 a maximum was observed at the sites NO99 and SE02, in the south of respectively Norway and Sweden. Also the level of the isomer α -HCH is decreasing (Fig. 4). The main source of α -HCH is use of technical HCH as a pesticide. Technical HCH contains 60-70% α -HCH, 5-12% β -HCH, 10-12% γ -HCH (which is the active pesticide component) and other minor components. Technical HCH is banned in most countries and replaced by lindane.

The general trend in atmospheric HCB levels is also decreasing. Fig. 4 shows annual means for two Norwegian and one Icelandic station. The important sources for HCB are production and use of chlorinated solvents and other chlorinated chemicals and various combustion reactions. These

processes have no seasonal variation and thus just produce a general background level, which is clearly seen from the results in Fig. 4. Neither the sampling methods nor the analytical methods have been harmonized between the labs producing the data. This may explain the difference in the general level detected.

A laboratory inter-comparison for PAH, pesticides and PCB using standard solutions was conducted in 2001, 18 laboratories were participating. The general impression from this first round was positive, most laboratories performed satisfactory. A second round of inter-comparison were done 2002; and a workshop discussing the results from these two laboratory inter-comparison will be arranged by CCC during the autumn 2003.

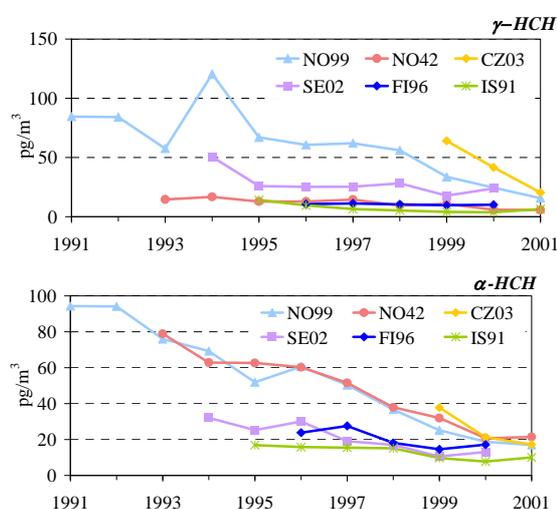


Fig. 3. Trend in annual average γ -HCH and α -HCH concentration in air and aerosols

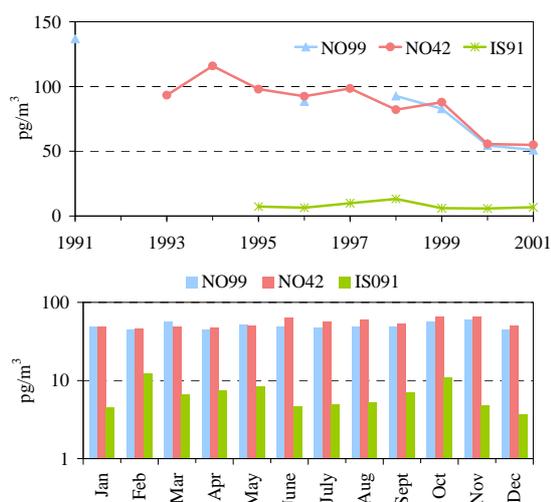


Fig. 4. Trends in annual average HCB concentration and in seasonal variation in HCB monthly average HCB concentration in air and aerosols in 2001

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

This chapter presents estimates of pollution levels caused by persistent organic pollutants (PAHs, PCDD/Fs, PCBs, γ -HCH, and HCB), as well as the evaluation of the long-range transport of these substances and their accumulation in the environmental compartments. This investigation, covering the EMEP region, was performed with the use of the MSCE-POP regional and hemispheric models. Special consideration was given to the evaluation of depositions, concentrations, and accumulation of POPs in the main environmental compartments, to the analysis of contamination trends over a long period of time, and to the estimation of transboundary transport of these species.

In subsection 2.1, we consider POP emission data used in the model computation. Total POP emissions and their spatial distribution were determined on the basis of official data complemented by expert estimates.

Subsection 2.2 describes levels of PAH and PCDD/F pollution in the EMEP region from European sources.

Subsection 2.3 is dedicated to the study of effects of PCB, γ -HCH, and HCB emissions from different regions of the Northern Hemisphere on the contamination of Europe. The transport of these pollutants from European sources outside the EMEP domain is also analyzed.

2.1. Emissions

The objective of the Protocol on POPs "is to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants" [ECE/EB.AIR/60]. The Protocol envisages that Parties shall submit official information about POP emissions to the UN ECE Secretariat. Data on emissions of POPs (PAHs, PCDD/Fs, PCBs, γ -HCH, HCB) for the period from 1980 to 2000 (for at least one year) were submitted by 30 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.

In model computations for PAHs and γ -HCH, the official data submitted to the UN ECE Secretariat in 2002 were used; for PCDD/Fs, the data submitted in 2003 were used. For countries that have not submitted their official emissions data, expert estimates were used.

Polycyclic aromatic hydrocarbons

Official data on emission totals of polycyclic aromatic hydrocarbons for 1980–2000 were submitted by 27 countries [Vestreng and Klein, 2002], and information about their spatial distribution was provided by 8 countries (Bulgaria, Denmark, Finland, Norway, Poland, Spain, the Netherlands, and the United Kingdom).

For emissions inventory purposes, the Protocol on POPs of 1998 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 (IP) [Annex III, ECE/EB.AIR/60]. This year, model calculations were performed for the most toxic carcinogenic compounds from this group (B[a]P and B[b]F).

Benzo[a]pyrene

Three countries – Denmark, Poland and Russia – submitted official data on benzo[a]pyrene emissions in 2000. For the remaining countries, expert estimates were used [Pacyna et al., 1999; Tsibylski et al., 2001; Berdowski et al., 1997; Coleman et al., 2001]. According to official data and expert estimates in the period from 1980 to 2000, European emissions of B[a]P decreased as much as 3.4 times. Total B[a]P emissions in the EMEP region amounted to 356 tonnes in 2000.

The spatial distribution of B[a]P emissions in 2000 was prepared on the basis of official data on spatial distribution of PAH emissions submitted by eight countries. For other countries, expert estimates were used [Pacyna et al., 1999, Berdowski et al., 1997].

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

Benzo[b]fluoranthene

Official information about total B[b]F emissions was submitted by Denmark and Poland. At present, expert estimates of B[b]F emissions in the European region are available only for 1990 [Baart *et al.*, 1995]. In computations, as a first approximation, B[b]F emissions were taken to be equal to B[a]P emissions. This assumption was made on the basis of the mean relationship 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]. It is rather rough assumption and introduces a significant uncertainty to the estimate of B[b]F emissions.

The B[b]F emission field was constructed with the use of expert estimates of B[a]P emissions in Europe prepared by Pacyna *et al.* [1999] for a number of basic years from 1970 to 1995. In the period from 1996 to 2000, the annual values of emissions were accepted to be equal to those of 1995.

In accordance with the assumptions made, B[b]F emissions in the EMEP region during 1980-2000 decreased from 1200 to 600 tonnes. In the model computations, seasonal variations in B[b]F emissions were taken from [Baart *et al.*, 1995].

Dioxins and furans

According to the data [Vestring and Klein, 2002], and also the data reported to the UN ECE Secretariat in 2003, there is official information about total emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) for the period from 1980 to 2000 for 24 European countries. The information about the spatial distribution was submitted by 9 countries (Belarus, Belgium, Bulgaria, Finland, France, the Netherlands, Norway, Poland, and Spain). For the remaining countries, we used expert estimates of PCDD/F total emissions and their spatial distribution in 1970-1995 [Pacyna *et al.*, 1999].

Of the entire diversity of PCDD/F congeners, only 17 are toxic. Since their properties are different, for modelling purposes, it is important to know the fraction of each in the overall emissions. On the basis of expert estimates of PCDD/F emissions [Pacyna *et al.*, 1999], we evaluated the individual contributions of these 17 congeners to the total emissions toxicity, for each European country and for the whole EMEP domain.

Variations in PCDD/F emissions in Europe for the period from 1970 to 2000 are illustrated in Fig. 5. The maximum emissions value was in 1980; during the following years, it decreased substantially. PCDD/F emissions reduced 4.5 times during 1980-2000 and amounted to 6.2 kg TEQ/y in 2000.

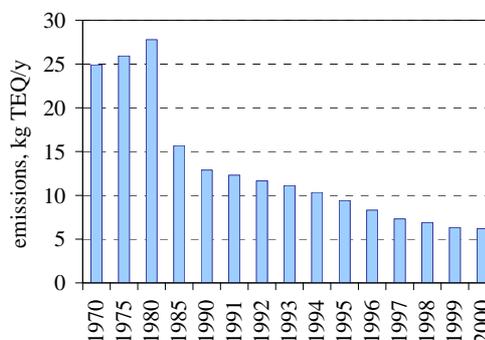


Fig. 5. PCDD/F emissions in Europe for the period from 1970 to 2000

Polychlorinated biphenyls

Official information about total emissions of polychlorinated biphenyls (PCBs) for the period from 1980 to 2000 was submitted by 14 countries [Vestring and Klein, 2002].

The long-range transport of individual PCB congeners (PCB-28, PCB-118, PCB-153, and PCB-180) was computed for the period from 1930 to 1996 by the MSCE-POP hemispheric model. 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 $2.5^{\circ} \times 2.5^{\circ}$ 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 [Breivik *et al.*, 2002], total emissions of the 22 PCB congeners in the Northern Hemisphere run up to their maximum value in 1970 and amounted to 3340 tonnes (High emission scenario). Total PCB emissions decreased 7 times in the period from 1970 to 2000. The value of PCB emissions (22 congeners) in the Northern Hemisphere amounted to approximately 660 tonnes in 1996. According to the expert estimates, total PCB emissions in the European region reduced 5 times in the period from 1980 to 2000.

In order to investigate the impact of PCB emissions from different sources of the Northern Hemisphere on the contamination of the EMEP domain, the

emission field was divided into six regions: Russia, North-western Europe, South-eastern Europe, America (both North and South), South-eastern Asia, and Central Asia and North Africa. For brevity, some regions were combined under one name. For example, the region-source "Central Asia" includes the central, western, and southern parts of Asia, and North America and a part of South America are considered as one source ("America"). The main sources of PCB emissions in the Northern Hemisphere in 1996 were America (24%), Russia (23%), South-eastern Europe (19%), and North-western Europe (16%) (Fig. 6).

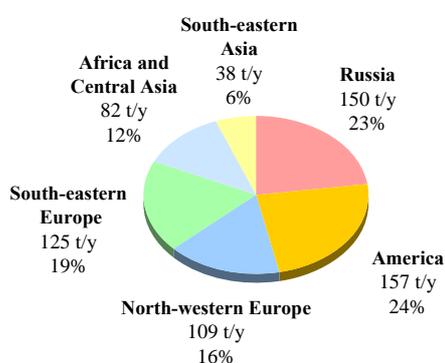


Fig. 6. The contribution of selected regions-sources to total PCB emissions in the Northern Hemisphere in 1996

γ -Hexachlorocyclohexane

The scenario on the distribution of γ -hexachlorocyclohexane (γ -HCH) emissions in the Northern Hemisphere was prepared with the use of official data [Vestrenng and Klein, 2002] and available expert estimates for 1990 -1996 [Pacyna et al., 1999; Revich et al., 1999; Yearbooks, 1992, 1993, 1999; Ananjeva et al., 1990; Li et al., 1996, 1998, 1999; Macdonald et al., 2000]. During the period considered, γ -HCH emissions in the Northern Hemisphere decreased 1.7 times, amounting to 3445 tonnes in 1996.

The distribution of γ -HCH emissions over a $2.5^\circ \times 2.5^\circ$ grid was made in relation to the distribution of cropland areas [Pacyna et al., 1999]. For the USA and Canada, emission totals were redistributed according to the spatial distribution of γ -HCH emissions in this region used by [Kozioł and Pudykiewicz, 2001]. For modelling purposes, the

seasonal distribution of γ -HCH emissions was taken from [Strand and Hov, 1996].

In the simulation of γ -HCH long-range airborne transport from sources of the Northern Hemisphere, nine groups of regions-sources were considered: Russia, West Europe, East Europe, South Europe, America (both North and South), China, India, Asia, and North Africa.

The contribution of the sources to the total γ -HCH emissions in the Northern Hemisphere in 1996 is illustrated in Fig. 7. India (53%) and West Europe (18%) contribute most greatly to total γ -HCH emissions in the Northern Hemisphere. North Europe was excluded from the consideration since γ -HCH was not used there in 1996.

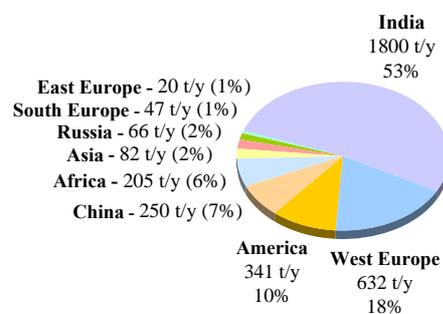


Fig. 7. The contribution of selected regions-sources to total γ -HCH emissions in the Northern Hemisphere in 1996

Hexachlorobenzene

Official data on HCB total emissions were submitted by 17 countries [Vestrenng and Klein, 2002]. According to these data, the HCB overall emissions in eight countries submitted information for 1990 and 2000 at the same time decreased 1.2 times during the period indicated.

Preliminary calculations of HCB airborne transport in the Northern Hemisphere from 1985 to 1996 were performed with the use of an emission scenario in which only European sources are considered. In these computations, we used expert estimates of HCB emissions for 1990 [Pacyna et al., 1999].

The specific data on POP emissions used in model calculations are presented in the MSC-E Technical report [Shatalov et al., 2003]

2.2. Pollution levels in the EMEP domain

This subsection provides estimates of the distribution of pollution by PAHs and PCDD/Fs over the European region and describes the results of investigation of long-term trends in their accumulation in different environmental compartments. In addition, a provisional estimate of the long-range transport of PCDD/Fs calculated by the MSCE-POP hemispheric model is given.

2.2.1. Polycyclic aromatic hydrocarbons

In the model computations, we consider two compounds – benzo[a]pyrene (B[a]P) and benzo[b]fluoranthene (B[b]F) – from the group of indicator polycyclic aromatic hydrocarbons (PAHs) [ECE.AIR/77/Add.2]. In previous studies, we evaluated the concentration distribution of B[a]P in the main environmental compartments and investigated its accumulation dynamics for the period from 1970 to 1999. In addition, we started to develop a model approach to the evaluation of B[a]P transboundary fluxes in the EMEP domain [Shatalov *et al.*, 2000, 2001, 2002]. This year, we proceed with computations of air concentration levels and deposition to the underlying surface. Much attention is given to the assessment of transboundary transport and its impact on the pollution levels in European countries in 2000.

Tentative calculations of B[b]F transport and accumulation have been made this year. This work was aimed at the assessment of B[b]F pollution levels (deposition and concentrations in environmental compartments) in 2000 and at the evaluation of B[b]F accumulation within the time period from 1970 to 2000.

Benzo[a]pyrene

Calculations of benzo[a]pyrene pollution levels in the EMEP region were performed with the model 50x50 km² and meteorological information for 2000. The emissions data include official data and expert estimates if official information is not available [Pacyna *et al.*, 1999] (see Subsection 2.1). The spatial distribution of B[a]P emissions used in the simulation is illustrated in Fig. 8. High values of emissions fluxes (100-200 µg/m²/y) are characteristic of some regions of Poland, Germany, the Czech Republic, Slovakia, Hungary, Georgia, and the countries of the former Yugoslavia.

The spatial distribution of pollution. The B[a]P deposition field estimated for the EMEP domain is shown in Fig. 9. High values of deposition fluxes (exceeding 100 µg/m²/y) were obtained for some regions of Poland and Germany; significant levels (50-100 µg/m²/y) are characteristic of the major part of Poland, Germany, the Czech Republic, Lithuania, and Latvia.

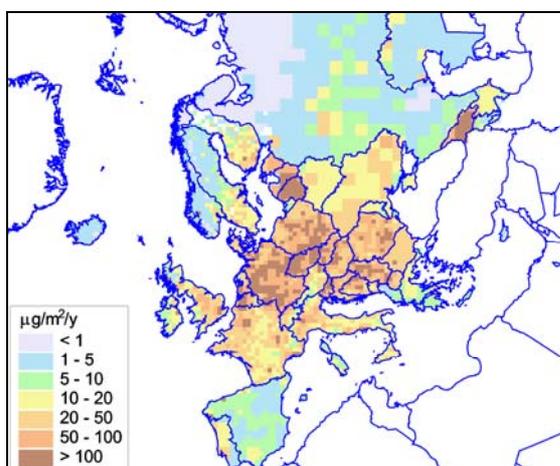


Fig. 8. Spatial distribution of B[a]P emission flux in 2000

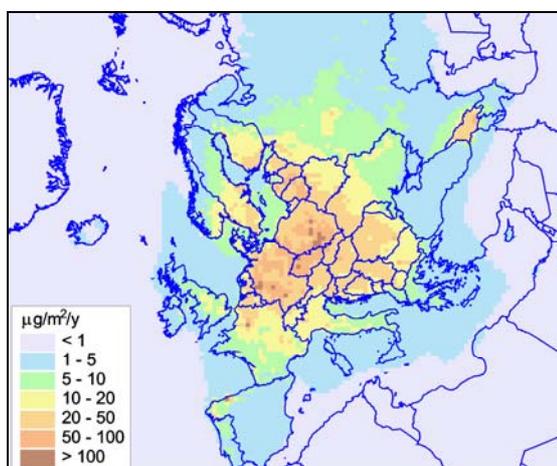


Fig. 9. Spatial distribution of B[a]P deposition flux in 2000

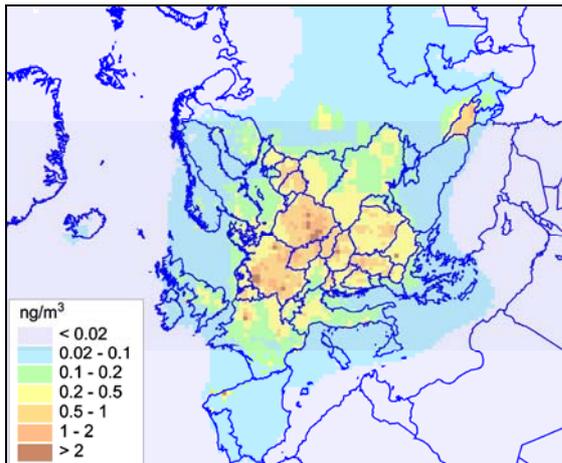


Fig. 10. Mean annual air concentrations of B[a]P in 2000

Mean annual air concentrations of B[a]P are shown in Fig. 10. In some regions of Poland, Germany, and the Czech Republic, concentrations exceed 1 ng/m^3 , which is higher than the limit value established for a number of European countries [Policy on ..., 1994; Zurek et al., 2000]. In regions with a high level of emissions – in the western part of Germany and in Poland – mean annual concentrations exceed 3 ng/m^3 . In the rest of the European countries, concentrations vary within $0.1\text{-}1 \text{ ng/m}^3$.

Mean diurnal air concentrations of this pollutant vary during the year. In the cold season, when B[a]P degradation slows down B[a]P emissions increase due to the increase of fuel combustion products released to the air. For this reason, mean diurnal concentrations are several times higher than in summer. The amplitude variation can be characterized by the maximum mean diurnal concentrations, which spatial distribution is illustrated in Fig. 11. On the average, maximum mean diurnal concentrations are as much as 5 times higher than mean annual concentrations. In the majority of countries of Central Europe, mean diurnal concentration values are within $0.5\text{-}5 \text{ ng/m}^3$. In some regions of Germany and Poland, they reach 20 ng/m^3 .

General description of transboundary transport. The half-life of B[a]P in the atmosphere is rather long; therefore, this pollutant can be transported with air masses over long distances. The transboundary transport from a country is estimated by the quantity of pollutant exported, i.e.,

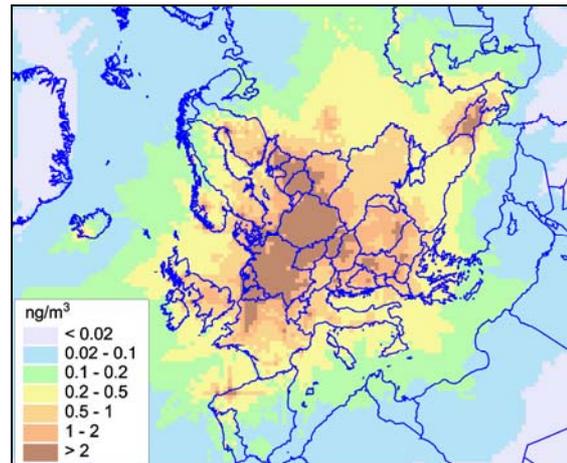


Fig. 11. Maximum mean diurnal air concentrations of B[a]P in 2000

by the contributions to the total depositions to other countries. Fig. 12 shows a diagram illustrating contributions of a number of countries to transboundary transport. The highest exporters of B[a]P are Germany (13 t), Poland (11 t), France (5.5 t), Romania (4.5 t), and the Czech Republic (4.5 t).

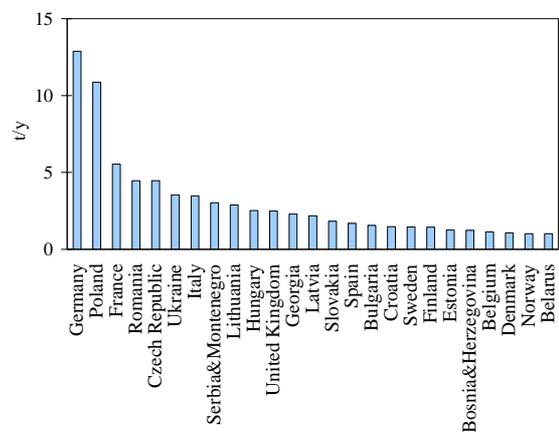


Fig. 12. Contributions of some countries to B[a]P transboundary transport

Transboundary transport can be also characterized by the contributions from external emission sources to the concentration levels of the country under study. Contributions of external sources to mean annual air concentrations in countries where this contribution exceeds mean European concentrations are shown in Fig. 13. The most significant impact of transboundary transport is observed in Slovakia (0.4 ng/m^3), the Czech Republic (0.33 ng/m^3), and Luxembourg (0.27 ng/m^3).

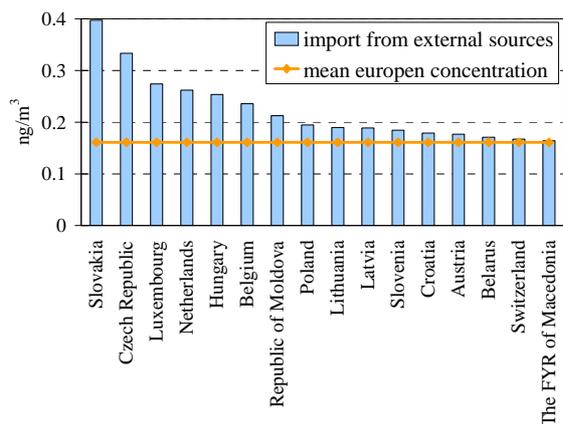


Fig. 13. Contribution of external sources to mean annual air concentrations of B[a]P of some countries. The orange line shows the mean annual air concentration value for Europe, equal to 0.16 ng/m³

Notice that the effect of the contribution of external sources to mean annual air concentrations is most pronounced in countries of Central Europe with relatively small territories. In order to perform more extended analysis, we consider the contribution of external emission sources to B[a]P total depositions to European countries (Fig. 14). The greatest external-source impacts on total depositions are characteristic of the Russian Federation (12 t), Poland (6 t), Ukraine (5 t) and Germany (4 t), i.e., countries with vast territories.

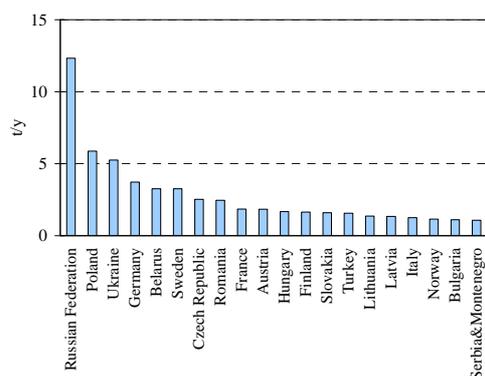


Fig. 14. Contribution of external emission sources to B[a]P total depositions to some countries

To evaluate the extent to which pollution in European countries is affected by transboundary transport, we compare the contributions of external and internal sources to mean annual air concentrations (Fig. 15). The effect of transboundary transport on air concentration is more significant than that of domestic emission flux

in such countries as Luxembourg (100% of the total concentration), Republic of Moldova (80%), and Albania (80%). At the same time, the contribution of transboundary transport to the total concentrations in Poland, Germany, and Georgia does not exceed 20% of these concentrations. In the majority of the countries considered, this contribution is within the range from 30 to 60%.

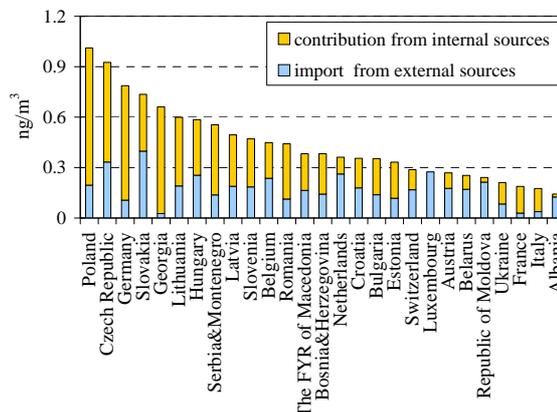


Fig. 15. Contribution of external and internal emission sources to mean annual air concentrations for some countries

It is pertinent to note that, in different countries of the EMEP region, the B[a]P pollution level depends, by and large, on their position and area.

The computations made allow us to analyze in detail the effect of transboundary pollution on each country and to reveal pathways of pollution by B[a]P from internal and external emission sources.

Peculiarities of transboundary transport in a particular country.

The analysis of B[a]P transboundary transport in a particular country is made on the example of France. First, we will consider the distribution of pollution over the EMEP region from internal sources; then, we will analyze pollution levels in the country resulting from internal and external sources.

According to expert estimates, total B[a]P emissions in France in 2000 were 26 tonnes. Twelve tonnes of this amount deposited over the EMEP domain; the remaining quantity partly degraded in the air (6 t) and was partly exported beyond the calculation grid (8 t). Twelve tonnes of depositions are distributed between France (6.5 t, or 54%), adjacent sea basins (1.5 t, or 14%), Germany (1 t, or 9%), and the remaining countries (less than 3 t, or 23%) (Fig. 16).

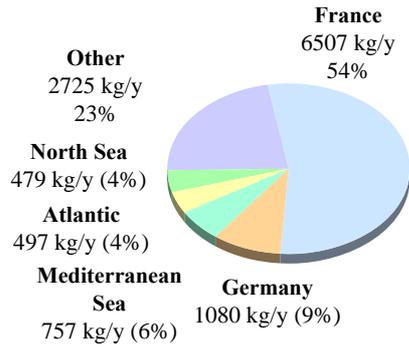


Fig. 16. The distribution of B[a]P depositions from French sources to European countries and regions

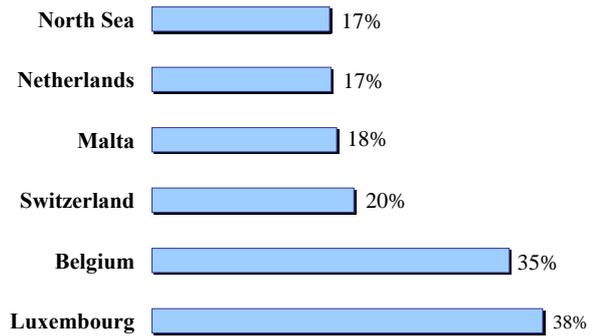


Fig. 17. The fraction of emissions from French sources deposited to some countries and sea surface

Let us consider the contribution of French domestic sources to depositions to European countries and regions (Fig. 17). The share of Luxembourg and Belgium exceeds one-third of the total depositions of B[a]P to these countries. The share of Switzerland, the Netherlands, Malta, and the North Sea basin is about 20% each.

The estimated field of B[a]P depositions from French sources is illustrated in Fig. 19. Significant B[a]P deposition fluxes (20-130 $\mu\text{g}/\text{m}^2/\text{y}$) are observed in France in regions with high emissions intensity (more than 100 $\mu\text{g}/\text{m}^2/\text{y}$; Fig. 18). In the larger part of the territory of France and Belgium, the deposition value varies from 5 to 20 $\mu\text{g}/\text{m}^2/\text{y}$. In neighboring countries, the flux value is from 0.5 to 5 $\mu\text{g}/\text{m}^2/\text{y}$. The same range is characteristic of regions located rather far from France, namely, the southern parts of Norway and Sweden.

Now, we will consider the contributions to B[a]P deposition levels to French territory from internal and external sources. The spatial distribution of the input from external sources is given in Fig. 20. It is clear that, over the major part of the territory, pollution import does not exceed 30%; however, in regions near boundaries with neighboring countries, the contribution to B[a]P deposition reaches 80%. The input of Germany to the total deposition of B[a]P to France is approximately 650 kg (8% of the total deposition to the country) (Fig. 21). Noticeable contributions to the contamination of France are made by Spain (349 kg, or 4%), Italy (244 kg, or 3%) and the United Kingdom (153 kg, or 2%). The integral contribution from the remaining European countries is 489 kg, or 6%. Approximately the same values of contributions are characteristic of air concentrations of this pollutant in France.

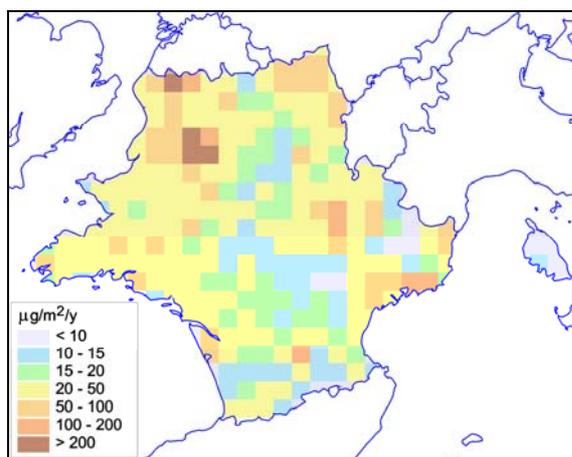


Fig. 18. Spatial distribution of B[a]P emission flux for French sources in 2000

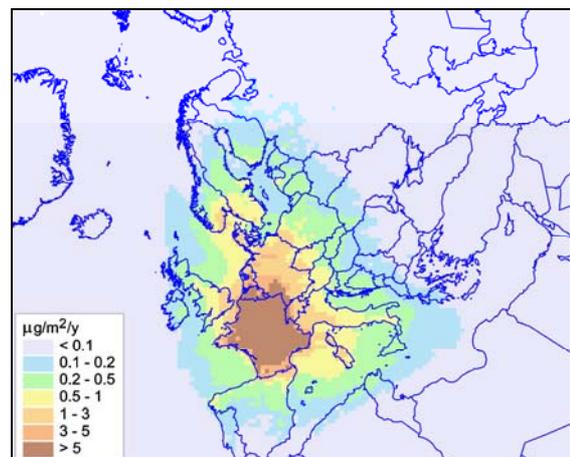


Fig. 19. Spatial distribution of B[a]P deposition flux from French sources in 2000

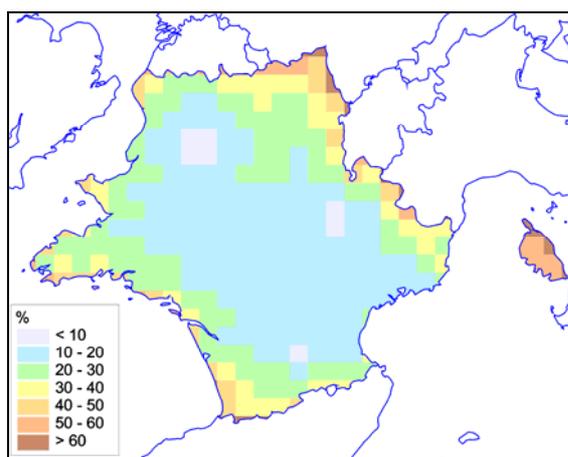


Fig. 20. Contribution of external sources to B[a]P deposition to France

The assessment of the transboundary transport for other European countries can be found on the site <http://www.msceast.org/countries/index.html>. More detailed analysis of depositions and air concentrations is given in the Technical Report [Shatalov *et al.*, 2003].

The comparison with measurements. The comparison of the calculation results with measurement data on depositions and mean annual concentrations of B[a]P in air and precipitation, revealed that about 70% of the calculated air concentrations were within a factor of 3 relative to the measured values and all the calculated concentrations in precipitation were within a factor of 4. The uncertainty of the calculation results obtained for B[a]P transboundary transport is conditioned by the uncertainty of emission data.

Benzo[b]fluoranthene

Calculations of B[b]F pollution levels covered the period from 1970 to 2000. The main objective of that computations was to make a provisional estimation of B[b]F pollution levels in the main environmental compartments, to analyze their long-term trends and to compare the calculation results

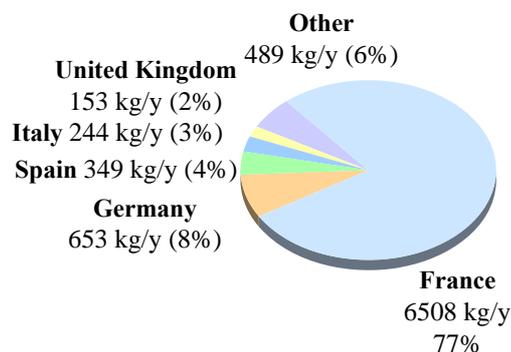


Fig. 21. Contribution of European countries to B[a]P deposition to France

with measurements. Expert estimates [Pacyna *et al.*, 1999] were used as emission data (see subsection 2.1). B[b]F initial accumulation in the environmental media (before 1970) was pre-estimated.

The analysis of B[b]F accumulation dynamics in the main environmental compartments. Plots of B[b]F content variations in the main environmental compartments as compared to emissions during 1970-2000 are illustrated in Fig. 22. B[b]F emissions moderately decreased from 1970 to 1985 (Fig. 22a). Then by 1995 the emission flux has drastically cut down. In calculations for 1995-2000 the emission is assumed to be constant. The dynamics of B[b]F accumulation in air (Fig. 22b) and sea (Fig. 22c) actually follows the emission variation. At the same time there are variations caused by meteorological conditions.

The dynamics of accumulation in soil (Fig. 22d) differs from that observed in other media. In spite of emission reduction from 1970 to 1980, B[b]F content in soil increases reaching the maximum in 1982. Then it smoothly decreases up to 2000. It is worth noting that the soil contains practically the whole mass of this pollutant accumulated in the environment (98%).

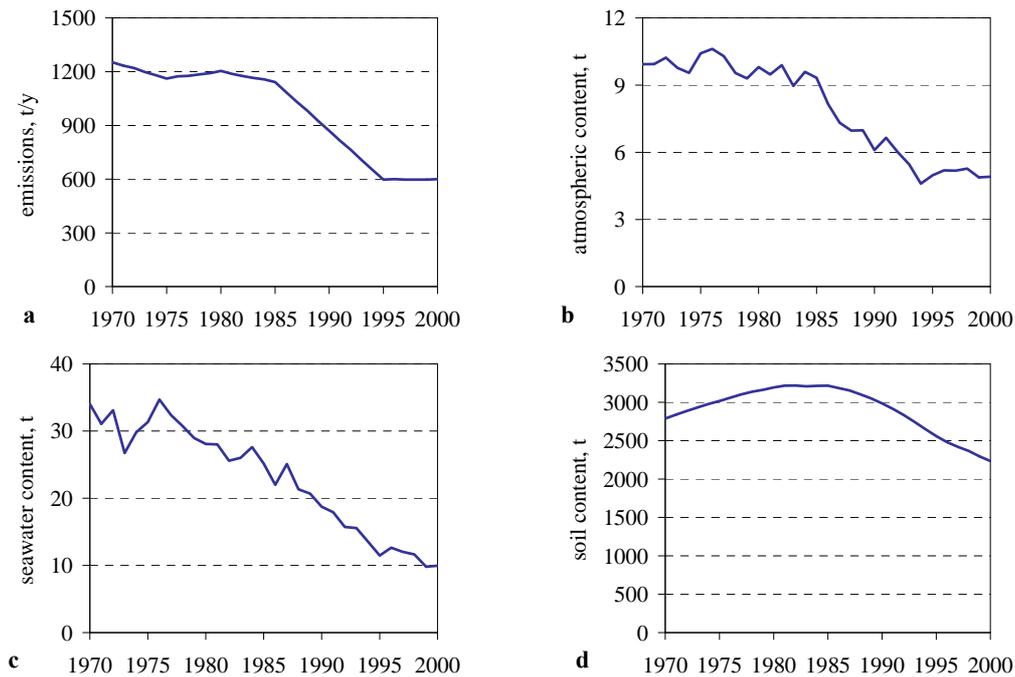


Fig. 22. B[b]F emission intensity variation (a) and accumulation dynamics in main environmental compartments of the EMEP domain (atmospheric air (b), seawater (c), soil (d) during 1970-2000

The spatial distribution of pollution. We proceed with the consideration of the calculated field of B[b]F environmental pollution and its deposition fluxes in 2000 and compare them with the emission spatial distribution. The average value of deposition flux for Europe is 15 $\mu\text{g}/\text{m}^2/\text{y}$. The most intensive fluxes of emissions (exceeding

200 $\mu\text{g}/\text{m}^2/\text{y}$) are estimated over vast areas of Poland, the Czech Republic, and the central part of Russia (Fig. 23). As evident from Fig. 24 the same regions have high deposition fluxes (more than 50 $\mu\text{g}/\text{m}^2/\text{y}$). Deposition flux values from 10 to 50 $\mu\text{g}/\text{m}^2/\text{y}$ are characteristic of Central and East Europe, western France, northern Italy, and the southern part of Sweden and Finland.

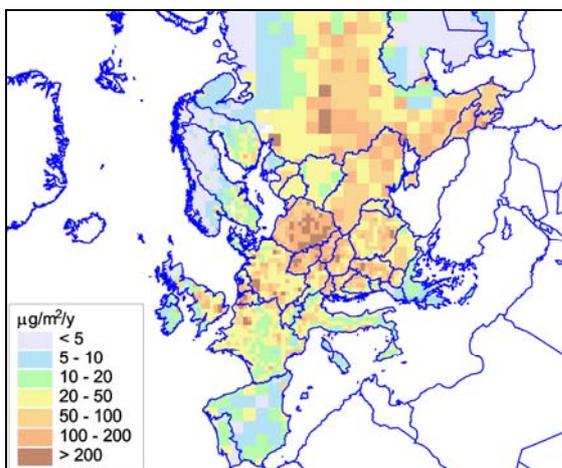


Fig. 23. Spatial distribution of B[b]F emission flux in 2000

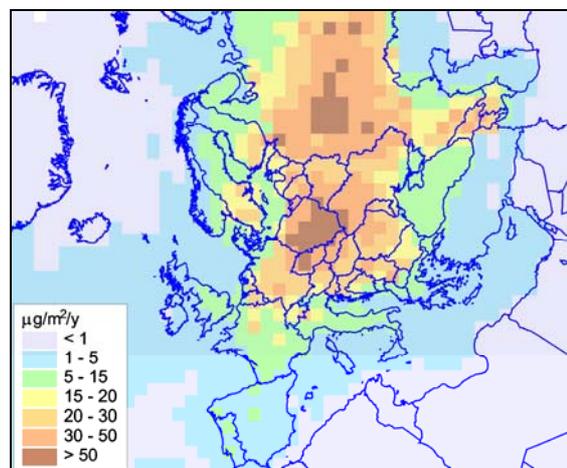


Fig. 24. Spatial distribution of B[b]F deposition flux in 2000

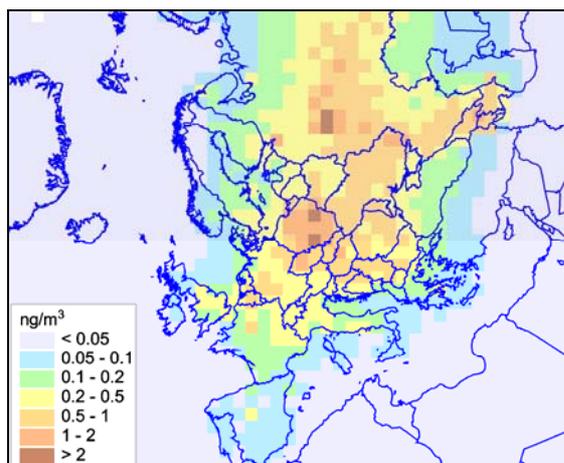


Fig. 25. B[b]F concentration in air in 2000

Deposition fluxes to a great extent are conditioned by B[b]F concentrations in the air surface layer (Fig. 25). The average value of surface air concentration of B[b]F for Europe is 0.28 ng/m^3 . In the polluted regions of Poland, the Czech Republic and Russia calculated mean annual concentration exceeds 1 ng/m^3 . The concentration level $0.5\text{-}1 \text{ ng/m}^3$ is characteristic of Slovakia, Hungary, Ukraine, Republic of Moldova, Serbia and Montenegro, Georgia, Belgium, vast territories of Germany, Russia, and Romania. For the majority of remaining European countries, the estimated B[b]F concentrations lie in the range from 0.04 to 0.5 ng/m^3 .

It might be well to point out that high levels of B[b]F concentration in soil are not always in line with high values of emissions in 2000 (Fig. 26). For example, in some regions of Germany, where in 2000 soil concentration values are essential ($> 5 \text{ ng/g}$) the emissions are relatively low (Fig. 23). The point is that the soil concentration has been accumulated for many years. Hence, in some regions high concentration levels in soil can be explained by intensive emission fluxes observed not only in the end of the calculation period, but at the previous time.

High levels of B[b]F soil concentration are estimated for Poland, the Czech Republic, and for central Russia. In the majority of countries of Central and East Europe the concentration levels are within $2 - 5 \text{ ng/g}$. The same levels of concentration were estimated for the United Kingdom, France, the south of Norway, Sweden, and Finland.

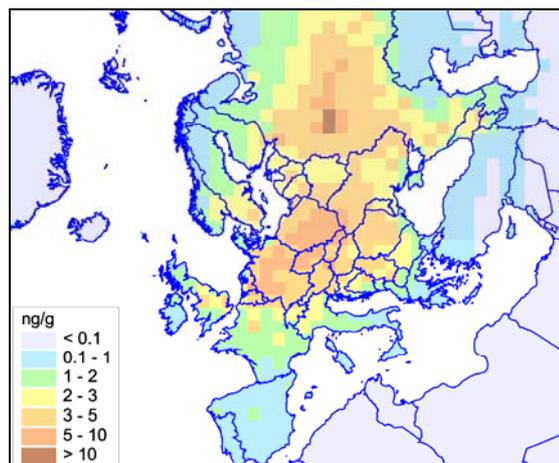


Fig. 26. B[b]F concentration in soil in 2000

The comparison with measurements. In comparison of modelling results with measurement data we used B[b]F mean annual concentrations observed in environmental compartments and precipitations as well as deposition fluxes measured in the period from 1988 to 2000. About 70% of concentrations are within a factor of 2 relative to measurements, all the remaining values – within a factor of 5. On the average the model underestimates air concentrations by 20%. All the computed values of concentration in precipitation are within a factor of 3 relative to measurement results, and again the model slightly underestimates the concentration (by 10% on the average). It is likely that after the refinement of emission data the agreement with measured values will be better. Three fourths of the calculated deposition fluxes are within a factor of 2 relative to measurements. It should be pointed out that the number of measurements in this case is limited (8 records). For concentrations in the marine environment about 70% of calculated values are within a factor of 3. Half the calculated concentrations of B[b]F in vegetation is within a factor of 2. As to soil concentrations calculated for all the stations but CZ3 (Kosetice, the Czech Republic), they differ from observation less than 5 times. The concentrations determined for the station Kosetice are underestimated as much as 7 times and more for different years. It is likely due to the effect of local relief and meteorological conditions. One could note that the agreement between calculated and measured values of B[b]F concentrations and deposition fluxes, by and large, is reasonable.

2.2.2. Dioxins and furans

On the previous stage of investigations the assessment of the EMEP domain contamination by dioxins/furans was fulfilled on the example of the "indicator congener" - 2,3,4,7,8-PeCDF. However, taking into account the difference in physical-chemical properties of individual PCDD/F congeners, it is reasonable to perform calculations for each congener separately.

The purpose of the study is further development of approaches for modelling PCDD/F transport. With this aim in view the annual transport and accumulation of eight congeners of dioxins/furans (accounting for 80% of overall toxicity of PCDD/F mixture) are estimated for the period of 1970-2000. PCDD/F overall toxicity is estimated as a sum of contributions of these congeners. To specify the distance of dioxins/furans transport and the impact of European emissions on the contamination of other regions, computations of their transport within the Northern Hemisphere is made for a one-year period (1996).

At the next stage it is intended to assess the transport and accumulation of all 17 toxic congeners of PCDD/F.

As evident from previous results, the soil is the dominant compartment of dioxins/furans accumulation. During the current year the model

description of POP behavior in this compartment was modified (see Annex B). As a result the agreement between model calculations and measurements improved not only for soil but also for vegetation and seawater due to the refinement of exchange fluxes between different environmental media.

Differences in the behavior of PCDD/F individual congeners in the environment and the assessment of their transport distance.

On the basis of tentative calculations with the use of the hemispheric MSCE-POP model, a provisional estimate of the long-range transport potential of the 8 dioxins/furans congeners is made.

Peculiarities of the behavior of the congeners in the environment due to their different physical-chemical properties affect their spatial distribution. It is evident from the analysis of the pattern of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD air pollution in the Northern Hemisphere from European sources (Fig. 27).

In spite of similar emissions fluxes (about 500 g TEQ/y), 1,2,3,7,8-PeCDD is transported much further than 2,3,7,8-TCDD. It happens because the first congener is more persistent in the air (its half-life in the atmosphere is about 15 days and the half-life of the second one – about 8 days) and its properties favor the accumulation in soil.

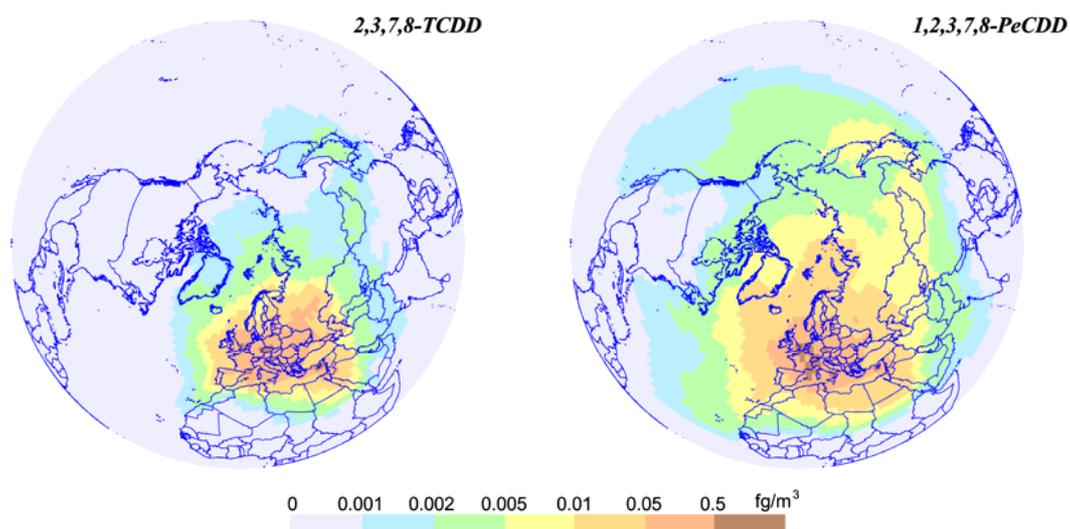


Fig. 27. Spatial distribution of air pollution by PCDD/F individual congeners from European sources in the Northern Hemisphere in 1996

The behavior of PCDD/F individual congeners is different both in peculiarities of their accumulation in various environmental compartments and in the distance of their airborne transport. The long-range transport potential of individual PCDD/F congeners is numerically specified as the *transport distance* (an average distance at which the substance concentration cuts down as much as 1000 times).

According to calculations the transport distance of the eight selected congeners varies from 4900 to 7100 km. Taking into account a significant persistence of dioxins/furans in the soil and sediments (the half-life is more than 60 years [Sinkkonen and Paasivirta, 1999]), even moderate depositions during a prolonged period of time result in substantial contamination of some remote regions (for example, such as the Arctic). At further stages of investigations for the assessment of contamination over "clean" areas it is intended to evaluate dioxins/furans transport and their accumulation in the environment with the use of the hemispherical model.

Estimates of European pollution levels specified by modelling the transport and accumulation of the 8 selected congeners of dioxins/furans in the EMEP domain for the period from 1970 to 2000 are discussed below.

The pollution partitioning between environmental compartments and its long-term trends. Long-term trends of emissions and the content of 8 PCDD/F congeners in air, soil and seawater are illustrated in Fig. 28.

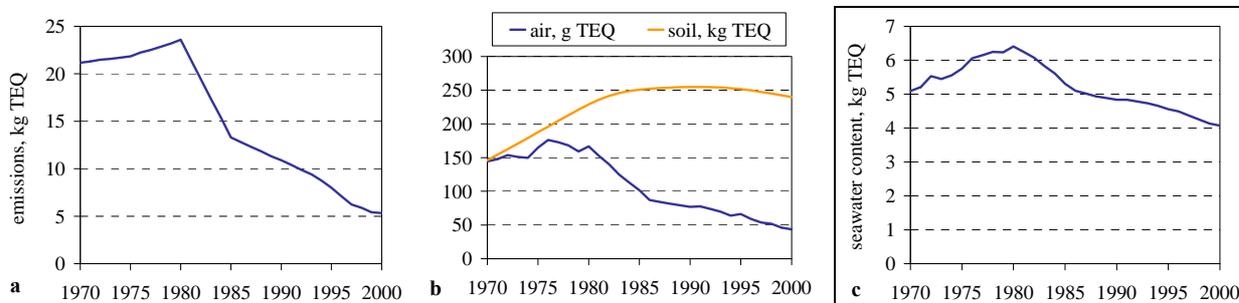


Fig. 28. The dynamics of emissions (a) and the content (b,c) of dioxins/furans in environmental compartments during 1970-2000

The calculation results demonstrate that the 4.5 times reduction of PCDD/F emission fluxes (in TEQ units) in the period of 1980-2000 (Fig. 28a) leads to the abatement of the air content 3.8 times (Fig. 28b). The value of seawater content (accounting for pollutants sedimented) drops 1.6 times. Since the mid 90s, PCDD/F soil content has been only slightly reduced.

Thus according to model estimates, the rate of PCDD/F content decrease in such media as water and especially soil can be well behind the emission reduction rate. It is due to low degradation rate of PCDD/Fs in soil and sediments. A slow decrease of the soil content against the emission reduction (and as a consequence reduction of air concentrations, Fig. 28b) results in lower gas flux from soil to air. Therefore air concentration reduction rate lags the emission reduction rate.

As it follows from the calculation results, the fraction of dioxins/furans toxicity in the environment, accumulated during a long period of time (30 years), is 90% in soil, about 4% in vegetation and approximately 3% in seawater (taking into account the accumulation in sediments).

The spatial distribution of pollution. The air pollution levels (in TEQ units) and emission fluxes of the selected congeners in 2000 are illustrated in Fig. 29.

The mean value of the emission flux from European countries varies from 0.004 to 8 ng TEQ/m²/y and amounts to 0.5 ng TEQ/m²/y in the EMEP region. High emission fluxes (more than 2 ng TEQ/m²/y) are estimated for the Czech Republic, Belgium, Switzerland, Luxembourg, Slovakia and Italy.

The comparison of spatial emission distributions with the calculated concentrations indicates that the high air concentrations coincide with regions of high emission intensity. The mean value of dioxins/furans concentrations in the surface air in different countries varies from 0.1 to 25 fg TEQ/m³ and is 2.5 fg TEQ/m³ in the EMEP domain. Air concentration levels exceeding 8 fg TEQ/m³ were determined mainly for the countries listed above. The impact of the long-range transport, however, leads to the increase of contamination in countries with relatively low emission flux. For instance, according to the calculation results, the air pollution level in Poland appears to be higher than in Italy, in spite of the fact that the emission flux intensity in Poland is 2.5 times lower than in Italy.

The marine environment can play the important role in the pollution accumulation and transport from

sources to remote regions. The spatial distribution of dioxins/furans concentrations in seawater is demonstrated in Fig. 30.

According to the calculation results, the mean value of dioxins/furans concentrations in seawater is about 1.1 fg TEQ/l. High concentrations in seawater were estimated for the regional seas and coastal water near major emission sources. The spatial distribution of sea concentrations is affected by the pollution transport by sea currents along the northern boundary of the Scandinavian Peninsula and Greenland.

Vegetation is important in the processes of the pollution transport from air to soil. The spatial distribution of PCDD/F pollution in vegetation is shown in Fig. 31.

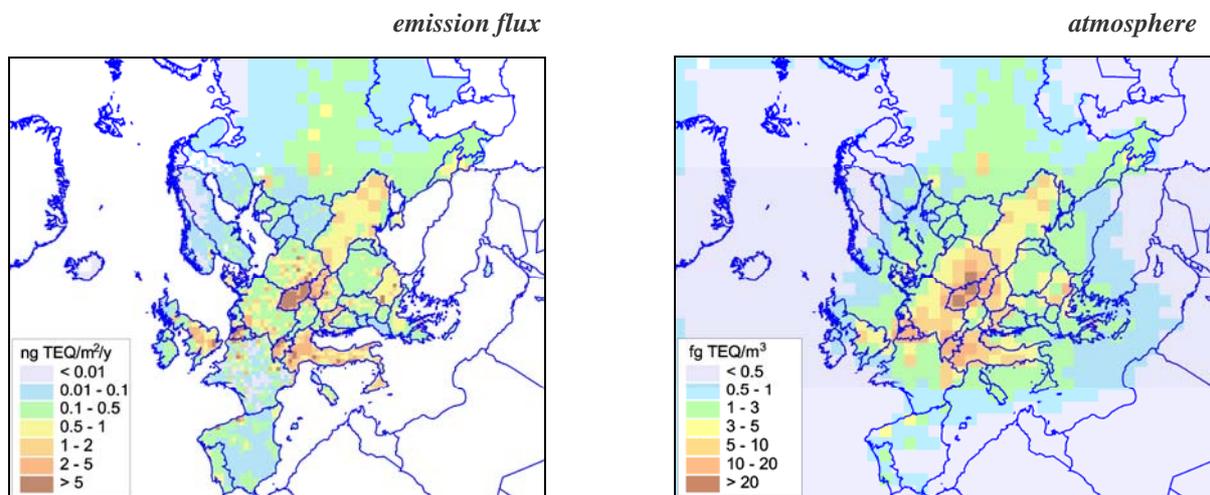


Fig. 29. Spatial distribution of emission flux and air levels of pollution by the eight selected congeners of dioxins/furans in 2000

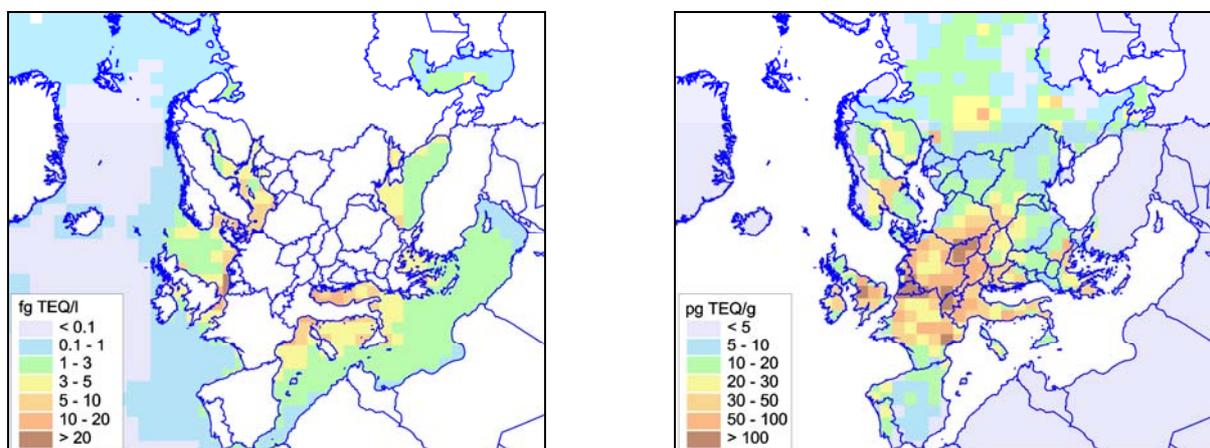


Fig. 30. Seawater levels of pollution by the mixture of the dioxins/furans 8 selected congeners in 2000

Fig. 31. Concentrations of the dioxins/furans 8 selected congeners in vegetation in 2000

The calculated mean concentrations in vegetation in different European countries vary from 0.04 to 5 pg TEQ/g and the mean value for the EMEP region is 1.3 pg TEQ/g. High concentration levels (exceeding 2 pg TEQ/g) are characteristic of Luxembourg, the Czech Republic, Belgium, Switzerland and Austria. Relatively high concentration values in vegetation over vast areas of the Scandinavian Peninsula and over the northern part of European Russia are explained by high deposition fluxes to forests.

The spatial distribution of the PCDD/F pollution in the topsoil layer is illustrated in Fig. 32.

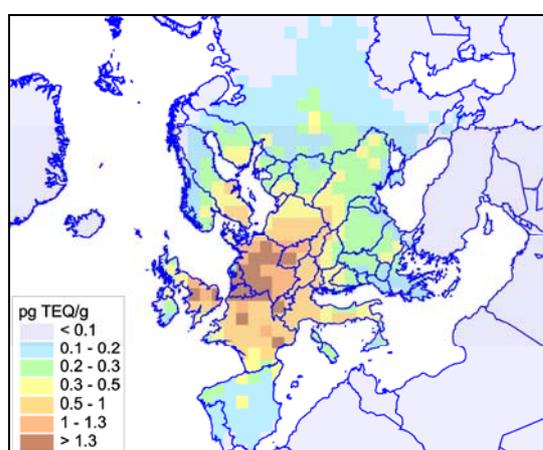


Fig. 32. Mean concentrations of the mixture of the 8 dioxins/furans selected congeners in the topsoil layer in 2000

The estimated mean concentration level of PCDD/Fs in the topsoil layer (5 cm) for the EMEP domain is equal to 0.3 pg TEQ/g. Mean levels in soil of European countries vary from 0.01 to 3 pg TEQ/g. The highest soil pollution levels (more than 1 pg TEQ/g) were calculated for Luxembourg, Belgium, the Netherlands, Germany, the Czech Republic and Switzerland. The regions with high concentrations in soil (contrary to air concentrations) do not coincide with those of high emission intensity. For instance, in the Netherlands where emission fluxes are moderate the soil

contamination considerably exceeds the mean European level. These differences can be caused by the long-range transport and by the long-term accumulation of dioxins/furans in soil. Relatively high PCDD/F concentrations in soil of some European regions (for instance, the Scandinavian Peninsula) can be explained by the role of forests in scavenging of dioxins/furans from the atmosphere and subsequent runoff to soil.

Data on countries. On the basis of calculation results, information about mean annual levels of pollution by dioxins/furans of environmental compartments in Parties to the Convention is prepared. This information can be found in the Internet (www.msceast.org) and in the Technical Report of the Centre. Table 2 exemplifies the presentation of these data.

The comparison with measurements. The model modification made at this stage of investigations improved the agreement between calculated and measured data in particular with regard to seawater and vegetation. The comparison of specified concentrations with available measured values for air indicates that about 70% of the calculated concentrations were within a factor of 3 relative to measurements. More than half the calculated and measured concentration in soil and vegetation agrees within a factor of 4. The estimated concentrations in seawater are consistent with measurements within an order of magnitude. At the same time more than half the calculated values differs from measured ones less than 6 times. It worth noting that the database on concentrations in seawater (the number of measurements) is very limited.

The main reasons for the discrepancies is the uncertainty inherited in the model and the uncertainty of emission data. As indicated in [Pacyna *et al.*, 1999] the uncertainty of expert estimates of PCDD/F emission values is an order of magnitude. Note that the official information submitted by countries is also somewhat uncertain.

Table 2. Mean annual pollution levels of some European countries (TEQ units)

Country	Air, fg/m ³	Soil, pg/g	Vegetation, pg/g	Seawater, fg/l
Albania	1.7	0.19	0.33	6.2
Armenia	2.8	0.10	0.32	-
...
United Kingdom	2.4	0.69	1.2	3.6

2.2.3. Levels of pollution by persistent organic pollutants in European regional seas

The assessment of pollution by polycyclic aromatic hydrocarbons (in particular, B[a]P) and polychlorinated dibenzo-p-dioxins and dibenzofurans of regional seas (the Baltic Sea, the North Sea, the Black Sea and the Mediterranean Sea) is made for 2000 with the use of the modified MSCE-POP regional model. Average values of POP deposition fluxes to these seas are given in Table 3.

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

Sea	B[a]P, $\mu\text{g}/\text{m}^2/\text{y}$	PCDD/Fs, $\mu\text{g TEQ}/\text{m}^2/\text{y}$
Baltic	8.5	97
North	3.6	85
Black	3.1	69
Mediterranean	1.5	53

According to the calculation results, the most intensive deposition fluxes of B[a]P and PCDD/Fs are characteristic of the Baltic Sea. The pollution levels of the North and the Black Sea are similar. The least values are determined for the Mediterranean Sea. Note that in calculations only European sources of these pollutants were considered.

The contribution of B[a]P emission fluxes from individual European countries to the pollution of the regional seas is estimated. As an example the diagram in Fig. 33 shows the distribution of contributions of different countries to B[a]P depositions to the Baltic Sea surface. Five countries making the greatest input to depositions of this pollutant are distinguished.

More detailed information on the pollution of the regional seas (including the data on different basins of the Baltic and Mediterranean Seas) can be found in the Technical Report of MSC-E [Shatalov *et al.*, 2003].

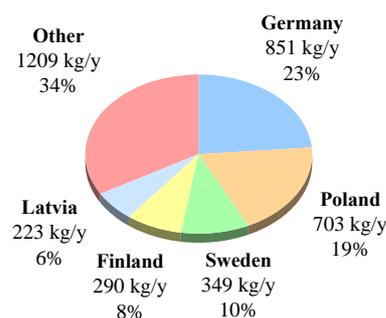


Fig. 33. The contribution of European countries to B[a]P depositions to the Baltic Sea basin

2.3. Pollution levels in the Northern Hemisphere

This subsection describes the results of the investigation of the spatial distribution of pollution by polychlorinated biphenyls, γ -hexachlorocyclohexane and hexachlorobenzene in air, seawater and soil in Europe and in the Northern Hemisphere. Particular emphasis has been placed to the evaluation of PCB and γ -HCH long-range transport and depositions to various European regions from emission sources located in the Northern Hemisphere and to the assessment of the impact of European sources on the pollution in remote regions. In addition we analyzed γ -HCH long-term trends of accumulation and distribution in environmental compartments and made a preliminary estimate of HCB long-range transport.

The calculation results for each pollutant considered are discussed below in appropriate subsections.

2.3.1. Polychlorinated biphenyls

Tentative computations of airborne transport of PCBs within the Northern Hemisphere from emission sources located in the EMEP region for one year (1990) were performed in 2002. It was demonstrated earlier [Dutchak *et al.*, 2002] that a substantial fraction (50%) of PCB emissions from such sources is transported outside the European region.

The object of this stage is to evaluate the pollution level of polychlorinated biphenyls with allowance made for their airborne transport and accumulation

in environmental media for several decades. Special consideration is given to the assessment of contamination in the EMEP domain and the Arctic. This study was made under EMEP/WMO/AMAP joint project on the assessment of the Arctic contamination.

For the description of the transport and accumulation of PCB congeners in the environment, a set of congeners representing the whole spectrum of PCB properties was selected. It involves light (PCB-28), medium (PCB-118) and heavy (PCB-153 and 180) congeners. Besides, PCB-118 also represents the group of toxic congeners. These congeners are included to the list of 7 congeners of ICES (International Council for the Exploration of the Seas), their physical-chemical properties are well studied and measurement data are available.

Long-term trends of accumulation and contamination partitioning between environmental compartments. To make a correct description of PCB accumulation in such media as soil and seawater, the assessment of the environmental pollution is performed on the basis of computation for a sufficiently long period of time (1970-1996). The estimated distribution of different PCB congeners in environmental compartments is given in Fig. 34.

The calculation results confirm the conclusion (made earlier on the basis of regional calculations [Shatalov *et al.*, 2001]) that soil is the main medium-accumulator of PCBs. The pollutant fraction accumulated in soil essentially depends on physical-chemical properties of a congener and it grows from 74% of the total content in the environment for a light congener (PCB-28) to 95% for the heaviest congener among the considered

ones (PCB-180). The fraction of light and medium congeners accumulated in seawater and vegetation reaches 5-10%. At the further stages of investigations it is supposed to proceed with estimation of PCB toxic congeners input to the pollution accumulated in the environment.

The spatial distribution of contamination.

Estimates of the spatial distribution of the four selected congeners in the main environmental media (air, soil, seawater and vegetation) are assessed on the basis of calculation results. As an example Fig. 35 illustrates the spatial distribution of PCB-153 ("indicator" congener [Pekar *et al.*, 1999]) concentrations in media in comparison with its emission and deposition fluxes distribution. Information about the remaining 3 congeners is presented in V.Shatalov *et al.* [2003].

The overall emissions of PCB mixture in the Northern Hemisphere in 1996 are estimated to be 660 tonnes [Breivik *et al.*, 2002]. The input of European sources (approximately 235 tonnes) amounts to 35% of the total emission flux. PCB-153 emissions are 15 tonnes of which about one-half is accounted for the EMEP region. The value of the emission flux in West Europe is highest and can reach more than $5 \mu\text{g}/\text{m}^2/\text{y}$. On the eastern coast of North America the emission flux is $1-3 \mu\text{g}/\text{m}^2/\text{y}$. In the remainder of the Northern Hemisphere the emission flux in the main is not higher than $1 \mu\text{g}/\text{m}^2/\text{y}$.

PCB-153 concentration in the air surface layer of the Northern Hemisphere varies from fractions of pg/m^3 to $30 \text{ pg}/\text{m}^3$. Least contaminated is the Pacific and the Indian Oceans (air concentration is not higher than $0.3 \text{ pg}/\text{m}^3$). The exception is coastal zones where concentrations can exceed $3 \text{ pg}/\text{m}^3$.

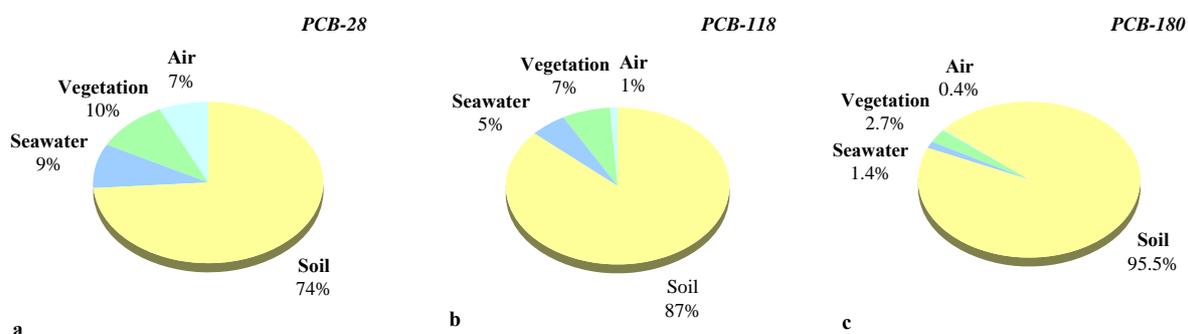


Fig. 34. Diagrams of the distribution of congeners: PCB-28 (a); PCB-118 (b); PCB-180 (c) in the main environmental compartments in 1996

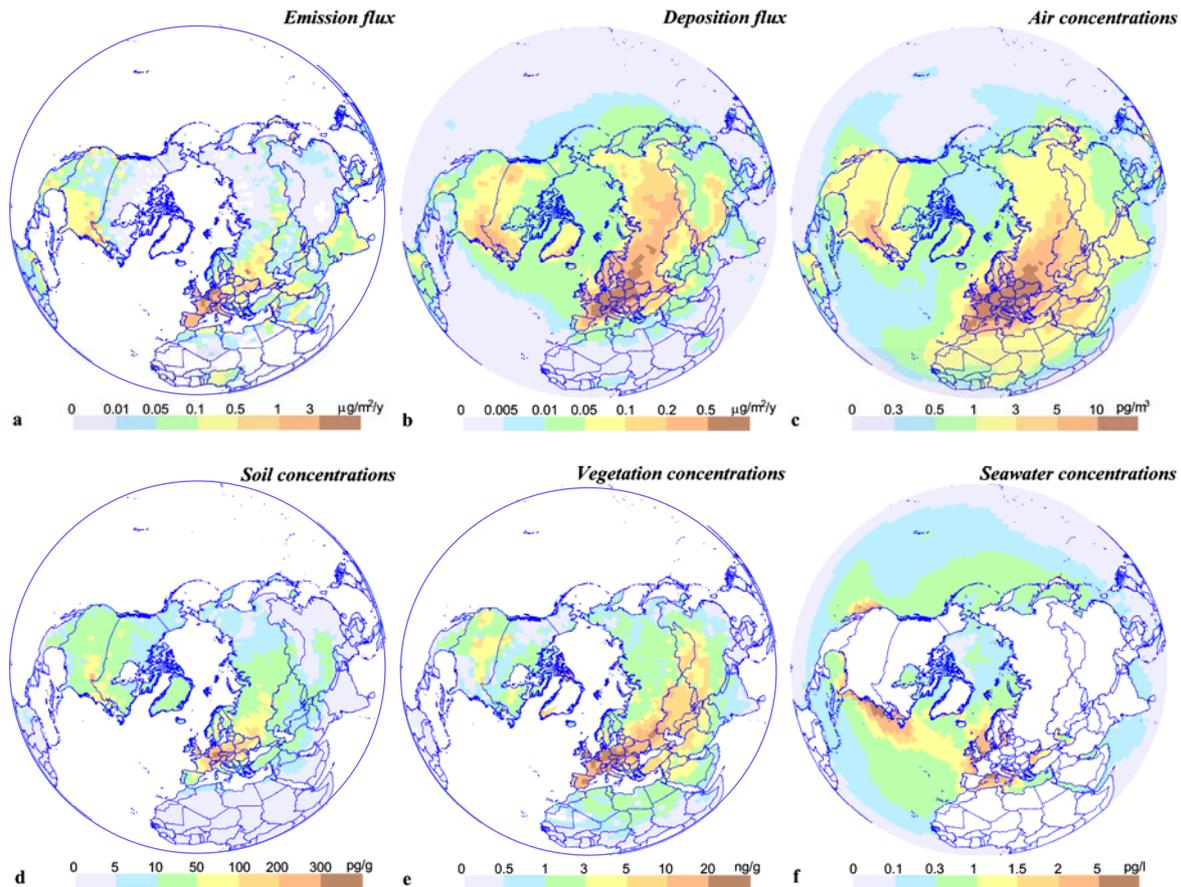


Fig. 35. Spatial distribution of emission (a) and deposition (b) fluxes and concentrations of PCB-153 in air (c), soil (d), vegetation (e) and seawater (f) within the Northern Hemisphere in 1996

The air pollution over the Polar Ocean is slightly higher and makes up $0.3\text{--}3\text{ pg/m}^3$ and in the vicinity of Scandinavian coast and Siberia it reaches 3 pg/m^3 . Over the greater part of the Atlantic the air contamination by PCB-153 is higher – from 1 to 3 pg/m^3 and in the coastal zone it can reach 5 pg/m^3 . Air pollution levels over North American continent are $0.5\text{--}1\text{ pg/m}^3$ in clean territories (the northern part of Canada and Alaska) and in polluted regions (the US eastern coast) they can reach 10 pg/m^3 . Characteristic levels of air concentrations over Asia and Africa amount to $0.5\text{--}3\text{ pg/m}^3$ and in some regions of Eastern Siberia and Central Asia – up to 10 pg/m^3 . The transport distance of PCB-153 is approximately 8000 km.

European air pollution level varies from $3\text{ to }30\text{ pg/m}^3$. Most clean is North Europe where air concentrations vary within the range from 1 to 5 pg/m^3 . Most contaminated are regions of West Europe where concentrations can be up to 20 pg/m^3 and higher. In other European regions air concentrations are within the range $3\text{--}20\text{ pg/m}^3$. The

distribution of mean air concentrations of PCB-153 in different European regions is illustrated in Fig. 36.

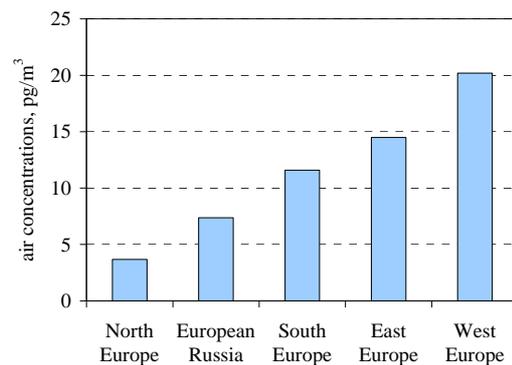


Fig. 36. PCB-153 mean concentrations in the air surface layer of different European regions in 1996

Soil concentrations of PCB-153 in the Northern Hemisphere reach 300 pg/g (and more) and vegetation concentrations – up to 30 ng/g . Comparatively high concentrations in vegetation

(exceeding 2 ng/g) are characteristic of Europe and of vast territories of Asia, Africa and America. Soil and vegetation of Africa and Asia are the least contaminated. Here in the clean areas soil concentrations vary from fractions of pg/g to 50 pg/g and vegetation concentrations do not exceed 10 ng/g. In some regions of Eastern Siberia and Central Asia soil concentrations reach 100 pg/g and concentrations in vegetation – up to 50 ng/g. On North American continent concentrations in the clean areas (the northern part of Canada and Alaska) do not exceed 50 pg/g in soil and 5 ng/g in vegetation. In the contaminated regions of North America soil concentrations can be up to 300 pg/g and in vegetation – up to 10 ng/g.

Soil pollution levels of PCB-153 in Europe vary from 10 to 300 pg/g and in vegetation – from 5 to 30 ng/g. The cleanest regions are North Europe, Spain, Portugal and southern Italy where concentrations in soil are from 10 to 100 pg/g and in vegetation – 5-20 ng/g. Higher levels in these media are estimated for some regions of Central and East Europe and the United Kingdom. Here concentrations in soils vary from 100 to 300 pg/g and in vegetation they reach 30 ng/g (and more).

Typical values of PCB-153 concentrations in seawater are within the range of 0.2-1 pg/l. In the North Atlantic the concentrations are somewhat higher – 1-2 pg/l. High concentrations in seawater (more than 2 pg/l) are estimated in sea basins in the vicinity of major emission sources and inland seas. The pattern of spatial distribution of PCB-153 concentrations in seawater of the North Atlantic, in particular, is defined by the pollutant transport by sea currents along the coast of the Scandinavian Peninsula from the Atlantic to the Arctic and back along the eastern coast of Greenland.

The assessment of the Arctic contamination.

The model assessment of the effect of various emission sources (in particular, European ones) on the Arctic pollution is made in the current year with the support of the AMAP. In future it is intended to investigate in detail the intercontinental and transboundary transport of PCBs within the Northern Hemisphere.

In the model calculations, major regions-sources of PCBs are distinguished in the Northern Hemisphere (Fig. 37). As an example, North-western and South-eastern Europe are set apart as regions-sources in the EMEP domain.



Fig. 37. *Regions-sources of PCB emissions in the Northern Hemisphere*

The calculation results show that the transport distance of the considered congeners of PCBs varies from 6000 to 7500 km. The contributions of European emission sources of PCB-153 to depositions to the Arctic region (Fig. 38b) is approximately 60%. It slightly exceeds the contributions of these sources to the overall PCB-153 emission flux of the Northern Hemisphere (about 50%, Fig. 38a). The contribution of Russian sources to depositions to the Arctic region is approximately 20%. It is a double amount of their input to the total emissions. The combined contribution of remote sources – Africa and Asia – is 8% of total depositions to the Arctic region. At the same time their combined contribution to the total emission flux is nearly 20%.

Using the calculated data, more detailed information about the contributions of different sources to depositions to the Arctic subregions can be specified. As an example Fig. 39 presents diagrams of the input of various sources of PCB-153 to depositions to Greenland and Alaska.

The contributions of different regions-sources of PCB-153 to depositions to the considered subregions of the Arctic essentially depend on their geographical location. The highest contribution to depositions to this region is made by North-western Europe (36 and 21% for Greenland and Alaska respectively) and America (32 and 30%). Emission sources located far away from Greenland and Alaska make an essential contribution to deposition to these subregions. Thus the integral contribution of African and Asian sources to depositions to Greenland is approximately 10 % and to Alaska – about 20%.

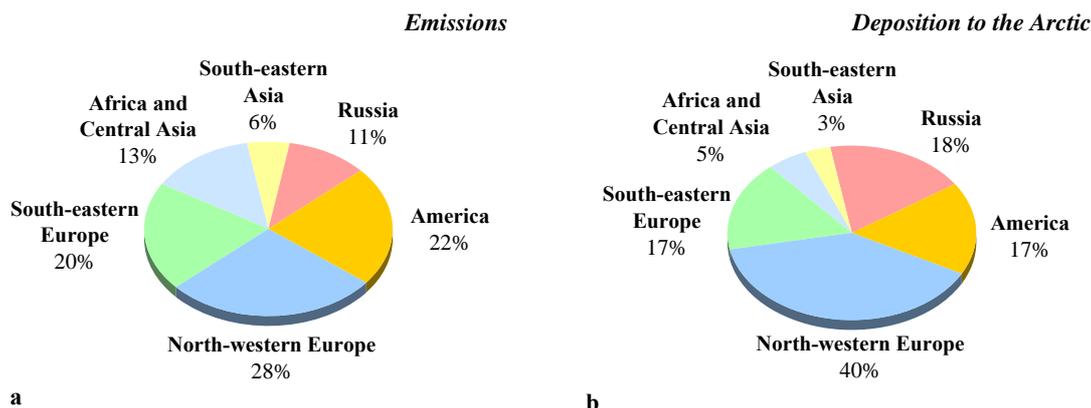


Fig. 38. The contributions of various regions-sources of the Northern Hemisphere to the overall PCB emissions and depositions to the Arctic

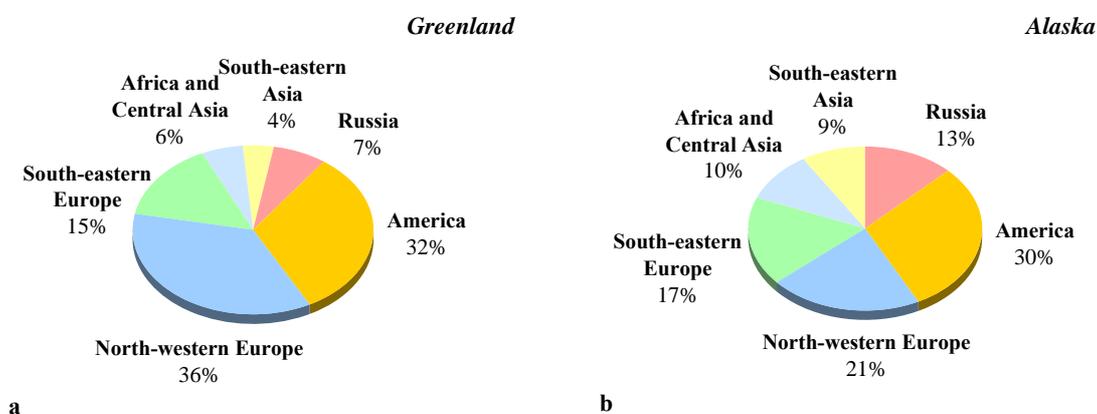


Fig. 39. The contributions of the PCB emissions from different regions-sources to depositions to some regions of the Arctic

The comparison with measurements. The comparison of calculated concentrations of the 4 selected PCBs in the air surface layer and precipitation with measurement data revealed that more than 70% of calculated concentrations of the four congeners (as to most studied PCB-153 – more than 90%) agree with measurements within a factor of 3.

Concentrations in precipitation are compared only with measurements made in 1995 and 1996. It is found that the model underestimates PCB-118 and 153 concentrations in precipitation within a factor of 3 and PCB-180 – within a factor of 2. PCB-28 concentration in precipitation is drastically underestimated. Thus in further study it is necessary to refine the parameterization of wet depositions, in particular, for light congeners. At the same time the measurement database (the number of measurements) is insufficient for the comparison of calculated versus measured concentrations in precipitation for a reliable verification of the model.

More detailed calculation results can be found in the Report [Dutchak et al., 2002] presented on the EMEP website and in the Technical Report of MSC-E [Shatalov et al., 2003].

2.3.2. γ Hexachlorocyclohexane

This year γ -HCH (lindane) long-range transport and accumulation is estimated for the period 1990-1996 with allowance made for emission sources of the Northern Hemisphere (see Subsection 2.1). Previous accumulation of lindane in environmental media (before 1990) is pre-calculated. Air concentrations and depositions of γ -HCH in various parts of the Northern Hemisphere are assessed as well as the impact of remote sources on the pollution of different European regions. The studies are made within the framework of EMEP/WMO/AMAP joint project on the assessment of the Russian Arctic contamination.

The analysis of γ -HCH accumulation dynamics in the main environmental media.

For a correct evaluation of γ -HCH pollution levels in the environment, it is necessary to study long-term trends of this substance accumulation in environmental compartments. Its emission and accumulation dynamics in the main environmental media of the Northern Hemisphere during 1990-96 is illustrated by Fig. 40.

In the period 1990-91 emission intensity sharply decreased, during the following five years its level cuts down rather slowly (Fig. 40a). γ -HCH accumulation dynamics in air and vegetation actually follows the dynamic of emission reduction (Fig. 40 b and c). The content of this pollutant in soil and seawater diminishes very slowly due to a long half-life of γ -HCH in these media. According to our estimates, seawater contains more than 80% of this pollutant accumulated in the environment by the end of 1996; the soil contains about 15%, the atmosphere – less than 3% of the γ -HCH total mass.

The spatial distribution of contamination. The spatial distribution of γ -HCH in the main environmental compartments, emission and deposition fluxes of this pollutant in 1996 are demonstrated in Fig. 41. As seen from modelling

results, substantial levels of γ -HCH depositions and concentrations in air and soil take place in countries and regions with high lindane emission intensity (India, China, West Europe and North America). At the same time, elevated air concentrations over the ocean and seawater caused by the γ -HCH long-range transport with atmospheric fluxes and sea currents are estimated. It is necessary to point to lindane elevated concentrations in soil of the European part of Russia, which are comparable with soil concentration in areas with essential emission fluxes. They are mainly determined by the long-term accumulation of this species in this compartment rather than by emissions in 1996.

On the basis of the computations, mean levels of γ -HCH concentrations in air and depositions in various parts of Europe are assessed. The conventional division of Europe into regions is presented in Fig. 37. The resulted estimates are shown in Table 4.

West Europe is the most contaminated area. It should be mentioned that in spite of an utter absence of lindane emission flux in North Europe the pollution level here is not much less than, say, in East Europe due to γ -HCH transboundary transport.

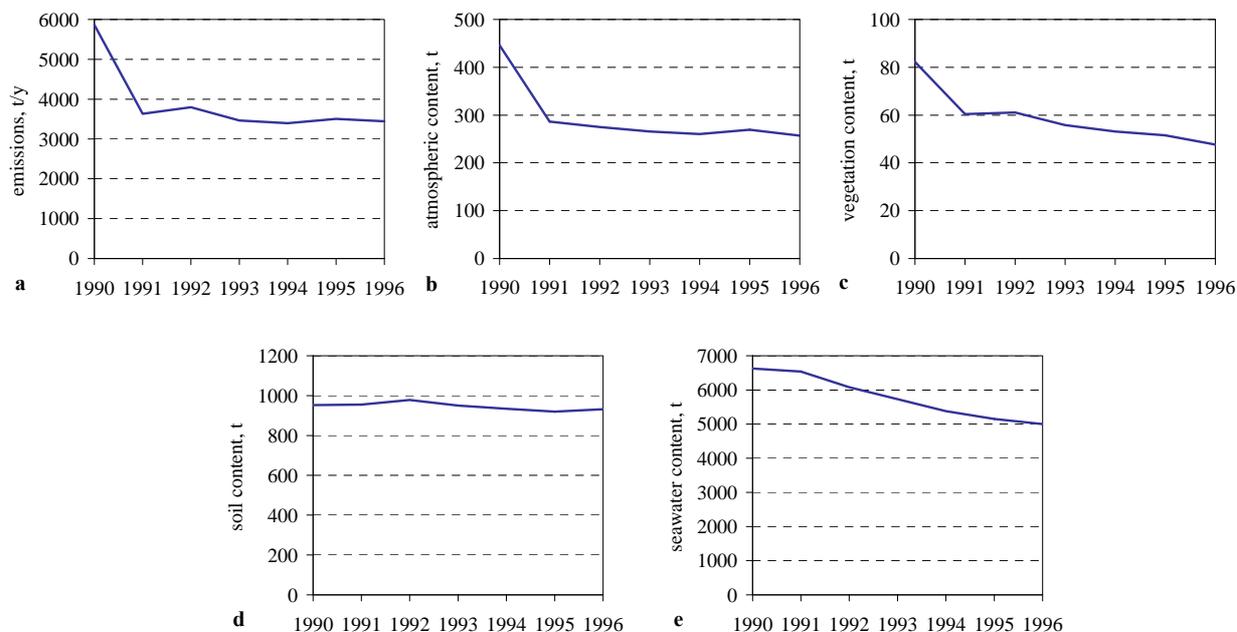


Fig. 40. The dynamics of γ -HCH emissions (a) and accumulation in air (b), vegetation (c), soil (d) and seawater (e) during 1990-96

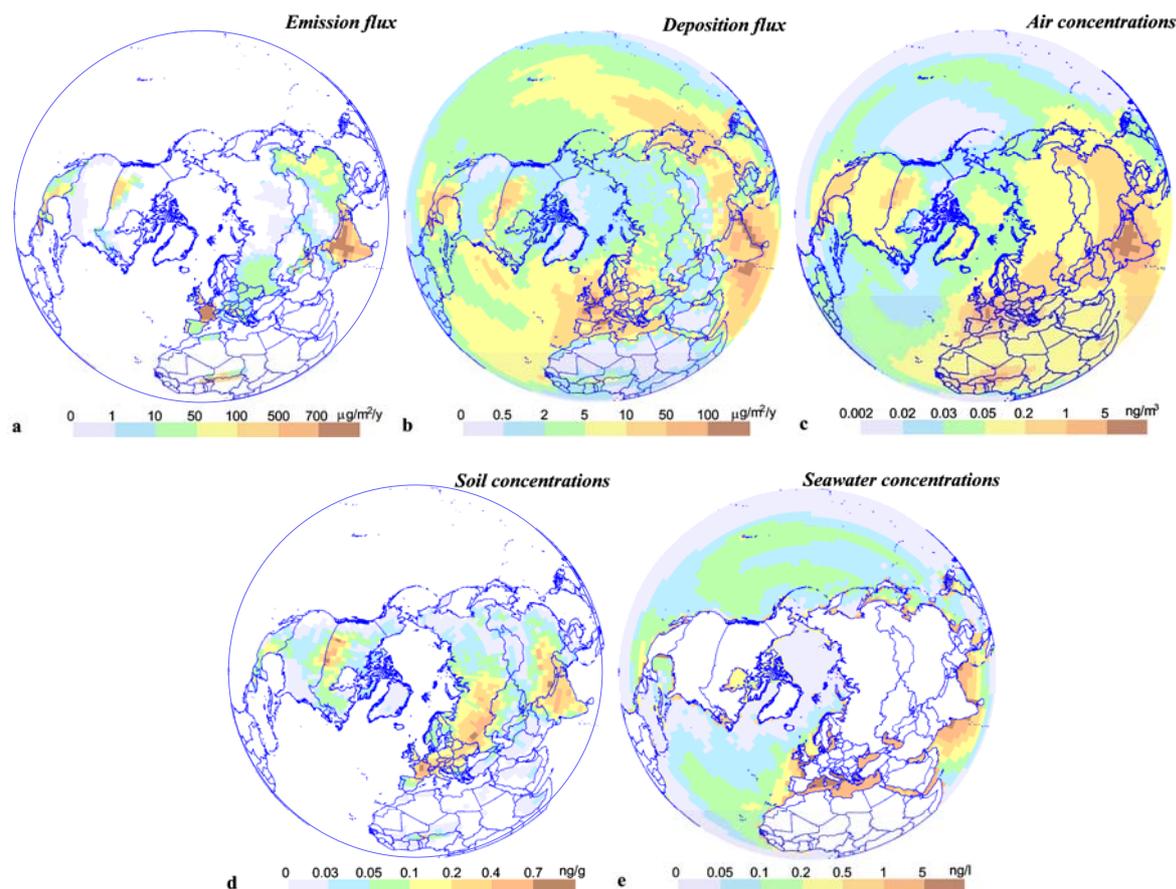


Fig. 41. Spatial distribution of γ -HCH emission (a) and deposition (b) fluxes; concentration in air (c), soil (d) and seawater (e)

Table 4. Mean annual levels of γ -HCH pollution in different European regions in 1996

Region	Air concentration, ng/m ³	Depositions*, µg/m ² /y
East Europe	0.47	7.3
European part of Russia	0.26	3.5
North Europe	0.10	1.9
South Europe	0.72	5.4
West Europe	2.21	18.8

* depositions include wet and dry depositions of the particulate phase and wet deposition of the gas phase

γ -HCH transboundary transport in 1996. To estimate the influence of remote emission sources on the contamination of various European regions in 1996, nine groups of the emission sources were set apart (Fig. 42). Emission fluxes from East, West and South Europe were considered separately. Russia was examined as an individual source. As regions-receptors the same five regions (Table 4) were considered.

γ -HCH transport distance is estimated to be equal to 6000 km. The performed calculations made it

possible to assess the contributions of regions-sources to γ -HCH depositions to the considered regions in Europe. Fig. 43 illustrates diagrams of contributions of different emission sources to depositions to East, South and North Europe. The sources of West Europe make the greatest contribution to deposition levels of the considered regions-receptors. It is worth noting that such remote regions-sources as India and America make a noticeable input to the contamination of North Europe.



Fig. 42. Regions-sources of γ -HCH emissions in the Northern Hemisphere

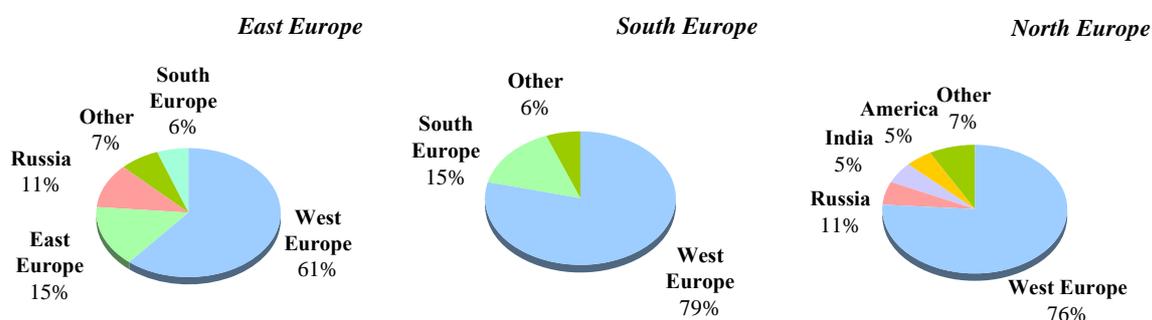


Fig. 43. Contributions of different regions-sources of emissions to γ -HCH depositions to some European regions

The comparison with measurement data.

The ratios of calculated and measured values of γ -HCH concentrations in air and precipitation indicate that the model overestimates air concentrations 2.5 times and the correlation coefficient between them is 0.5. Nearly 60% of calculated air concentrations and 100% of calculated concentrations in precipitation are within a factor of 3 relative to the observed levels. The mean ratio of measured concentrations in precipitation to calculated values equals 1.15. The correlation coefficient between calculated and measured values is 0.8.

2.3.3. Hexachlorobenzene

This year we have studied further the long-range transport and accumulation of hexachlorobenzene with the use of hemispherical model MSCE-POP. At the previous stage [Shatalov *et al.*, 2002] HCB

airborne transport during 1990 from European sources is estimated.

The task of the present stage is to make a preliminary analysis of HCB transport from European sources within the Northern Hemisphere and to make provisional estimates of European pollution from local sources. Since HCB accumulation processes in environmental compartments can essentially affect the long-range transport, the assessment is performed allowing for the description of HCB accumulation in environmental compartments during a long period of time (from 1985 to 1996). To compare the results obtained at the previous and at the present stage, the data on emissions from European sources in 1990 (emission spatial distribution is given in Fig. 44a below) is used in modelling.

In further studies it is supposed to evaluate the contamination of European domain taking into account remote sources of HCB emissions in the Northern Hemisphere.

The spatial distribution of pollution. The spatial distribution of HCB concentrations in the main environmental media calculated with allowance made for the long-term accumulation of this species in the environment is illustrated in Fig. 44. For the analysis of the estimated distribution, the same figure shows the emission distribution used and the gaseous flux of exchange with the underlying surface in 1996 (the last year of the calculations).

The analysis of spatial emission distribution shows that the major sources of pollution in Europe are located in its central, southern and eastern parts (Fig. 44a). The highest air concentrations (Fig. 44c) are observed in the regions with high emission intensity, while air pollution embraces appreciable areas of Europe and Asia and sea basins. The calculations point out that over the most part of the Northern Hemisphere HCB air concentrations are

lower not more than 30 times compared to mean European values. Over 10% of the Northern Hemisphere area (that exceeding the entire European area as much as 2.5 times) the concentration reduction in air is 10 times compared to mean European level.

Estimated mean values of HCB concentrations in the surface air of Europe and the Arctic in 1996 are illustrated below.

Region	Concentration, ng/m ³
East Europe	13
South Europe	8.9
West Europe	8
European Russia	7.9
North Europe	2.4
Arctic region	0.34

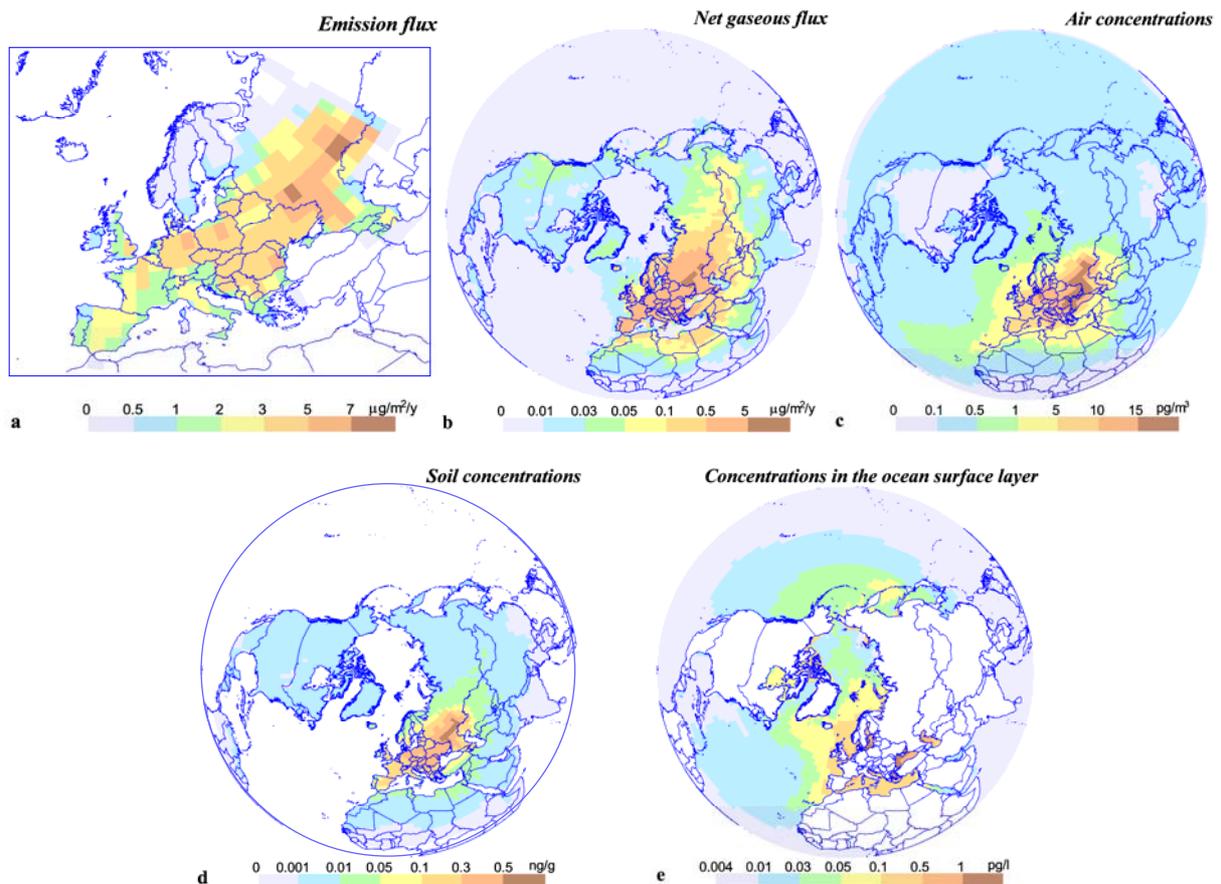


Fig. 44. Spatial distribution of emission flux (a), the flux of gas exchange with the underlying surface (c) and the calculated levels of HCB pollution in the air surface layer (b), soil (d) and in the ocean top layer (e) in 1996

Air concentrations over land far from the major emission sources (in North America and southeast Asia) are lower than over sea surface. This phenomenon is conditioned by the intensive gaseous flux to soil (Fig. 44b) in these regions. This fact evidences that by the end of the calculation period soil concentrations have not reached the equilibrium with air concentrations. To make a correct assessment of air pollution in these regions it is necessary to consider emission sources located in America and Asia and to perform calculations for a longer period of time. Reasoning from preliminary estimates, the model underestimates air concentrations as much as several times. It can be explained by the consideration of European emission sources only and underestimation of their intensity.

The impact of European emission sources on soil contamination is not limited by the EMEP domain but extends to the adjacent territories (Fig. 44d). Taking into account the gas exchange between the surface air and soil, it may be supposed that soil concentration will grow with the increase of the calculation period. For the EMEP region modelling covering 12-year period (1985-96) provides reasonable values of concentrations in soil (slightly underestimated). In particular, measured background concentration levels are equal to units of ng/g and calculated ones are 0.3-0.7 ng/g. It might be well to point out that the modification of air/soil exchange module improved considerably the consistency between calculated and measured concentration in soil.

In the marine environment (Fig. 44e), HCB pollution is transported from emission sources to some remote regions. Unfortunately data on HCB concentrations measured in seawater are insufficient for model verification. The comparison of estimated concentrations with measured values in regional seas (the Baltic Sea, the North Sea and the Mediterranean Sea) [Shatalov *et al.*, 2001] shows that the model underestimates concentrations in seawater within an order of magnitude. Sufficiently high concentrations of HCB in seawater of the Arctic point to the necessity of accounting for sea ice in modelling (Annex B).

Preliminary computations indicate that during the calculation period more than half the HCB emission flux (60%) is kept in different environmental compartments and only 40% of the emission flux is removed from the environment due to degradation processes and export beyond the calculation grid.

Provisional estimates of the transport distance. The presented analysis of concentration distribution in air, soil and seawater is indicative of extremely high potential of HCB to be transported over long distances. According to modelling results, the transport distance of HCB calculated as a mean distance from a source, at which the concentration drops 1000 times, is approximately 10000 km. This distance appreciably exceeds the transport distance of other pollutants considered. For the sake of comparison, the transport distance of different congeners of dioxins/furans is 4900-7100 km.

The consideration of HCB emission sources of the Northern Hemisphere located outside the EMEP domain will refine appreciably the estimates of the contamination in Europe. This work will be done in the subsequent investigations.

3. CO-OPERATION

In the current year the activity of the EMEP Centres was carried out in co-operation with subsidiary bodies to the Convention: the Working Group on Strategies and Review (WGSR), the Working Group on Effects (WGE), and international organizations and programmes: the Arctic Monitoring and Assessment Programme, the United Nations Environment Programme, the World Meteorological Organization, The Oslo-Paris Commission for the Protection of the Marine Environment of the North-East Atlantic and the Baltic Marine Environment Protection Commission. Special attention was given to collaboration with national experts of the Parties to the Convention.

3.1. Co-operation with subsidiary bodies to the Convention

Expert group on POPs (Working Group on Strategies and Review)

At the meeting of the Expert Group on POPs (Oslo, Norway, March 2003) MSC-E proposed a modelling procedure for the assessment of new species suggested by the experts for the inclusion to the POP Protocol.

Expert Group on POPs uses the approach based on the evaluation of substance toxicity, persistence in the environment, long-range transport potential and bio-accumulation in compliance with the accepted criteria. The half-life in the atmosphere (more than two days) is taken as a criterion of the long-range transport potential; the overall persistence in the environment is assessed by the half-life in the marine environment (not less than two months) or the half-life in soil and sediments (not less than six months) [ECE/EB.AIR/66].

To assess new substances by these criteria with the use of the hemispheric version of the multi-compartment POP transport model (MSCE-POP) the following procedure was proposed.

The long-range transport potential. In modelling POP transport from a point source of a conventional power (1 t/y), the **transport distance** (TD), i.e. mean distance at which air concentration of a substance is reduced 1000 times (Fig. 45), is specified. Such an approach is similar to that suggested in [Rodan *et al.*, 1999] (see also [Mackay *et al.*, 2001]). Based upon the prescribed characteristic half-life in the atmosphere (2 days), it is possible to calculate the threshold value of the transport distance. On preliminary calculations the threshold value of the transport distance is 1000-3000 km [Shatalov *et al.*, 2003]. The threshold value is to be refined in future.

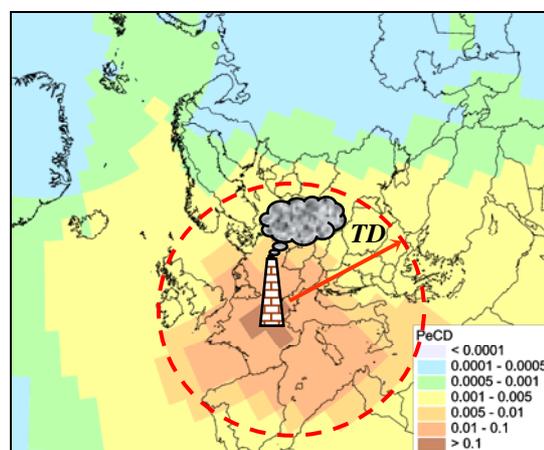


Fig. 45. Estimation of the transport distance

The overall persistence (P_{over}) is estimated by the time period during which the total pollutant content in the environment is twice reduced in the absence of emissions. This period is estimated [Mackay *et al.*, 2001] as the average of the characteristic half-lives of a pollutant in environmental compartments weighted by calculated fractions of it in these compartments. With the persistence criteria mentioned above (2 months in seawater and 6 months in soil and sediments), P_{over} value should be 60-180 days.

At the present stage model assessments of TD and P_{over} are made for the following species: **hexachlorobutadiene (HCBd)**, **pentachlorobenzene (PeCB)**, **polychlorinated naphthalenes (PCN-47 congener)**, **α -endosulfan**, **dicofol**.

The results are illustrated in Fig. 46. A point source located in Europe (France) was considered in calculations.

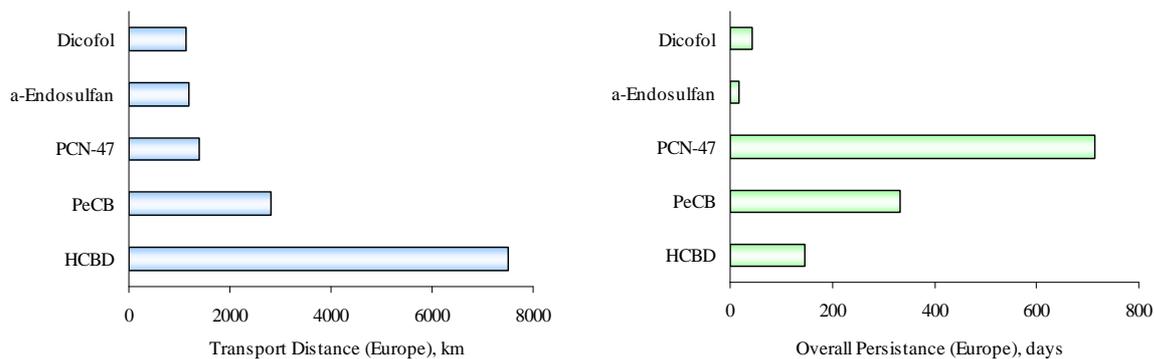


Fig. 46. The transport distance and the persistence in the environment calculated for a source located in Europe

The results allow ranking the species according to the considered criteria (TD and P_{over}). Thus among the species in question HCBBD demonstrates the highest long-range transport potential and PCN-47 is most persistent in the environment.

The model approach reveals the distribution of pollution from a country, region or continent. The

spatial distribution of the listed pollutants from a point source located in France is illustrated in Fig. 47. To make the comparison more convenient, concentrations on the maps are given in relative values (the maximum concentration is taken as the unit).

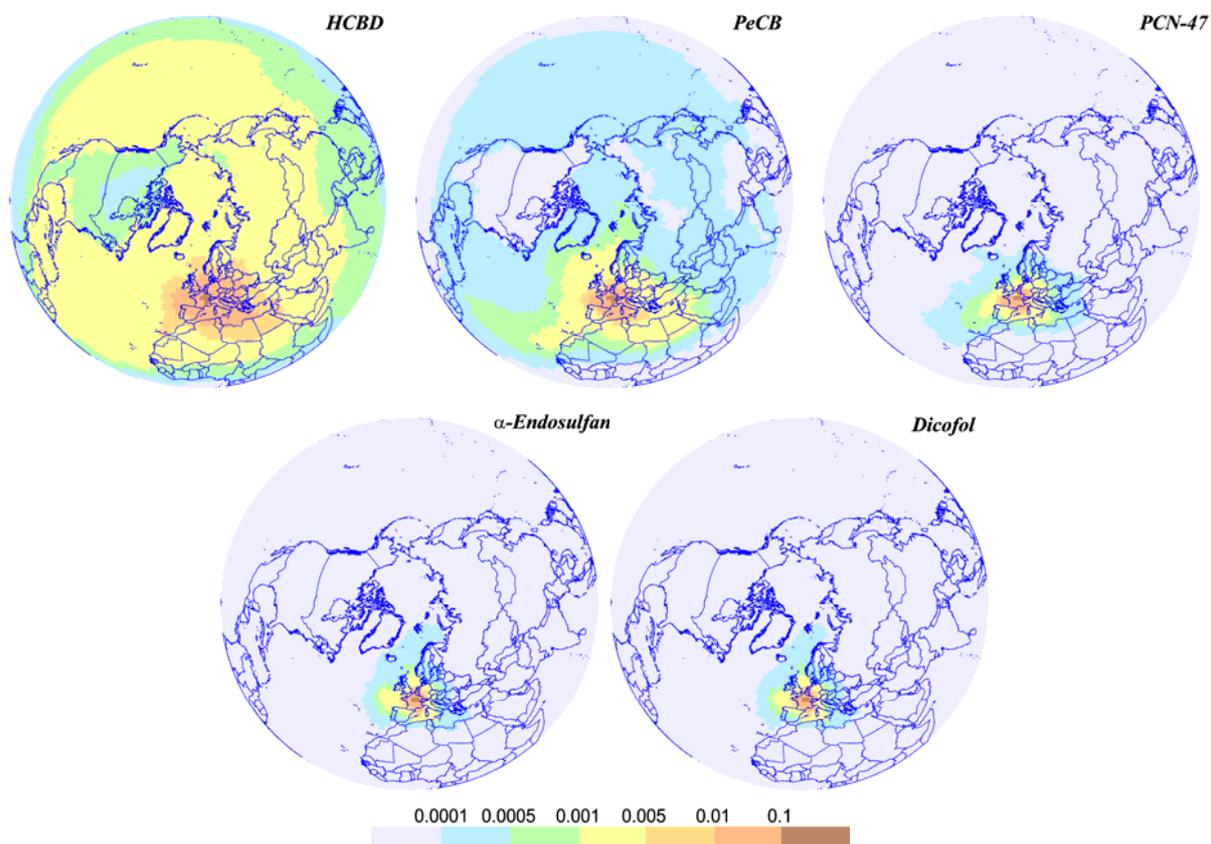


Fig. 47. The spatial distribution of air pollution from a source located in France for 1996 (in relative units)

The estimated distribution reveals the regions mostly affected by the source.

Thus on estimation of new substances the considered numerical criteria can be essentially complemented by the calculated spatial distribution of pollution from emission sources of different geographical location. This information can be beneficial for the decision whether this or that species should be included to international agreements on environmental protection.

The Working Group on Effects

This year MSC-E continued investigations, which could be useful for the development of the effect-based approach for the evaluation of POP impact on ecosystems and human health. POP pollution levels and accumulation dynamics in different environmental compartments of Europe are under investigation. Media, which accumulate the bulk of this or that pollutant mass, are distinguished. Studies focused on estimations of POP depositions to various types of the underlying surface are initiated.

According to the model results, 90% of PCDD/F overall toxicity accumulated in the environment during a long time period (30 years) is concentrated in soil. High soil concentrations of this pollutant (up to 3 pg TEQ/g) were estimated in the majority of European countries in 2000. Values of these concentrations are comparable with limit values set up in a number of countries (0.13-27 pg TEQ/g) [Vakar *et al.*, 1998].

Limit value of B[a]P annual average concentration in air recommended and accepted in a number of European countries is 1 ng/m³. In Europe this value varies from 0.25 to 2 ng/m³ [PAH Position Paper, 2001]. The analysis of the modelling results of B[a]P mean annual air concentrations points out that in some regions of Poland and the Czech Republic these values exceed 1 ng/m³ in 2000. In the majority of European countries calculated mean diurnal concentrations exceed mean annual ones as much as several times.

3.2. Co-operation with national experts and programmes

MSC-E has launched the intercomparison study of POP models. The first meeting was held in Moscow (Russia) in November 2002. Experts from Canada, the Czech Republic, Denmark, France, Germany, Japan, Norway, Switzerland, the United Kingdom, and the USA approved the intercomparison programme and submitted the description of 15 POP models. At the first stage it is envisaged to compare model description of the main processes of POP behavior in the environment, their parameterization and results of model experiments.

MSC-E continues to collect and review POP measurements in various environmental media. Additional data on POP measurements in the framework of bilateral collaboration with national experts were received from the Czech Republic, Germany, Sweden, and the United Kingdom.

3.3. Co-operation with international organizations

Arctic Monitoring and Assessment Programme and World Meteorological Organization

On the basis of agreement between EMEP, AMAP and WMO, MSC-E participated in the project "Persistent toxic substances, food safety and indigenous people of the Russian North". The Technical Report "Assessment of long-range transport of Hg, PCBs, and γ -HCH to the Russian North" [Dutchak *et al.*, 2002] prepared by MSC-E under this project was approved by independent experts from Canada and Norway and accepted by the AMAP Secretariat in January 2003. The calculation results show pollution levels of the considered POPs in five northern regions of the Russian Federation and in the Arctic as a whole. In the course of studies the main sources of PCB and γ -HCH emissions in the Northern Hemisphere, which make the crucial contribution to the Arctic contamination were identified. The Technical Report and its Executive Summary were

discussed at the fourth meeting of EMEP/TFMM (Valencia, Spain, April 2003).

The Baltic Marine Environment Protection Commission

In accordance with the contract between MSC-E and HELCOM, lindane depositions to the Baltic Sea and adjacent area are estimated and the results are described in the joint report of EMEP Centres presented to HELCOM [*Bartnitcki et al.*, 2002].

The UN Environment Programme

MSC-E continued its activity under the UNEP/GEF project "Regionally-Based Assessment of Persistent Toxic Substances" aimed at evaluating the pollution of Region III (Europe), IV (the Mediterranean area) and VII (Central and northwestern Asia). The results were included to the Final reports of regional groups [*RBA PTS*, 2002a, 2002b, 2002c].

CCC together with MSC-E took part in the development of POP monitoring global strategy under the auspices of UNEP. The Centres prepared a joint document, which summarizes the experience gained in this field under EMEP.

CONCLUSIONS

The EMEP Centres' activities in the field of monitoring and modelling are aimed at studying the pollution of the European region by persistent organic pollutants (PAHs, PCDD/Fs, PCBs, γ -HCH and HCB). The research involves an estimation of POP contamination in different environmental compartments, calculations of spatial distribution and the analysis of long-term trends of the considered pollutants. Much attention is given to studying POP transboundary and intercontinental transport in the Northern Hemisphere. A number of new substances is considered in terms of their potential to be transported over long distances and overall persistence in the environment. The regional and hemispheric versions of the MSCE-POP model are further modified. The description of processes defining POP behavior in soil and seawater are improved.

The progress in studying the environmental pollution by POPs is reviewed below:

Emissions

- The official data on emissions (PAHs, PCDD/Fs, PCBs, γ -HCH, HCB) for the period of 1980-2000 were submitted by 30 countries. During recent years the number of countries, which provide the POP emission totals and their spatial distribution, increased.
- According to the official data and expert estimates, total POP emissions in Europe tend to decrease due to the emission reduction in the majority of European countries.

Monitoring

- Thirteen measurement sites have reported POP data to CCC for 2001. Six of these were measuring POPs in both precipitation and air. The number of sites is still unsatisfactory in EMEP and especially in south and east of Europe.
- The general trends in concentrations of atmospheric α - and γ -HCH and HCB are decreasing since the first measurements started in 1991.

- The concentration of benzo[a]pyrene (and other PAHs) shows a clear seasonal variation, with peak concentrations during winter. The concentration level is decreasing towards the north of Europe.

Modelling

- Long-term trends of environmental content of PAHs (on the example of B[b]F) and PCDD/Fs (eight congeners) are analyzed. The level of pollution by these substances in the European region in 2000 is estimated.
 - PAHs and PCDD/Fs are mainly accumulated in soil containing more than 90% of their mass in the environment.
 - The two-fold emission decrease of B[b]F from 1980 to 2000 resulted in decrease of soil concentrations 1.5 times. In different regions of Europe soil concentration levels in 2000 are within the range of 0.1-14 ng/g with the mean value equal to 1.8 ng/g. B[b]F air concentrations amount to 0.05-5 ng/m³, the mean value is 0.3 ng/m³.
 - Considerable PCDD/F emission reduction (4 times) during 1980-2000 resulted only in minor decrease of their soil concentration. In European countries in 2000 PCDD/F concentration levels in soil are within 0.01-2.7 pg TEQ/g. High air concentrations are estimated for the Czech Republic, Belgium, Switzerland, Luxembourg, Slovakia, and Italy. Among regional seas the highest deposition values are estimated for the Baltic Sea and the lowest one – for the Mediterranean Sea.
- POP transboundary transport essentially influences the pollution level in European countries. On the example of B[a]P, it is demonstrated that in the majority of countries in 2000 the input of transboundary transport to concentration levels in air and to depositions is from 30% to 70%. Mean annual B[a]P air

concentrations are 0.1-1 ng/m³ in the majority of countries. In some regions of Poland, Germany, and the Czech Republic air concentrations exceed 1 ng/m³. Mean diurnal concentration values can exceed the mean annual ones more than 5 times. B[a]P deposition fluxes to regional seas are as much as 1.5 µg/m²/y for the Mediterranean Sea and 9 µg/m²/y for the Baltic Sea.

- The assessment of PCB and γ-HCH pollution level in the Northern Hemisphere in 1996 showed that:
 - Typical levels of air pollution by PCB-153 over the oceans in the Northern Hemisphere are from 0.004 to 3 pg/m³, over land – from 0.3 to 5 pg/m³. Higher air pollution levels are estimated for some regions of West Europe (up to 30 pg/m³) and over the US eastern coast (up to 20 pg/m³).
 - Typical levels of air pollution by γ-HCH over the oceans in the Northern Hemisphere are from 0.01 to 0.2 ng/m³, over land – from 0.2 to 1 ng/m³. Higher air pollution levels are estimated for some regions in West Europe (up to 6 ng/m³) and over southeastern Asia (above 7 ng/m³).
- An investigation of the long-range transport potential of PCDD/Fs, PCBs, γ-HCH and HCB is made. The transport distance of these POPs is from 5000 km (some congeners of PCDD/Fs) to 10000 km (HCB).
- The long-range transport potential and overall persistence is investigated for a number of new substances: hexachlorobutadiene, pentachlorobenzene, polychlorinated naphthalenes, α-endosulfan and dicofol. Hexachlorobutadiene and pentachlorobenzene possess the highest potential to the long-range transport and can be referred to the global pollutants.
- POP intercontinental transport can make a noticeable contribution to the regions of the Northern Hemisphere, in particular to the Arctic. On the example of PCB-153 it is demonstrated that European emission sources make the main contribution to the Arctic pollution (approximately 60%). The combined contribution of African and Asian sources is

around 10% of PCB-153 total depositions to the Arctic region.

- Model estimates of the environmental pollution are compared with monitoring data. A large share of calculated concentrations and depositions is within a factor of 3 relative measured values. For further model verification MSC-E carries out an intercomparison study of POP models, in which experts from a number of European countries, Canada and the USA take part.

CCC and MSC-E activity in the field of environmental pollution assessment was carried out in close co-operation with subsidiary bodies to the Convention and international organizations (UNEP, AMAP, HELCOM, WMO, OSPAR) and national experts. The principal results were presented for the discussion and examination at a number of international conferences, workshops and expert meetings.

Further efforts in the assessment of the environment pollution by POPs should be directed to the refinement of emission data; acquisition of measurement data on POP content in various environmental media; the refinement of the parameterization of POP behavioral processes in environmental media; the investigation of POP transport on the hemispherical/global level; further development of the model approach for the evaluation of new species.

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Annex A

EMEP WORK-PLAN FOR 2003

EMEP work-plan elements in 2003 [ECE/EB.AIR/77/Add.2]

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

Main activities and time schedule:

- a) MSC-E will prepare information for 2000 on: transboundary transport of Benzo[a]pyrene (B[a]P) (deposition and concentration fields and country-to-country matrix); transport and accumulation of PCDD/Fs in various compartments; pilot calculations for long-range transport on a hemispheric scale of PCBs, HCB and γ -HCH; and deposition of selected POPs to the regional seas. It will furthermore present: 1970-2000 pollution trends for B[b]F and PCDD/Fs. It will support the Expert Group on POPs and its national experts in their work and contribute to work to develop an effects-based approach under the Working Group on Effects;
- b) MSC-E will further develop its models by: modifying the modelled behavior in soil; modifying modelled air/sea exchange; refining the physico-chemical properties of PAHs, PCBs, γ -HCH, PCDD/Fs and HCB; evaluating the influence of sea ice on hemispheric transport of the POPs; and refining the model input data. It will start the model intercomparisons study and organize the first meeting with experts from the Czech Republic, Lithuania, Switzerland, the United Kingdom and the United States. Stage I will compare model descriptions of behavior in environmental media and parameterization for long-range transport and accumulation in multi-compartment models;
- c) In cooperation with Parties, CCC will enhance the completion of the superstation network (five to ten sampling sites). In cooperation with MSC-E, it will complement EMEP data with data from other international and national programmes for comparison with model results;
- d) CCC and MSC-E, in consultation with the Task Force on Emission Inventories and Projections and Parties, will improve the POPs emission data quality. 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.

Fulfillment of the EMEP work-plan for 2003 in field of model evaluation of POP pollution is presented in Tables A.1 and A.2:

Table A.1. EMEP domain

POPs	Model development	Modelling	Assessment of the environment pollution	Comparison with monitoring data
PAHs	<p>1. For B[a]P, B[b]F and 8 toxic congeners of PCDD/Fs – refinement of physical-chemical properties and collection of available measurement obtained for the EMEP domain under different international and national programmes.</p> <p>2. Modification of the model description of POP behavior in soil.</p>	<p>1. For B[a]P – deposition and concentration field and “country-to-country” matrix for 2000.</p> <p>2. For B[b]F - pollution trends for 1970 - 2000 (50x50 km²).</p>	<p>1. For B[a]P – source-receptor analysis in the EMEP domain in 2000.</p> <p>2. For B[a]P and B[b]F – assessment of pollution distribution in environmental media for 1970-2000.</p> <p>3. For B[a]P – assessment of levels of depositions to regional seas.</p>	<p>1. Comparison of B[a]P concentration in air and precipitation during 1991-2000.</p> <p>2. Comparison of B[b]F concentrations in air, precipitation, surface water, soils and vegetation and deposition fluxes for 1991-2000.</p>
PCDD/Fs		<p>1. For 8 congeners of PCDD/Fs and their mixture – pollution trends in 1970-2000 with the use of official and expert data on emissions.</p> <p>2. Transport and accumulation of PCDD/Fs in different environmental media.</p>	<p>1. Assessment of spatial distribution of PCDD/F toxicity on the basis of modelling 8 congeners for 2000.</p> <p>2. Exploration of long-term trends of PCDD/F pollution in different media.</p> <p>3. Assessment of congener composition of PCDD/Fs in environmental compartments.</p> <p>4. For 8 congeners of PCDD/Fs estimation of levels of depositions to regional seas.</p>	<p>1. Comparison of calculated and measured congener composition of PCDD/Fs in air, soil and vegetation.</p> <p>2. Comparison of calculated and measured concentrations of PCDD/Fs in air, soil, seawater and vegetation and deposition fluxes.</p>

Table A.2. Northern Hemisphere

POPs	Model development	Modelling	Assessment of the environment pollution	Comparison with monitoring data
PCDD/Fs	<p>1. For PCBs, γ-HCH 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.</p> <p>2. Modification of the model description of POP behavior in soil.</p> <p>3. Modification of the model description of POP behavior in the marine environment.</p>	Modelling PCDD/F long-range transport within the hemispherical scale for 1996 from European emission sources.	Assessment of the long-range transport of 8 congeners.	-
PCBs		Modelling PCB long-range transport within the hemispherical scale for 1996 from all the emission sources of the Northern Hemisphere (expert estimates).	Assessment of pollution of the Northern Hemisphere and the EMEP region from emission sources of the Northern Hemisphere.	Comparison of measured and calculated pollution levels in the Northern Hemisphere.
γ-HCH		Modelling γ -HCH long-range transport within the hemispherical scale for 1996 from all the emission sources of the Northern Hemisphere (official data + expert estimates).	Assessment of pollution of the Northern Hemisphere and the EMEP region from emission sources of the Northern Hemisphere.	Comparison of measured and calculated pollution levels in the Northern Hemisphere.
HCB		Modelling HCB long-range transport within the hemispherical scale for 1996 from European emission sources (expert estimates).	Preliminary estimate of pollution of the North Hemisphere from European sources and assessment of the transport distance.	Provisional comparison of calculated and measured levels of European pollution.

MODEL MODIFICATION

B.1. The modification of the model description of POP behavior in the marine environment

In modelling POP behavior in the marine environment one of the most important transport process is turbulent diffusion. The parameterization of turbulent diffusion process is a complicated problem not solved for the time being. In problems of pollution transport in the ocean it is common practice to use empirical values of turbulent diffusion coefficients depending on the problem scale [Okuba, 1971].

The MSC-E grid model describing the POP transport in the Northern Hemisphere [Malanichev *et al.*, 2002] takes into account horizontal and vertical turbulent diffusion in the ocean. In the model the horizontal turbulent diffusion is constant, homogeneous and isotropic. The vertical diffusion is constant and homogeneous in the main depth of the ocean. In the upper mixed layer, which is dynamically changed, the vertical diffusion is also constant and homogeneous but essentially more intensive.

As estimated, the contribution of turbulent diffusion to POP transport process is comparable with other constituents of the transport. Coefficients of large-scale turbulent diffusion in a grid model, in a way, parameterize the transport processes on a sub grid level and should depend on their intensity. For a difference grid with spatial resolution $1^\circ \times 1^\circ$, these processes can be represented by tides, mesoscale oceanic gyres, internal waves, and a number of other phenomena bringing about heterogeneity of

the velocity field with sizes from tens to hundreds kilometers. The availability of such heterogeneities obviously can depend on time and co-ordinates. For example, near the coastal line tidal waves and at the boundaries of ocean currents so-called frontal gyres are formed. At the same time the condition in deep water depressions can be nearly stationary and the diffusion processes are sufficiently weak.

At present the module of POP transport in the marine environment is under improvement. The parameterization of large-scale turbulent diffusion takes into account the dependence of diffusion coefficients on parameters of the input field of current velocities. Diffusion coefficient values are related to a derivative of this velocity component. It is supposed that spatial derivatives of prescribed sample of velocity components (in grid knots in discrete time moments) allow projecting the dispersion of velocity components for a sub grid scale and consequently turbulent diffusion intensity. In a first approximation the turbulent diffusion coefficients are assumed to be proportional to a sum of modules of the first partial derivatives. The normalization of diffusion coefficient values follows the equality condition of pre-calculated experimental mean value. Fig B.1 illustrates examples of calculated dependences of turbulent zonal diffusion coefficients on latitude and on depth.

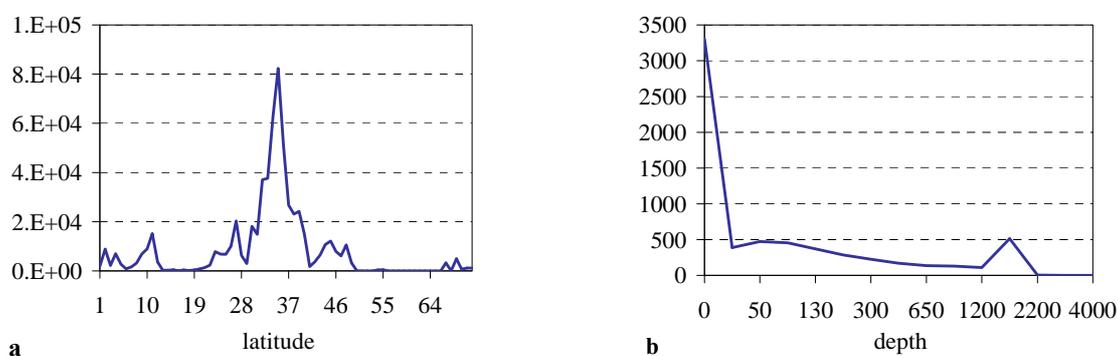


Fig. B.1. Characteristic dependence of large-scale zonal turbulent diffusion coefficient on latitude for the upper ocean layer (a) and depth (b) (a - January, $\lambda = 20^\circ\text{W}$, b - January, $\varphi = 60^\circ\text{N}$, $\lambda = 20^\circ\text{W}$)

Peculiarities of these dependences - significant values of the coefficients in the upper layer (exceeding 1-2 orders of experimental values accepted before) with maximum values in some regions. The coefficient values of horizontal diffusion decrease with depth.

To evaluate the effect of the dependence of large-scale turbulent diffusion on time and co-ordinates in terms of pollution transport in sea basins of the Northern Hemisphere, we carried out numerical experiments with the use of a complete global POP transport model [Malanichev *et al.*, 2002]. PCB-153 was selected as a pollutant. The experiment embraced the time period from 1970 to 1980. Fig. B.2 shows characteristic deviations of PCB-153 concentration values relative to constant coefficients accepted before.

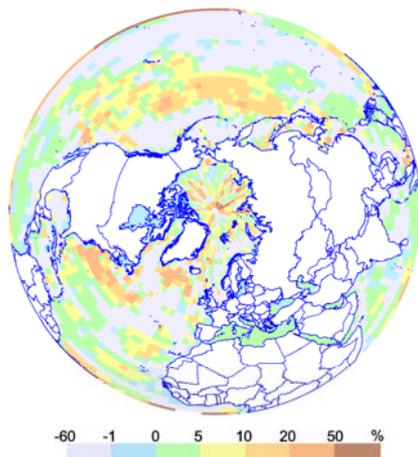


Fig. B.2. The difference in concentrations of PCB-153 in the upper ocean layer with variables of large-scale turbulent diffusion in comparison with concentrations with constant diffusion coefficient (January, 1977)

As seen from the figure in the case of variable coefficients of turbulent diffusion PCB-153 concentrations essentially increased (by 10-50%) mainly in zones of sea currents and they cut down in remaining regions.

B.2. The modification of the model description of POP behavior in soil

Some classes of POPs are accumulated in soil in appreciable quantities with possible subsequent re-emission to air. As it is shown in [Shatalov *et al.*, 2001] against a background of radical decrease of PCB emissions in the 90s the contribution of re-

emission flux from soil to air became comparable with that of anthropogenic emissions. In this context a correct description of POP behavior in soil is very important for modelling their long-range transport.

Up till now a simplified description of POP behavior in soil was used allowing for the following processes:

- POP redistribution between different phases in soil (gaseous, dissolved and sorbed on the particle soil phase) under the assumption that the equilibrium between phases is established instantaneously;
- POP vertical transport in the dissolved phase and vertical diffusion;
- POP degradation in soil;
- POP scavenging from the atmosphere to soil and gas exchange between these compartments.

Recent investigations, however, show [Cousins *et al.*, 1999] that POP transports with the dissolved organics in soil solution and (particularly) bioturbation make an essential impact on POP behavior in soil. The assumption on instantaneous equilibrium establishment between the POP dissolved and sorbed phase roughens the situation. The consideration of these processes refines appreciably the model description of POP behavior in soil, in particular, more correctly gives an account of vertical pollutant distribution.

In this context this year the model description of POP behavior in soil has been modified with allowance made for the following processes:

- POP transport with dissolved organics in soil solution;
- POP transport with ascending soil solution fluxes;
- bioturbation.

The dynamic character of POP partitioning between soil phases is also taken into account.

In order to evaluate the influence of the introduced processes on calculation results the analysis of model sensitivity to these processes and their parameters is made on the example of PCB-153. It is shown that:

- *The consideration of PCB-153 transport with dissolved organics strongly affect the gas exchange process between soil and vegetation and drastically increases POP penetration*

depth in soil (up to 15 times) compared to that calculated with the use of the previous model version. The specified penetration depth agrees with the experimental data [Cousin et al., 1999]. The calculated concentrations increased up to 2.5 times that are also more consistent with measured concentrations.

- The consideration of the dynamic character of PCB-153 partitioning between different phases of the pollutant in soil results in a change of the flux between soil and the atmosphere and essentially affects the vertical concentration profile (20-40%) The main changes are characteristic of emission reduction periods.
- The consideration of bioturbation strongly affects the vertical profile of soil pollution (the

concentration in the top layer decreases 2-3 times and in the lower layer it increases up to 6 times) These changes lead also to essential variations of the gas exchange flux between soil and the atmosphere.

To compare the results obtained by the previous and modified versions of the model PCB-153 transport for the period of 1970-99 is calculated on the assumption of zero initial pollution of media. The concentration spatial distribution in soil is shown in Fig. B.3.

As a result of modifications made mean concentration increased about 6 times and in some grid cells – up to 16 times. Since the previous model version underestimated soil concentrations the modification improved the agreement between the calculated and measured values.

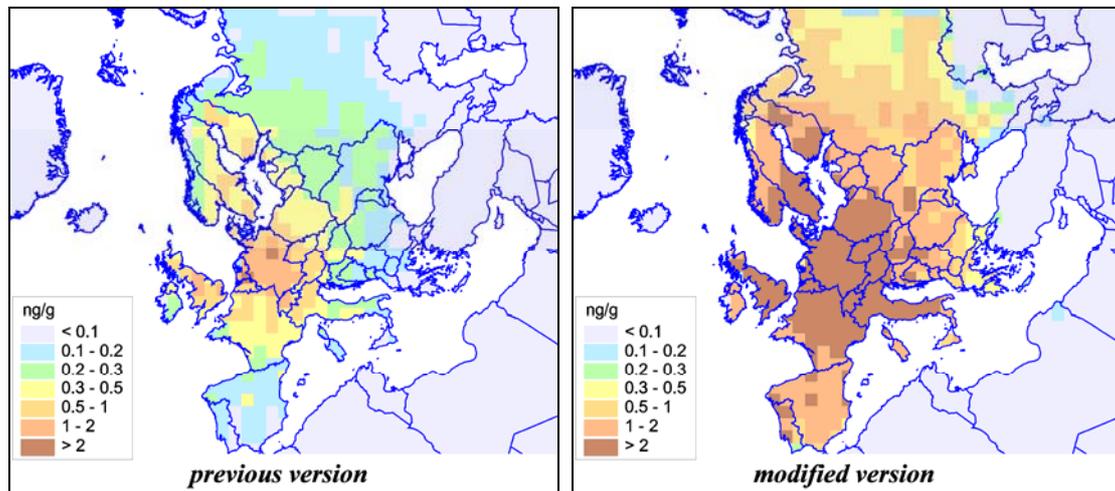


Fig. B.3. PCB soil concentration in the upper 5-cm layer calculated for 1999 by the previous and modified model versions